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Metal derivatives of tetrazoles

P N Gaponik, S V Voitekhovich, O A Ivashkevich

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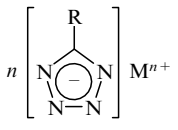
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Abstract. Published data on the synthesis, structure, properties and applications of metal derivatives of tetrazoles are generalised and described systematically. Compounds based on the anionic and neutral tetrazole forms, *C*- and *N*-mono- and *C*,*N*-disubstituted tetrazoles are considered. The bibliography includes 464 references.

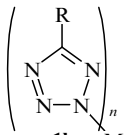
I. Introduction

In recent years a new direction has been developed in the tetrazole chemistry, which has appeared at the border with inorganic chemistry and is related to the synthesis and studies into the structure and properties of metal tetrazole derivatives (MT). This is due to the practical and theoretical significance of these unique compounds and diversity of their properties, depending on both the nature of the metal atom and the functional groups attached to the tetrazole ring.

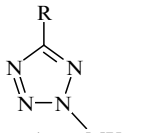
Tetrazoles are a peculiar class of heterocyclic compounds exhibiting properties of both acids and bases.[1–3] Therefore, they can exist in neutral, anionic and cationic forms. The metal atom (M) in MT can be bound to the heterocycle by a covalent, ionic or coordination bond or can be incorporated into a neutral molecule, anion or cation. When considering the enormous array of existing data in terms of these peculiar features, one can distinguish several main types of MT (**1**–**5**) (R^A is the substituent generating the anionic centre, X is an inorganic or organic ligand, A is the anion, MA is the metal-containing anion).



1a



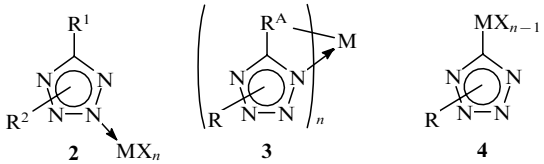
1b



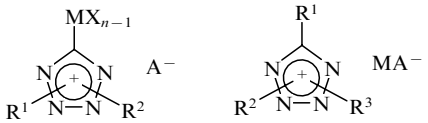
1c

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2 **3** **4**



5a **5b**

Compounds **1a**,**b** are formed upon deprotonation of 5-substituted tetrazoles and, in the case of alkali and alkaline earth metals, are mainly ionic (**1a**). For other metals, a more or less covalent bond of the type **1b** is formed; this also occurs for mixed-ligand complexes (**1c**). Compounds **2** are nv-complexes in which neutral mono- and disubstituted tetrazoles are present as ligands. A separate type of MT is represented by chelates **3** formed by *C*- and *N*-substituted tetrazoles in which substituents generate the anionic centre. The metal atom in MT **4** and **5a** is directly linked to the carbon atom of the tetrazole ring, while in tetrazolium salts **5b**, the metal is a part of the anion.

Owing to the availability and good prospects for the practical use, derivatives of types **1**–**3** are most studied. And only in the last decade, more than 300 relevant papers were published. However, numerous data on the synthesis, structures and properties of these compounds have not been described systematically as yet. Data on transition metal compounds of tetrazoles and tetrazolate anions published before 1987 have been surveyed.[4] Two reviews devoted to complexes of 1,5-disubstituted tetrazoles[5] and thermo- and photochromic iron(II) complexes with 1-alkyltetrazoles[6] have been published. In addition, a recent review[7] devoted to organometallic complexes of azoles contains some data on the tetrazole derivatives.

The purpose of the present review is to describe systematically and generalise the existing data on the synthesis, structure, properties and applications of MT of types **1**–**3** prepared using anionic and neutral forms of unsubstituted and *N*-substituted tetrazoles. Organometallic compounds **4** and tetrazolium compounds **5**, which are somewhat different and much less studied, are beyond the scope of the review. However, judging from the latest publications, the attention to these derivatives increased owing to

the prospects of their use in organic synthesis[8] and analytical chemistry.[3,9]

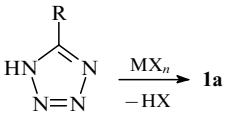
The information is systematised according to the type of tetrazole that forms MT, because the structure of the tetrazole derivative, *i.e.*, the presence, positions and the nature of substituents in the ring, determines the formation of metal–tetrazole bonds of different nature and, hence, dictates the methods used to synthesise the MT. The attention is focused on the synthetic aspects and applications of MT. Structural features and properties of MT are also discussed.

II. Metal derivatives of unsubstituted and 5-substituted tetrazoles

5-Substituted tetrazoles are the most readily available tetrazole derivatives.[1–3,10] This accounts for the considerable interest in them as the starting compounds in the synthesis of MT. Due to their unique structures and properties, tetrazoles of this type form diverse metal derivatives; the methods of their synthesis can be divided into two groups. The first one includes the reactions of 5-substituted tetrazoles with bases, metal salts or other metal-containing compounds and transformations of the MT formed. Due to acidic properties of 5-substituted tetrazoles, the pK_a of which ranges from −0.8 to 6 depending on the nature of substituent R,[1–3,11,12] it is possible to prepare salts **1a** and similar metal derivatives **1b**,**c**. In some cases, tetrazoles are not deprotonated, complexes **2** (R^2 = H) being formed with involvement of the lone pair of the tetrazole nitrogen. The second group of methods comprises heterocyclisations of linear polynitrogen structures with metal salts or complexes; this gives metal derivatives **1a**–**c**.

1. Synthesis of metal derivatives from tetrazoles

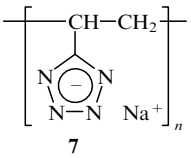
The reactions of 5-substituted tetrazoles **6** with bases (alkali and alkaline earth metal hydroxides,[13–18] alkoxides[19–25] or hydrides[16,26]) afford tetrazolates **1a**. In most cases, the reaction is carried out in water, ethanol or acetonitrile, and the resulting salts are often used for subsequent transformations without isolation from the reaction medium.



6

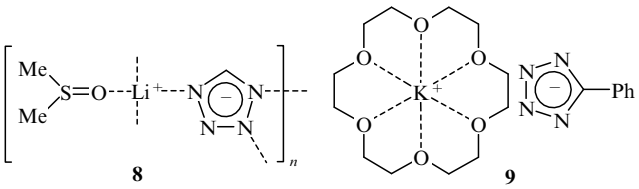
M is alkali or alkaline earth metal; X = H, OH, OAlk.

This reaction is also suitable for the synthesis of poly(5-vinyltetrazole) (PVT) salts. However, the reaction in water or ethanol does not proceed to completion despite an excess of the base.[27] In other organic solvents, sodium poly(5-vinyltetrazolate) (**7**) with a metal content of 99.9% of the stoichiometric amount was obtained.[28]



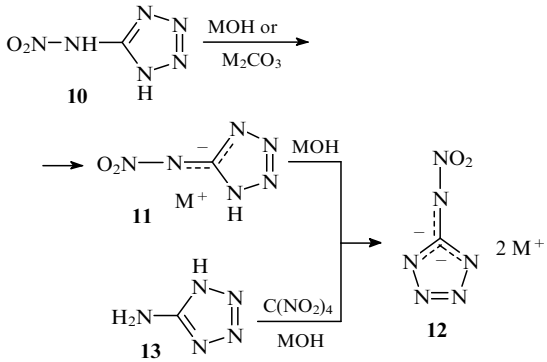
7

In the presence of complex-forming compounds, this reaction may give salts with a more intricate composition. In particular, the reaction of tetrazole with lithium hydroxide in DMSO afforded lithium tetrazolate **8**, incorporating a DMSO molecule, in 33% yield.[29] Treatment of 5-phenyltetrazole with potassium hydride and 18-crown-6 in THF at room temperature gave 5-phenyltetrazolate of the potassium complex with 18-crown-6 (**9**) in 94% yield.[26] The structures of compounds **8** and **9** were determined by X-ray diffraction analysis.



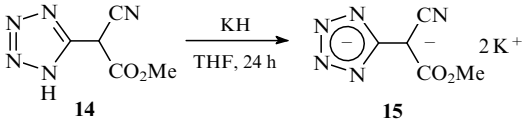
8 **9**

The substituent at the heterocycle carbon atom can also exhibit acidic properties; in this case, the tetrazole forms salts of different types. For instance, 5-nitraminotetrazole (**10**) is converted into salts **11** and **12** containing singly and doubly charged tetrazole anions, respectively.[30–33] According to X-ray diffraction data, in caesium[31] and lithium (hydrate)[33] salts **11**, the negative charge is delocalised over the anion. Salts **12** are often prepared using more readily available 5-aminotetrazole (**13**) instead of tetrazole **10**. Upon nitration with polynitro compounds in the presence of an alkali, compound **13** is converted into 5-nitraminotetrazolate(2−) salts (**12**) (yields 68%–91%).[30]

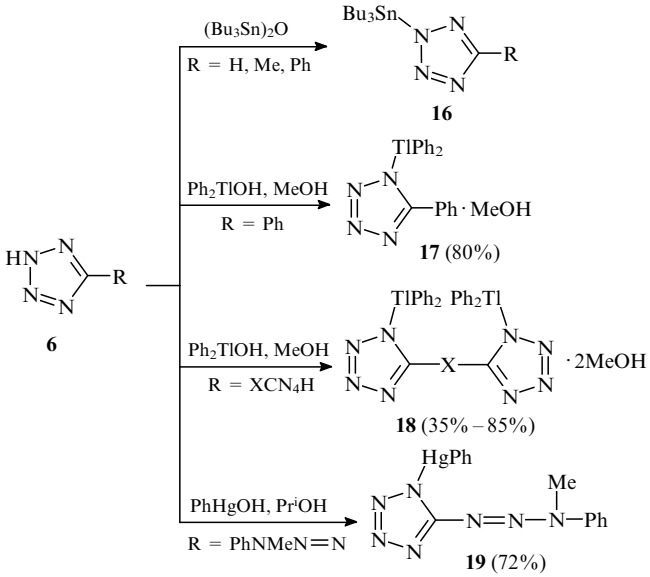


M = Li, Na, K, Rb, Cs.

5-Substituted tetrazole **14** reacts with potassium hydride as a dibasic acid to give dipotassium salt **15** in a quantitative yield.[34]



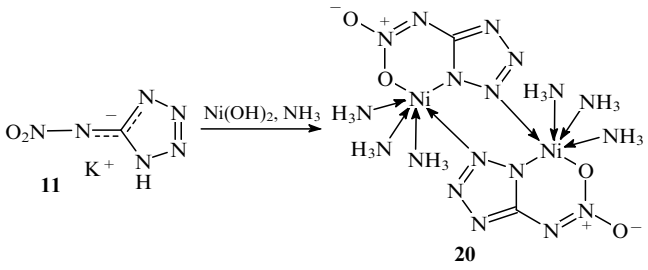
A series of MT **1c** have been prepared by the reaction of 5-substituted tetrazoles **6** with organometallic bases and oxides, in particular, tributyltin oxide[1,2] and diphenylthallium[21] and phenylmercury[1] hydroxides dissolved in lower alcohols. MT **16**–**19**



X = 1,3-C_6H_4, $(CH_2)_n$ (n = 1, 2, 4).

obtained in this way may have more complex structures in the crystalline state due to the additional coordination of the metal atom to the tetrazole ring. According to X-ray diffraction data, compound **17** is a dimer formed through the N(1),N(2)-binding of the tetrazole ring to the metal atom, and MT **18** [X = $(CH_2)_4$] is polymeric owing to the tridentate coordination of the heterocycle by the N(1), N(2), N(3) atoms to different metal atoms.[21]

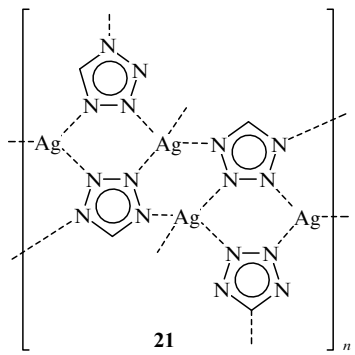
The use of the methods to prepare compounds **1b**, where M is a transition metal, is virtually unexplored. The reaction of 5,5′-bitetrazole with copper(II) oxide or copper(II) basic carbonate gave [35] copper(II) bitetrazolate. These reactions proceed more smoothly in the presence of ammonia or ethylenediamine, which are incorporated into the final product.[35–37] Thus the reaction of potassium 5-nitraminotetrazolate (**11**, M = K) with nickel(II) hydroxide in aqueous ammonia furnished triammine(5-nitraminotetrazolato)nickel(II) (yield 80%) having dimeric structure **20** according to X-ray diffraction data.[37]



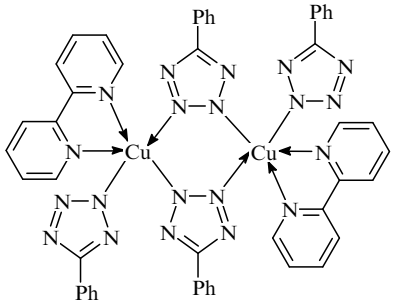
11 **20**

The reaction of tetrazoles **6** with metal chlorides, sulfates, acetates and other salts is a convenient method for the preparation of MT **1b**. Due to poor solubility, the target compounds are formed on mixing aqueous or aqueous ethanolic solutions of reactants at room temperature. This procedure was used to prepare silver (**21**) [38] and copper(II) tetrazolates [39] and nickel(II) and copper(II) 5-vinyltetrazolates [40] having a stoichiometric composition. Due to the possibility of inclusion of a reagent into the final product, the composition of the resulting salt depends on the starting reactant ratio. In particular, tetrazole reacted with excess silver nitrate to give the double salt $2\,Ag(HCN_4)\cdot AgNO_3$ (**22**).[38]

According to X-ray diffraction, the structure of tetrazolate **21** is a 3D network of three- and four-coordinate silver ions linked by tri- and tetradentate tetrazolate ligands. In salt **22**, the silver atoms are two- and three-coordinate, while the tetrazole ring is linked to the metal atoms through four nitrogen atoms. The Ag–N bond lengths in these compounds are in the range of 2.197(4)–2.410(4) Å.[38] Note that participation of all four nitrogen atoms of the tetrazole ring in metal coordination is a rare case. This coordination mode has also been found recently by X-ray diffraction analysis in the structure of copper(I) 5-methyltetrazolate.[41] More often, the tetrazolate anion acts as a bidentate bridging ligand or a monodentate ligand. According to X-ray diffraction data, both types of coordination exist in the mixed-ligand copper(II) complex **23**, prepared by the reaction of 5-phenyltetrazole with copper acetate in aqueous ethanol in the presence of 2,2′-bipyridine.[42]

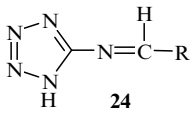


21



23

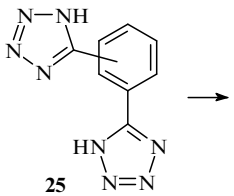
The reaction of salts MX_2 (M = Cu, Cd, Zn; X = Cl, OAc) with Schiff bases **24** in methanol resulted in the complexes $M(HL)_2(MX_2)_n$, where $n = 0–2$, HL is the singly deprotonated ligand, and the complexes ML, where L is the doubly deprotonated ligand. The diversity of compositions of the complexes obtained is due to the ability of metal atoms to substitute the hydrogen atoms in the tetrazole ring and the hydroxy group, polydentate nature of the heterocycle and participation of the azomethine group in the coordination, as indicated by IR spectroscopic data.[43]



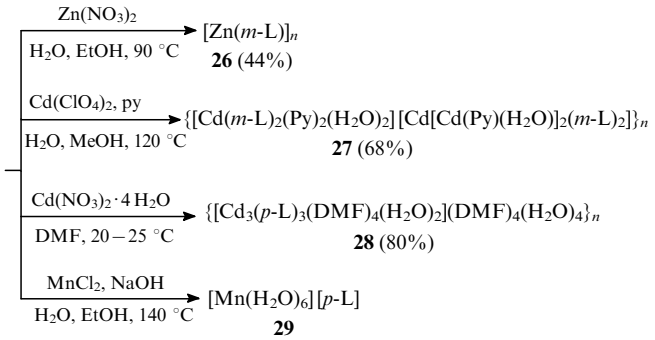
24

R = 2,4-$Cl_2C_6H_3$, 2-MeO-3,5-$Cl_2C_6H_2$, 2,4-$(MeO)_2C_6H_3$, 4-$Me_2NC_6H_4$, 2-HOC_6H_4, 2-HO-5-BrC_6H_3, 2-HO-5-$NO_2C_6H_3$.

Depending on the reaction conditions, *meta*- and *para*-5,5′-phenyleneditetrazoles **25** react with Cd, Zn and Mn(II) salts to give essentially different, as regards both composition and structure, complexes **26**, **27**,[44] **28**,[45] **29**.[46] The structures of compounds **26**–**29** were determined by X-ray diffraction. Compounds **26**–**28** in which the doubly charged anions derived from tetrazole **25** function as bridges are two- and three-dimensional coordination polymers. Conversely, compound **29** is a mononuclear aqua complex containing no metal–tetrazole coordination bond. In the structure of complex **28**, one-dimensional channels were found which occupy up to 35% of the void volume and encapsulate tetrameric cyclic water clusters and DMF molecules. On heating to 150 °C, water and DMF are removed from the channels, which accounts for the interest of researchers in this type of compound for the preparation of inclusion compounds and sorbents. A coordination polymer with a composition similar to complex



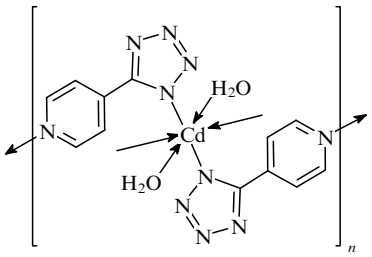
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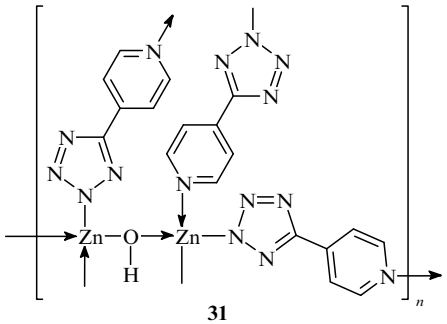
L = $N_4CC_6H_4CN_4$.

26 is formed upon the reaction of 3-(tetrazol-5-yl)benzoic acid with zinc chloride under hydrothermal conditions.[47]

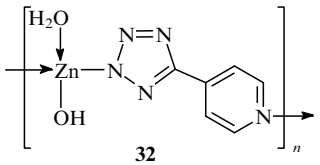
The 5-(4-pyridyl)tetrazole anion also acts as a bridging ligand forming two-dimensional coordination polymers **30**–**32** upon the reaction with Cd [48] and Zn [49] ions under hydrothermal conditions. The products were characterised by X-ray diffraction. Under the same conditions, Cu(II) ions are reduced and the process ends in the formation of Cu(I) complex **33**, having a 3D structure.[49]



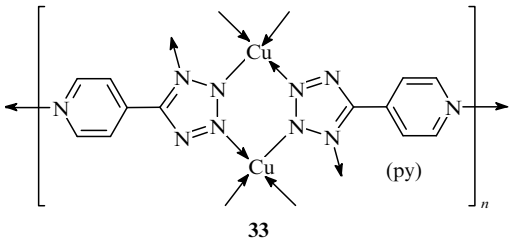
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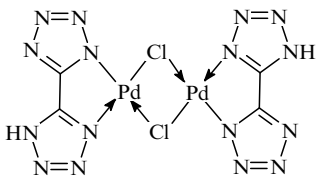
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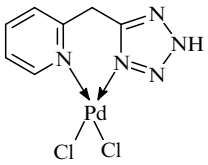
33

The high thermal stability, insolubility in most of solvents and photophysical properties of complexes **28** and **30**–**33** induce interest in these compounds as promising fluorescent materials.[45, 48, 49]

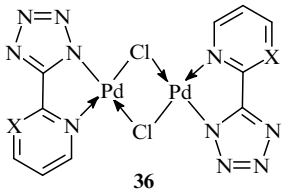
Not only derivatives of tetrazolate anions **1b** can be isolated as the reaction products of 5-monosubstituted tetrazoles with transition metal salts, but also complexes **2** containing the molecular form of tetrazoles. This is true first of all for palladium salts. Unlike copper(II) and nickel(II) chlorides, palladium(II) chloride reacts with 5-vinyltetrazole in water [40] or chloroform [50] to give the molecular complex $Pd(CH_2=CH-CN_4H)_2Cl_2$. However, 5,5′-bitetrazole and 5-monosubstituted tetrazoles containing a pyridyl or pyrimidyl group react under the same conditions to give complexes **34**–**36** in which the tetrazole ring occurs in the anionic or neutral form.[51]



34



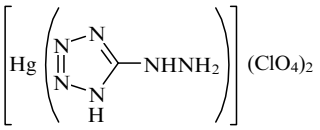
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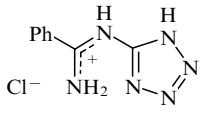
X = CH, N.

The preparation of nv-complexes of neutral 5-substituted tetrazoles with other metal salts has been reported. In particular, the synthesis of compound **37** by the reaction of mercury(II) salts or oxide with 5-hydrazinotetrazole in aqueous perchloric acid has been described.[52]

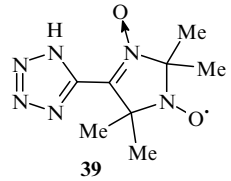


37

A complex of *N*-(tetrazol-5-yl)benzamidine hydrochloride (**38**), *viz*., $CoLCl_2$ (L is ligand **38**),[53] and complexes of 2,2,5,5-tetramethyl-4-(tetrazol-5-yl)-3-imidazole-1-oxyl 3-oxide (**39**),[54] *viz*., $NiLCl_2(H_2O)$ and $CuLCl_2$ (L is ligand **39**), have been prepared. According to IR spectroscopy, diffuse reflectance spectroscopy and magnetochemical measurements, neutral ligands in these complexes are coordinated in the bidendate mode, namely, by a nitrogen atom of the tetrazole ring and either the amidine nitrogen atom (compound **38**) or the oxygen atom of the N→O group (compound **39**). In the complexes of tetrazole **39**, weak interaction between the unpaired electrons of the metal and the ligand was found.[54]

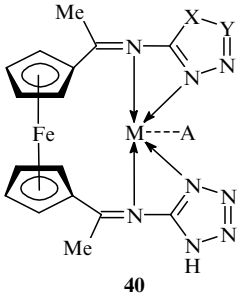


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39

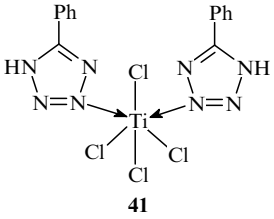
Refluxing in ethanol of divalent metal salts with Schiff bases prepared from 1,1′-diacetylferrocene, 5-aminotetrazole or some other azoles gives rise to MT having apparently chelate structure **40** in which the metal atom can be additionally coordinated by the anion.[55–57]



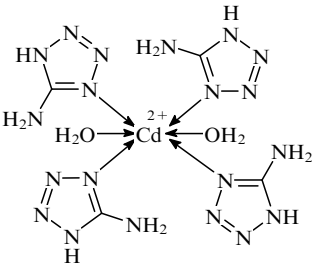
40

X–Y = SCH, NHCH, NHN; M = Co, Cu, Ni, Zn;
A = NO_3, SO_4, C_2O_4.

