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Tautomerism and various coordination modes of typical chelating ligands with metals †

A D Garnovskii, I S Vasil'chenko

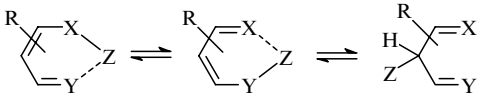
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Abstract. Data on the tautomerism of classical chelating ligands, *viz*., β-diketones and nitrogen- and sulfur-containing analogues, are surveyed. The possibilities of the stabilisation of specific tautomers of these organic compounds due to coordination with metals are discussed. The bibliography includes 455 references.

I. Introduction

Investigations into tautomerism [1–6] and complex formation [1, 7–10] is an important direction of the research activity of the Rostov school of chemists headed by V I Minkin. Proto- and elementotropic tautomerism [1–3, 11] was elucidated, the acylotropy phenomenon (*i.e*., the intramolecular transfer of a COMe group) [5, 12] was discovered, and stereochemically non-rigid structures in their ground and electronically excited states were studied [13, 14] using β-diketones and functionalised aliphatic, aromatic or heterocyclic azomethines **1** as examples of typical chelating ligands.

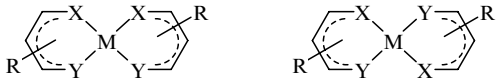


(1)

1a **1b** **1c**

R = H, Alk, Ar; X, Y = O, S; Z = H, COR′, MR′, MR'_2, MR'_3 (R′ = Alk, Ar; M = Hg, B, Ga, Tl, In, Si, Sn, Sb).

V I Minkin and co-workers [7, 8] developed original methods for the synthesis of azomethine intracomplex compounds with metallacycles containing chalcogen atoms (S, Se), and undertook fundamental investigations into the stereochemistry, stereodynamics [13, 14] and photochemistry [15, 16] of the type **2** metal chelates.



2a **2b**

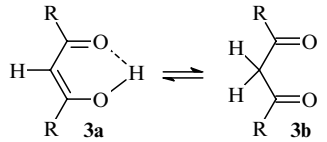
X = O, S, Se; Y = NR′; M = Be, Cd, Hg, Pb, Co, Ni, Cu, Zn.

The above aspects served as a background for the development of an important direction in modern coordination chemistry, *viz*., the coordination-dependent stabilisation of specific tautomeric forms of organic compounds.[6]

The present review surveys the state-of-the-art structural studies of free and coordinated tautomeric chelating ligand systems, which are of great importance for the chemistry of not only complex compounds but of organic and organometallic compounds as well.

II. β-Diketones and their coordination compounds

The problem of stabilisation of a specific tautomeric form of β-diketones upon complexation with metal ions was discussed for the first time by Kukushkin.[17] It is known that β-diketones exist in two tautomeric forms, *viz*., ketoenol (**3a**) and diketone (**3b**) with the former predominating.[2–5]



(2)

3a **3b**

R = Alk, Ar.

Coordination compounds of these chelating ligands are widely represented by intracomplex compounds ML_n (L^- is an anionic ligand). Contributions of specific tautomeric forms of the ligands to the solid-state or solution structures of such complexes cannot be estimated due to the equality of the intrachelate bonds M – O (from X-ray diffraction data [18–24]).

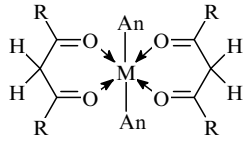
In those cases where β-diketones act as neutral proton-containing ligands (LH),[19–30] the ketone form **3b** is realised (for instance, in complex **4**). This has been proved using X-ray

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† Dedicated to Academician Vladimir Minkin on the occasion of his 70th birthday.

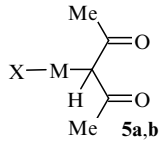
diffraction studies with the objective localisation of all hydrogen atoms.[18, 25, 26]



4

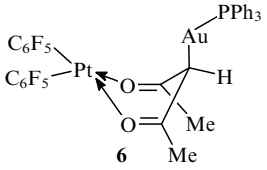
An is a monocharged anion.

The same structure is typical of mono- (compounds **5**)[18, 25, 26] and polynuclear (compounds **6** and **7**)[31, 32] complexes as well as of compound **8**, in which two β-diketone fragments are differently bound to a metal atom.[18]

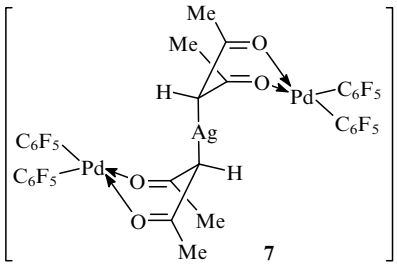


5a,**b**

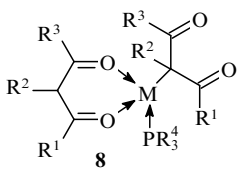
5a: M = Hg, X = Cl, OAc;
5b: M = Au, X = Ph_3P.



6



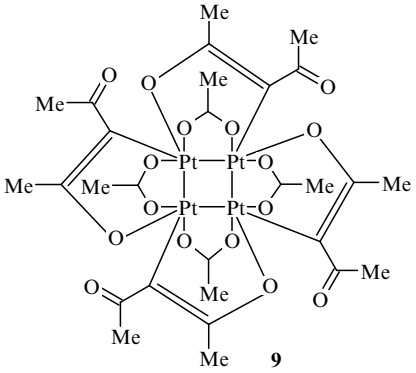
7



8

M = Pd, Pt;
R^1, R^2, R^3, R^4 = Alk, Ar.

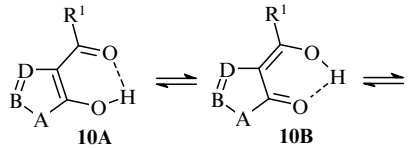
Unusual C,O-coordination of the β-diketonate ligands was observed in complex **9**.[33]



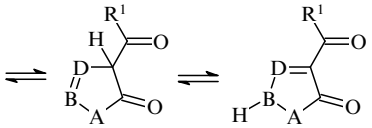
9

The type **2** (X = Y = O), **4** and **5** β-diketonate complexes can be prepared by both chemical (from metal salts)[34, 35] and electrochemical (from zero-valent metals)[34–37] methods. The structures of coordination compounds **2**, **4**–**9** were unequivocally established by X-ray diffraction studies.

Studies of the tautomeric forms of heterocyclic β-diketone ligands **10** showed[6, 21, 38, 39] that the tautomeric equilibrium (3) in solution is shifted towards the formation of the ketoenol form **A**, which is typical of these ligand systems in the crystalline phase as well.[6, 21, 38–44]



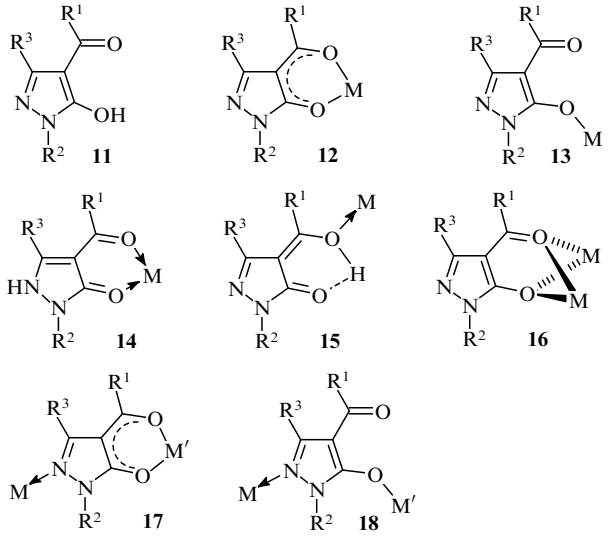
10A **10B** (3)



10C **10D**

A = NR^2, O, S, Se; B, D = CR^3, N; R^1, R^2, R^3 = H, Alk, Ar.

4-Acylpyrazol-5-ones **11** are the most studied ligands.[6, 21, 38] Characteristic types of their coordination with different metals are shown below. Different tautomeric forms of these ligand systems (complexes **12**–**18**) are realised depending on the nature of the metal atom.[21]

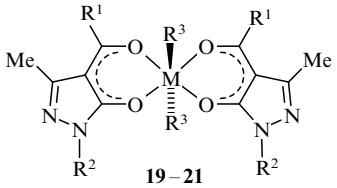


11 **12** **13**
14 **15** **16**
17 **18**

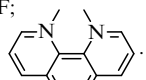
R^1, R^2, R^3 = Alk, Ar.

Studies devoted to β-diketonates **12** with equalised intrachelate bonds are most numerous.[6, 21, 39–43, 45–48]

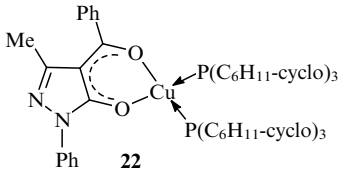
Nearly identical M—O bond lengths in complexes **19**–**21** confirm the delocalisation of the intrachelate bonds within the ligands.[48, 49]



19–**21**

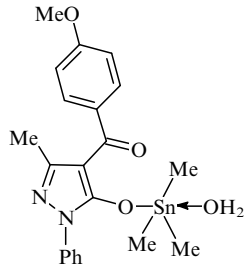
19: M = Sn, R^1, R^3 = Alk, R^2 = 4-MeC_6H_4;
20: M = Zn, R^1 = R^2 = Ph, R^3 = DMF;
21: M = Cu, R^1 = CF_3, R^2 = Ph, R_2^3 = .

A similar type of coordination was also revealed in the monochelate complex **22** using X-ray diffraction.[50]

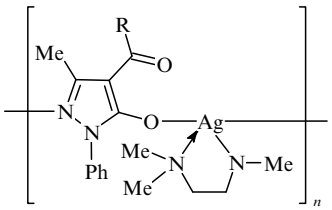


22

According to the X-ray diffraction data, the β-diketonate ligand in the organometallic derivative **23**[51, 52] and in polymeric complex compounds **24** exists in the enol form.[53]

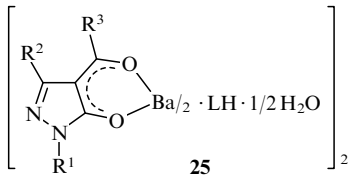


23



24

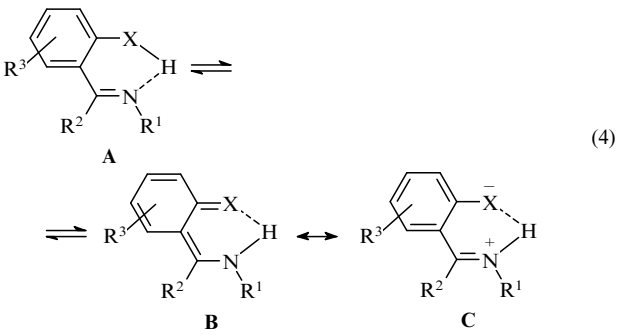
Of particular interest is complex **25** where the chelate form and the diketone form of the molecular ligand (LH) are simultaneously present.[21]



25

III. Hydroxy-, amino-, thio- and seleno-substituted aromatic azomethines and their metal complexes

It is known that azomethines with the general formula *o*-HXArC(R^2)=NR^1 can exist in three tautomeric forms **A**, **B** and **C** [equilibrium (4)].



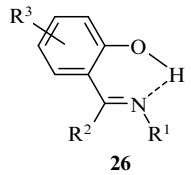
(4)

X = O, NR^4, S, Se.

The tautomeric equilibrium (4) is strongly affected by the nature of the donor atom X.

1. Schiff bases with one OH group

Among such tautomeric systems, azomethines of salicylaldehyde and *o*-hydroxynaphthaldehyde **26** are the most abundant.[1–5, 8, 11, 54–58]

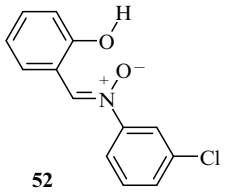


26

R^1 = Alk, Ar, Het; R^2 = H, Alk, Ar; R^3 = H, 5,6-benzo.

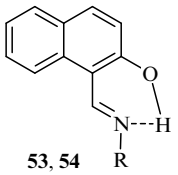
The existence of the tautomeric equilibrium (4) in solutions of azomethines **26** and of their derivatives has been confirmed by diverse physical methods,[1–6, 8, 11, 54–56] whereas its involvement in crystalline phases has been observed only in a few examples. The large body of X-ray diffraction studies on the structures of this class of compounds published in 1990–2000 (compounds **27**–**51**, Table 1) suggested that it is form **A** of the ligand that is virtually always realised in the crystalline phases.[59–86] It is of note that the presence of bulky substituents (compounds **31**–**36**)[63–67] or coordinatively active fragments (compounds **37**–**49**)[68–84] at the nitrogen atom of the imino group does not affect the type of tautomeric form of the azomethine ligand.

The enolimine tautomeric form is also retained in other modifications of the imine; for instance, this was found in *o*-hydroxyazomethine *N*-oxide **52**.[87]



52

The structures of the Schiff bases of *o*-hydroxynaphthaldehyde are of particular interest.[68, 88–94] As has been established using ^{1}H, ^{13}C and ^{15}N NMR spectroscopy, UV and IR spectroscopy in solution,[11, 55, 56, 68] equilibrium (4) is shifted towards the formation of tautomer **B** (X = O)[88] with an increase in the bulk of the aromatic fragment annulated to the azomethine system of the aromatic fragment (*i.e.*, on going from salicylaldehyde to *o*-hydroxynaphthaldehyde). Meanwhile, tautomeric form **A** prevails[89, 92–94] in crystals (*e.g.*, in compounds **34**, **53**, **54**).

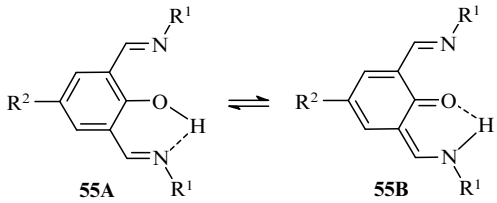


53, **54**

53: R = C_6H_4X-4 (X = Cl, F);
54: R = 3-pyridyl.

The study by Nazir *et al.*[68] is worth a special note: they synthesised both tautomers of the Schiff base of 2-hydroxy-1-naphthaldehyde and 2-aminopyridine and proved their co-existence in the crystalline phase using X-ray diffraction.

Substituted 2,6-diformylphenol diimines **55** are of significance as alterdentate[13, 95, 96] ligands.[97–99]



(5)

55A **55B**

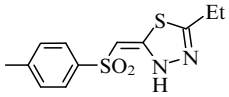
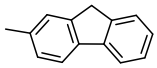
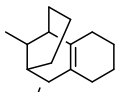
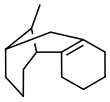
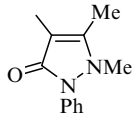
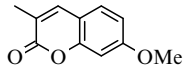
R^1 = Ph, Pr^i, *p*-Tol, cyclo-C_6H_{11}; R^2 = Me, Bu^n, OMe, Br, NO_2.

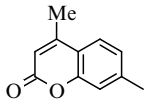
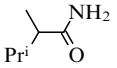
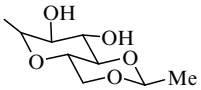
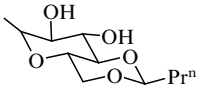
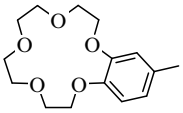
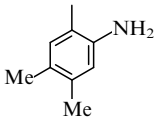
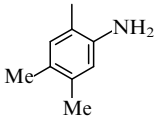
A study of the photo- and thermochromic properties of compounds **55** with consideration of the character of the R^1 and R^2 substituents and the solvent nature has shown that equilibrium (5) is shifted towards the formation of the enolimine tautomer **55A**[97] (this form is also present in the crystalline phase according to X-ray diffraction data[99]) in nonpolar solvents, whereas it is shifted towards the formation of the quinomethide tautomer **55B** in polar solvents (*e.g.*, in DMSO). An increase in temperature shifts equilibrium (5) in a similar way. Alkyl substituents R^1 at the nitrogen atom shift the equilibrium towards the formation of tautomer **B**, whereas aryl substitutents shift it towards tautomer **A**. The presence of donor substituents R^2 in the aldehyde fragment stabilises the enolimine form of ligand **55A**, whereas acceptor substituents shift equilibrium (5) to the right.

2. Schiff bases with two and more hydroxy groups

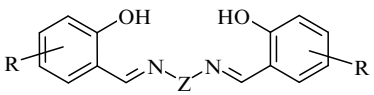
Many mono- and binuclear metal complexes containing Schiff bases with several OH groups as ligands are known.[34, 35, 100, 101] Among them, ligands with two hydroxy groups where two azomethine fragments are bound to each other by a bridge Z through the imine nitrogen atoms (compounds **56**–**65**),[102–111] or the carbon atoms of the aldehyde moieties (compounds **66a**,**b**,

Table 1. Azomethines of salicylaldehyde and 2-hydroxynaphthaldehyde (type **26**) and their derivatives with known crystal structures.