Note that in the studies cited above,[40, 50–57] involvement of the molecular form of 5-substituted tetrazoles in the coordination was proposed relying on the results of spectroscopic studies and chemical analysis. X-Ray diffraction data confirming the existence of complexes of neutral tetrazoles have been obtained only for compounds **41**[58] and **42**.[59] Complex **41** in which 5-phenyltetrazole is coordinated by the metal ion through the N(3) atom has been prepared in 94% yield by the reaction of the ligand with titanium(IV) chloride at room temperature. Studies of the mass spectra of this complex and its behaviour in a THF solution indicate that the tetrazole ligand is bound rather weakly to the metal ion; this restricts the suggested use of compound **41** for the synthesis of titanium nitride.[58] In complex **42** obtained by the reaction of 5-aminotetrazole with cadmium picrate on heating in water, neutral tetrazole is also coordinated in the monodentate mode, but by the N(4) atom.[59]



41



$[C_6H_2(NO_2)_3O^-]_2(H_2O)_2$

42

Poly(5-vinyltetrazole) behaves with respect to metal salts like monomeric 5-substituted tetrazoles. It reacts with nickel(II) and copper(II) chlorides in water to give the salts $[M\{CH_2CH(CN_4)\}_2]_n$, while with palladium chloride, molecular complexes $[Pd\{CH_2CH(CN_4H)\}_3Cl_2]_n$ are formed.[40] The reaction of poly(5-vinyltetrazole) with excess copper(II) nitrate is accompanied by a decrease in the solution pH to give a water-insoluble complex containing three tetrazole fragments per metal ion.[60] A specific feature of the complexation of PVT with copper(II) ions is the formation of complexes, under certain conditions, with a high local concentration of copper stabilised by both coordination bonds and hydrogen bonds between the tetrazole units. The mutual strengthening of these bonds results in the cooperative stabilisation of the whole system.[61] The reaction of PVT with chromium(III) chloride is accompanied by a slight decrease in pH; this gives soluble complexes in which the chromium atom coordinates both the tetrazole ring and water molecules.[62] A method for the synthesis of iron poly(5-vinyltetrazole) complex from the monomer has been reported.[63] Some of the Fe^{2+} ions arising upon electrochemical dissolution of an iron electrode (with potassium peroxydisulfate as the electrolyte) form a redox system, $Fe^{2+} - S_2O_8^{2-}$, which initiates the radical polymerisation of 5-vinyltetrazole; other Fe^{2+} ions interact with the tetrazole ring as complex-forming agents. This yields the polymer $[Fe\{CH_2CH(CN_4)\}_2]_n$ insoluble in water or organic solvents.

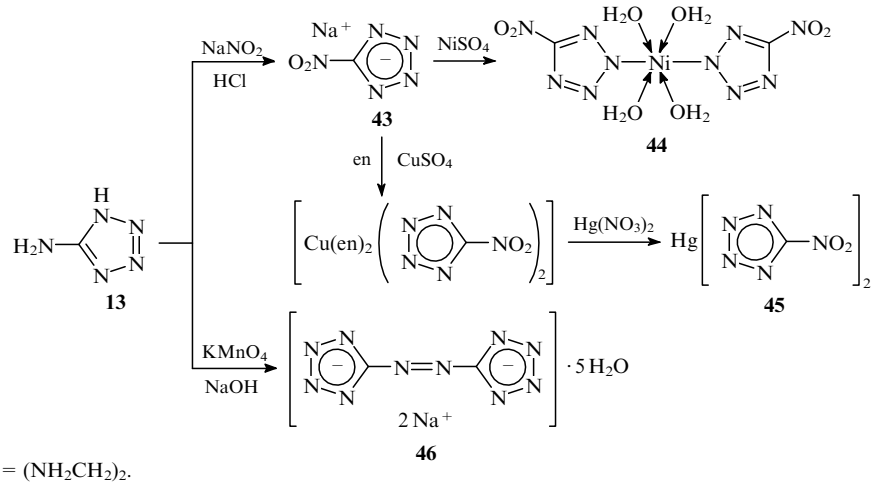
The replacement of neutral tetrazole in the reactions with transition metal salts by water-soluble ammonium and alkali or alkaline earth metal tetrazolates rules out the possibility of formation of complexes **2** and is used successfully for the synthesis of MT **1b**. This method was employed to prepare silver 5-nitraminotetrazolate (**12**, M = Ag),[64] a number of fluorine-containing silver tetrazolates $Ag(RCN_4)$, where $R = CF_3$, NF_2CF_2, NF_2CFCl, and transition metal tetrazolates $Ni(RCN_4)_2 \cdot 2MeOH$, $Cu(RCN_4)_2 \cdot 2.5\,MeOH$ and $[Fe(RCN_4)Cl] \cdot MeOH$, where $R = NF_2CF_2$.[65] The transformation of 5-aminotetrazole (**13**) *via* sodium salts **43** or copper salts and the 5-nitrotetrazolate anion afforded nickel(II) (**44**)[66] and mercuric (**45**)[67] 5-nitrotetrazolates (Scheme 1). The presence of inner-sphere water and the monodentate mode of coordination of the tetrazolate anion in complex **44** were established by X-ray diffraction analysis.

Sodium 5,5′-azoditetrazolate pentahydrate (**46**),[68] which is also readily prepared from tetrazole **13**, serves as a convenient starting compound for the synthesis of other 5,5′-azoditetrazolates. Recently, a large group of 5,5′-azoditetrazolates of other alkali and alkaline earth metals, aluminium, yttrium, some lanthanides (La, Ce, Nd, Gd),[69] and thallium(I)[21] have been synthesised by this method (as hydrates) and characterised by X-ray diffraction analysis. It is noteworthy that these compounds easily eliminate water even at room temperature. This makes the salts sensitive to friction or impact; therefore, handling these salts requires special care.[69]

The reaction of sodium salt of 2-(tetrazol-5-yl)-4,4,5,5-tetramethyl-4,5-dihydroimidazol-1-oxyl 3-oxide (**47**) with manganese(II) and nickel(II) acetates gave ionic complexes **48** and **49** (Scheme 2) in which (according to X-ray diffraction data) the paramagnetic tetrazolate anion acts as a bidentate chelating or bridging ligand. Due to intermolecular hydrogen bonds, these complexes form high-dimensional heterospin structures whose magnetic properties are of obvious interest.[70]

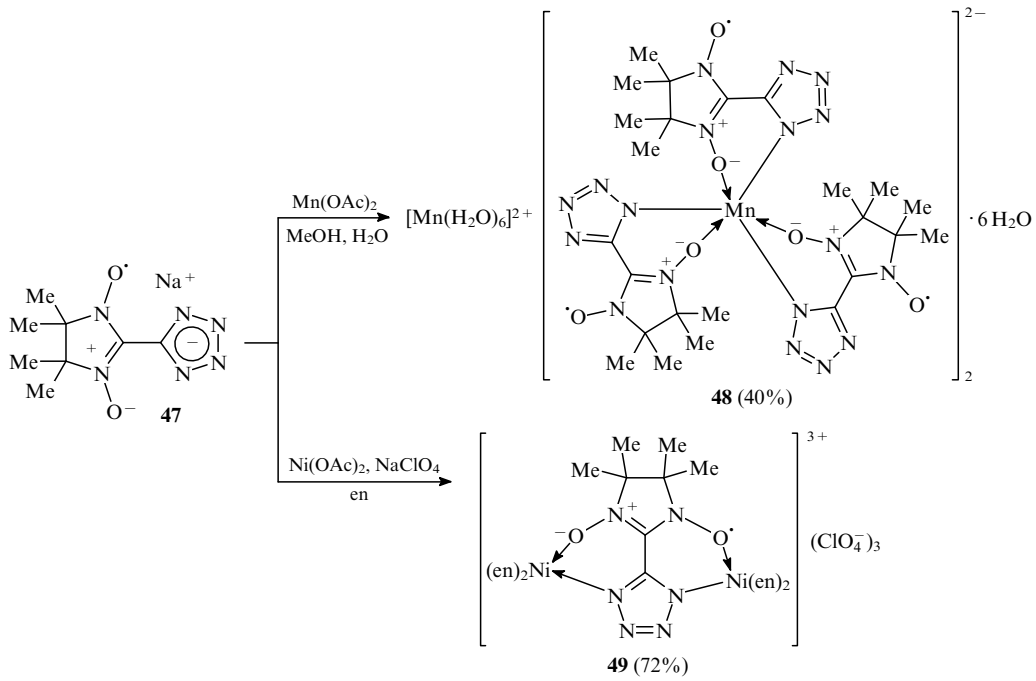
A number of neutral water-soluble highly stable gadolinium(III) **50**, **51** and zinc **52** complexes with 5-(2-pyridyl)- and 5-(2-pyridyl 1-oxide)tetrazoles have been prepared by the reactions of metal salts with potassium or barium tetrazolates obtained *in situ* from tetrazoles and the corresponding carbonates in water. Compounds **50**–**52** were prepared in 48%–76% yields. According to X-ray diffraction data, in these complexes tetrazoles are bidentate ligands forming stable five- and six-membered chelate rings. In gadolinium compounds **50**, **51**, the second coordination sphere includes additional water molecules, which

Scheme 1

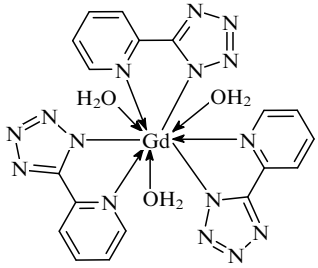


en = $(NH_2CH_2)_2$.

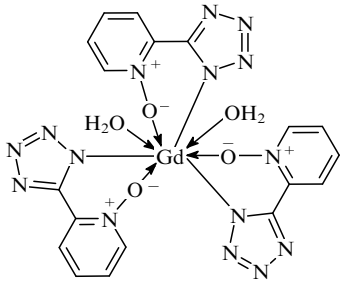
Scheme 2



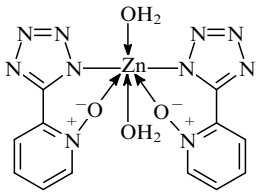
makes the complexes readily soluble and provides high proton relaxation ability.[71]



50



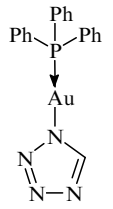
51



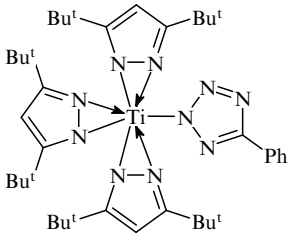
52

Synthesis of MT by the reaction of 5-R-tetrazolates with transition metal salts is of interest due to the fact that the resulting compounds are capable of subsequent transformations involving the initial tetrazolate. In particular, cobalt(II) and nickel(II) nitrates react with sodium 5-R-tetrazolates in aqueous solutions to give metal tetrazolates as the solid phase, which is gradually dissolved on treatment with excess 5-R-tetrazolate anion. The dissolution is accompanied by an increase in the solution viscosity and gives rise to water-soluble polymers. The rate of dissolution depends substantially on the nature of substituent R; in particular, it increases in the oder $NH_2 < 4\text{-}MeC_6H_4 < CH=CH_2 < Ph < H < Bu < Et < Me$. In the case of $R = NO_2$, CF_3, the process stops after the formation of solid products insoluble in an excess of the ligand. Presumably, polymeric complexes are formed in the case of azoles with pK_a and pK_{BH^+} values in the 3.5 to 12 and −4 to 5 ranges, respectively.[72]

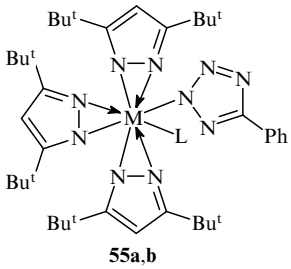
The tetrazolate anion has a fairly high nucleophilicity and can replace some groups in coordination compounds; this is used for the synthesis of mixed-ligand complexes. In these processes, the tetrazolate anion is introduced in the reaction as alkali metal tetrazolates or is generated *in situ* from 5-R-tetrazole and a base. The ligand being replaced is, most often, a halogen atom. The reaction of complex $[AuCl(PPh_3)]$ and tetrazole in the presence of sodium hydroxide in acetone according to this synthetic protocol gave complex **53** in 52% yield.[73] The reaction of chlorotris(3,5-di-*tert*-butylpyrazolato)titanium(IV) with sodium 5-phenyltetrazolate in THF (23 °C, 48 h, 74%) resulted in tris(3,5-di-*tert*-butylpyrazolato)-5-phenyltetrazolatotitanium(IV) (**54**). The replacement of two chlorine atoms in analogous niobium(V) and tantalum(V) dichloride complexes requires more drastic conditions (refluxing), and in the latter case, only one chlorine atom is substituted despite the use of excess tetrazolate.[74] According to X-ray diffraction data, the tetrazole ring in the resulting complexes **53**–**55** is coordinated as a monodentate ligand.



53



54

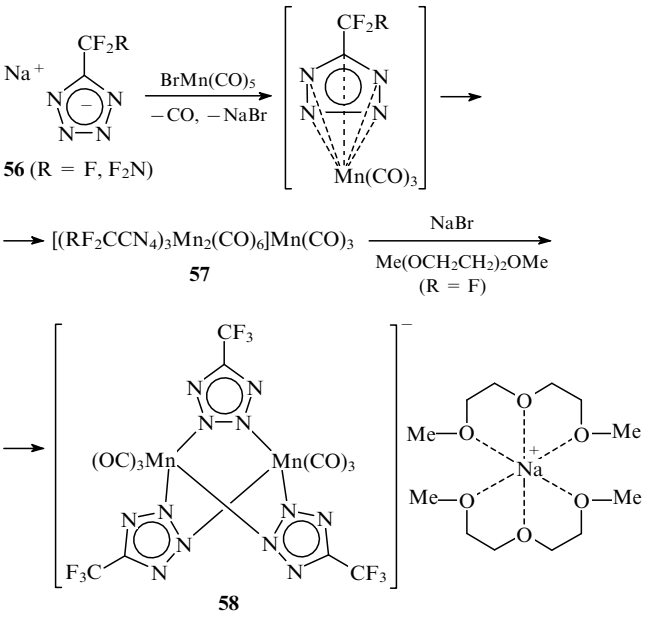


55a,b

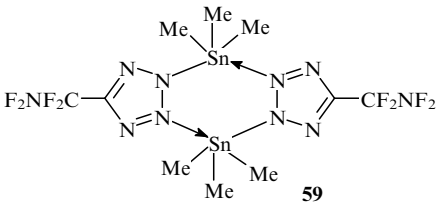
M = Nb, L = 2-(5-phenyltetrazolato) (**a**); M = Ta, L = Cl (**b**).

When sodium 5-perfluoroalkyltetrazolates **56** react with (pentacarbonyl)bromomanganese, the bromide ion and some of the

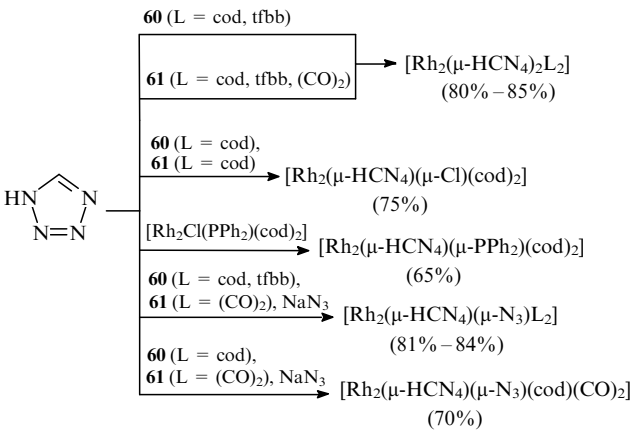
carbon monoxide molecules are substituted. On the basis of IR spectroscopic data, it was assumed that the tetrazolate anion forms a π-complex in solution, which is transformed into σ-complex **57** upon removal of the solvent. Attempts to grow single crystals of the obtained compounds from a diglyme solution in the presence of sodium bromide resulted in ionic complex **58** (for R = F) with the N(2),N(3)-bridging bidentate coordination of the heterocycle (X-ray diffraction data).[75]



A similar bridging bidentate coordination of the tetrazole ring has been proposed on the basis of mass spectrometry and ^{19}F and ^{1}H NMR spectroscopy for complex **59** synthesised by the reaction of silver 5-(difluoroamino)difluoromethyltetrazolate with Me_3SnCl in THF.[65]



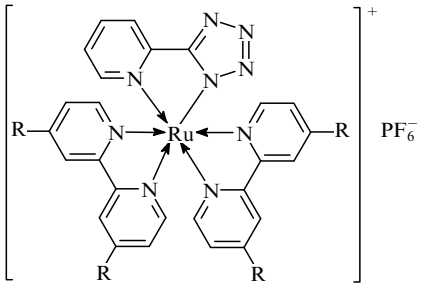
A series of homo- and heterobridged rhodium complexes with the tetrazolate anion and other ligands have been prepared by replacement of the chloride ions or acetylacetone molecules in rhodium diene compounds $[RhCl_2L_2]$ (**60**), [Rh(acac)L] (**61**), *et al.*[76,77]



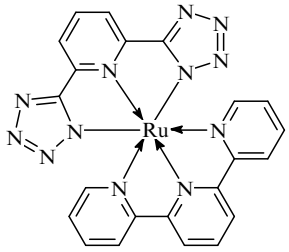
cod is cycloocta-1,5-diene; tfbb is tetrafluorobenzo[5,6]bicyclo-[2.2.2]octa-2,5,7-triene.

These reactions of tetrazole with rhodium compounds readily proceed at room temperature in the presence of triethylamine, and in the case of rhodium acetylacetonate, no base is required. However, in the synthesis of the complex with a bridging diphenylphosphide group, the best results are attained with lithium tetrazolate. The resulting compounds are of interest for the synthesis of trinuclear complexes, for example, $[Rh_3(\mu_3\text{-}HCN_4).(\mu\text{-}Cl)Cl(CO)_6]$, which represent (according to X-ray diffraction data) unusual examples of metal – metal interaction; the tetrazolate anions in these complexes are bound in the tridentate bridging mode.[76]

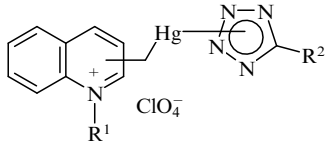
Similarly, the substitution of 5-(2-pyridyl)tetrazole and 2,6-bis(tetrazol-5-yl)pyridine for chlorine in the complexes RuL_2Cl_2 (L is 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine)[51] and $Ru(tpy)Cl_3$ (tpy is 2,2′ : 6′,2″-terpyridine)[78] gave ruthenium-containing tetrazoles **62** and **63** in 55% – 84% yields. The UV-spectroscopic and electrochemical studies have shown that the introduction of a tetrazolyl group having strong σ-donor properties into the $Ru(tpy)Cl_3$ complex results in destabilisation of the ground energy state and decreases the metal oxidation potential.



62 (R = H, Me)



63



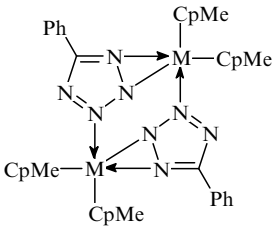
64

R^1 = Me, R^2 = H;
R^1 = Ph: R^2 = H, SMe, $MeSO_2$

This is also accompanied by a decrease in the emission energy and an increase in the luminescence time from 1 to 80 ns.[78]

The 5-R-tetrazolate anion replaces the acetoxy group in 2- and 4-mercuriomethylquinolinium salts. The ^{1}H NMR characteristics of compounds **64** prepared in this way in 76% – 96% yields indicate that only one *N*-isomer is formed in each case; however, the available data are insufficient for assigning the reaction products to either N(1)- or N(2)-isomeric tetrazoles.[24]

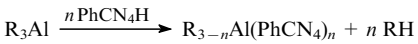
The presence of an active hydrogen atom in 5-substituted tetrazoles accounts for their ability to replace the alkyl and cyclopentadienyl groups in organometallic compounds susceptible to hydrolytic decomposition. For example, 5-phenyltetrazole replaces one methylcyclopentadienyl ligand in $(CpMe)_3M$, where CpMe = η-C_5H_4Me, M = Yb, Er, at room temperature to give binuclear complexes **65** in 60% – 78% yields. According to X-ray diffraction data, the phenyltetrazolate anion in these complexes is coordinated by three nitrogen atoms as a bridging and chelating ligand.[79] Attempts to prepare a similar praseodymium complex failed: complete substitution took place to give the salt $Pr(PhCN_4)_3$. For M = Dy or Gd, the reaction gave crystals of complexes containing, apart from the methylcyclopentadienyl ligand, a cyclopentadienyl ligand, the formation of which was attributed to the presence of a small amount of cyclopentadiene in the starting methylcyclopentadiene.



65

M = Yb, Er.

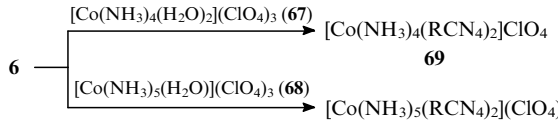
In the case of trialkylaluminium, the reaction smoothly proceeds in toluene and, depending on the reactant ratio, may give the substitution products of the 5-phenyltetrazolate anion for one, two or three alkyl groups, *viz*., compounds **66**.[80]



66

R = Me, n = 1–3; R = Et, Bu^i, n = 1.

Yet another possibility of MT synthesis is provided by displacement of neutral ligands (water, THF, ammonia) from various complexes. Water present as a ligand in cobalt(III) ammine complexes **67** and **68** is bound weaker to the central atom than the ammonia molecules and can be easily replaced by the tetrazolate anion. This underlies the preparation of cobalt(III) tetra- (**69**) and pentaammine (**70**) complexes, which contain a metal-coordinated 5-substituted tetrazole ring.[81–87]



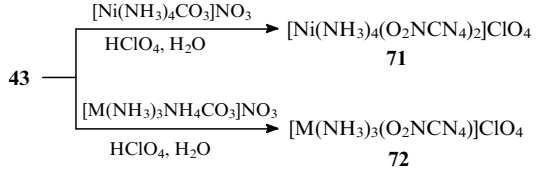
69

70

R = H, Me, NH_2, NO_2, CH_2N_3, $C(NO_2)_3$, $(NNO_2^-)(NH_4^+)$, Ph, 3-$NO_2C_6H_4$,  [X = NH_2, NO_2, N_3, $(NNO_2^-)(NH_4^+)$].

In the case of 5-phenyl-[82] and 5-(3-nitrophenyl)tetrazoles,[85] compounds $[Co_2(NH_3)_8(RCN_4)(H_2O)_2](ClO_4)_5 \cdot n\,H_2O$, where R = Ph, 3-$NO_2C_6H_4$, were isolated in addition to the expected complexes **69**. With microwave heating, 5-phenyltetrazole replaces not only water in complex **67**, but also the ammonia molecule to give compound $[Co(NH_3)_3(PhCN_4)_3]$.[82] More readily available precursors of cobalt(III) aqua ammine complexes, *viz*., tetraamminecarbonatocobalt salts,[81,83,84,86] are often used in these syntheses instead of the Co(III) complexes themselves.

Compounds **71** and **72** [M = Cu(II), Zn(II)] potentially useful as initiating explosives were prepared from similar ammine complexes of other metals.[88]

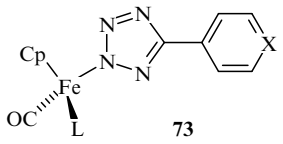


71

72

M = Cu, Zn.

5-(4-Pyridyl)tetrazole[89] and 5-(4-cyanophenyl)tetrazole[90] react with the complexes $[CpFe(CO)L(THF)]CF_3SO_3$ in the presence of triethylamine. They replace the coordinated THF molecule to give compounds **73** containing, according to ^{1}H and ^{13}C NMR spectroscopy, a Fe–N(2) σ-bond.

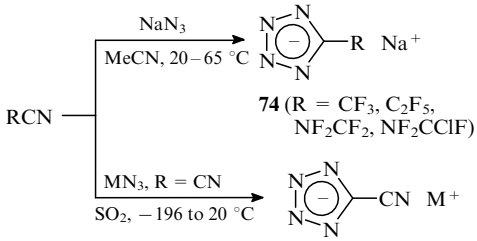


73

L = CO, PPh_3, $P(OMe)_3$; X = N, CCN; Cp = η-C_5H_5.

2. Synthesis of metal derivatives of tetrazoles by heterocyclisation

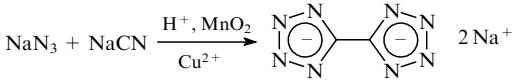
Among heterocyclisation reactions, [3 + 2]-cycloaddition of azides to systems containing C≡N bonds is most significant for the synthesis of tetrazoles.[1–3,10] This method allows one to prepare both 5-substituted tetrazoles and their metal derivatives.[91] The starting compounds include nitriles and organic or inorganic azides, in particular, sodium or ammonium azide prepared *in situ*. Sodium azide, like other alkali metal azides, is less reactive than ammonium azide and reacts only with activated nitriles containing electron-withdrawing substituents. The reaction occurs smoothly at room temperature or on moderate heating to give 5-R-tetrazolates **74**[65,75,92] and **75**[93] in quantitative yields.



74 (R = CF_3, C_2F_5, NF_2CF_2, NF_2CClF)

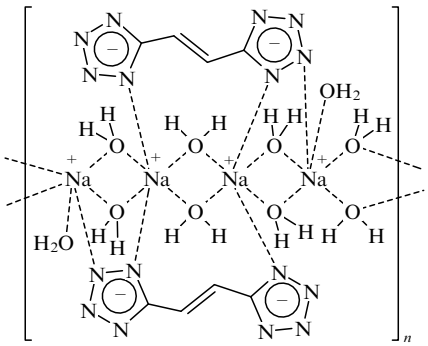
75 (M = K, Cs)

Salt **47** containing a paramagnetic anion has been obtained in a somewhat lower yield (77%) by treatment of the appropriate nitrile with a mixture of sodium azide and ammonium chloride in DMF.[70] An attempt to prepare caesium 5,5′-bitetrazolate from dicyanogen and excess caesium azide was unsuccessful.[93] 5,5′-Bitetrazole salts, in particular, sodium salt **76**, can be synthesised by the reaction of sodium cyanide and azide with manganese dioxide in the presence of copper(II) salts.[13]



76 (65%)

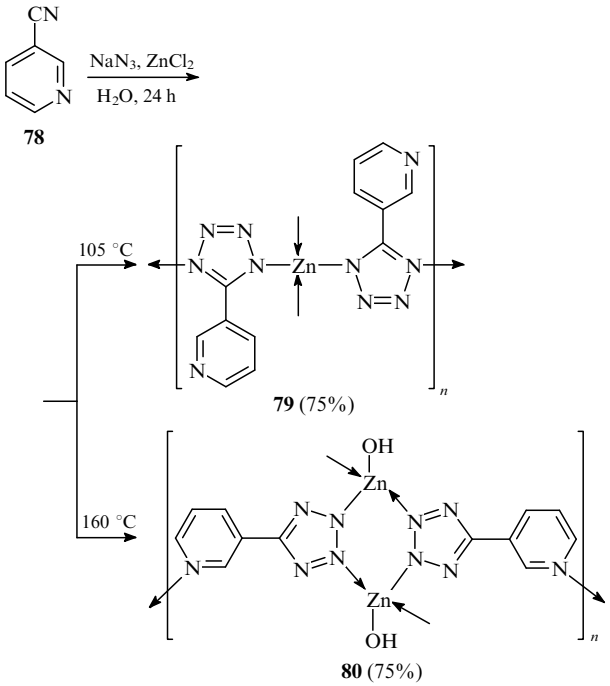
Under hydrothermal conditions (water, 130 °C), dicyanoethylene reacts with sodium azide in the presence of zinc chloride and sodium hydroxide[94] to give the sodium salt of *trans*-1,2-di(tetrazol-5-yl)ethylene (**77**) (yield 35%). According to X-ray diffraction, salt **77** is a one-dimensional coordination polymer in the crystalline state.



77

In this synthesis, zinc chloride acts as a catalyst of cycloaddition, which is typical of Lewis acids. This route is suitable for the preparation of complexes of some other metals.[95–107]

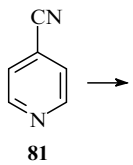
The synthesis of MT from cyanopyridine isomers has been studied rather comprehensively. Depending on the temperature of the reaction carried out in the presence of zinc chloride, 3-cyanopyridine (**78**) forms zinc 5-(3-pyridyl)tetrazolate (**79**) [95] or hydroxy complex **80**,[96] which are polymeric (according to X-ray diffraction data).

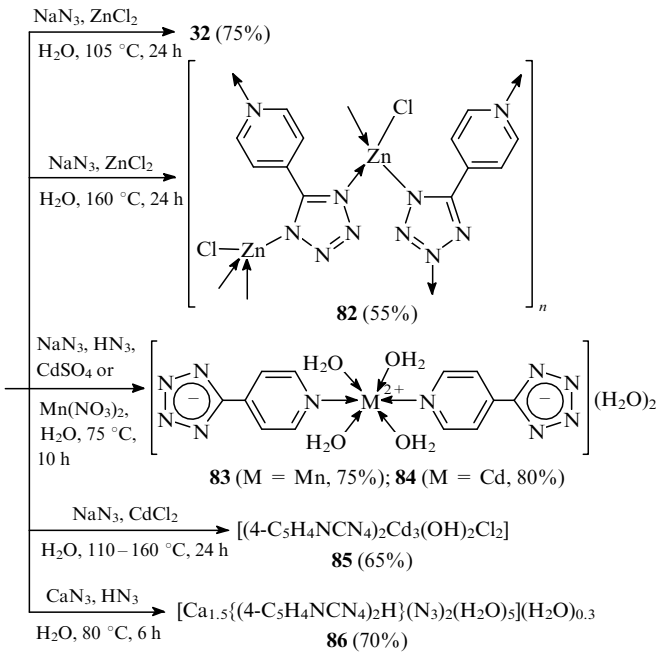


The complex $(3\text{-}C_5H_4NCN_4)CdN_3$ was isolated in 55% yield upon the reaction of nitrile **78** with sodium azide and cadmium chloride in water at 120 °C. According to X-ray diffraction data, the metal atoms in this compound are linked by bidentate azide and tetradentate pyridyltetrazolate [N(1), N(2), N(4) and N(Py) atoms] bridges to form an intricate 3D structure.[96]

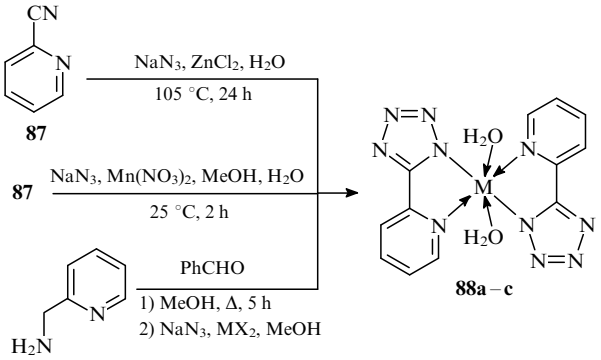
According to this procedure, nitrile **81** was converted into 5-(4-pyridyl)tetrazolate complexes of zinc **32** [95] and **82**,[96] manganese **83**,[97] cadmium **84** [97] and **85** [48] and calcium **86**.[97] Recently, it has been shown in relation to the synthesis of complex **83** that cycloaddition can also be accomplished at room temperature.[98] After a 2-h reaction of 4-cyanopyridine with manganese nitrate and sodium azide in a water–methanol mixture, the yield of complex **83** was 48%.

Complex **85** is a three-dimensional coordination polymer in which each cadmium cation has a nearly square planar environment composed of four anions (two *trans*-Cl^- and two *trans*-HO^-); the other two *trans*-positions are occupied by the nitrogen atoms of two tetrazole ligands. The latter function as tridentate ligands, being coordinated through the N(2), N(3) and N(Py) atoms. This complex has high thermal stability (stable up to 450 °C) and is attractive as a material with light-blue fluorescence and phosphorescence.[48]





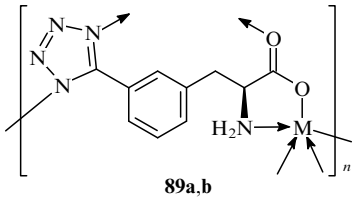
Similarly, 2-cyanopyridine (**87**) has been converted into zinc (**88a**) [95] and manganese (**88b**) [98] 5-(2-pyridyl)tetrazolate dihydrate. Complex **88b** was prepared [like a similar copper(II) derivative **88c**] using a somewhat unusual protocol, *viz*., by refluxing a methanolic solution of 2-aminomethylpyridine and benzaldehyde with subsequent addition of sodium azide and the corresponding metal salts followed by slow evaporation (the yield was 20%). The mononuclear blocks of complexes **88** are linked to one another by hydrogen bonds to form a 2D framework.[99]



M = Zn (**a**, 85%), Mn (**b**, 54%; 20%), Cu (**c**, 15%); X = ClO_4, BF_4.

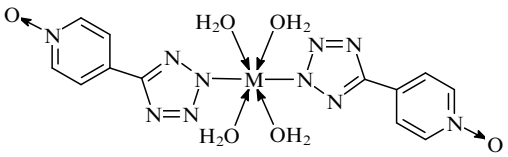
Tetrazolates **89**,[100] **90a**,[101] **90b**,[102] **91** [103] and **92** [104] have been prepared from the appropriate nitriles and metal salts; all these compounds were studied by X-ray diffraction. Complexes **90** are smoothly formed at room temperature in high yields (81%–84%), which is apparently due to good solubility of the starting nitrile in water and the electron-withdrawing properties of the substituent attached to the cyano group. Complex **92** has a high thermal stability (stable up to 345 °C) and is a second harmonics generator 80 times as active as urea.[104]

Dinitriles react with sodium azide in water in different ways. Indeed, in the presence of zinc chloride and 1,10-phenanthroline, 4,5-dicyanoimidazole is converted after 24 h at 160 °C into crystals of one-dimensional polymeric complex of 4,5-di(tetrazol-5-yl)imidazole **93** (yield 53%).[105] Similar treatment of 1,2-

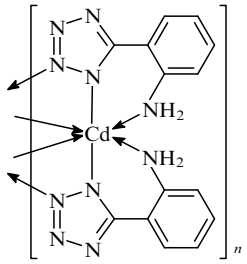


89a,b

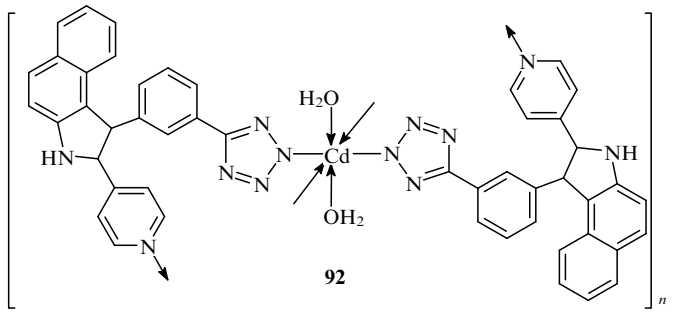
M = Zn (**a**), Cd (**b**).



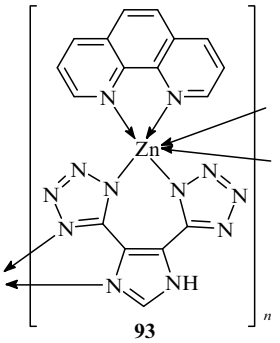
90a,b



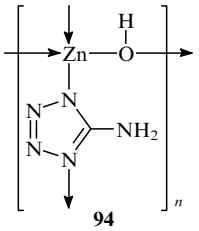
91



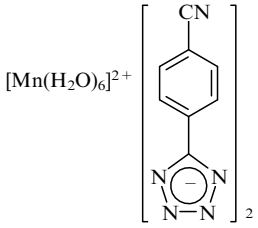
92



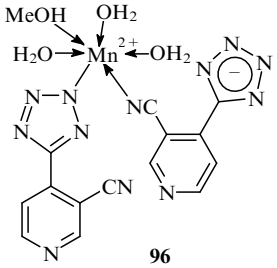
93



94



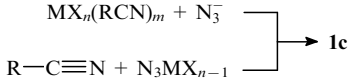
95



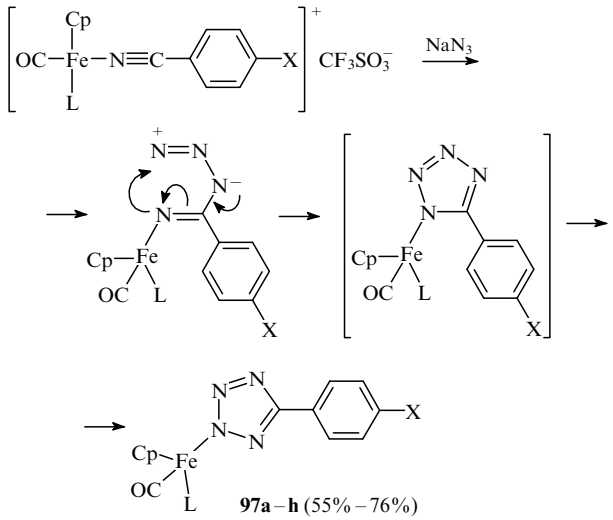
96

dicyanohydrazine is accompanied by cleavage of the N—N bond to give (5-aminotetrazolato)hydroxyzinc (**94**).[106] In the case of terephthalonitrile and 3,4-dicyanopyridine, the reaction in the presence of manganese salts is limited to azidation of only one cyano group to give complexes **95**[107] and **96**[98] in which the tetrazolate anion is not involved in coordination (X-ray diffraction data). A similar structure has been found for some other tetrazole-containing manganese aqua complexes.[46, 97]

Other methods based on cycloaddition of azides to nitriles require introducing the metal into the reaction as a nitrile or azide complex, which somewhat restricts their synthetic scope. However, these approaches are quite efficient in the synthesis of different-ligand metal complexes **1c** in which one of the ligands is represented by 5-substituted tetrazole.[108, 109]



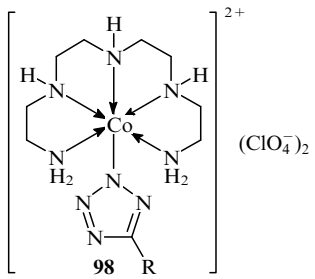
A series of iron(II) complexes of this type **97a**–**h** have been synthesised; high yields are attained at room temperature for several hours.[90, 110] Presumably, the process starts with a nucleophilic attack by the azide ion on the nitrile carbon atom to give the N(1) derivative, which is rapidly converted in the N(2)-isomer.[110] Despite the excess of sodium azide, in the case of binuclear nitrile complexes, the reaction stops after the formation of monotetrazole derivatives **97f**–**h**.[90] The coordination to the N(2) atom of the tetrazole ring in these products was confirmed by X-ray diffraction data for complex **97c** and by similarity of the spectroscopic (^{1}H and ^{13}C NMR) characteristics to those of other complexes **97**.[110]



97a–**h** (55%–76%)

X = CN: L = CO (**a**), PPh_3 (**b**), $P(OMe)_3$ (**c**), 2,6-$Me_2C_6H_3CN$ (**d**);
X = NO_2: L = $P(OMe)_3$ (**e**); X = $CNFeCp(L)(CO)^+CF_3SO_3^-$:
L = CO (**f**), PPh_3 (**g**), $P(OMe)_3$ (**h**).

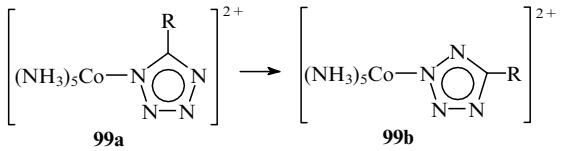
On the basis of kinetic studies, a similar mechanism has been proposed also for the formation of cobalt(III) complexes **98** from the nitrile complexes and sodium azide.[111]



98

R = Me, Ph.

The kinetics and mechanism of isomerisation have been studied in substantial detail for *N*-coordinated pentaamminocobalt(III) 5-R-tetrazolates **99a**,**b**.[112–115] The isomerisation is due to higher thermodynamic stability of N(2)-coordinated complexes compared to the 1-isomers. This is indicated, in particular, by quantum chemical calculations for silver(I) 5-chlorotetrazolate complexes.[116]

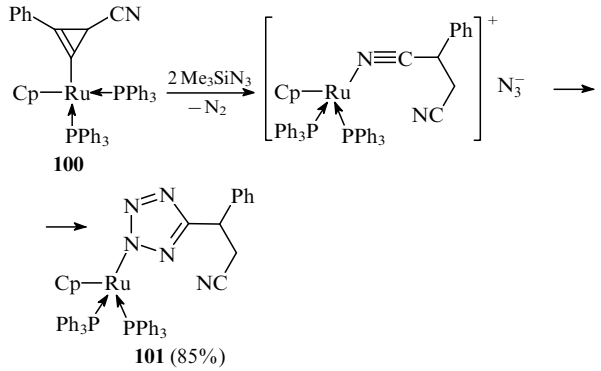


99a **99b**

R = Me, Ar.

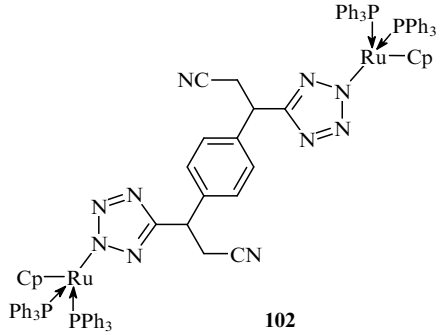
The cycloaddition of the azide ion to nitrile complexes prepared by N-cyanation of histidine has been used to introduce Mn(II)-,[117] Fe(II)- [118] and Fe(III)-coordinated [119] tetrazolyl group into myoglobine derivatives.

Complex-type tetrazolates can be synthesised not only from coordinated nitriles, but also from their synthetic precursors. Recently, it has been found [120,121] that the reaction of cyclopropenyl complex **100** with an excess of trimethylsilyl azide yields ruthenium(II) tetrazolate complex **101**. A ruthenium nitrile complex is formed as an intermediate in this reaction.



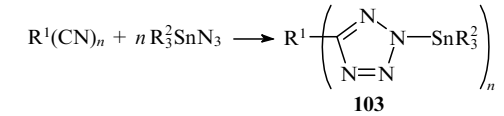
100 **101** (85%)

Bis-tetrazolate complex **102** was prepared in a similar way from the corresponding binuclear ruthenium complex.[122] Coordination by the N(2) atom of the tetrazole ring has been proposed for compounds **101** and **102** on the basis of X-ray diffraction data.[121]



102

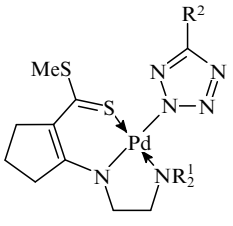
Reactions of metal azide complexes are often used for the synthesis of MT. In recent years, the addition of organic derivatives of stannyl azides to nitriles, resulting in tetrazoles with an organotin substituent at N(2), has been studied in detail. Researchers focused the attention on the use of this reaction for the synthesis of bis-, tris- and tetrakis- and functionally substituted 2-(trialkylstannyl)tetrazoles **103**.[58,123–130] Note that the compounds synthesised have a fairly complex structure in the crystalline state due to coordination of different nitrogen atoms of the heterocycle to the metal, as followed from X-ray diffraction data for compounds of this series.[58,126–130]



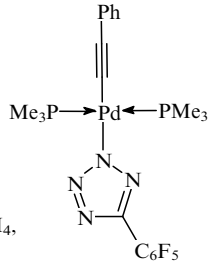
103

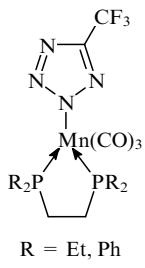
R^1	R^2	*n*	Yield (%)	Ref.
$Ph_2P(CH_2)_m$ (*m* = 3, 4, 7)	Bu	1	–	123
$Ph_3Sn(CH_2)_m$ (*m* = 2, 3)	Bu	1	97–100	124
Ph	Bu	1	80	125
2-MeC_6H_4	Bu	1	100	58
2-$Ph_2PC_6H_4$	Et, Bu	1	–	123
1*H*-Indol-3-yl	Bu	1	60	125
1*H*-Indol-3-yl(phenyl)-methyl	Bu	1	60	125
2-, 3-, 4-Py	Et, Bu	1	47–88	126
CH_2	Me, Pr^i, Bu	2	22–45	127
$(CH_2)_m$ (*m* = 2, 4, 5, 6)	Bu	2	13–65	127
$(CH_2)_4$	Et	2	62	127
1,2-C_6H_4	Me, Pr^i, Bu	2	48–63	128
1,3-C_6H_4	Et, Bu	2	68–77	128
1,4-C_6H_4	Pr^i, Bu	2	33–70	128
$[2\text{-}C_6H_4O(CH_2)_2]_2O$	Bu	2	98	126
$O_2NC(CH_2CH_2)_3$	Me, Et, Bu	3	42–63	129
1,3,5-C_6H_3	Me, Et, Bu	3	52–70	129
$CHCH_2CH$	Et, Bu	4	24–80	129
$C(CH_2CH_2)_2$	Et, Bu	4	68–70	130
1,2,4,5-C_6H_2	Et, Bu	4	30–56	130

The same method was used to prepare complex palladium(II),[131–133] manganese(II),[134] ruthenium(II),[135] platinum(II) [136] and thallium(III) [21] 5-R-tetrazolates shown below.