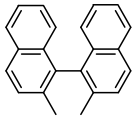
Compound	R^1	R^2	R^3	Ref.
27	Ph	H	5-Cl	59
28	C_6H_4F	H	H	60
29	C_6H_4F	H	OMe	61
30		H	H	62
31	2,6-$Pr^i_2C_6H_3$	H	3-Me	63
32	2,6-$Pr^i_2C_6H_3$	H	3,5-Cl_2	64
33		H	H	65
34		H	4,5-benzo	66
35		H	H	67
36		H	H	67
37	2-C_5H_4N	H	H	68
38	2-C_5H_4N	H	3,4-benzo	68
39		H	H, 3,4- and 4,5-benzo, 4,5-(15-crown-5)	69–73
40		H	H	74

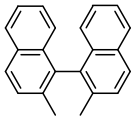
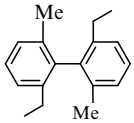
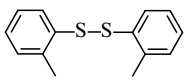
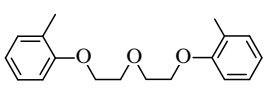
Compound	R^1	R^2	R^3	Ref.
41		H	3-CH_2NEt_2-5-Br	75
42		H	3-CHMePh-5-Me	76
43		H	H	77, 78
44		H	H	79
45		H	5-Br	80
46	2-$NH_2C_6H_4$	H	H, 5,6-benzo	81, 82
47	2-$NH_2C_6H_4$	Ph	5-Me	83
48		Me	H	84
49		Ph	5-Me	83
50	Pr^n	Me	4-Me-5-Cl	85
51	CHMePh	Ph	3,6-[$(CH_2)_2C_6H_4(CH_2)_2$-*p*]	86

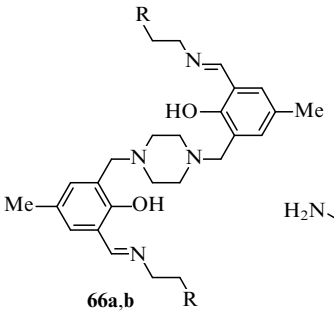
67)[112–114] or through the N and C atoms simultaneously (compounds **68**, **69**)[112,115–117] are the most abundant. Various alkyl, aryl, aralkyl, O-, N- and S-containing cyclic or acyclic fragments,



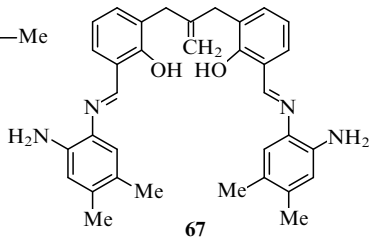
56–**65**

Compound	Z	R	Ref.
56	$(CH_2)_2$	5-Br	102
57		3,5-Bu^t_2	103
58		5-Br	104
59		3,5-Bu^t_2	105
60		3-OMe	106

Compound	Z	R	Ref.
61		3-OEt	107
62		5-Br	108
63		H	109
64		3-OMe	110
65		H	111

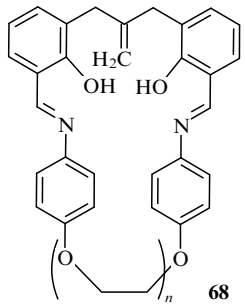


66a,b

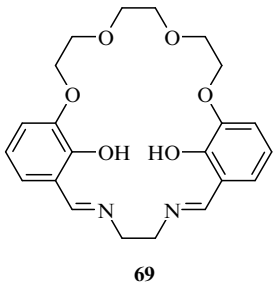


67

R = NMe_2 (**a**), OH (**b**).



68

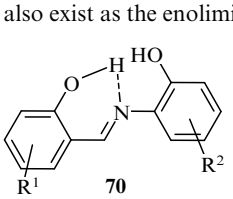


69

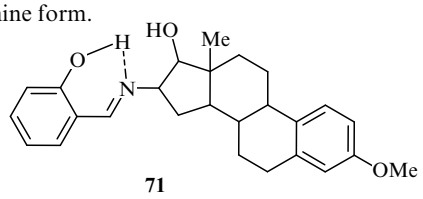
n = 3, 4.

etc. can act as the bridges. The hydroxyimine tautomeric form of these ligands predominates in both solution and crystalline phases.

Salicylaldehyde derivatives with OH-containing substituents at the nitrogen atom, *e.g*., compounds **70** and **71**,[118,119] represent another class of azomethine ligands with two OH groups. They also exist as the enolimine form.



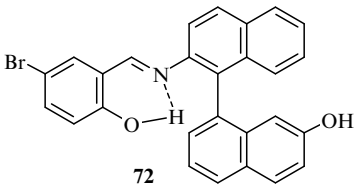
70



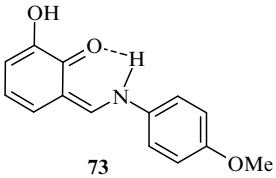
71

In these derivatives, the formation of intramolecular H-bonds can involve both OH groups giving rise to five- or six-membered rings. X-Ray diffraction studies have shown that six-membered rings are formed in bishydroxy imines **70** and **71**.

In the recently synthesised and structurally characterised[120] derivative **72**, only one of two possible H-bonded rings[11,58] is formed, which involves the OH group of salicylaldehyde; the substituent at the nitrogen atom is rotated in such a way that the OH group is far from the nitrogen atom.



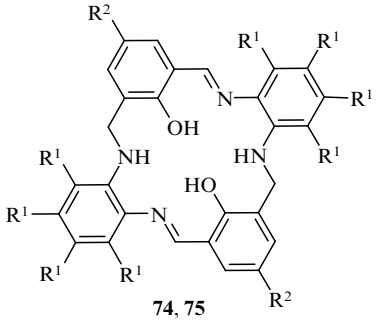
72



73

A similar situation occurs in the case of 2,3-dihydroxyazomethine **73**,[121] which exists in the ketoenamine form in the crystal. One of the OH groups of this compound, *viz*., in the *ortho*-position with respect to the imino group, is involved in the intramolecular H-bonding (closure of a six-membered ring), while the second one forms H-bonds with the carbonyl oxygen atom of a neighbouring molecule. This gives rise to dimers with a ten-membered H-bonded pseudocycle. According to ^{1}H and ^{13}C NMR spectroscopy, fast exchange between the ketoenamine and enolimine forms is observed in solution at room temperature.[121]

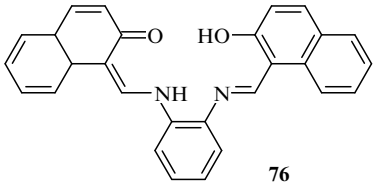
Macrocyclic azomethines (*e.g*., compounds **74** and **75**)[122–124] and Schiff bases containing crown-ether fragments (*e.g*., compounds **68** and **69**)[112,115–117] exist in the enolimine tautomeric form in both solution (as evidenced by ^{1}H NMR data) and the crystalline phase (according to X-ray diffraction).



74, **75**

74: R^1 = F, R^2 = Bu^t; **75**: R^1 = H, R^2 = Me.

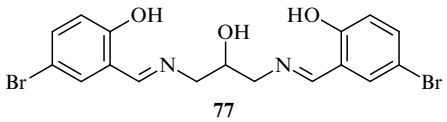
The crystal structure of compound **76** is of considerable interest; this has been determined using X-ray diffraction and the positions of all hydrogen atoms have been revealed objectively. Two tautomeric forms, *viz*., enolimine and ketoenamine, co-exist in molecules of **76** at 200 K.[125]



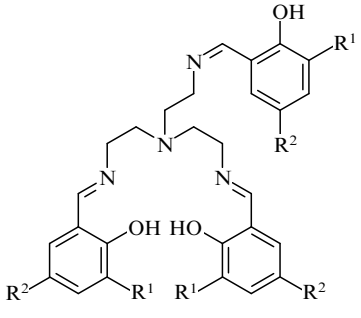
76

The co-existence of two tautomeric forms in one molecule of **76** is also supported by IR spectroscopy (KBr pellets): two bands at 1605 cm^{-1} and 1622 cm^{-1} are observed in the region 1600–1700 cm^{-1} Although Popovic *et al*.[125] attributed both bands to vibrations of the C=N bond (see Refs 126–129), there are reasons to re-assign the higher-frequency band to vibrations of the C=O group involved in the formation of the intramolecular H-bond. There is some experimental evidence that both of the above tautomeric forms also occur in solution (according to ^{1}H NMR spectroscopy). Nevertheless, the use of dimethylformamide, which is a strong donor, as a solvent in these spectral studies makes their results doubtful. In particular, a strict assignment of the signals to the fragments OH···N and O···HN is hardly possible.

Prototropic tautomerism is also observed for Schiff bases containing a larger number of OH groups. Typically, these compounds exist in the enolimine tautomeric form. Several Schiff bases containing three (compounds **77**–**80**)[130–132] and four (compounds **66b**, **81**, **82**)[113,133–135] OH groups are listed below.

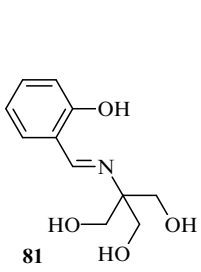


77

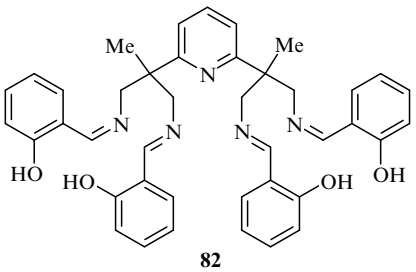


78–**80**

R^1 = H, R^2 = Cl (**78**); R^1 = Bu^t, R^2 = H (**79**);
R^1 = CHO, R^2 = Me (**80**).

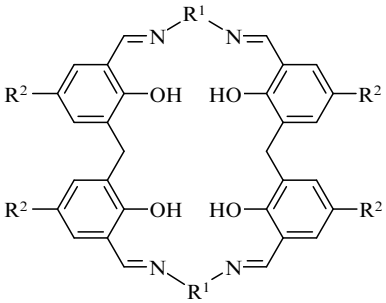


81



82

Macrocyclic compounds (*e.g.*, ligands **83**, **84**, *etc.*)[112, 114, 136–138] constitute another group of tetrahydroxyazomethine derivatives.

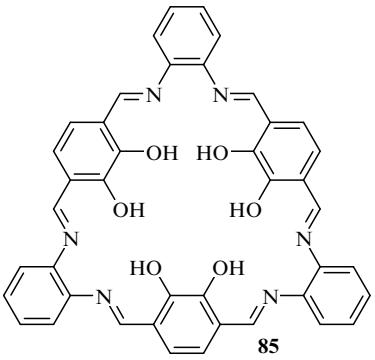


83, **84**

83: R^1 = , R^2 = Bu^t;

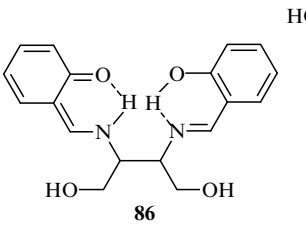
84: $R^1 = -(CH_2)_2O(CH_2)_2O(CH_2)_2-$, R^2 = Me.

To our knowledge, no pentahydroxyazomethine structures have been characterised so far; Schiff bases with six OH groups are represented by single macrocyclic structure **85**.[139]

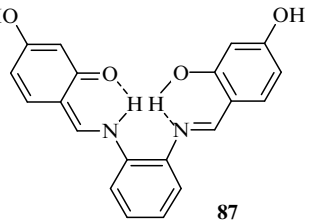


85

Derivatives **86**[140] and **87**[141] are worth a special note among the Schiff bases with four OH groups; their molecules contain two different tautomeric forms simultaneously, which co-exist both at room temperature and at 116 K (according to X-ray diffraction data). The reported ^{1}H NMR data (in $CDCl_3$) concerned only the possibility of the existence of compound **86** in the open or cyclic forms rather than tautomeric equilibrium.



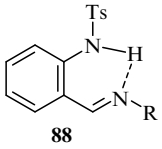
86



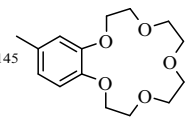
87

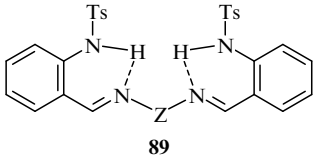
3. Tosylamino- and mercaptoazomethines

Tosylaminoazomethines (X = NTs) exist predominantly in the benzenoid form **A** [like the hydroxyazomethines (X = O) considered above], *i.e.*, equilibrium (4) is shifted to the left.[142–144] This form is typical of the majority of tosylaminophenyl imines **88**[143–146] and bis-*o*-tosylaminobenzylidene derivatives **89** with various bridges Z.[147–149]



88

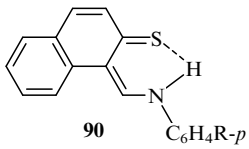
R = Ph,[142] Bn,[143] Bu^t,[144] C_6H_4OH-*o*,[145]  (see [146]).



89

Z = C_2H_4,[147]  (see [148]),  (see [149]).

In contrast, in the case of sulfur-containing analogues of hydroxyazomethines (X = S), equilibrium (4) is shifted towards tautomer **B**, as evidenced by data from UV, IR and ^{1}H NMR spectroscopy and supported by quantum-chemical calculations.[150, 151] The fraction of tautomer **B** increases with an increase in the polarity of the solvent, nucleophilicity of the substituent at the nitrogen atom (R^1) and acceptor properties of the substituent R^3 (see Ref. 150). In particular, it was established [151] that the thioderivative **90** exists virtually exclusively in the tautomeric form **B** in solution (DMSO, ethanol).

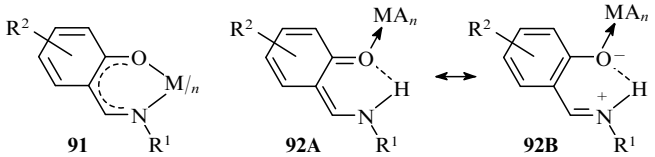


90

R = H, Me, Cl, OMe, NO_2.

4. Coordination compounds of azomethines

Coordination compounds of hydroxyazomethines can be subdivided[1, 8, 22, 27, 28, 34, 35, 57, 58] into traditional chelates **91** and nonstandard molecular complexes **92A** and **92B**.



91 **92A** **92B**

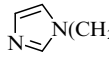
R^1 = Alk, Ar; R^2 = H, Hal, NO_3; A = Hal, NO_3; n = 3, 4.

There is experimental evidence[58, 152, 153] that interconversion is possible between the chelate (**91**) and molecular (**92**) complexes.‡

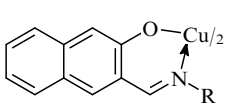
Intracomplex compounds of type **91** were the subject of numerous monographs[34–37] and reviews,[8, 22, 58, 154–159] thus only compounds with crystal structures established over the last five years will be considered below. The respective copper, zinc and cobalt intracomplex compounds (structural data published in 2000–2004)[63, 152, 160–169] are listed in Table 2.

‡ In the majority of schematic drawings of chelate structures, the enol-imine tautomeric form **A** [equilibrium (4)] is depicted, although the bonds in anionic azomethine ligands (complex **91**) are substantially delocalised.

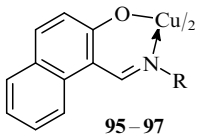
Table 2. Mononuclear chelate complexes of 3d metals with hydroxyazomethine ligands of the type **91**.