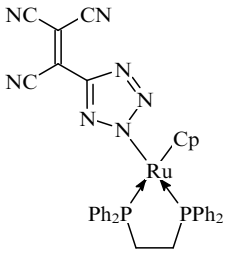


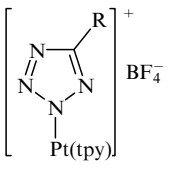
R^1 = H, Me, Et;
R^2 = Me, Et, Ph, 4-$O_2NC_6H_4$, 4-$MeOC_6H_4$, 4-ClC_6H_4



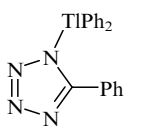


R = Et, Ph



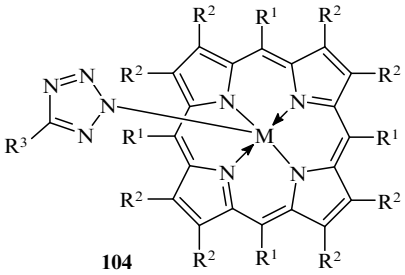


R = Me, Ph



Mixed tetrazolate complexes **104** with 2,3,7,8,12,13,17,18-octaethyl- and 5,10,15,20-tetraarylporphyrin anions as ligands

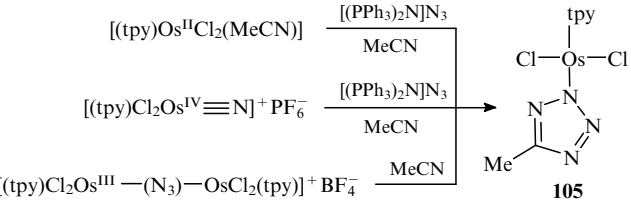
have been prepared by cycloaddition of azide complexes to nitriles.



104

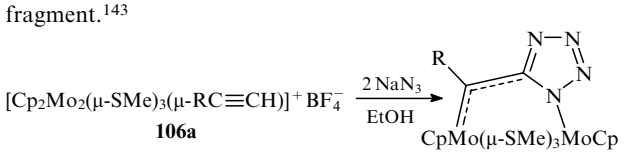
M	R^1	R^2	R^3	Yield (%)	Ref.
Mn	Ph	H	Et, Ph, CH=CH_2, CH=CH−CN	31–77	137
Fe	H	Et	Me, Et, Ph, 3-MeC_6H_4, 4-MeC_6H_4	46–75	138
Fe	2,4,6-$Me_3C_6H_2$	H	Me, Ph	55–60	138
In	H	Et	Me, Et, Ph, 4-$O_2NC_6H_4$	55–88	139
In	Ph, 4-$CF_3C_6H_4$	H	Me, Et, Ph, 4-$O_2NC_6H_4$	32–65	139

The first Os(III) tetrazolate complex **105** was prepared from terpyridine-stabilised complexes of osmium in different oxidation states using three methods. X-Ray diffraction data confirm the *trans*-geometry of the complex compound, the N(2)-coordination of the 5-methyltetrazolate anion and coplanarity of the tetrazole ring and terpyridine.[140–142]



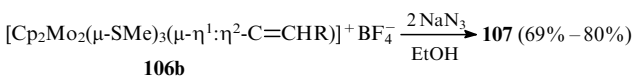
105

Organometallic compounds containing alkyne and vinylidene fragments can also be used as the starting compounds in the synthesis of tetrazolate complexes by cycloaddition. On treatment of molybdenum complexes **106a**,**b** with sodium azide at room temperature, complexes **107** were isolated as the major products. Presumably, the reaction proceeds through the intermediate coordination of azides and nitriles to the metal and intramolecular 1,3-dipolar cycloaddition. According to X-ray diffraction data, complex **107** (R = Ph) contains two cluster molybdenum atoms [the Mo−Mo bond length is 2.7913(6) Å], one being bonded to the heterocycle N(1) atom, while the other, to the α-carbon atom; substantial electron delocalisation occurs in the Mo−C−C(5) fragment.[143]



106a **107** (61%)

R = Ph;



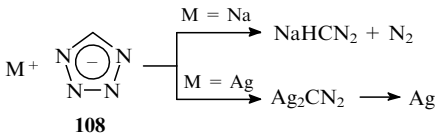
106b

R = Pr, C(Me)=CH_2, Ph, MeC_6H_4.

3. Physicochemical properties and chemical transformations

Salts of 5-substituted tetrazoles are rather stable compounds; however, some of them are known to be sensitive to mechanical impact or heating. The sensitivity of these salts is mainly determined by the nature of the substituent at C(5) in the tetrazole ring and the nature of the cation. Electron-withdrawing substituents increase the N(1)−N(2) bond polarity and hence decrease the thermal stability of the heterocycle.[144] Tetrazole salts with alkali and alkaline earth metal cations are rather stable. Lithium tetrazolate melts at 318 °C, and sodium and potassium tetrazolates melt at 284 and 228 °C, respectively. Calcium tetrazolate melts at 282 °C, whereas analogous strontium and barium salts explode (before melting) at 374 and 344 °C, respectively.[20] Metal tetrazole derivatives stable up to 400–450 °C are also known.[100]

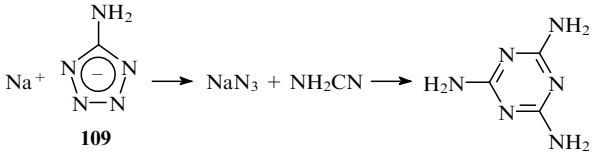
Sodium tetrazolate monohydrate undergoes a polymorphic transformation after dehydration at 192 °C, melts at 284 °C and decomposes with explosion above 323 °C. Decomposition is accompanied by nitrogen evolution to give sodium hydrocyanamide.[17] Silver tetrazolate (**108**, M = Ag) decomposes at 224 °C with heat evolution to give silver cyanamide, which also decomposes at 600 °C to give metallic silver.[38]



108

Study of the combustion of mixtures of tetrazole with alkali and alkaline earth metal tetrazolates resulted in the discovery of new types of combustion, *viz*., liquid-flame[19,145–147] and layer-by-layer combustion,[147] which are distinguished by a high self-organisation level and a number of specific features. This opens up prospects for the design of new types of non-expendable gas generants and for the development of self-propagating high-temperature synthesis techniques in combustion waves.

A different fragmentation pathway is observed for 5-substituted tetrazole salts. For example, sodium 5-aminotetrazolate (**109**) decomposes to give sodium azide and cyanamide in the first stage (290–460 °C). Secondary reactions include decomposition of sodium azide with nitrogen evolution and cyclotrimerisation of cyanamide to give melamine and its condensation products.[22] A similar mechanism is observed in the first stage of thermal decomposition of PVT sodium salt (**7**), which takes place at 340–400 °C with heat evolution and gives rise to polyacrylonitrile and sodium azide.[28]

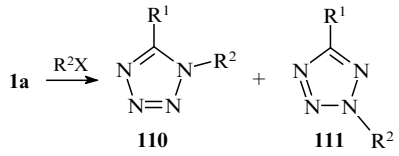


109

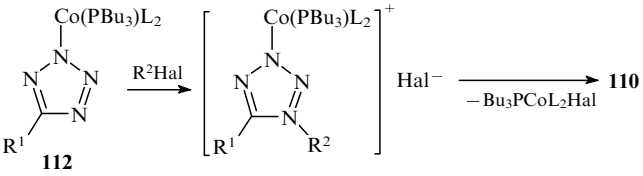
Complex tetrazolates and some salts of 5-substituted tetrazoles are promising as initiating explosives (IE) and serve as components of gas generating compositions (see Section V); therefore, their thermal transformations have been studied rather comprehensively. The mechanism of thermal decomposition giving condensed or gaseous products depends appreciably on the conditions of thermolysis, the nature of the metal and the reactivity of gaseous products.[31,32,37,69,86,88,148]

Among the chemical transformations of metal derivatives of 5-substituted tetrazoles, N-alkylation reactions have a high practical value, because they underlie the most facile and general method for the synthesis of *N*-substituted tetrazoles.[1–3] The use of 5-substituted tetrazole salts in the synthesis of *N*-mono- and *C*,*N*-disubstituted tetrazoles by alkylation is more expedient than the use of neutral 5-substituted tetrazoles. This is due to higher nucleophilicity of the tetrazole ring in tetrazole salts resulting from their ionic structure. The mainly ionic type of the metal–tetrazole bond follows from X-ray diffraction data obtained in recent years for alkali and alkaline earth metal tetrazolates.[29,69,70,93,149–152] A distinctive feature of the structure of these salts is a symmetric structure of the tetrazole ring in which the C−N(1) and N(1)−N(2) bond lengths are equal to C−N(4) and N(3)−N(4) bond lengths, respectively. This structure of the

heterocycle accounts for the high aromaticity of the tetrazolate anion (which is the highest among the tetrazoles); therefore, the nature of the cation has an insignificant influence on the selectivity of alkylation of metal tetrazolates and, in most cases, a mixture of 1- and 2-substituted tetrazoles **110** and **111** is formed. The product ratio is mainly determined by the electronic and spatial structure of the R^1 substituent at the C atom.

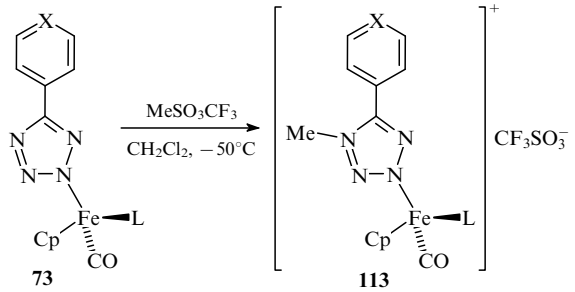


A more pronounced influence of the nature of the metal should be expected for salts and complexes of p- or d-elements with a covalent bond between the metal and the ring nitrogen atom. Indeed, the selectivity of alkylation of cobalt(III) 5-R-tetrazolate complexes **112** in which the tetrazole ring is bound to the metal through the N(2) atom (X-ray diffraction data) differs sharply from the selectivity of alkylation of alkali metal tetrazolates. In the former case, only 1,5-disubstituted tetrazoles **110** without any isomeric tetrazoles **111** were found among the reaction products with alkyl halides in chloroform and nitrobenzene at 36–57 °C. A ^{1}H NMR study of the alkylation kinetics has shown that the reaction occurs in two stages *via* a 1,5-disubstituted tetrazole complex.[153]



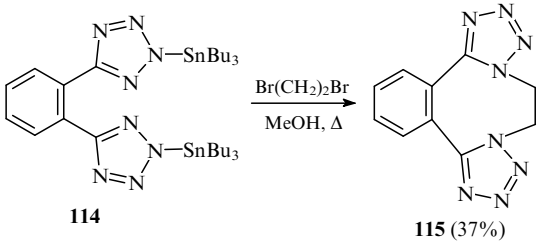
R^1 = Me, $PhCH_2$, Ph, CF_3, 4-FC_6H_4, 3-FC_6H_4; R^2 = Me, $PhCH_2$; L = HONC(Me) = C(Me)NO.

The alkylation of iron(II) complexes **73** also proceeds selectively. At lower temperatures, the process ends in the formation of complexes of 1,5-disubstituted tetrazoles **113** isolated from the reaction mixture in high yields (67%–98%).[89, 90, 110]

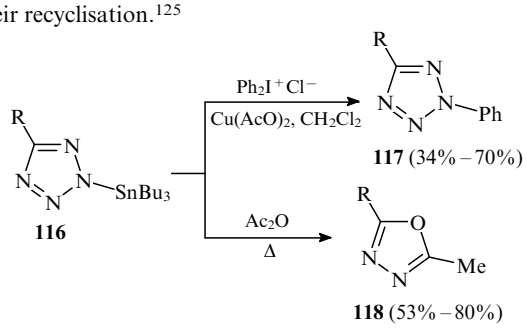


X = CCN: L = CO, PPh_3, $P(OMe)_3$; X = N, L = CO; X = $CCNFeCpL(CO)^+CF_3SO_3^-$: L = PPh_3, $P(OMe)_3$.

Several examples of alkylation of complex tetrazolates used for the synthesis of *N*-substituted tetrazoles has been described.[69, 121] However, the selectivity of these reactions has not been discussed. The alkylation of 5-substituted 2-(tributylstannyl)tetrazoles has been studied in more detail. Methylation of these compounds with some reagents is selective and gives 1,5-disubstituted tetrazoles.[1, 2] However, in the case of other alkylating reagents, mixtures of 1- and 2-substituted tetrazoles have been obtained. This behaviour of stannyl derivatives is attributed to different degrees of their association in solutions. In recent years, alkylation of stannyltetrazoles has been employed for the synthesis of poorly accessible disubstituted tetrazoles. Thus the reaction of *o*-phenylenedi(2-tributylstannyltetrazole) (**114**) with an excess of 1,2-dibromoethane in methanol resulted in cyclophane **115**.[154] In dibromoethane, alkylation of tetrazole **114** is accompanied by dehydrohalogenation to give *N*-vinyltetrazoles.[155]



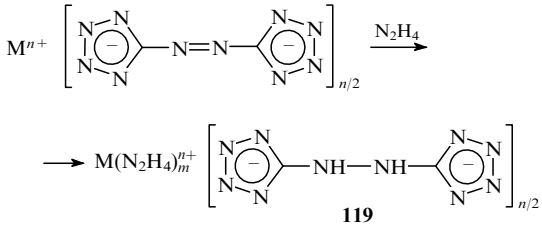
Arylation of 2-tributylstannyltetrazoles **116** with diphenyliodonium chloride at room temperature afforded 5-aryl- and 5-hetaryl-2-phenyltetrazoles **117**.[156] The reaction was selective unlike a similar reaction of sodium 5-phenyltetrazolate in which approximately equal amounts of 1,5- and 2,5-diphenyltetrazoles are formed.[23] On refluxing with acetic anhydride, tetrazoles **116** are converted into 2-R-5-methyl-1,3,4-oxadiazoles **118**. The reaction proceeds apparently with formation of *N*-acyltetrazoles and their recyclisation.[125]



117: R = Ph, 4-MeC_6H_4, 4-BrC_6H_4, 1*H*-indol-3-yl, 1*H*-indol-3-ylmethyl; **118**: R = Ph, 1-acetylindol-3-yl, 1*H*-indol-3-yl(phenyl)methyl.

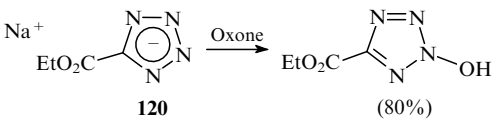
Most complexes and salts of 5-substituted tetrazoles are sensitive to the action of acids. Upon the reaction with an equimolar amount of acids under mild conditions, N(2)-coordinated ruthenium(II) **100**[121] and iron(II) **73**[89, 90, 110] complexes are protonated at the N(4) atom of the heterocycle. Under more drastic conditions, this type of compounds are destroyed to give tetrazoles **6**, which is used for the synthesis of the latter.[1–3, 10, 98, 157–162]

The behaviour of MT towards oxidising and reducing agents has not been systematically studied. However, the tetrazolate anion is known to be stable against these reagents, only substituents being affected. Thus upon dissolution in hydrazine, alkali and alkaline earth metal 5,5′-azoditetrazolates are reduced to give 5,5′-hydrazoditetrazolates **119**.[152]



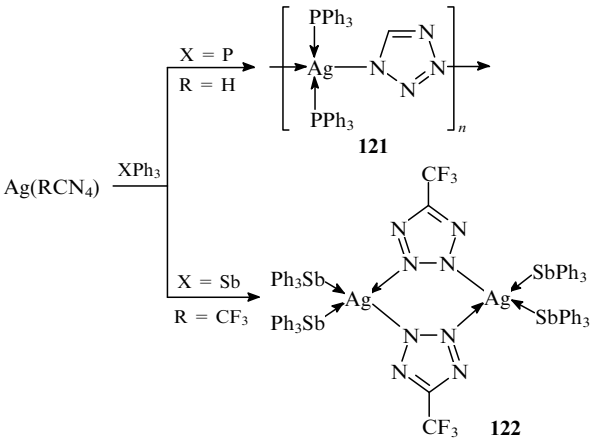
M = Li, Na, Ba; *n* = 1, 2.

The action of oxone ($2\,KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) on sodium 5-(ethoxycarbonyl)tetrazole **120** allows a hydroxyl group to be introduced into the heterocycle at N(2) position.[163]

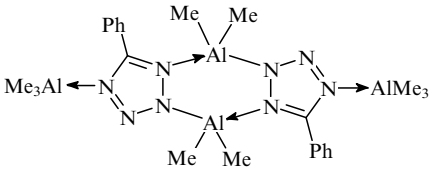


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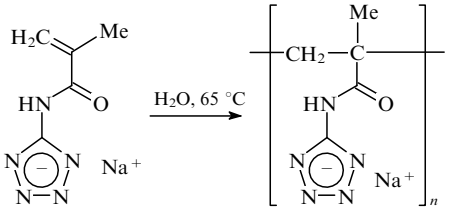
Other known transformations of this type of MT have been used to prepare bi- and polynuclear metal-containing tetrazoles the structures of which were determined by X-ray diffraction analysis. Silver tetrazolates react with triphenylphosphine in dichloromethane to give polymeric complex **121** through bridging N(1),N(3)-coordination of the heterocycle.[73] Silver 5-trifluoromethyltetrazolate reacts with triphenylantimony in acetone to give binuclear complex **122** with the N(2),N(3)-coordination of the heterocycle.[65]



Mono- and dimethylaluminium 5-phenyltetrazolates **66** (R = Me; n = 1, 2) react with trimethylaluminium to give bi- and tetranuclear complexes $[(PhCN_4)_2AlMe-AlMe_3]$ and compounds **123**, respectively.[80]



Worthy of note is also radical polymerisation of sodium 5-(methacrylamido)tetrazole (**124**) to give polymer **125**. Copolymerisation of this salt with 0.08 mol.% of *N*,*N*′-methylenebis(acrylamide) affords a polymeric gel absorbing up to 200 g of water per gram.[18]



124 **125**

III. Metal derivatives of neutral *N*-substituted tetrazoles

The introduction of an *N*-substituent into the tetrazole ring, instead of the hydrogen atom capable of migration (prototropy) and dissociation, gives rise to two isomeric *N*-substituted tetrazoles **110** and **111**,[1–3] which behave as weak bases ($-pK_{BH^+}$ = 2–4); note that 1-substituted tetrazoles are much more basic than the 2-isomers.[164] In these compounds, the N(4) atom is the most basic; however, the sequences of variation of the proton affinity (according to quantum-chemical calculations) are different: N(4) > N(3) > N(2) > N(1) for 1-substituted tetrazoles; N(4) > N(1) > N(3) > N(2) for 2-isomers.[165, 166]

In early studies, complexes of 1-substituted tetrazoles have been prepared by procedures based on the use of non-aqueous solvents and forced removal of water from the starting salt hydrates.[4, 5] Only in the 1980s, did publications appear (see, for example, Ref. 4) describing the synthesis of transition metal complexes with *N*-substituted tetrazoles directly from metal salt hydrates in organic solvents, their mixtures with water and even in water. The solvent is selected considering its electron-donating activity, the ability to dissolve the reactants and precipitate or function as a crystallisation medium for the final product. Most often, the complex is isolated by partial concentration of the reaction mixture, its storage for a certain period of time or cooling. In most cases, the reactions of 1-substituted tetrazoles in weakly coordinating solvents (alcohols, acetone, diethyl ether, acetonitrile, *etc.*) smoothly proceed at room temperature to give solid complexes.

2-Substituted tetrazoles are more sensitive to the conditions under which the complex formation is carried out, in particular, to the presence of water in the reaction mixture.[167, 168] In addition, the formation of solid complexes of 2-substituted tetrazoles is prevented by their high solubility. Therefore, high concentrations of components and dry solvents are required to obtain such complexes (although in some cases, the presence of a minor amount of water is allowed). In some cases, the reaction mixture must be heated and then concentrated. Many *N*-substituted tetrazoles are liquids, which allows preparing complex-type compounds by the reaction of the starting components without a solvent.

Complexes of 1-substituted tetrazoles **110** (R^1 = H) have been studied in most detail, first of all, due to the discovery, for these derivatives, of spin transitions accompanied by thermo- and photochromism (Fe^{2+} complexes) and ferromagnetic ordering of the electron spins (Cu^{2+} compounds). More than a hundred complex-type compounds have been prepared and characterised; their compositions vary over a broad range, being mainly dependent on the nature of the metal cation and the counter-ion (Table 1). In some cases, the compositions of the complexes formed are affected by the starting reactant ratio, the solvent, and the nature and the size of the substituent in 1-substituted tetrazole. For example, metal (Cu^{2+}, Co^{2+}, Ni^{2+}) chlorides and 1-alkyl-, 1-vinyl- and 1-allyltetrazoles form the ML_2Cl_2 complexes irrespective of the reactant ratio. Copper(II) bromide and thiocyanate behave in a similar way. In the case of weakly coordinating anions (BF_4^-, ClO_4^-, PF_6^-, *etc.*), the greatest number of coordinated ligands corresponds to the formula ML_6X_2 (M = Zn, Fe, Cu, Co, Ni). Metal nitrates occupy an intermediate position, being capable of forming compounds with a MX_n : L ratio of 1 : 2, 1 : 3, 1 : 4 and 1 : 6. For 1-substituted tetrazoles containing bulky substituents (Bu^t, Ph, Mes, 3-Cl-4-FC_6H_3), complexes with a smaller number of coordinated tetrazoles, in particular, equimolar complexes, $CuLCl_2$, $CuL(BF_4)_2$, have been isolated. In some cases (for L = 1-propyl-, 1-chloroethyl- or 1-phenyltetrazole), during the growth of single crystals, additional uncoordinated tetrazole molecules were incorporated in the crystals.

2-Substituted tetrazoles **111** (R^1 = H) behave in complexation reactions in a different way. It has been shown in relation to 2-alkyltetrazoles and copper(II) chloride that, depending on the reactant ratio, the resulting complexes may be described as $CuLCl_2$, CuL_2Cl_2 or $Cu_3L_4Cl_6$ (Table 2), the last-mentioned complexes being also formed during recrystallisation of CuL_2Cl_2 or during their synthesis with low reactant concentrations. The greatest number of coordinated 2-substituted tetrazole molecules is four in the case of copper(II) tetrafluoroborate or two with the nitrate.

Table 1. Complexes ML_nX_2 prepared by the reaction of 1-R-tetrazoles (L) with metal salts MX_2.

R	Complex composition	Ref.	R	Complex composition	Ref.
n-C_nH_{2n+1} (n = 1–10, 12, 16, 18)	$FeL_6(BF_4)_2$	169, 170	$CH_2=CH-CH_2$	$ML_6(NO_3)_2(H_2O)$ (M = Co, Ni)	195
				CuL_2Cl_2	167, 195, 198
n-C_nH_{2n+1} (n = 1–4, 6, 8)	CuL_2X_2 (X = Cl, NCS)	167			
				$CuL_2(NCS)_2$	167
Me	$FeL_6(BF_4)_2$	171–173		$CuL_2(NO_3)_2$, $CuL_6(NO_3)_2$, $CuL_6(ClO_4)_2$	199
	$FeL_6(ClO_4)_2$	172			
	$FeL_6(PF_6)_2$	174	CH_2CH_2Y (Y = F, Cl, Br, I)	$FeL_6(BF_4)_2$	169
	$FeL_6(CF_3SO_3)_2$	175, 176			
	$NiL_6(CF_3SO_3)_2$	176	CH_2CH_2Y (Y = F, Br, I)	FeL_6X_2 (X = BF_4, ClO_4)	200
	CuL_2Cl_2	177, 178			
	CuL_2Br_2	179	CH_2CH_2Cl	FeL_6X_2 (X = BF_4, ClO_4, PF_6)	201
	$ML_6(BF_4)_2$ (M = Cu, Zn)	180		CuL_2X_2 (X = Cl, Br)	202
Et	$FeL_6(BF_4)_2$	181		CuL_6X_2L (X = BF_4, ClO_4)	203
	$ML_2Cl_2(H_2O)$ (M = Co, Ni)	182		$CuL_2(NO_3)_2$	204
	$CoL_6(NO_3)_2$, $NiL_6(NO_3)_2$,	183		$(CuL_5)_2(CuL_6)[PMo_{12}O_{40}]_2(H_2O)_2$	205
	$CdL_3(NO_3)_2(H_2O)_2$		CH_2CH_2OMe	α-CuL_2Br_2, β-CuL_2Br_2	206
	CuL_2Cl_2	182, 184	$CH_2CH_2N_3$	CuL_2Cl_2	207
	CuL_2Br_2	185	CH_2CH_2Y (Y = CN, Ac)	CuL_2Cl_2	177
	$CuL_2(NO_3)_2$	186			
	$CuL_3(NO_3)_2$	187	CH_2CO_2Et	CuL_2Cl_2	177
Pr	$FeL_6(BF_4)_2$	172, 188, 189	$CH_2CONHNH_2$	$ML_2(ClO_4)_2$ (M = Co, Ni, Cu), $NiL_3(ClO_4)_2$	208
	$FeL_6(ClO_4)_2$	190		ML_2X_2 (M = Zn, Cd); X = NO_3, ClO_4)	209
	$FeL_6(PF_6)_2$	191			
	$FeL_6(CF_3SO_3)_2L_2$	173		PbL_2X_2 (X = NO_3, ClO_4)	210
	$ZnL_6(BF_4)_2$	189	cyclo-C_3H_7	$ML_6(BF_4)_2$ (M = Ni, Cu)	211
n-C_6H_{13}	CuL_2Br_2	185	Ph	$ML_2Cl_2(H_2O)_{0.5}$ (M = Co, Ni)	182
n-C_nH_{2n+1} (n = 8, 12, 18)	$FeL_6(BF_4)_2$	192		$CuLCl_2$, CuL_2X_2 (X = Cl, Br)	182
				$CuL_2Cl_2L_{0.5}$	212
Bu^t	$CuLCl_2$, $CuL_4(BF_4)_2$, $CuL_6(BF_4)_2$	193		$CuL_2(NO_3)_2(H_2O)_2$	182, 213
	CuL_2Cl_2	193, 194		$CuL_n(BF_4)_2$ (n = 2–5)	214
$CH_2=CH$	CoL_2Cl_2, $CuL_4(NO_3)_2(H_2O)$	195		$CuL_5(BF_4)_2$	215
	ML_2Cl_2 (M = Cu, Ni)	40, 195	Mes	CuL_2Cl_2	214, 216
$CH_2=CH$	$CuL_2(NCS)_2$	167		$CuLCl_2$, $CuL_n(BF_4)_2$ (n = 1, 2)	214
$CH_2=CH-CH_2$	CoL_2Cl_2	195–197	3-Cl-4-FC_6H_2	$CuLCl_2$, $CuL_n(BF_4)_2$ (n = 4, 5)	214
	$NiL_2Cl_2(H_2O)$, CuL_2Br_2	195	2-$PyCH_2$	$PdLCl_2(H_2O)_2$	51

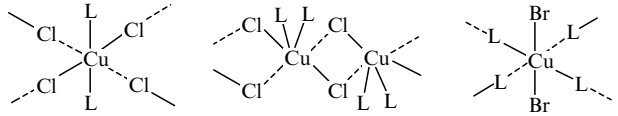
Some syntheses of copper(II) chloride complexes with 2-alkyltetrazoles were accompanied [223] by the formation of tetranuclear oxychloride $Cu_4OL_4Cl_6$ complexes, as a result of hydrolysis of copper chloride and due to high thermodynamic stability of this type of cluster. Such a transformation has also been observed [224] on attempted synthesis of the 1-ethyltetrazole complex with copper(II) bromide carried out by slow concentration of a solution of the reactants in 96% ethanol, which gave single crystals of the $Cu_4OL_4Br_6$ complex.

Table 2. Complexes ML_nX_2 prepared by the reaction of 2-R-tetrazoles (L) with metal salts MX_2.

R	Complex composition	Ref.
n-C_nH_{2n+1} (n = 1–4, 6)	CuL_2X_2 (X = Cl, NCS)	167
n-C_nH_{2n+1} (n = 1–3, 6); Bu^t	$CuLCl_2$	167
Me, Et	$Cu_3L_4Cl_6$	167
Me	CuL_2Cl_2	217
Et	CuL_2Cl_2	218
	$CuL_2(NO_3)_2$	183, 187
	$CuL_4(BF_4)_2$	187
	$ML_2(NO_3)_2(H_2O)_n$ (M = Co, Ni: n = 4; M = Cd; n = 2)	183
Pr	CuL_2Cl_2	219
Bu^t	CuL_nCl_2 (n = 1, 2); $CuL_4(BF_4)_2$	193
	$CuLCl_2$	220
n-C_6H_{13}	$CuLCl_2$	221
$CH_2=CH-CH_2$	$Cu_3L_4Cl_6$	222
	CuL_2Cl_2	219
2-$PyCH_2$	$PdLCl_2$	51

The structures of complexes of *N*-substituted tetrazoles have been studied by spectroscopic techniques and by X-ray diffraction analysis. Most often, 1-substituted tetrazoles are monodentate ligands, complex formation involving the N(4) atom. Hence, the environment of the copper atom in the halide complexes CuL_2X_2, where X = Cl, Br; L is 1-R-tetrazole (R = Me; Et; $CH_2=CHCH_2$; CH_2CHY, Y = Cl, Br, N_3), is completed to a square bipyramid due to contacts with halogen atoms coordinated to the neighbouring copper atom,[179, 182, 184, 185, 195, 202, 207] *i.e.*, halide ions are bridges connecting the CuL_2X_2 fragments into layers (structure **126**). The *trans*-coordinated tetrazole ligands occur in the interlayer space; the size of the substituent in the ligand determines the interlayer spacing. All complexes of copper(II) halides with 1-monosubstituted tetrazoles having such structure are low-temperature ferromagnets.[185, 198, 199, 202, 225] According to electronic and IR spectroscopy, this type of a layered polymeric structure is also characteristic of cobalt(II) and nickel(II) chloride complexes with 1-ethyl- [182] and 1-allyltetrazoles [195], ML_2X_2. Recently,[196] this has been confirmed by X-ray diffraction analysis carried for cobalt 1-allyltetrazole complex.

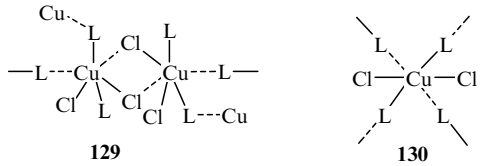
The key difference between the structures of these copper(II) and cobalt(II) complexes is that in the latter compound, the bridging bonds have the same length (2.54 Å), whereas in the copper complex these bonds are markedly dissimilar due to the Jahn–Teller effect (2.30 and 2.99 Å). It was found, however, that the cobalt complex is a weak ferromagnet with $T_N = 102 \pm 1$ K having spontaneous magnetisation of $\sigma_s(5\,K) = 710 \pm 5$ G cm^3 mol^{-1}. In the case of bulky substituents (R = Bu^t, Ph, Mes), the CuL_2Cl_2 complex exists as linear polymeric structure **127** due to chloride bridges, while the tetrazole ligands are coordinated in the *cis*-position.[194, 212, 216]



126 **127** **128**

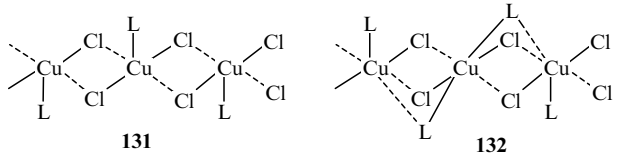
1-(2-Methoxyethyl)tetrazole (**110**, $R^1 = H$, $R^2 = CH_2.CH_2OMe$) shows an unusual ligand behaviour compared to other 1-alkyltetrazoles. It reacts with copper(II) bromide in methanol or ethanol to give two isomeric complexes, α- and β-CuL_2Br_2, which differ substantially in physicochemical properties and structure.[206] The α-form obtained from methanol is a 2D structures **128** in which the copper ions are connected by the N(4),N(2)-bridging tetrazole ligands and the bromide ion is monodentate. In this species, no magnetic interaction occurs between the copper ions. Conversely, the β-form, which crystallises from ethanol, exhibits ferromagnetic properties ($C = 0.41$ cm^3 K mol^{-1}, $J/k_B = 16.4$ K, $\theta = 30.5$ K) and has structure **126**.

A substantial influence of the substituent on the structure of the complex is also observed for 2-substituted tetrazoles. Indeed, complexes Cu(2-R-tetrazole)$_2$Cl$_2$ (R = Me, Et) have a layered polymeric structure **129** joined by bridges formed by some of the chlorine atoms and tetrazole ligands coordinated through the N(4) and N(1) atoms. The second tetrazole ligand is coordinated in the monodentate mode through the N(4) atom.[217, 218] As the substituent bulk increases (R = Pr, $CH_2=CHCH_2$), both tetrazole ligands become bridging and are coordinated by the N(4) and N(1) atoms (structure **130**).[219]



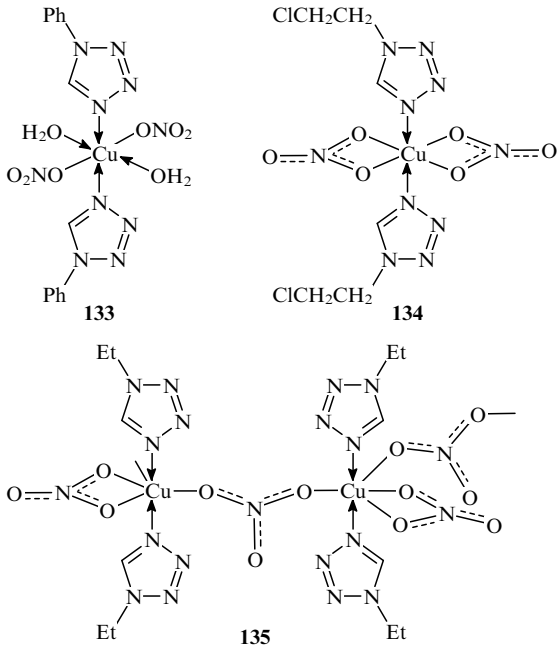
129 **130**

Note that complexes **128**–**130** are the first examples of layered polymeric structures formed by *N*-substituted tetrazoles through two nitrogen atoms of the heterocycle. The complexes $CuLCl_2$ and $Cu_3L_4Cl_6$ are polymeric chains **131** and **132**, respectively, formed owing to the bridging coordination of chlorine atoms;[220–222] in **132**, the neighbouring copper atoms are additionally linked by the tetrazole ring [N(3), N(4) atoms]; hence, a half of the tetrazole ligands in the structure are bridging.[222]



131 **132**

The main feature of the metal nitrate complexes is related to different coordination modes of nitrate anions even in compounds with similar compositions. According to X-ray diffraction data, in three copper(II) complexes, **133**,[213] **134**,[204] **135**,[186] in which 1-substituted tetrazole ligands are coordinated through the N(4) atom and occupy *trans*-positions, the nitrate anions are coordinated as monodentate, bidentate and bridging ligands. Moreover, compound **135** is a 2D coordination polymer. The linear chain packing of mononuclear complexes **134** gives rise to a weak ferromagnetism ($\theta = 0.30$ K and $C = 0.44$ cm^3 K mol^{-1}).



133 **134**

135

No structural data for the thiocyanate or chloride complexes $CuL_2(NCS)_2$ and $CuLCl_2$ (L is 1-substituted tetrazoles) have been reported. The IR and EPR data indicate a bridging type of the Cu–NCS–Cu bond, while in the case of $CuLCl_2$, a bridging coordination of 1-substituted tetrazoles through the N(3) and N(4) atoms is assumed.[167] The salts of bivalent metals (Fe, Ni, Cu, Zn) with weakly coordinated anions (BF_4^-, ClO_4^-) react with an excess of 1-substituted tetrazole to give mononuclear complexes containing MN_6 coordination octahedra. The coordination involves the N(4) atom of the ring. In compounds with fewer coordinated tetrazole molecules, the copper coordination sphere contains anions (according to IR spectroscopic and X-ray diffraction data).[215, 226]

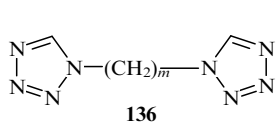
The structures and properties of six-coordinate iron(II) complexes FeL_6X_2 (see Table 1) have been studied in most detail; these compounds possess unique properties related to the extremely high sensitivity of their electronic characteristics to relatively weak impact of temperature, pressure or light with a definite wavelength. This induces easy reversible spin transitions (ST)

$$^1A_1(O_h) \rightleftharpoons {}^5T_2(O_h)$$

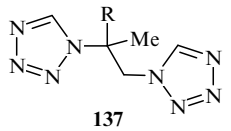
between the ground diamagnetic low-spin (LS, S = 0) and paramagnetic high-spin (HS, S = 2) states the nature of which for iron(II) complexes has been studied in fair detail and considered in reviews[6, 227, 228] and references cited therein. Characteristics of the ST (a broad range of temperatures, 45–200 K, the character and sharpness of transitions, the presence of hysteresis and the width of the hysteresis loop) are determined by structural features of the complexes. Numerous publications describe X-ray diffraction, magnetochemistry, and Mössbauer, EXAFS, photoelectron, FT IR and Raman spectroscopic studies of the structures, physicochemical properties and their variation in the series of related iron(II) complexes and those diluted over broad ranges with isomorphous zinc[229–232] and nickel[233] complexes (Refs 169–176, 181, 188–192, 199, 200, 234–250). It was found that the ST may be accompanied by a structural phase transition, which results in shortening of the Fe–N bond in the coordination polyhedron by ~0.2 Å and distortion of the polyhedron symmetry.[6, 228, 249, 251] Therefore, ST characteristics may be sensitive to the external pressure.[6, 191, 251]

The obtained data suggest that the change in the magnetic and optical properties upon spin transitions in Fe(II) complexes with 1-substituted tetrazoles is largely related to the cooperative mechanism of transfer of the electronic effects and is determined by the efficiency of intermolecular contacts, including hydrogen bonds, π–π and other interatomic interactions between the structural fragments of the compounds. Recent theoretical descriptions of spin transitions for a series of iron(II) complexes with 1-(2-haloethyl)tetrazoles in terms of physical [252] and quasi-chemical [253] models of the intermolecular interactions are in fairly good agreement with experimental data.

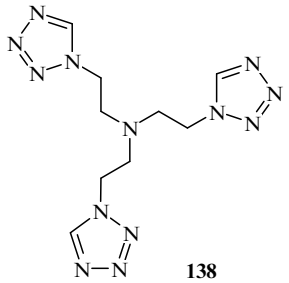
These results have stimulated the research aimed at the development of methods for the synthesis and study of the properties of iron(II) complexes with binuclear monosubstituted tetrazoles, the structure of which could ensure effective cooperative interactions through bridging ligands. A number of recent publications have been devoted to the iron(II) complexes FeL_3X_2, where L is di(tetrazol-1-yl)alkanes **136** ($m = 2$, $X = BF_4$;[254] $m = 4$: $X = ClO_4$,[255] PF_6 [256]) and **137** (R = H, $X = ClO_4$;[257] R = Me, $X = BF_4$).[258] A broader set of these compounds based on tetrazoles **136** ($m = 1-8$, 10, 12) have been described in dissertations.[169, 259] However, it was noted [169] that for $m = 6$, 8, 12, complexes $FeL_3(BF_4)_2$ with a sufficient purity could not be isolated.



136



137

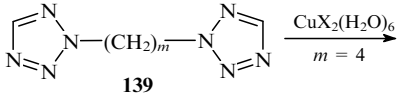


138

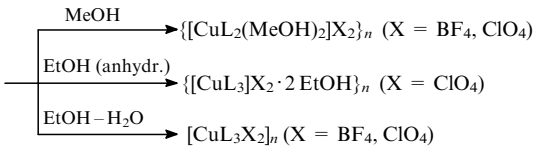
An important feature of iron(II) complexes with bistetrazoles is that they form one- [254, 257] and three-dimensional [255, 256, 259, 260] polymeric structures. This stimulated further investigations into the self-assembly of supramolecular structures and self-organisation of molecules through coordination to transition metal ions. Of special note is the structural, chemical and functional diversity of the resulting objects. A series of 2D polymeric complexes based on tetrazolylamine **138** described as ML_2X_2 (M = Fe, Cu, Co, Zn; $X = BF_4^-$ and M = Fe, Zn; $X = ClO_4^-$) and a series of double compounds $[Cu_{0.01}M_{0.99}L_2](BF_4)_2$ (M = Zn, Fe); $[Fe_xZn_{(1-x)}L_2](BF_4)_2$ ($x = 0.0062-0.970$) [259] have been synthesised and studied. Research into the formation of this type of supramolecular structures is needed to study systematically the mechanism of transfer of electronic effects.[252, 259]

It has been noted [6, 259] that spin transition characteristics depend essentially (apart from the nature of the ligand and counter-ion) on the formation conditions of the crystals of complexes. The investigation of compounds such as $FeL_6(CF_3SO_3)_2 \cdot L_2$ (L is 1-propyltetrazole),[173] $FeL_3(PF_6)_2 \cdot Solv$ [L is **136** ($m = 4$), Solv is 0.5 MeOH or H_2O],[256] $FeL_3X_2 \cdot MeCN$ [L is **136** ($m = 5$), X = BF_4, PF_6] [259] has shown that inclusion of uncoordinated tetrazole or solvent molecules into the structure changes substantially the characteristics of spin transitions.

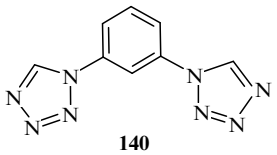
The structures and physicochemical properties of several complexes of other transition metals with bis-tetrazoles similar in composition to iron(II) complexes have been studied, in particular, the complex $CuL_3(ClO_4)_2$ [L is **136** ($m = 2$)],[261] the Ni(II) and Cu(II) complexes with 1,4-di(tetrazol-1-yl)butane (**136**, $m = 4$).[255] The first representatives of coordination polymers based on 2-substituted bis-tetrazoles **139** have been prepared and characterised: one-dimensional $ZnL_3(ClO_4)_2$ complex [L is **139** ($m = 2$)],[168] one- and three-dimensional polymers, $CuL_3(ClO_4)_2$ and $ZnL_3(ClO_4)_2 \cdot 2\,EtOH$ [L is **139** ($m = 3$)],[262] and five copper complexes with 1,4-di(tetrazol-2-yl)butane (**139**, $m = 4$).[263] The synthesis of the last-mentioned compounds shows an essential dependence of the composition and structure of MT on the nature of the solvent used.



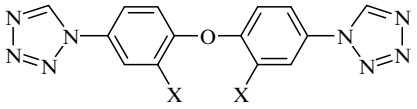
139



Generally, binuclear tetrazoles function most often as bridging ligands and give coordination compounds containing fewer ligands than in the case of mononuclear *N*-substituted tetrazoles. Apart from those mentioned above, a number of such compounds with 1,1′-*m*-phenyleneditetrazole (**140**) have been obtained, in particular, ML_2X_2, where M = Ni, Co, Cu; X = NO_3, ClO_4;[199] CuL_2X_2, where X = NO_3, BF_4, and $CuLCl_2$.[264] An equimolar ratio has also been found for copper(II) chloride complexes with *para*- and *ortho*-isomers of compound **140** [264] and with bis-tetrazoles based on diphenyl ethers **141a–c**.[265]



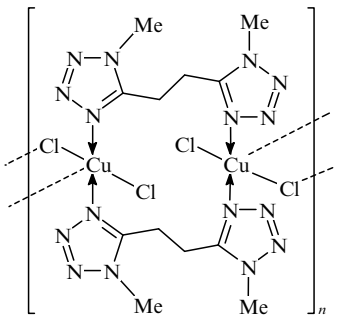
140



141a–c

X = H (**a**), NO_2 (**b**), tetrazol-1-yl (**c**).