M	R^1	R^2	Ref.
Cu	$CHPh_2$	H	160
Cu	n-C_8H_{17}	H	161
Cu	C_6H_4OMe-*p*	H	162
Cu	C_6H_4F-*p*	H	163
Cu	C_6H_4Cl-*p*	H	164
Cu	C_5H_9-cyclo	H	165
Cu	C_6H_{11}-cyclo	H	165
Cu		3,5-Bu^t_2	166
Zn	Pr^n	H	152
Zn	$C_6H_3Pr^i_2$-2,6	3,5-Bu^t_2	63
Zn	CHMePh	4-OMe	167
Zn	CHMePh	4-NO_2	167
Zn	$C_6H_3Pr^i_2$-2,6	4-NO_2	168
Co	cyclo-$C_6H_9Pr^i$-2-Me-5	H	169

A series of copper complexes **93**–**97** containing azomethines of naphthaldehyde as ligands have been characterised structurally.[165, 170–173]



93, **94**

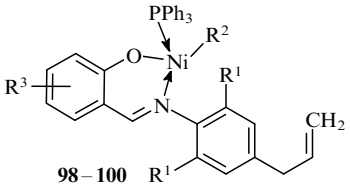


95–**97**

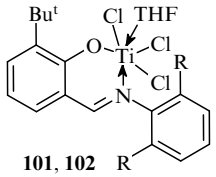
R = $CHEt_2$ (**93**),[170] cyclo-C_7H_{13} (**94**).[165]

R = C_6H_4Cl-*o* (**95**),[171] C_6H_4I-*o* (**96**),[172] $C_6H_3(NMe_2)_2$ (**97**).[173]

Monochelates **98**–**102**[176–179] are of great potential importance as catalysts of polymerisation processes.[174, 175]



98–**100**



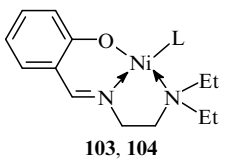
101, **102**

98: R^1 = Me, R^2 = Ph, R^3 = 3-Ph;[176]
99: R^1 = Pr^i, R^2 = Ph, R^3 = 3,5-$(NO_2)_2$;[177]
100: R^1 = Pr^i, R^2 = Cl, R^3 = 3-Ph.[178]

R = H (**101**), Pr^i (**102**).[179]

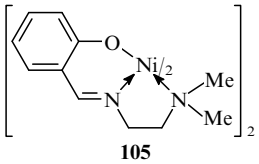
In complexes **101** and **102**, trimethylsilyl derivatives of salicylideneaniline are used as ligands.[179]

In complexes of hydroxyazomethines containing coordinatively active fragments with N-, P-, O- or S-donor centres at the nitrogen atom of the imino group,[180–186] additional coordination with the metal atom is observed. For instance, this is typical of complexes **103**–**108**.[181, 184, 186–188]

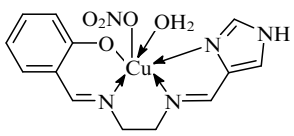


103, **104**

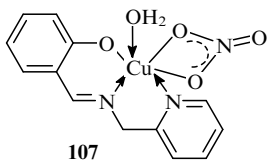
L = N_3 (**103**), NCS (**104**)



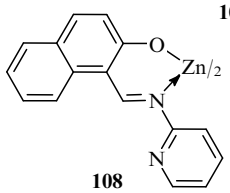
105



106



107

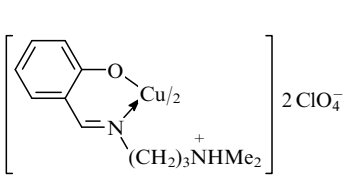


108

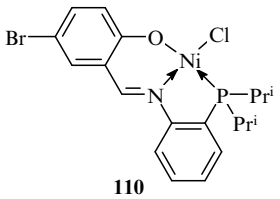
The dependence of the coordinative activity of the nitrogen atom of the pyridine fragment on the size of the metallacycle formed was analysed by several authors.[34, 35, 57, 58] It was found that five-membered rings are more stable than four-membered ones. The molecular structures of compounds **107** and **108** support this conclusion.

Protonation of the amino group in the coordinatively active substituent at the nitrogen atom of the imino group (compound **109**)[189] suppresses the donor properties of the substituent.

Among phosphorus-containing azomethine compounds, we are aware of only one complex **110** with the coordination core NiNPOCl.[190]

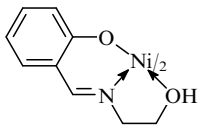


109

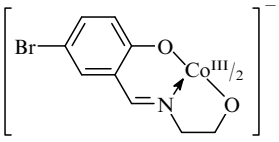


110

Intracomplex compounds of azomethines with coordinatively active oxygen-containing fragments[57, 58, 191] include mononuclear complexes with a protonated (compound **111**)[192, 193] or deprotonated (compound **112**)[194] OH group.

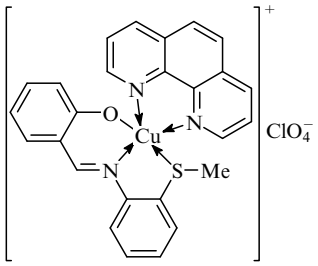


111

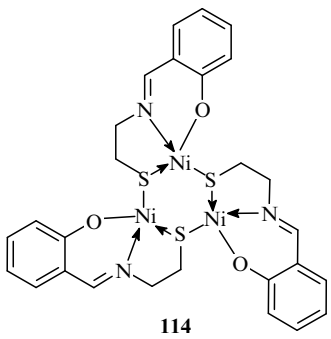


112

In the case of hydroxyazomethine ligands with sulfur-containing coordinatively active substituents, both mono- (compound **113**)[195–197] and polynuclear (compound **114**)[198] complexes have been synthesised.

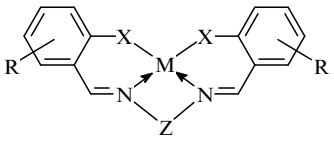


113



114

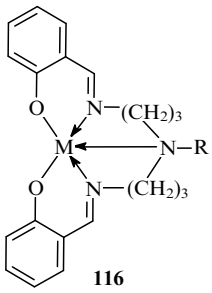
The structures of chelates **115** for the Group III elements of the Periodic Table have recently been reviewed[199] and structures of complexes of 3d metals (copper, nickel, cobalt) are considered in Refs 200–204.



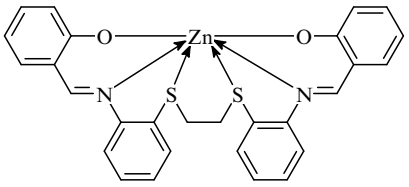
115a–e

115a: M = Cu, Z = $(CH_2)_3$, X = O, R = H;[200]
115b: M = Ni, Z = $(CH_2)_3$, X = O, R = 6-OMe;[201]
115c: M = Ni, Z = $(CHPh)_2$, X = O, R = H;[202]
115d: M = Ni, Z = $(CHPh)_2$, X = O, R = NEt_2;[203]
115e: M = Co, Z = , X = O, R = 3,5-Bu^t_2.[204]

If the bridge Z contains coordinatively active donor atoms, the dentate numbers of ligands and coordination numbers of the complex-forming metal atoms increase (complexes **116**[205] and **117**[206]).



116



117

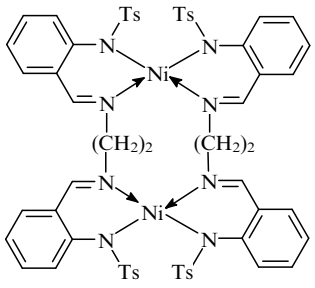
M = Co, Cu; R = H, Pr^n, $SiMe_3$, $Si(OMe)_3$.

Azomethine compounds with three OH groups (*e.g.*, **78–80**) form complexes with lanthanides with the composition LnL (Ln = La, Ce, Sm, Tb, Y or Lu) where triply deprotonated molecules act as the ligands L^{3-}. In these complexes, a complex-forming metal atom binds three nitrogen atoms of the C=N groups and a nitrogen atom of the amino group (according to X-ray diffraction data).[132]

Coordination of ligand **86**, which exists in two tautomeric forms, gives rise to a series of chelates **115** (M = Mn, X = O, R = H, Z = CH_2OH-CH_2OH) with structures typical of bis-salicylideneiminates.[140]

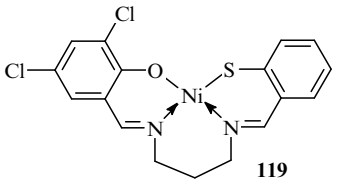
Similar complexes are formed upon coordination of ligands **89**.[207–211] In particular, metal chelates with the coordination core MN_4 [Z = $(CH_2)_3$, M = Cu;[208] Z = $(CH_2)_2CHOH$, M = Zn;[209] Z = 1,2-C_6H_4, M = Ni;[210] Z = 1,2-C_6H_{10}, M = Ni;[149] Z = 1,2-C_6H_4, M = Cu (see Ref. 211)] analogous to **115** (X = NTs) have been prepared.

The ligands **89** (Z = C_2H_4) can form binuclear chelates in some specific cases as well (*e.g.*, complex **118**).[212]



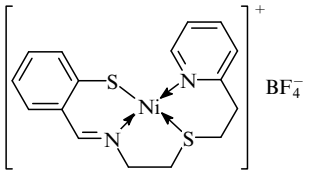
118

The Schiff bases with N,N,O,S- and N,N,S,S-donor centres form intracomplex compounds **119**[213] and **115** (X = S, M = Cu, Z = C_2H_4),[214] which are characterised by the *cis*-planar configuration of the cordination core.



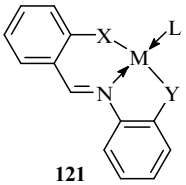
119

The mercaptoazomethine ligand with the substituent $(CH_2)_2S(CH_2)_2(C_5H_4N\text{-}2)$ with coordinatively active N and S atoms at the nitrogen atom of the imino group forms a nickel complex with the NiN_2S_2 coordination core (complex **120**, X-ray diffraction data).[215]



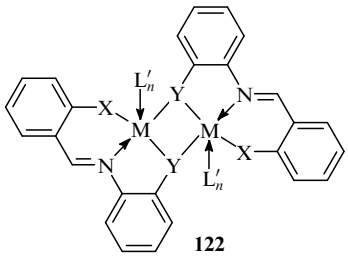
120

Numerous mono- (**121**) and binuclear (**122**) structures with tetra-, penta- and hexa-coordinated metal sites have been synthesised based on bishydroxyazomethines **70** (O,N,O-) and related N,N,N-, N,N,O-, N,N,S- and N,O,S-tridentate azomethines.



121

X, Y = NTs, O, S; L = Het.

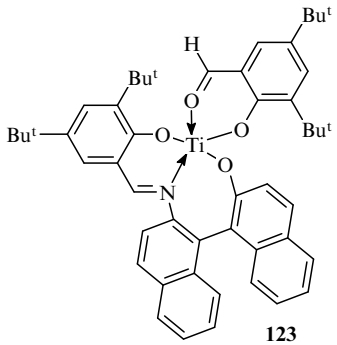


122

X = NTs, O, S; Y = O, S; L′ = H_2O, MeOH.

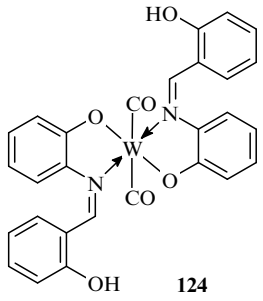
The structures of these complexes have been surveyed in several monographs[34–37] and a review[58]. Recently, the structures of nickel, copper and zinc complexes with tosylaminoazomethine ligands (X = NTs, L = 2-aminopyridine, L′ = MeOH) have been reported.[216–218]

Compound **123**[120] containing six- and seven-membered metallacyclic fragments represents an interesting example of complex formation involving a tridentate azomethine ligand.



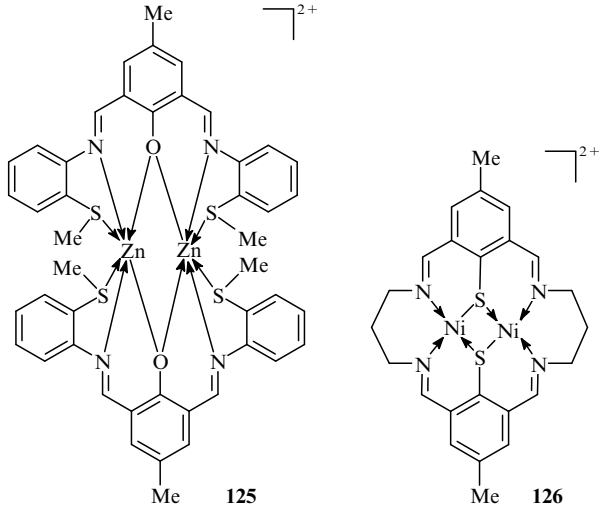
123

The presence of two OH groups in positions suitable for double chelation does not guarantee the realisation of structures **121** or **122**. For instance, ligand **71** afforded mononuclear intracomplex compounds due to coordination of only one hydroxy group of the hydroxyazomethine fragment.[119] An unusual structure of tungsten complex **124** was suggested by El-Medani.[219] Unfortunately, no reliable X-ray diffraction data confirming this structure are available for this compound.



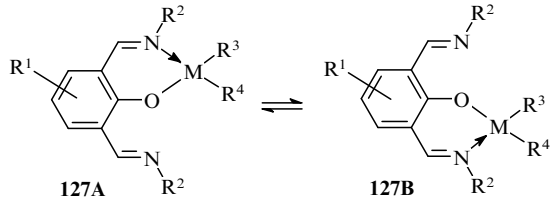
124

Complexes based on the alterdentate ligand systems **55** or on their sulfur-containing analogues [220–222] have predominantly binuclear structures. The metal atom is coordinated by both imine nitrogen atoms and an oxygen (complex **125**) [221] or sulfur (complex **126**) atom.[222] Similar complexes are formed with macrocyclic Schiff bases.[158, 159, 220]



125 **126**

Sometimes, both imine nitrogen atoms of the alterdentate ligands **55** [13, 14, 97] cannot be involved in coordination with a metal atom simultaneously due to spatial restrictions. In these cases, intermediate structures (**127**) are formed with equally probable involvement of any of the two nitrogen atoms in coordination with the metal.

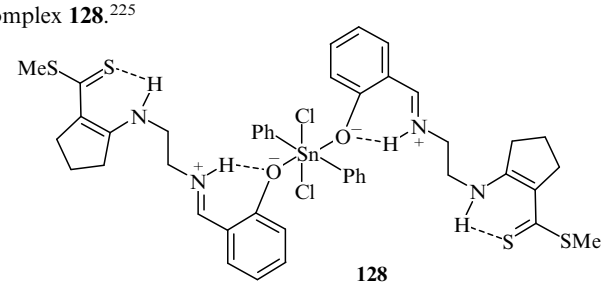


127A **127B**

M = B, Ga, In; R^1 = H, 5-NO_2, 5,6-benzo;
R^2 = Me, Pr^i, Bn; R^3 = OMe, OPr^i, OBn; R^4 = Ph, C_6H_4OMe-4.

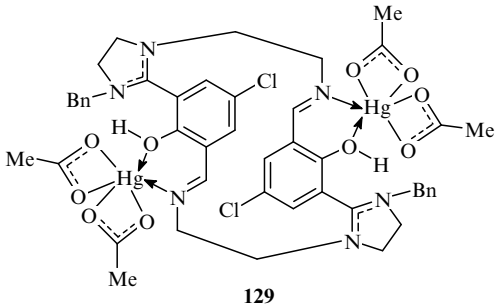
Similar coordination is typical, for instance, of organoboron derivatives.[223]

The intrachelate bonds in complexes **91** with anionic ligands are delocalised. Meanwhile, according to X-ray diffraction studies with objective localisation of all hydrogen atoms, the ligand exists in molecular complexes **92** in the ketoenamine (quinomethide) form.[34, 35, 58] This form was also revealed in complexes of salicylidene imines (**92**: R^1 = Ar, R^2 = H) [152] and hydroxynaphthylmethylidene (**92**: R^1 = Ph, R^2 = 4,5-benzo) [89] with zinc dichloride. Although the proton is reliably localised at the nitrogen atom and the coordination of the oxygen atom with the metal atom is confirmed in such complexes, the formation of enolimine [224] and zwitter-ionic [152] structures cannot be totally ruled out. In particular, a zwitter-ionic structure was suggested for the molecular complex **128**.[225]



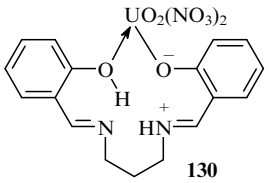
128

Compound **129** [226] manifests the N,O-chelate coordination that is unusual for molecular complexes of hydroxyazomethines.



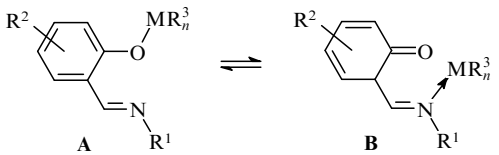
129

The structure of **130** [227] confirms the possibility of the coexistence of two tautomeric forms in one molecule of bishydroxyazomethine.



130

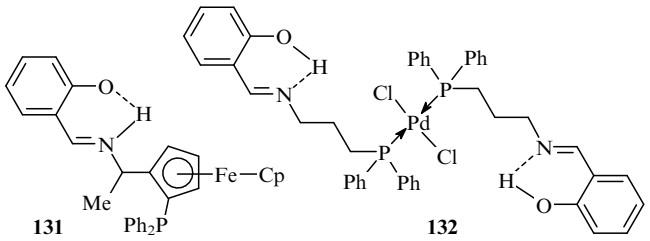
The tautomeric metallotropic equilibrium (6) invlolving organometallic derivatives of azomethines was studied using spectroscopic [228] and X-ray diffraction [229] methods. It was established that coordination of the oxygen atom with a metal atom stabilises the enolimine (benzenoid) form **A**, whereas coordination of the nitrogen atom stabilises the ketoenamine (quinomethide) tautomeric form **B**.