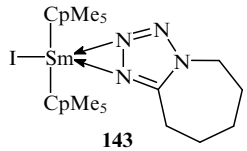
Bis-tetrazole **141c** reacts with copper(II) chloride to give compounds $CuL_{0.5-0.75}Cl_2$ with composition depending on the reactant ratio.[265] It was shown by X-ray diffraction that 1,2-bis(1-methyltetrazol-5-yl)ethane functioning as a bridging ligand with respect to copper(II) chloride forms polymeric complex **142** containing both monodentate and bridging chlorine atoms.[266]



142

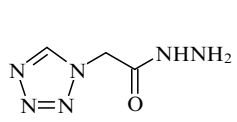
The presence of second substituent in the tetrazole ring (tetrazoles **110**, **111**) and a substituent capable of complexation has a pronounced influence on the compositions and structures of the coordination compounds. Unlike 1-monosubstituted tetrazoles, which form the complexes CuL_2Cl_2 and CuL_6X_2 (X = BF_4, ClO_4) (see Table 1), 1,5-disubstituted tetrazoles form compounds $CuLCl_2$ (see Ref. 177) and CuL_4X_2 (see Ref. 267) under the same conditions. For 1 : 1 complexes, a bidentate bridging tetrazole coordination is assumed, which is in line with the results of quantum-chemical calculations of the proton affinity [165] and

with experimental data on quaternisation,[268] indicating that 1,5-disubstituted tetrazoles contain two clear-cut nucleophilic centres [N(4) and N(3)], coordination through these atoms being energetically favourable.[269] According to X-ray diffraction data,[5] the ligand in $Ag_2L_4(NO_3)_2$, where L is perhydroazepino[1,2-*e*]tetrazole, is coordinated in the bidentate bridging mode, two ligand molecules being coordinated through the N(3) and N(4) atoms, while the other two ligand molecules, through N(4). However, in the polymeric-chain complex $CuLCl_2$, where L is 5,5-dimethyl-5,6-dihydrotetrazolo[5,1-*a*]isoquinoline,[270] as well as in palladium(II) chloride complexes with isomeric 5-vinyl-1(2)-methyltetrazoles,[271,272] only the N(4) atom of the tetrazole ring is involved in coordination (X-ray diffraction data). In the case of steric restrictions (aryl substituent in position 5), palladium chloride forms a bond with the N(3) atom.[273] X-Ray diffraction data have been obtained, indicating that perhydroazepino[1,2-*e*]tetrazole can also function as a bidentate ligand giving formally nine-coordinate complex of samarium(III) **143**.[274]

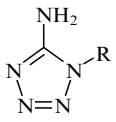


143

N-Substituted tetrazole **144** containing an acetohydrazide group, which can act as a chelating ligand, forms complexes ML_2X_2 with metal nitrates and perchlorates; various types of coordination of this tetrazole to the metal are encountered in the complexes. According to X-ray diffraction data, coordination through the N and O atoms of the acetohydrazide group and the N(4) atom of the tetrazole ring giving linear polymeric chains is found in copper(II)[208] and cadmium(II)[209] perchlorate complexes. IR data indicate that the same coordination mode is also characteristic of zinc(II),[209] nickel(II) and cobalt(II)[208] coordination compounds. In the case of lead(II)[210] and nickel(III)[208] complexes, the interaction occurs only through the hydrazide fragment. It was shown by X-ray diffraction analysis[210] that polymeric chains of the lead nitrate complex are formed due to the tridentate chelating-and-bridging coordination of the nitrate group.



144

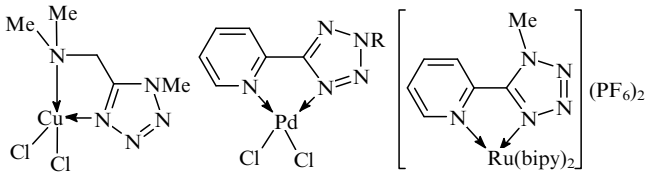


145a–c

R = NH_2 (**a**), Me (**b**), CH_2=CH (**c**).

The amino groups of 1-R-5-aminotetrazoles **145a–c** can also coordinate the metal atom. A number of complexes of these ligands with transition metals have been prepared and studied.[40,84,88,275] It was found[275] that in the compound $NiL_2Cl_2(H_2O)_{0.5}$, where L is tetrazole **145a**, the exchange interaction between the unpaired electrons of the Ni^{2+} ion is ferromagnetic. According to X-ray diffraction data,[276] the complex CuL_2Cl_2 is a 2D coordination polymer in which 1,5-diaminotetrazole functions as a bridging ligand coordinated by the N(4) atom of the ring and the nitrogen atom of the 1-amino group. It is also worth noting that in the octahedral complex $[Co(NH_3)_4L_2]\cdot(ClO_4)_3$ (L is tetrazole **145b**), the monodentate tetrazole ligands are coordinated in different ways, namely, by the N(3) or N(4) atom.[277] Several compounds of this type, *viz*, $[Co(NH_3)_4L_2]\cdot(ClO_4)_3$ and $[Co(NH_3)_5L](ClO_4)_3$ (L are ligands **145a**,**b**[88,278] or perhydroazepino[1,2-*e*]tetrazole),[279] prepared from cobalt ammine complexes **69**, have been reported (see Section II). Their physicochemical properties were studied in detail.[84,88,278,279]

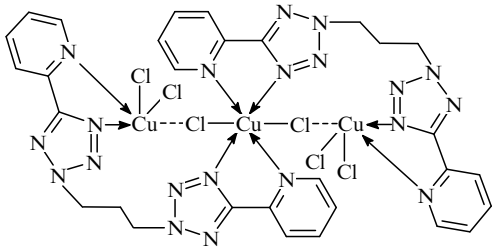
It was shown by X-ray diffraction[280] that 1-methyl-5-dimethylaminotetrazole reacts with copper(II) chloride as a bidentate chelating ligand to give complex **146.** 2-Pyridyltetrazole ligands are also coordinated in the bidentate mode when react (in 1 : 1 ratio) with palladium and ruthenium chlorides to give five-membered metallacycles **147** and **148**, respectively.[51]



146 **147** **148**

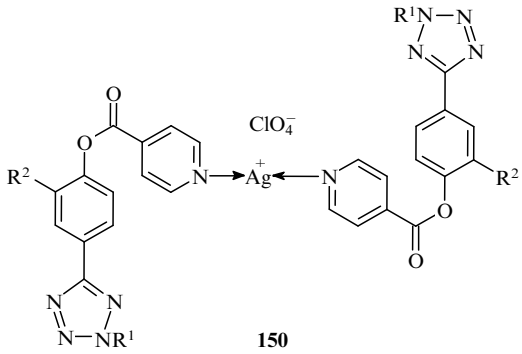
R = Me, Bu^t

A compound with two pyridyltetrazole fragments and copper(II) chloride form a trinuclear linear complex **149** (X-ray diffraction data) in which the ligand occupies a bridging position between two neighbouring copper atoms.[281]



149

In a search for new metal-containing mesogens, complexes of long-chain 2-alkyltetrazoles containing additionally a 4-pyridyl fragment have been synthesised. The coordination in these complexes was found[282] to involve the pyridine nitrogen atom, as for example, in compounds **150**.

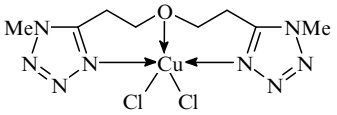


150

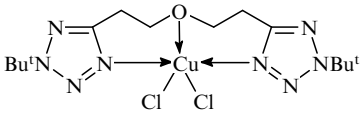
R^1 = Alk; R^2 = H, OMe.

It was shown[282] that only silver complexes **150** (R^1 = n-C_9H_{19}, n-$C_{14}H_{29}$; R^2 = H) exhibit mesomorphic properties, smectic S_A phases arising in the temperature range of 174–204 °C. It is noteworthy that analogous ligands containing no pyridine rings are coordinated through the tetrazole N(4) atom and form palladium(II) complexes giving no liquid-crystalline phases.[283]

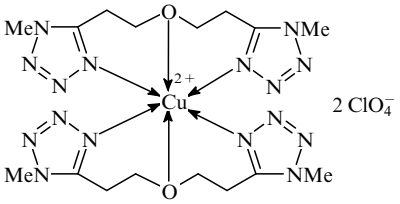
According to X-ray diffraction data,[284,285] in copper(II) complexes **151–153**, the exocyclic oxygen atom also participates in the coordination of the metal ion to binuclear tetrazoles. Note that 1,5-bis(1-methyltetrazol-5-yl)-3-oxapentane isolated as perchlorate reacts with copper(II) chloride to yield complex **151** or **153**, depending on the nature of the solvent. In complex **151**, the intermolecular interactions of the C–H···Cl and C–H···N types are responsible for the formation of infinite one-dimensional chains.[285]



151

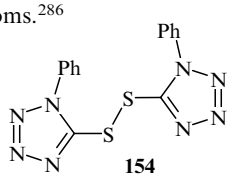


152



153

On the basis of IR spectra of disulfide **154** and the complexes $MO_2L_2Cl_2$ (M = Mo, W; L is compound **154**), it was concluded that the ligands are coordinated through one of the sulfur atoms.[286]

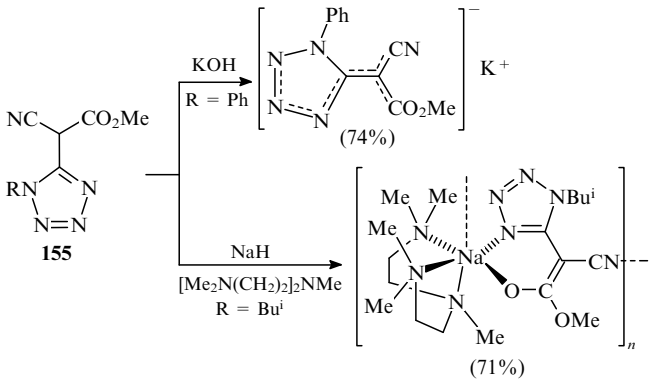


154

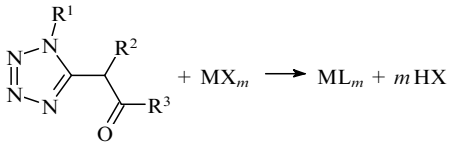
The complex formation of the tetrazole analogues of peptides deltorphin,[287] β-casomorphin,[288] enkephalin[289] and tetraalanine[290] has been studied by potentiometric and spectroscopic methods. The stability constants of the copper(II) complexes formed in aqueous solutions were determined; it was shown that the introduction of a 1,5-tetrazolyl fragment, which mimics the *cis*-amide group, into the peptide gives rise to peptide agents that efficiently chelate copper(II) ions under physiological conditions. The site of introduction of the tetrazolyl fragment into the amino acid residues has a crucial influence on the coordinating ability of the compounds. The obtained data may underlie the simulation of the peptide – metal binding sites.

IV. Metal derivatives of *C*,*N*-substituted tetrazoles generating anionic centres in the substituent

N-Substituted tetrazoles containing electron-withdrawing proton-containing substituents in the 5-position of the ring are capable of tautomeric transformations. They can be deprotonated to give various anionic forms that react with metal cations to give, as a rule, chelate complexes **3**. In recent years, the ways of synthesis of MT of various dimensions based on tetrazole-containing cyanoacetates **155** have been studied in detail. Depending on the nature of reactants and synthesis conditions, these tetrazoles react with alkali metal compounds to give (according to X-ray diffraction data) salts or complexes.[291, 292]



The reactions of these ligands or enol forms of compounds **156** with transition metal salts occur in different ways. By varying the nature of substituents and using metal ions with appropriate coordination properties, one can obtain mono- and binuclear complexes and also polymeric structures of different dimensionality. The composition and dimensionality of the ML_m complexes are presented in Table 3.



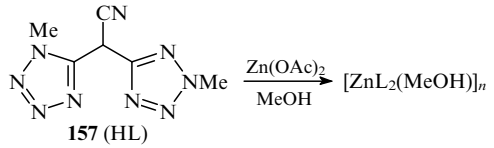
156 (HL)

Table 3. Composition and dimensionality of the complexes ML_m derived from ligand **156**.

R^1	R^3	MX_m	Complex ML_m			Yield (%)	Ref.
			composition	dimensionality	polyhedron		
Et	Ph	$FeCl_3$	FeL_3 [a]		FeN_3O_3	60 – 90	293
Bu^t	Ph	$FeCl_3$	FeL_3 [a]		FeN_3O_3	84 – 89	294
Bu^i	OMe	$FeCl_3$	FeL_3		FeN_3O_3	84 – 89	294
Bu^t	OMe	$Cu(OAc)_2$	$[CuL_2]_n$	1	CuN_4O_2	71	295
Bu^t	Bu^t	$Cu(OAc)_2$	$[CuL_2]_n$	2	CuN_4O_2	86	296
Bu^t	Bu^t	$Cu(OAc)_2$	$[CuL_2]_n$	3	CuN_4O_2	90	297
neo-C_5H_{11}	OMe	$FeCl_3$	FeL_3		FeN_3O_3	–	293
neo-C_5H_{11}	OMe	$FeSO_4$	$[FeL_2]_n$	3	FeN_4O_2	–	293
neo-C_5H_{11}	OMe	$Cu(OAc)_2$	$[CuL_2]_2$		CuN_3O_2	–	295
Bn	OMe	$FeCl_3$	FeL_3		FeN_3O_3	84 – 89	293
Bn	OMe	$FeSO_4$	$[FeL_2]_n$	3	FeN_4O_2	–	293
Ph	Me	$Cu(OAc)_2$	$[CuL_2]_n$	2	CuN_4O_2	82	296
Ph	Me	$Zn(OAc)_2$	$ZnL_2(MeOH)_2$		ZnN_2O_4	65	296
Ph	OMe	$Cu(OAc)_2$	CuL_2		CuN_2O_2	95	296
4-MeC_6H_4	Bu^t	$Cu(OAc)_2$	$[CuL_2(MeOH)_2]_n$	1	CuN_2O_4	88	295
4-EtC_6H_4	OMe	$FeCl_3$	FeL_3		FeN_3O_3	84 – 89	293
4-EtC_6H_4	OMe	$FeSO_4$	$[FeL_2]_n$	3	FeN_4O_2	–	293

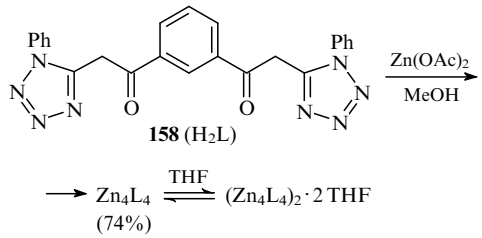
[a] In these cases, R^2 = H, in other cases, R^2 = CN.

The second tetrazole ring can also act as an electron-withdrawing substituent in the carbon chain. Thus, bistetrazole **157** reacts with zinc acetate in methanol to give a complex (in 78% yield), representing, according to X-ray diffraction data, a one-dimensional coordination polymer with rather short (2.257 Å) intermolecular Zn···N≡C bonds.[298]



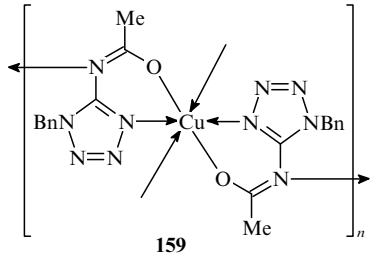
157 (HL)

Bis(tetrazolylmethyl ketone) **158** undergoes double deprotonation in the reaction with zinc acetate to give the tetranuclear chelate Zn_4L_4, which crystallises from THF as cryptatoclathrate (according to X-ray diffraction data); this dissociates in solution.[299] In the 3D structure of this compound, each zinc ion is connected to three ligands, and the coordination sphere is a distorted trigonal bipyramid. When made to react with iron(III) chloride in the presence of triethylamine, compound **158** forms the complex Fe_2L_3 with D_3 symmetry and the (Δ,Δ)-(Λ,Λ)-*fac*-configuration of the Fe(III) coordination polyhedron (octahedron), and the *p*-phenylene ligand of this type forms a tetranuclear adamantane-like chelate complex.[299]



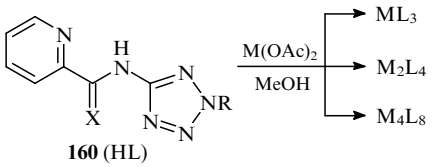
158 (H_2L)

The reactions of acyl derivatives of *N*-alkyl-5-aminotetrazoles with metal salts proceed in a similar way, the amide group being deprotonated. For example, 5-acetylamino-1-benzyltetrazole reacts with copper(II) acetate to give complex **159** (in 74% yield), which is self-assembled into a stair-like one-dimensional supramolecular structure owing to the intermolecular interaction between the coordinatively unsaturated copper(II) ion and the nitrogen atom of the amide group. The copper(II) environment in this complex is a tetragonal bipyramid.[295]



159

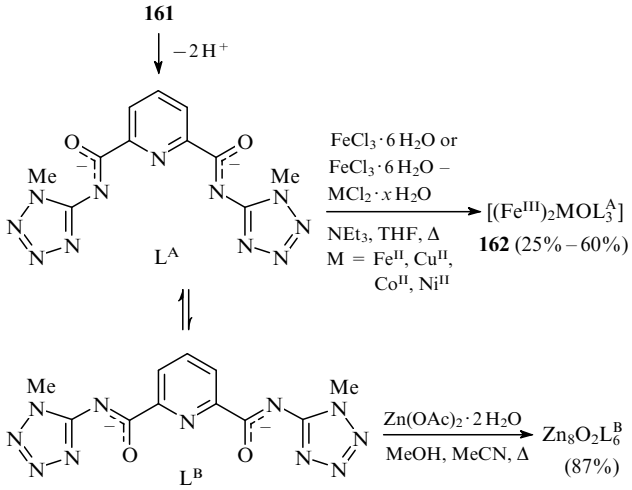
The introduction of an α-pyridyl group into these ligands changes considerably their coordination properties. *N*-(2-Alkyltetrazol-5-yl)pyridine-2-carboxamides and -thioamides **160** were shown [300, 301] to react with copper(II), zinc(II), cobalt(II) and nickel(II) acetates at 20 °C to give a series of mono-, bi- and tetranuclear complexes differing appreciably in the structure of the coordination unit, which decompose only at temperatures above 250 °C [note that during the synthesis Co(II) was oxidised to Co(III)]. For the Ni_4L_8 complexes and their solvates with metal–metal distances of 5.56–5.57 Å, a weak intramolecular ferromagnetic interaction has been found [300, 302]



160 (HL)

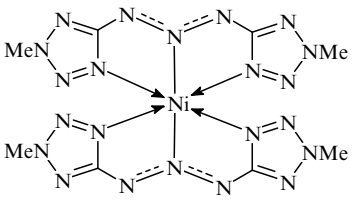
X	R	M	Complex composition	Coordination polyhedron	Yield (%)	Ref.
O	Me	Zn	Zn_4L_8	ZnN_5O	86	300
O	Me	Co(II)	$Co(III)L_3$	CoN_6	85	301
O	Et	Cu	Cu_2L_4	CuN_5	82	301
O	Et	Ni	Ni_4L_8	NiN_5O	85	300
S	Et	Ni	Ni_4L_8	NiN_5S	79	301
S	Et	Cu	Cu_2L_4	CuN_3S_2	51	301

A ditetrazole derivative of this type, *N*(2),*N*(6)-bis(1-methyltetrazol-5-yl)pyridine-2,6-dicarboxamide (**161**), has been used [303, 304] for the synthesis of transition metal oxo complexes. This compound undergoes double deprotonation, and the doubly charged anion exists in solution as two rotamers, L^A and L^B; these species selectively form oxo complexes of two different types, Fe_2MOL_3 [M = Fe(II), Cu(II), Co(II), Ni(II)] and $Zn_8O_2L_6$. These complexes are considered as models of metalloproteins and promising oxidation catalysts.



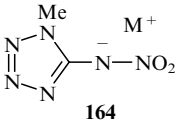
The structures and properties of trinuclear oxo-centred complexes have been studied in most detail using a variety of spectroscopic, electrochemical and spectroelectrochemical methods and X-ray diffraction analysis. In these compounds, the ligand acquires the shape of a helix and binds all three metal atoms by five electron-donating nitrogen atoms, giving rise to complexes stable in solution and in the solid state (m.p. > 250 °C with decomposition). These complexes show unusual electronic properties of the central $Fe_2^{III}M^{II}O$ core, which imply the possibility of fine tuning of the parameters of the reversible electron transitions $Fe^{III} \rightleftharpoons M^{II}$ by external action. According to X-ray diffraction data, compounds **162** (M = Fe, Ni, Cu) correspond to the D_3 point group of symmetry, three metal ions being indistinguishable in these structures. The metal–metal distances (3.267–3.287 Å) are somewhat shorter that those in similar complexes with carboxylate bridges (3.306–3.308 Å). Mixed-valence iron complex **162** can be easily converted into $[Fe_3^{III}OL_3]$ by treatment with cerium(IV) nitrate; the reaction of $FeCl_3 \cdot 6H_2O$ with the ligand under consideration in the presence of triethylamine at room temperature affords the ionic complex $(HNEt_3)[Fe^{III}L_2]$ (yield 87%).[304]

The triazene ligand RNHN=NR (R is 2-methyltetrazol-5-yl) is also easily deprotonated in the reaction with nickel chloride. The resulting dark red crystals of mononuclear complex **163** are thermally stable despite the high content of nitrogen, and undergo no changes below 250 °C.[305]

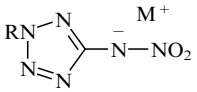


163

Like the initial 5-aminotetrazole (**13**), its 1- and 2-methyl derivatives react with tetranitromethane in alkaline media to give 5-nitraminotetrazole salts **164**, **165** (yields 65%–85%), which vigorously decompose at temperatures of 248–325 °C. In the case of *N*-cyanoethyl derivatives, this reaction occurs smoothly only for the 2-isomer. The nitration of 5-amino-1-cyanoethyltetrazole is accompanied by dealkylation to give salts **12**.[306]



164

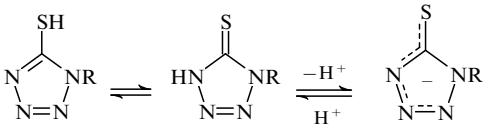


165

M = Li, Na, K, Rb, Cs (**164**); R = Me, CH_2CH_2CN; M = Na, K (**165**).