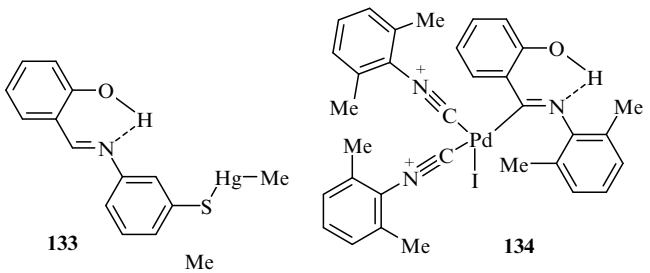
A **B** (6)

R^1 = H, Me, C_6H_4OMe-*p*; R^2 = H, 5,6-benzo; R^3 = Me, Ph;
M = Hg, Tl; *n* = 1, 2.

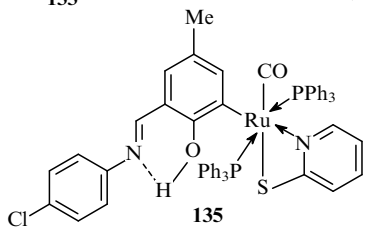
The fraction of the latter increases with an increase in the solvent polarity (*e.g.*, DMSO) and with a lowering of the temperature.[228] Apparently, both tautomeric forms occur in crystalline phases.[229] Although the tautomeric equlibrium (6) has not been studied in detail with other organometallic derivatives of hydroxyazomethines, X-ray diffraction data indicate the predominance of the enolimine tautomers **A**. The enolimine form of the ligand is also realised in complexes **131**–**135** [230–235] where substituents at the nitrogen (compounds **131**–**133**) or carbon (compound **134**) atoms of the imino group or at the carbon atom of salicylaldehyde (compound **135**) contain metal-bearing fragments.



131 **132**

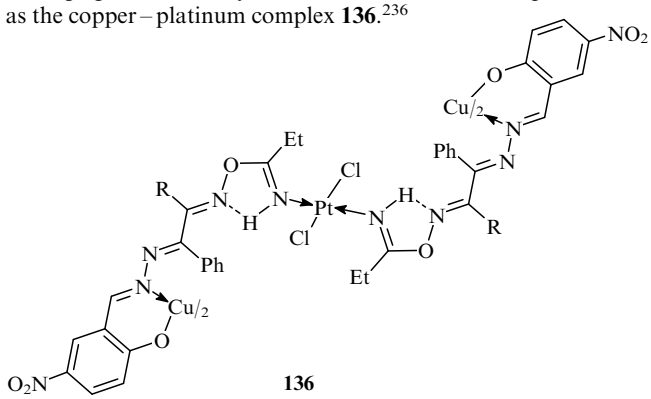


133 **134**



135

Compounds similar to **131**–**135** can be used as metal-containing ligands for the synthesis of heteronuclear complexes, such as the copper–platinum complex **136**.[236]

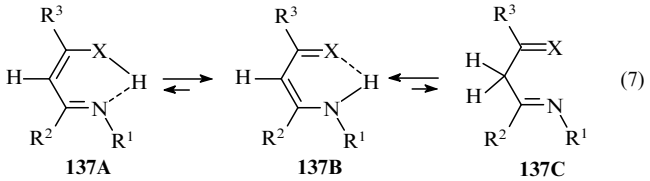


136

Thus, functionalised azomethines exist predominantly in the enolimine tautomeric form independently of the nature of the substituents. Intracomplex compounds **91** containing this ligand system are characterised by delocalised intrachelate bonds, whereas the ketoenamine tautomeric form of ligand **92** is stabilised in molecular complexes due to metal coordination.

IV. β-Aminovinyl ketones, thiones, imines and their complexes

In contrast to the functionalised aromatic Shiff bases, the tautomeric equilibrium (7) in solutions of enamino ketones (X = O), thiones (X = S) and imines (X = NR^4) **137** is shifted towards form **B**, as evidenced by data from NMR and electronic spectroscopy and supported by quantum-chemical calculations.[11, 55, 56, 237, 238]

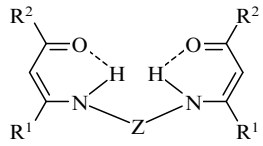


137A **137B** **137C** (7)

X = NR^4, O, S; R^1–R^4 = H, Alk, cyclo-Alk, Ar.

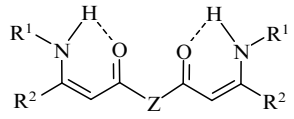
X-Ray diffraction studies[239–253] of enamino ketones (X = O) **138**–**153** confirmed the existence of form **B** in the crystalline phases as well (Table 3).

This form is also typical of bisenamino ketones containing various bridges Z (compounds **154**–**159**).[254–261]



154–**157**

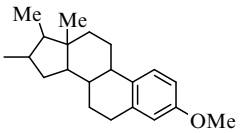
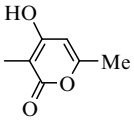
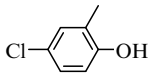
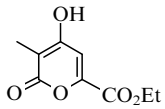
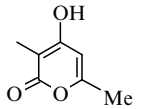
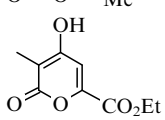
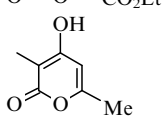
154: Z = C_2H_4, R^1 = R^2 = Me, Ph, Bn; **155**: Z = *o*-C_6H_4, R^1 = Me, R^2 = Ph; **156**: Z = *p*-C_6H_4, R^1 = CO_2Et, R^2 = (η^5-C_5H_4)FeCp; **157**: Z = (η^5-C_5H_4)$_2$Fe, R^1 = R^2 = Me.



158, **159**

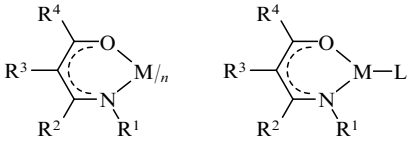
158: Z = $(CF_2)_4$, R^1 = Pr^i, R^2 = Me;
159: Z = (η^5-C_5H_4)$_2$Fe, R^1 = Ph, R^2 = CO_2Et.

Table 3. β-Aminovinyl ketones (type **137**) with known crystal structures.

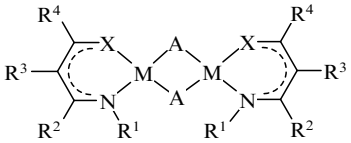
Compound	R^1	R^2	R^3	Ref.
138	4-BrC_6H_4	Me	Me	239
139	4-$NO_2C_6H_4$	Me	Me	240
140	C_6F_5	Me	Me	241
141	XC_6H_4 (X = H, Br, NEt_2)	C(O)Ph	Ph	242
142	2-MeC_6H_4	Bz	Ph	243
143	Bu^n	CO_2Et	(η^5-C_5H_4)FeCp	245
144		Me	Me	119
145		CO_2Et		246
146	2-NH_2-5-$NO_2C_6H_3$	4-$NO_2C_6H_4$	Ph	247
147	2-C_5H_4N	Me	Ph	248
148	2-HOC_6H_4	Me	Ph	249
149	2-HOC_6H_4	Me	Me	250
150		Me	Me	251
151a	1-$C_{10}H_7$	Me		252
151b	1-$C_{10}H_7$	CO_2Et		252
152	4-$MeOC_6H_4$	Me		253
153	4-$MeOC_6H_4$	CO_2Et		253

Metal chelates **160** are the most common complex compounds of β-aminovinyl ketones; their structures have been considered in numerous publications, including reviews,[8, 27, 58, 262] theses [263–265] and monographs.[35, 36] Metal chelates of the type **160** are widely used for the deposition of metal films; thus they attract undying interest. For instance, the structures of copper and palladium metal chelates have recently been reported.[266–268]

In addition to intracomplex compounds **160**, the deprotonated ligands also form mononuclear complexes **161** [269, 270] and binuclear bridged complexes **162**.[264]

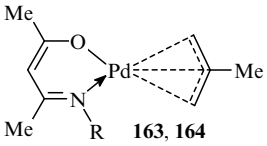


160 **161**



162

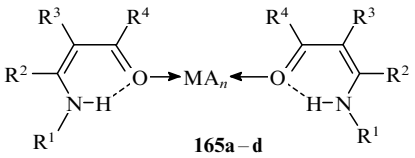
Organopalladium compounds **163** and **164** [269, 270] can be considered as examples of mono-β-aminovinylketonate complexes.