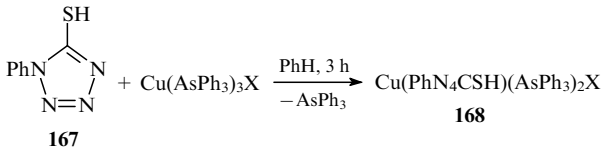
Silver(I) complexes based on *N*-nitraminotetrazole anions **110** (R^1 = H, R^2 = $NHNO_2$) and **111** (R^1 = H, R^2 = $NHNO_2$; R^1 = $NHNO_2$, R^2 = Me) have also been reported.[64] These 1 : 1 complexes were prepared in almost quantitative yields from ammonium salts of tetrazoles and silver nitrate in water; they are stable under ambient conditions and susceptible to explosive decomposition on heating; their decomposition temperatures lie in the range of 180–275 °C.

Of substantial value for MT synthesis are *N*-substituted 5-mercaptotetrazoles **166**, which may exist in thiol **166a** and thione **166b** tautomeric forms, form **166b** predominating in the condensed state.[307] These compounds are readily deprotonated to give tetrazolethiolate anion, which is a stable 6π-electron cyclic system.



166a **166b**

Depending on the reagents and reaction conditions, 5-mercaptotetrazoles **166** (R = Ph, 4-MeC_6H_4, 3-MeC_6H_4, 4-ClC_6H_4) form complexes involving both deprotonated (L) and neutral (HL) forms, for example, $Bi(HL)_2Cl_3$, $Bi(HL)(H_2O)Cl_3$,[308] $VO_2(HL)_2Cl(H_2O)$, $NbL_2(H_2O)Cl_3$ and $TaL_5(H_2O)$.[309] Complexes with a neutral form of the ligand are prepared by reactions of tetrazoles **166** with a metal salt in ethanole or aqueous ethanole solution with heating and with maintaining of the required pH. The nature of the substituent R and metal cation also influence the composition of the complex and the form of existence of the ligand in the complex. The data from IR, electronic and ^{1}H NMR spectroscopy provided the conclusion[310] that neutral 1-substituted mercaptotetrazoles are coordinated in the thione form **166b**. It was also shown that 5-mercapto-1-phenyltetrazole (**167**) displaces triphenylarsine from copper(I) triphenylarsine complexes to give complexes **168** involving the neutral form of the tetrazole ligand, which is coordinated in the thione form through the sulfur atom.[310]

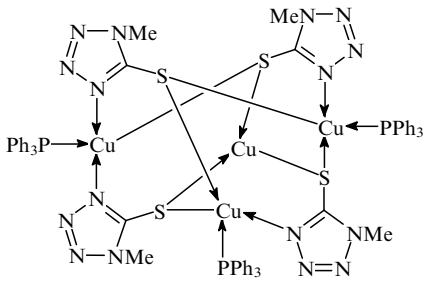


167 **168**

X = Cl, Br, I.

However, no structural data are still available for this type of complexes. In some cases,[308,311] data on the composition and properties of complexes have been improperly interpreted.

Complexes with mercaptotetrazole anions are mainly prepared by substitution of an appropriate thiolate anion (taken as the ammonium or sodium salt) for a halide ion. They can also be prepared by the reaction of the metal salt with a neutral ligand in the presence of an amine. A number of neutral and ionic complexes of 1-methyl- and 1-phenyltetrazole-5-thiones have been prepared by this method; their molecular structures have been studied by X-ray diffraction: $(Ph_3P)_3Cu_4(MeN_4CS)_4 \cdot CH_2Cl_2$ (**169**), $[Ph_3PAu(MeN_4CS)]_2$ (**170**), $Ph_3PAu(PhN_4CS)$ (**171**), $(Ph_3P)_2Ag(PhN_4CS) \cdot CH_2Cl_2$ (**172**), $(Ph_3P)_2Hg(MeN_4CS)_2$ (**173**), $(AsPh_4)_2[Hg(MeN_4CS)_4]$ (**174**), $(AsPh_4)_2[Pd(MeN_4CS)_4]$ (**175**), $AsPh_4[Au(PhN_4CS)_2]$ (**176**), $AsPh_4[Au(PhN_4CS)_4]$ (**177**),[312] $NEt_4[Au(MeN_4CS)_4]$ (**178**),[313] $PPh_4[Au(MeN_4CS)_4] \cdot 0.5\,H_2O$ (**179**),[314] $(Ph_3P)_2Ag(PhN_4CS) \cdot MeOH$ (**180**).[315] Note that tetranuclear complex **169** is formed upon crystallisation of the dimeric compounds $[Ph_3PCu(MeN_4CS)]_2$ existing in solution and has an unusual asymmetric structure. One copper atom not bound to triphenylphosphine is coordinated only by three sulfur atoms and the other three copper atoms are tetracoordinated by the P, N and S atoms.

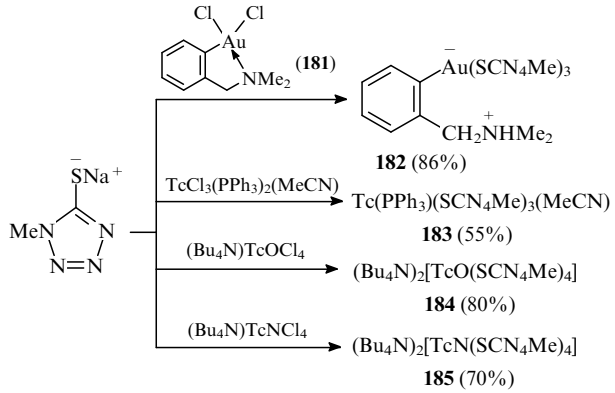


169

In complexes **170**–**180**, 1-R-5-mercaptotetrazoles are coordinated to the metal atom in the monodentate mode through the sulfur atom. Complex **170** is a dimer owing to the intermolecular Au–S bonds, while the other compounds are monomers. Unexpectedly, the M–P bonds in all triphenylphosphine complexes were found to be shorter than the M–S bonds. On the basis of Raman spectra and quantum-chemical calculations for tetrazole **167**, its sodium salt and the complex $Ag(PhN_4CS)$, one can conclude that in the absence of other ligands, this tetrazole is bound to silver(I) by two donor atoms, S and N(4).[316]

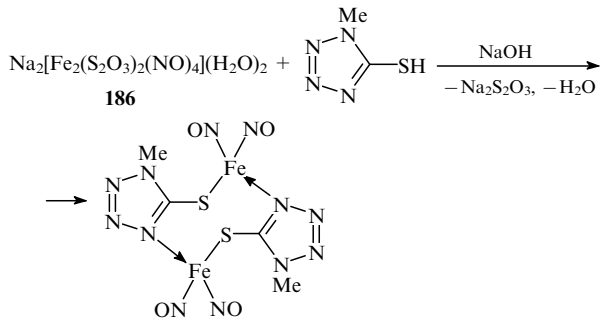
The substitution reaction in gold(III) complex **181** on treatment with sodium 1-methyltetrazole-5-thiolate was found[313] to involve Au–N bond cleavage, protonation of the dimethylamino group and the formation of zwitter-ion complex **182** in which the gold atom (X-ray diffraction data) has a distorted square planar environment ($AuCS_3$). Compound **181** exhibits an antitumour activity; therefore, studies of the ligand exchange in this complex and the biological activities of the products obtained arouse considerable interest.[313,317] The replacement of chloride ions in complex **181** by successive treatment with diphenylthiocarbazone and 5-mercapto-1-methyltetrazolate anion to give mixed-ligand complex has been carried out.[317]

The 5-mercapto-1-methyltetrazolate anion also reacts as a monodentate ligand to form technetium(III) and (V) complexes **183**–**185**.[318] During the synthesis of nitride complex **185**, Tc(VI) is reduced to Tc(V), which is also typical of reactions with other

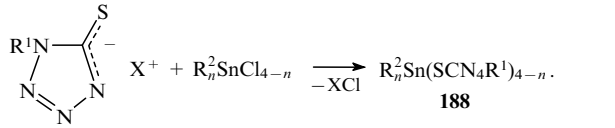


S-donor ligands. According to X-ray diffraction data, ionic complexes **184** and **185** have a square pyramidal structure, while neutral complex **183** has a trigonal bipyramidal geometry in which the triphenylphosphine and acetonitrile molecules are coordinated in the axial positions. An attempt has been made [319] to carry out quantum-chemical prediction of the spin state of transition metal complexes, including the technetium(III) complex **183**.

By exchange of thiosulfate ligands in complex **186** for the 1-methyltetrazole-5-thiolate anion, binuclear nitrosyl iron complex **187** has been synthesised.[320] On the basis of IR and Mössbauer spectroscopy data, it was concluded that in this complex, tetrahedrally coordinated iron atoms are bound to each other by two N=C–S bridges. Complex **187** is stable in air and can be used as a model to study the mechanism of transformations of the nitrosyl adducts of [2Fe,2S]-proteins *in vivo*.



The synthesis and structure of the complexes of organotin 1-R-5-thiotetrazoles **188** have been studied in detail. The complexes are obtained at room temperature according to the following scheme:

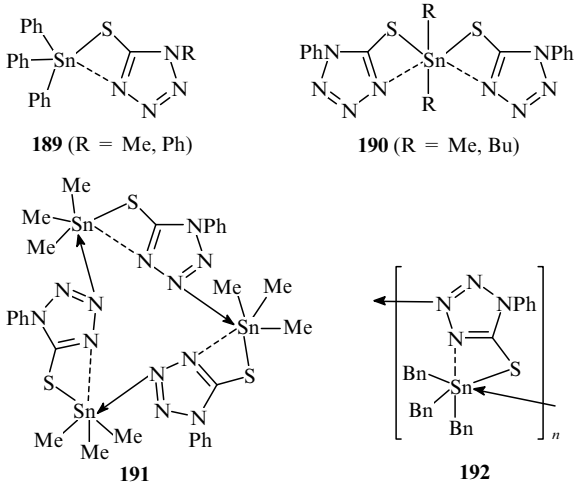


R^2	n	X	Yield (%)	Ref.
Ph [a]	3	Na	88	321
Me	3	Na	67	322
Me	3	NH_4	59	323
Bu	3	Na	74	322
CH_2Ph	3	NH_4	74	323
Ph	3	Na	70	322
Me	2	NH_4	26	323
Bu	2	Na	58	322
CH_2Ph	2	NH_4	79	323
Ph	2	Na	69	322
Me [b]	2	Na	52	322

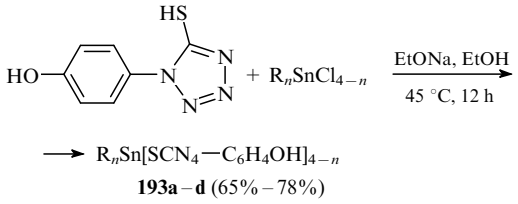
[a] In this case, R^1 = Me, and in other cases, R^1 = Ph; [b] only one chloride ion is replaced under the synthesis conditions to give $Me_2SnCl(SCN_4Ph)$.

These compounds can also be prepared by cycloaddition of organic isothiocyanates to R_3SnN_3 but this route is seldom used. Syntheses of the complexes $Bu_3Sn(SCN_4Me)$ and $Bu_3Sn(SCN_4Ph)$ have been reported.[322]

All the obtained complexes have been studied by ^1H, ^{13}C and ^{119}Sn NMR and Mössbauer spectroscopy and X-ray diffraction analysis. In solution, these compounds are monomers, the tin atom has a tetrahedral coordination and is bound to the tetrazole ligand through the donor sulfur atom. In the solid state, X-ray diffraction analysis shows the formation of an additional weaker intramolecular bond, Sn–N(4), the length of which is 2.94–3.28 Å [for example, in compounds **189** (R = Me,[321] Ph [324]) and **190** (R = Me,[325] Bu [322])]. In the complexes $R_3Sn(SCN_4Ph)$ [R = Me (**191**),[326] Bn (**192**) [323]], the tetrazole ligand forms an intermolecular Sn–N(3) bond thus increasing the coordination number of the central atom to 6. This bond (2.6–2.7 Å) is essentially shorter than the intramolecular bond (3.2–3.3 Å). As a result, the complex is a trimer for R = Me and a linear polymer for R = Bn.



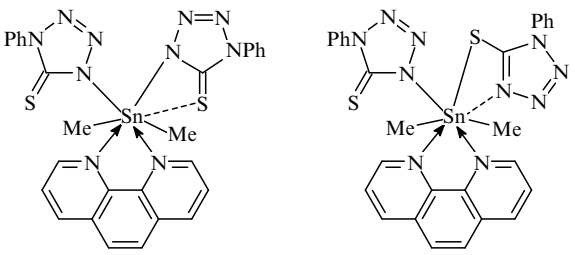
The presence of a hydroxy group in the benzene ring of 5-mercapto-1-phenyltetrazole was found [327] to have a substantial influence on the structure of di- and trialkyltin compounds. A series of such compounds **193** have been prepared and studied by IR and ^1H NMR spectroscopy.



n = 3: R = Ph (**a**), Bn (**b**); n = 2: R = Me (**c**), Bu (**d**).

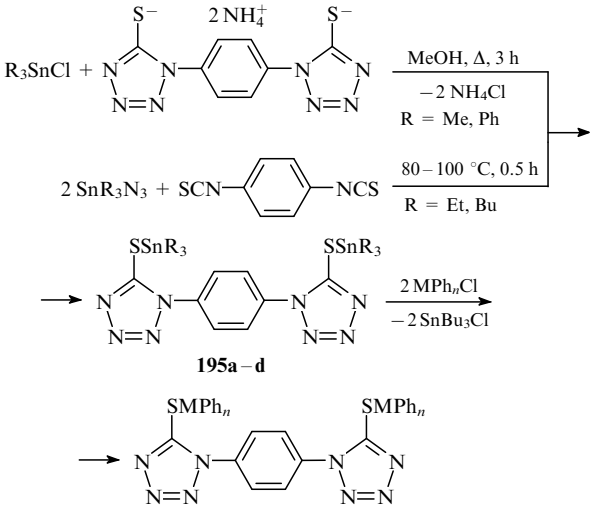
Complexes **193a–d** have also been studied by X-ray diffraction. The presence of an intermolecular Sn–N bond in complex **193b** and intermolecular O–H···X hydrogen bonds (X = O, N, S) in the crystal structures of compounds **193a**,**c** gives rise to polymeric chains and two-dimensional networks. In addition, strong π–π interaction of the hydroxyphenyl fragments was found in complexes **193b**,**c**. In compound **193c**, the intramolecular Sn–N bond (2.704 Å) is shorter than that in related complex **190** (R = Me) (2.947 Å).

The 5-mercapto-1-phenyltetrazolate anion can be coordinated only through the tetrazole N(4) atom. According to X-ray diffraction data,[328] the unit cell of the crystalline mixed-ligand complex **194** contains two independent molecules **A** and **B**, which are formally bond isomers.



A **194** **B**

Organotin complexes **195** were prepared from 1,4-phenylenedi(tetrazolethiols) by two methods;[329] the same ligands were used to synthesise lead- and mercurio-thiotetrazoles.



195a–d

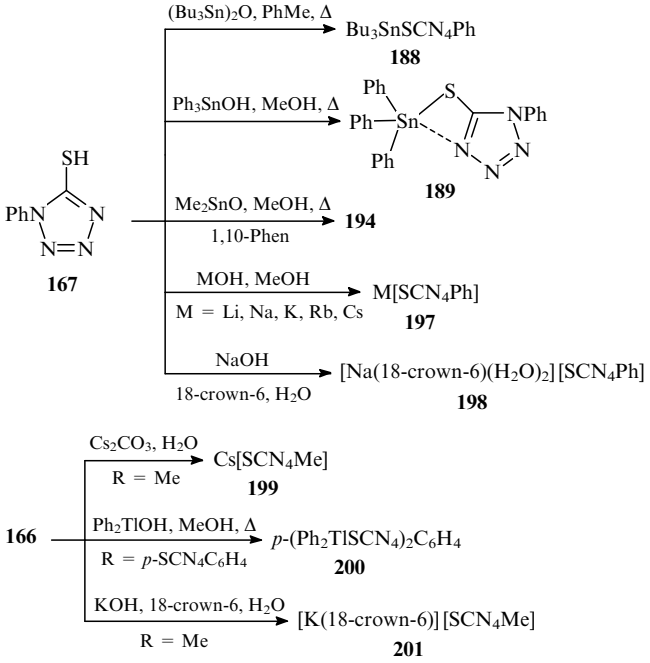
196a,b

195: R = Me (**a**, 77%), Et (**b**, 53%), Bu (**c**, 55%), Ph (**d**, 40%);
196: M = Pb, n = 3 (**a**, 33%); M = Hg, n = 1 (**b**, 80%).

According to X-ray diffraction, the supramolecular structure of compound **195c** is a 2D polymer consisting of 32-membered rings $(NC_4CSSnN_2CSSnN_3)_2$. The asymmetric cell contains two trigonal bipyramidal *trans*-$NSSnC_3$ fragments. The tin atom is bound to the ligand through sulfur and is coordinated by the N(4) atom of the tetrazole ring of the neighbouring molecule. Conversely, trimethyltin derivative **195a** crystallises with two methanol molecules and gives a linear polymeric structure due to hydrogen bonds, the tin atom having a trigonal bipyramidal environment, *trans*-$SOSnC_3$. The polymer is formed by 14-membered rings $(SnSCN_2HO)_2$ connected by phenylene bridges. A similar coordination polyhedron geometry and a polymeric structure were also found for complex **195b** by Mössbauer spectroscopy. Complex **195d** is monomeric and might contain a weak intramolecular Sn–S bond. According to ^{119}Sn NMR data obtained in DMSO, the metal atom in compounds **195c**,**d** has a tetrahedral coordination environment, while in the case of methyl and ethyl derivatives **195a**,**b**, the coordination number of tin increases to 5 due to coordination of the solvent. According to ^{207}Pb NMR data, a similar coordination mode is observed for the lead atom in compound **196a**.

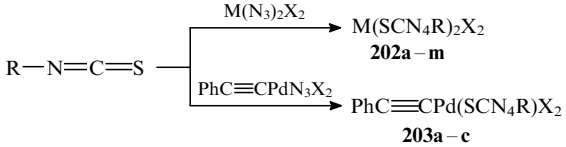
Interesting data have been obtained[330] for the compound Ph_3PbSCN_4Ph synthesised by the exchange reaction of Ph_3PbCl with the ammonium salt of tetrazole **167**. The compound has a one-dimensional polymeric structure formed due to the intermolecular Pb–N(2) contact (the bond length is 3.339 Å). The unusual orientation of the tetrazole ring with respect to the lead atom [the intermolecular Pb–N(2)–N(1)–N(4) dihedral angle is 126.1°] prompted the hypothesis of π-coordination of the tetrazole ring to the metal atom.

Due to the rather high acidity of 5-mercaptotetrazoles **166** (pK_a = 2.8–3.6),[11] their metal complexes, for example, compounds **188**,[331] **189**,[324] **194**,[328] **197**,[332] **198**,[333] **199**,[334] **200**,[328] **201**,[335] can be prepared by the reaction of these tetrazoles with basic reagents.



X-Ray diffraction data confirm the different coordination modes of the anion of tetrazole **167** in compounds **197**.[332] The coordination number of the cations increases from 5 to 8 following an increase in the ionic radius on passing from Na^+ to Cs^+. In K^+, Rb^+ and Cs^+ complexes, four-membered MSCN rings are formed upon bidentate coordination of the ligand by the S and N(4) atoms, while in Rb^+ and Cs^+ compounds, Rb···C and Cs···C contacts with the carbon atom of the phenyl group were also found. As was to be expected, the alkali metal ion in complexes **198**[333] and **201**[335] is coordinated by the crown ether and, in the case of the sodium compound, no direct reaction between the metal and tetrazole takes place. Conversely, in the crystal structure of **201**, the potassium ion has a contact with the N(4)–C(5)–S fragment of the tetrazole ligand [bond lengths: K–N(4) 2.934(4) Å, K–C 3.469(4) Å, K–S 3.373(2) Å]; in this respect, this complex bears the similarity with the complexes of organotin compounds considered above where the Sn–S and Sn–N distances are in the range of 2.617–3.255 Å.

A series of Pd(II) and Pt(II) complexes with 1-R-5-mercaptotetrazoles **202**[336] and **203**[133] have been obtained by 1,3-cycloaddition of the azido complexes of these metals to organic isothiocyanates.

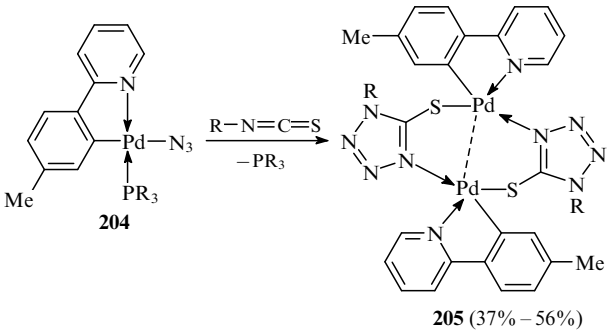


Compound	M	R	X or X_2	Yield (%)
202a	Pd	Et	PMe_3	88
202b	Pd	$CH_2CH=CH_2$	PMe_3	75
202c	Pd	$PhCH_2$	PMe_3	81
202d	Pd	Ph	PMe_3	59
202e	Pd	Ph	PMe_2Ph	93
202f	Pd	2,6-$Me_2C_6H_3$	PMe_3	45
202g	Pd	2,6-$Me_2C_6H_3$	PEt_3	72
202h	Pt	Et	PMe_3	91
202i	Pt	Ph	PMe_3	92
202j	Pt	Ph	PEt_3	64

Compound	M	R	X or X_2	Yield (%)
202k	Pd	Ph	$Et_2P(CH_2)_2PEt_2$	76
202l	Pt	Ph	$Et_2P(CH_2)_2PEt_2$	66
202m	Pt	2,6-$Me_2C_6H_3$	$Et_2P(CH_2)_2PEt_2$	92
203a	Pd	Et	PMe_3	61
203b	Pd	2,6-$Me_2C_6H_3$	PMe_3	71
203c	Pd	2,6-$Me_2C_6H_3$	PEt_3	82

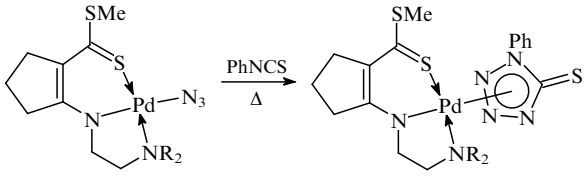
The binuclear complex 1,4-$[PhC{\equiv}CPd(PEt_3)_2SCN_4]_2C_6H_4$ was synthesised in a similar way from *p*-phenylene diisothiocyanate in 37% yield.[133] Treatment of azide complex **204** with alkyl isothiocyanates results in unusual binuclear palladium complexes **205**, which may contain an intramolecular metal–metal bond.

According to X-ray diffraction data, the Pd–Pd distance in complex **205** (R = Pr^i) is equal to 2.9704(6) Å, which is smaller than twice the covalent radius of palladium (1.380 Å), but larger than the length of the single Pd–Pd bond (2.55–2.8 Å) in other binuclear palladium complexes.[337]



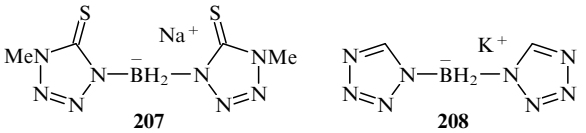
R = Et, Pr^i, Bu^n, $CH_2{=}CHCH_2$.

The data from IR and ^1H, ^{13}C and ^{31}P NMR spectroscopy and X-ray diffraction analysis of compounds **202b**,**d**,**h**,**m** and **203b** are indicative of S-coordination of thiotetrazoles in these complexes. The Pd–S bond lengths (2.325–2.365 Å) are typical of analogous neutral and anionic Pd and Au tetrazolethiolate complexes **170**, **171**, **175**–**177** prepared in a different way. Note that coordination of the tetrazole ring through the nitrogen atom has previously been suggested based on IR and ^1H NMR spectra for Pd(II) complexes **206** prepared by cycloaddition of azide complexes to phenyl thiocyanate.[132] Apparently, spectroscopic data alone are inadequate to draw this conclusion, as the vibration frequency of the C=S fragment bound to nitrogen atoms has not been reliably assigned as yet.[316]



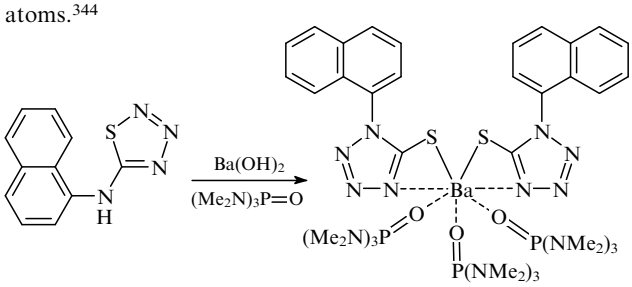
R = H, Et.

A number of MT based on tetrazolyldihydroborate anions have been synthesised; they were formed as salts **207**[338] and **208**[339,340] from sodium and potassium borohydrides and tetrazoles.

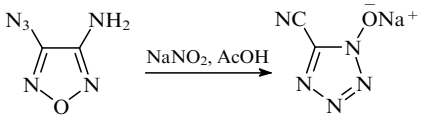


Compounds **207** and **208** react with bivalent metal salts in methanol and water, respectively, to give crystalline complexes $M[H_2B(SCN_4Me)_2]_2$ [**209**; M = Co (**a**), Ni (**b**)][338] and $[M\{H_2B(CHN_4)_2\}_2(H_2O)_2](H_2O)_2$ (**210**; M = Co, Zn, Cd, Mn, Fe).[341–343] The reaction of compound **208** with nickel(II)[342] and copper(II)[343] salts in water results in loose amorphous precipitates, which can be dissolved in ammonia and then crystallised as polymeric complexes $[M\{H_2B(CHN_4)_2\}_2(NH_3)_2]_n$ (**211**; M = Cu, Ni).[341,342] The structures of the resulting complexes were investigated by various spectroscopic methods and X-ray diffraction. It was shown[338] that the dihydrobis(1-methyl-5-thiotetrazol-4-yl)borate anion is coordinated as a bidentate ligand (k^2-S,S) in complex **209a** and as a tridentate ligand (k^3-S,S,HB) in complex **209b**, *i.e.*, rather strong Ni···H–B interaction is manifested. Conversely, in compounds **210**, dihydrobis(tetrazolyl)borate anion acts as a bridging ligand, being coordinated through the N(4) atoms of both rings and forming a 2D structure. Complexes **211** also have a 2D structure with polyhedron distortion due to the Jahn–Teller effect typical of copper. The coordination polyhedron is formed by four nitrogen atoms of two bis(tetrazolyl)borate ligands and two ammonia molecules in *trans*-positions.[341–343]

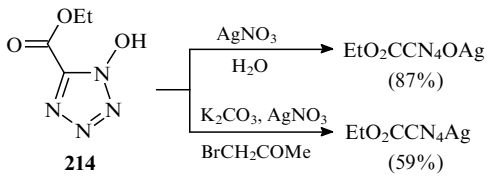
The properties and structures of two MT prepared by an unusual method, namely, by recyclisation, have been reported.[344,345] 5-Aminothiatriazoles are known to isomerise into 5-mercaptotetrazoles on treatment with an aqueous solution of sodium hydroxide. Using 5-(1-naphthylamino)-1,2,3,4-thiatriazole as an example, it was shown[344] that this isomerisation occurs more efficiently under the action of barium hydroxide in toluene in the presence of hexamethylphosphoramide. This gives solvated complex **212** in which the ligands form chelate rings due to coordination of the tetrazole ring through sulfur and nitrogen atoms.[344]



An unexpected transformation of aminoazidofurazan induced by sodium nitrite yields rather stable (m.p. = 255 °C) sodium salt of 5-cyano-1-hydroxytetrazole (**213**).[345] In the crystal structure of the hydrate of salt **213**, the sodium atom in the NaN_3O_4 polyhedron is coordinated by the nitrogen atom of the nitrile group, by the N(3) and N(4) atoms of three anions and by oxygen atoms of four water molecules.



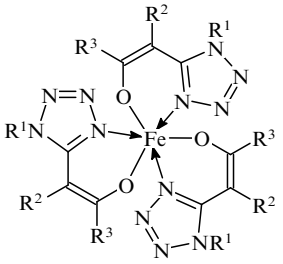
It is noteworthy that, being rather strong OH acids, 1-hydroxytetrazoles are capable of ready formation of stable salts with metals or nitrogen bases. A sequence of transformations of ethyl 1-hydroxytetrazole-5- carboxylate (**214**) has been reported;[346] compound **214** readily forms a silver salt and, like other 1-hydroxytetrazoles, reacts with bromoacetone in the presence of potassium carbonate to be reduced to ethyl tetrazole-5-carboxylate, which was isolated as the silver salt. The structure of silver compounds of this type has not been determined as yet.



V. Applications of metal tetrazole derivatives

A key application of MT is organic synthesis, where they are used as the starting and intermediate compounds for the preparation of practically valuable substances. First, this is synthesis of *N*-substituted tetrazoles from various metal tetrazolates.[1–3, 15, 16, 23, 347–349] By using metal derivatives **1b** and **2** containing covalently bound metal, it is possible in some cases to obtain selectively one of the possible *N*-substituted tetrazole isomers **110** and **111**.[69, 89, 110, 121, 347–349] This approach is successfully used not only to prepare simplest *N*-alkyltetrazoles, but also for the synthesis of *N*-aryl- and *N*-hetaryltetrazoles[23, 156, 186, 350] and for introduction of tetrazolyl groups into complex biologically active compounds.[351, 352] The replacement of traditional alkylating agents in these processes by other halogen-containing compounds provides the route to 2-phosphinotetrazoles,[348] 2,5-disubstituted triazolo[3,4-*b*][1,3,4]thiadiazoles,[353] tetrazolylmethylaminoglyoximes and furazans[354] difficult to prepare by other methods. Alkylation of metal 5-mercaptotetrazolates plays an important role in the synthesis of biologically active compounds incorporating a 1-R-tetrazole-5-thiolate fragment.[355–365] Treatment of *N*-alkylstannyltetrazoles **16**, **103**[88, 157–159, 161, 162] and metal tetrazolates[75, 94] with acids is the final stage of a popular synthesis of 5-substituted tetrazoles **6** from nitriles. More readily available alkali and alkaline earth metal bis-tetrazolates, for example, salts **46** and **76**, are often used to prepare the corresponding ammonium and hydrazinium salts and salts of organic bases.[366–368]

Metal derivatives of tetrazoles find use as catalysts. For example, iron(III) complexes **215a**,**b** demonstrated[294] high efficiency as oxidation and dehydrogenation catalysts in the epoxidation of olefins and dehydrogenation of dihydropyridine with dioxygen and aldehydes. Owing to the use of mentioned compounds, these processes smoothly occur at room temperature and atmospheric pressure.



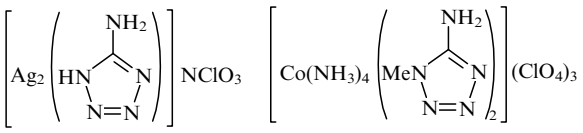
215a,**b**

R^1 = Bu^i, R^2 = CN, R^3 = OMe (**a**); R^1 = Bu^t, R^2 = H, R^3 = Ph (**b**).

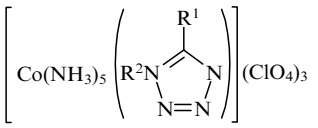
Palladium(II) acetate complexes with *m*-phenylenedi(1*H*-tetrazole)[369] and 1-(2-iodo-phenyl)tetrazole,[370] prepared *in situ*, proved to be good catalysts in the Suzuki and Heck coupling reactions.

Many energetic MT able to pass from the combustion mode to detonation are promising as initiating explosives (IE) for safe initiating means including those operating from a low-voltage current sources or on exposure to laser radiation.[31, 83] First of all, these are cobalt(III) ammino tetrazolate complexes **69**–**71**,[83, 87, 148, 371] which have a substantially lower impact sensitivity and are less toxic than traditional IE, namely, lead azide, fulminating mercury or lead trinitroresorcinolate.[87] Compound **69** (R = NO_2) is successfully used in light igniting charges applied in the pyrocontrol of guided missile systems.[83] Good operation parameters were found for non-hygroscopic and low-toxic complex **70**, which has a reduced sensitivity to the static electric discharge. The use of this compound as a key component in perforating equipment meant for operation in deep oil and gas wells markedly increases oil and gas condensate production rates and decreases the time of development of exploratory and producing wells.[83]

An extremely high susceptibility to laser pulse was found recently for the complexes of 5-hydrazinotetrazole with mercury(II) perchlorate **37** and 5-aminotetrazole with silver(I) perchlorylamide **216**.[52, 83, 371] For complex **37**, the initiation threshold by a neodymium laser (λ = 1.06 μm, pulse duration τ_q = 30 ns) is ~5 mJ cm^{-2}. This complex has found use for the production of film light-sensitive charges employed for the formation of shaped shock waves and blast hardening of steels.[83] Other MT of type **1** proposed as IE include silver[148] and mercury salts of 5-nitrotetrazole,[67, 148] caesium salts of 5-nitrotetrazole and 5,5′-azoditetrazole,[372] cobalt(III), nickel(II), copper(II) and zinc(II) complexes with ammonia and 5-nitrotetrazole **71**, **72**[88] and cobalt(III) complexes with ammonia and *N*-substituted tetrazoles **217**, **218**.[87, 277–279] These MT show a number of advantages over the conventional IE; many of them can be considered as promising low-toxic explosives valuable for the development of environmentally safe (green) energetic materials (see, for example, Ref. 279).



216 **217**



218

R^1 = NH_2: R^2 = Me, NH_2; R^1–R^2 = $(CH_2)_5$.

It has been shown[373] that 5,5′-bitetrazole or bis(tetrazol-5-yl)amine or their barium, strontium and copper salts can underlie the development of low-smoke pyrotechnic compositions to be used in colour fireworks.

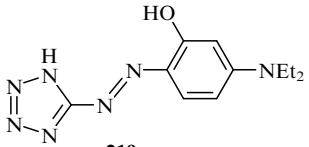
An important field of MT application is gas generation. Of most interest in this respect are salts of 5-substituted tetrazoles as they are safer than azides used previously.[374] The compositions proposed for the use in car safety pads usually include an oxidant represented by metal oxides or salts (perchlorates, nitrates, *etc.*), and a fuel. As such fuells, 5-aminotetrazole,[375–379] 5-nitraminotetrazole,[380–382] 5,5′-bitetrazole[35, 36, 379, 383] and salts with alkali, alkaline earth and transition metal cations [copper(II), zinc, cobalt(II), iron(III)] were patented. In addition, some of these compounds are catalysts of carbon monoxide and nitrogen oxide burning and conversion into carbon dioxide and nitrogen, respectively. Minor additives of these salts, in particular, those based on unsubstituted 5-aminotetrazole, decrease the toxicity of other gaseous products to a reasonable extent.[377, 378] The formation of environmentally safe gaseous products from aminotetrazole-based compositions, for example, potassium salt of 5-aminotetrazole, has been proposed as a fire extinguishing means, instead of Freons or other halogenated compounds used currently in fire extinguishers.[384, 385] The use of 5-substituted tetrazole salts **1a**,**b** (M = Na, K, Ca, Zn), which produce nitrogen at temperatures above 300 °C or above 230 °C, for the design of fire-resistant thermoset[386] and thermoplastic[387] polymers has been patented. Copper(II) 5-methyltetrazolate and other salts of 5-substituted tetrazoles and 5,5′-bitetrazole with melting points above 200 °C have been proposed[388, 389] for the manufacture of high-quality moulds for casting of foamed materials. The decomposition of tetrazoles accompanied by gas evolution and change in the state of the plastic surface underlies the laser beam marking of polymeric articles containing tetrazole derivatives, including their alkali and alkaline earth metal, zinc and copper salts.[390]

The ability of tetrazoles to form stable complexes with various metal ions is widely used in photoprocesses and for corrosion protection of metals.[316, 391–395] 5-Substituted tetrazoles and their

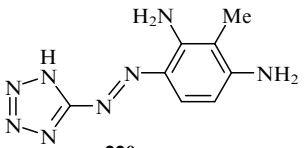
salts as well as 5-mercapto-1-phenyltetrazole and its derivatives are used as light-sensitive materials and reagents that improve sharpness, enhance the mechanical and thermal stability of the image and prevent bleaching.[396–399] 5-Mercapto-1-phenyltetrazole is the most effective metal corrosion inhibitor in the series of heterocyclic compounds. On a metal surface, this compound forms inert, insoluble and stable complexes with metal ions, which prevent the material from destruction.[400–402] The film of these complexes inhibits corrosion of copper,[403–407] nickel,[408] iron,[409] steel,[410–413] bronze,[406,414] and Cu–Zn[415] and Fe–B[416] alloys in acidic media. Treatment of silver,[417,418] copper[419] and brass[420] surfaces with compositions containing 5-mercapto-1-phenyltetrazole prevents them from dimming even in the presence of corrosive reagents such as sulfur-containing gases. It has been noted[420] that this treatment is more efficient than that with agents used traditionally. 5-Phenyltetrazole and its potassium and sodium salts are fairly effective copper and steel corrosion inhibitors in aqueous solutions of sodium sulfate and chloride.[421,422] In addition, tetrazoles inhibit not only electrochemical but also microbiological corrosion of metals.[423]

The interaction of tetrazoles with the surface of various parts and articles, resulting in a substantial change in their physicochemical properties has been used for the manufacture of printed circuit cards,[424–428] semiconductor devices,[429] layered materials;[430] for stabilisation of CdS colloid solutions[431] and Mo–S–Cu thermochromic films formed on the copper surface,[432] and for surface modification of silver nanoparticles.[433] The use of tetrazolylacetic acid as a bidentate ligand allows the design of polynuclear heterometallic clusters, $Cu_{12}Gd_6$ and $Cu_{12}Nd_6$ (Ref. 434).

The formation of coloured metal complexes of azotetrazoles **219** and **220** stable in solution is used for spectrophotometric determination of traces of iron(III),[435] bismuth(III)[436] and palladium(II)[437] in various mixtures and articles.



219



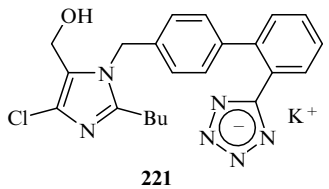
220

The high stability of the 5-diazotetrazole complex with copper(II) ions also underlies the voltammetric method for quantitative determination of copper present in low concentration (10^{-9} mol litre^{-1}).[438] The ability of 1-substituted tetrazoles **110** to form easily separable crystalline complexes with copper(II) chloride, which liberate free tetrazole ligand upon hydrolysis, has been used[439] for purification of this class of compound. This method is especially convenient for the production of low-volatile *N*-substituted tetrazoles sensitive to mechanical impact and capable of polymerisation. Since isomeric 1- and 2-substituted tetrazoles differ in the complexation properties, this process proved to be convenient for the separation of isomer mixtures.

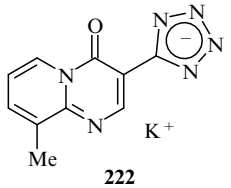
Immobilisation of tetrazoles on a polymeric matrix furnishes sorbents for selective binding of copper[440] and europium,[441] filtering materials[442] and hydrogels[443–445] suitable for purification of biological fluids and water from heavy metals and radionuclides. The ability of salt **7** to form hydrogel compositions under the action of Cr^{3+} ions is exploited in the application of this compound as a thickening agent in slurry explosives.[446]

Owing to high ionic conductivity and stability, lithium salts with heterocyclic anions, in particular, 5-cyanotetrazolate anion,[447] and alkali metal salts with 1-methyltetrazole-5-thiolate anion[334,448–451] are promising as components of polymeric electrolytes in galvanic and electrochemical (photovoltaic) current sources.

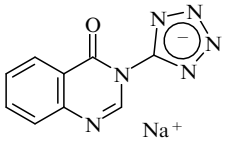
5-Substituted tetrazoles are known to be bioisosteres of the carboxy group, possessing a comparable acidity and lower toxicity. Tetrazoles are ionised in the physiological pH range, the tetrazolates thus formed being much more lipophilic than the corresponding carboxylates. This explains the interest in tetrazoles for the design of new effective drugs.[10] The structures of such drugs can incorporate the tetrazole ring in the form of a salt having higher solubility in water and ability to crystallise. Examples are Losartan Potassium (**221**),[10] which is a representative of new-generation antihypertensive drugs, and Pemirolast Potassium (**222**)[452] and MDL-427 (**223**),[14] which are effective as antiallergenic and antiasthmatic drugs.



221

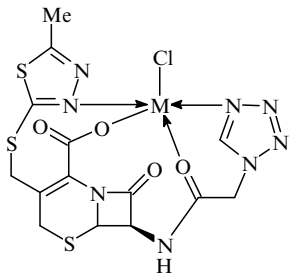


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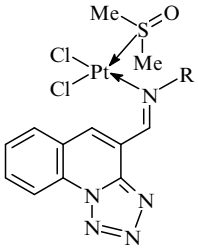


223

The complexes prepared by the reaction of the widely used antibacterial agent cephazolin or its sodium salt with metal(II) chlorides, ML_2Cl_2 and MLCl (**224**), $Ag_2L_2Cl_2$ (L is the deprotonated cephazolin), exhibit higher antibacterial activities *in vitro* compared to cephazolin with respect to *Staphylococcus aureus*, *Escherichia coli*, *Klebsiella pneumoniae*, *Proteus mirabilis* and *Salmonella enteriditis*.[453,454]



224 (M = Cu, Co, Ni, Zn)

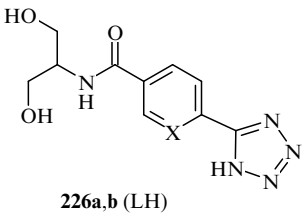


225a–e

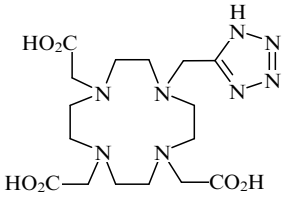
R = Ph (**a**), 4-MeC_6H_4 (**b**), 4-ClC_6H_4 (**c**), NHPh (**d**), NHMe (**e**)

A similar activity should be expected of complexes of another tetrazole-containing antibiotic, cefamandole, with copper,[455] cadmium[456] and zinc[457] salts. An antibacterial activity was also found for silver tetrazolate[73] and complexes **40**.[55–57] Platinum(II) complexes **225** possess a cytotoxic action with respect to malignant cells; compounds **225d**,**e** are similar in activity to cisplatin, while complexes **225a–c** demonstrate a higher activity.[458] Salt **7** shows a clear-cut polyelectrolyte activity toward an aseptic inflammatory process, which may be used to accelerate healing of wounds and to suppress scar formation.[459] Trialkylstannyl derivatives of 5-aryl- and -hetaryltetrazoles **103** were patented as herbicides and animal parasite control means.[460]

Gadolinium(III) complexes **50** and **51**[71] and the complexes $GdL_3(H_2O)_n$ and $Na[GdL(H_2O)]$ obtained from ligands **226**[71] and **227**,[461] respectively, are promising for the use in medicine as contrasting agents for magnetic resonance diagnostics. They show a high proton relaxation ability, good solubility in water, high stability and low osmotic pressure. These complexes surpass conventional reagents in many performance characteristics.



226a,b (LH)
X = N (**a**), N^+O^- (**b**).



227 (LH_4)

For many MT, practically valuable properties were found, demonstrating good prospects for their use in various fields of science and engineering. These properties include photo- and thermochromism,[6, 227, 228] ferromagnetism,[185, 199, 202, 225, 276] mesomorphism,[281, 282] nonlinear optical properties,[100, 104] luminescence,[44, 48, 49, 462, 463] and electrolytic production of nitrogen.[464]

VI. Conclusion

The ready availability of tetrazole and its derivatives containing four electron-donating atoms in the five-membered ring and existing as different isomeric forms and the high reactivity of the functional groups attached to the heterocycle ensured successful development of the investigations dealing with synthetic routes to, and physicochemical properties of, diverse MT. Numerous MT containing almost all known metals have now been obtained. The substituents in the tetrazole ring and the method used to prepare MT have a pronounced influence on the MT composition, structure and properties. Of course, the classification of MT proposed in this review is not all-round. There exist a number of compounds that cannot be assigned unambiguously to any type of metal tetrazole derivatives. Nevertheless, analysis based on this classification allows one to carry out deliberate selection of the rational routes to new MT with specified structure and properties. The successful development of synthetic methods forms the grounds for the practical use of many MT in various fields of science and engineering. For other compounds of this series, new practically valuable properties, not always predictable, have been found. Owing to the ability of tetrazole derivatives to be coordinated through different nitrogen atoms of the ring and donor atoms of substituents and to the structural, chemical and functional diversity of the MT formed, these compounds present considerable interest for the study of self-assembly of supramolecular structures and self-organisation of molecules through coordination to transition metal ions and the design of polymeric structures of different dimensionality. The subsequent systematic studies would provide information of what structural features of MT determine the appearance of particular useful properties and would enable targeted synthesis of such derivatives.

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