163, **164**

R = CHMePh (**163**), Ph (**164**).

Neutral β-aminovinylketonate ligands (LH) form molecular adducts **165** with the stoichiometry $(LH)_2 \cdot MA_n$.[8] As in the case of free molecules of these enamino ketones, the amino ketone form of the ligands was found [271–276] in these complexes.

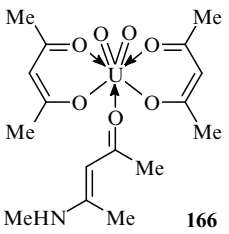


165a–d

165a: $MA_n = TiCl_4$, R^1 = Ph, $R^2 = R^4$ = Me, R^3 = H (taken from Ref. 8);
165b: $MA_n = ZnI_2$, $R^1 = Bu^i$, $R^2 = R^4$ = Me, R^3 = H (see Ref. 271);
165c: $MA_n = MoO_2Cl_2$, R^1 = Ph, $R^2 = R^4$ = Me, R^3 = H (see Refs 272 and 273);
165d: $MA_n = ZrCl_4$, $R^1 = Pr^i$, $R^2 = R^4$ = Me, R^3 = H (see Ref. 274).

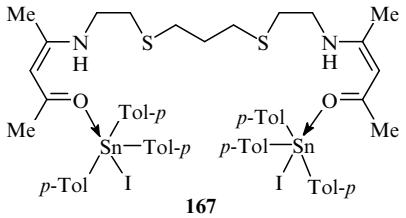
A spectroscopic study of the adduct **165a** has been performed [8] in order to determine the type of ligand coordination (*i.e.*, through the N or O atom). A decrease in the frequency of the stretching vibrations of the carbonyl group in the range 1610–1650 cm^{-1} (which can be due to the formation of a M–O bond) was used as the criterion for localisation of the coordination bond. Notwithstanding, it should be taken into account that the absorption band of the azomethine group shifted to higher frequencies due to M–N coordination can also fall in the same range. This problem was unambiguously solved by X-ray structural investigation of the adducts **165**.

For the first time, coordination of the neutral ligand LH through the oxygen atom was established for a mixed-ligand complex **166**.[271]



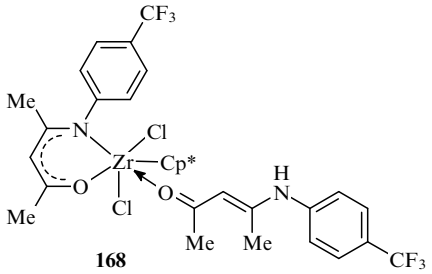
166

The bisenaminoketone adduct **167** [276] reveals similar coordination of the ligand.



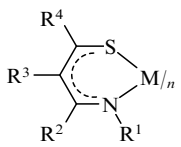
167

Complex **168** is of particular interest since it contains the ligand system in the anionic and neutral forms simultaneously.[277]

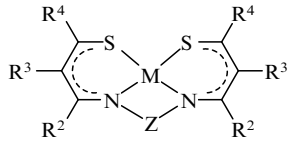


168

Like enamino ketones, their sulfur-containing analogues, enamino thiones **137** (X = S), exist in the β-aminovinylthione tautomeric form **B**.[278–281] Metal salts and deprotonated ligands yield complex compounds **169** and **170** with delocalised chelate bonds.



169



170

Depending on the nature of the metal atom and the substituent R^1 at the nitrogen atom, the metal cores in chelates **169** adopt the *cis*-planar (M = Ni; R^1 = Me, Et),[281] tetrahedral (M = Zn, R^1 = cyclo-C_6H_{11}) [8, 282] or square-pyramidal (M = Cu, R^1 = 8-quinolyl) [283] configurations. Despite the fact that octahedral coordination of the copper atom might be expected for copper complex with the β-aminovinylthione ligand contaning a coordinatively active quinoline fragment, X-ray diffraction data indicated that only one nitrogen atom of the azine substituent is involved in coordination.[264]

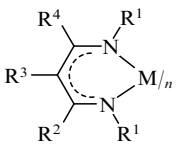
The nickel complex **169** (n = 2) possesses the *cis*-planar structure, whereas analogous copper (n = 2) and zinc (n = 2, 4) complexes are characterised by tetrahedral chelate structures.[8]

It was assumed that neutral β-aminovinylthione ligands form molecular complexes of the type **165** with metal salts (*e.g.*, with MoO_2Cl_2).[8] The formation of an Mo–S bond therein was suggested based on IR data (which cannot be considered reliable since the frequency of the stretching vibrations of the C=S bond is not characteristic), thus this requires independent confirmation using X-ray diffraction.

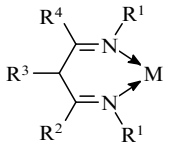
According to X-ray diffraction studies,[284–287] the tautomeric forms **A** and **B** for β-aminovinyl imines **137** (X = NR^4) can hardly

be distinguished, especially in the case of similar types of substituents R^1 and R^4; form **C** has never been detected.

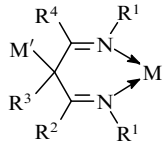
A series of coordination compounds synthesised from β-aminovinyl imines (X = NR^1) has been analysed by Bourget-Merle *et al.*;[288] they proposed that their structures can be classified into several types with **171** – **173** being the most interesting.



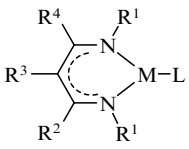
171



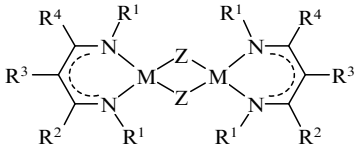
172



173

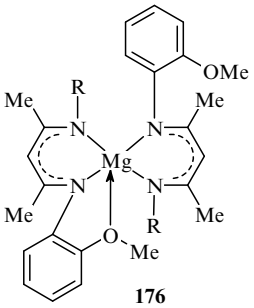


174



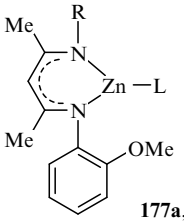
175

Examples of metal chelates of anionic β-aminovinylimine ligands with delocalised coordination bonds include both mono- (types **171** and **174**) and binuclear (type **175**) structures.[288 – 291] Recently reported synthesis [292] of a non-symmetrically substituted β-aminovinyl imine [2-(2-methoxyphenylimino)-4-(2,6-diisopropylphenylimido)pent-2-ene, BDI] and its magnesium and zinc complexes $(BDI)_2Mg$, (BDI)MgPr^i, (BDI)MgNPr$^i_2$, $(BDI)ZnN(SiMe_3)_2$ and (BDI)ZnEt are worth a special note. The structures of the bischelate magnesium complex (**176**) and two monochelate zinc complexes were determined using X-ray diffraction.



176

R = $C_6H_3Pr^i_2$-2,6.



177a,b

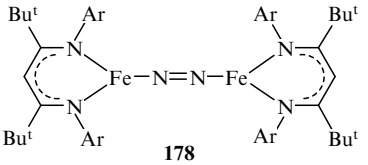
R = $C_6H_3Pr^i_2$-2,6; L = Et (**a**), $N(SiMe_3)_2$ (**b**).

It was found that the two BDI ligands in the bischelate magnesium complex are coordinated differently to the metal atom.

Since the number of publications devoted to monochelate anionic complexes **174** is very large, we mention here only recent structural studies of tricoordinated iron [R^1 = 2,6-$Pr^i_2C_6H_3$, R^2 = Bu^t, L = Me;[293] R^1 = 2,6-$Pr^i_2C_6H_3$, C_6F_5, Mes, 2,6-$Me_2C_6H_3$, 2,6-$Cl_2C_6H_3$, R^2 = Me, L = $N(SiMe_3)_2$;[294] R^1 = Ar, R^2 = Alk, L = Et, CH_2Bu^t, Pr^i;[295] R^1 = 2,6-$Pr^i_2C_6H_3$, R^2 = Me, Bu^t, L = Et, Bu^i, Bu^t (see Ref. 296)], cobalt [R^1 = 2,6-$Pr^i_2C_6H_3$, R^2 = Bu^t, L = Cl, Me;[293] R^1 = 2,6-$Pr^i_2C_6H_3$, R^2 = Me, L = $N(SiMe_3)_2$;[294] R^1 = 2,6-$Cl_2C_6H_3$, R^2 = Bu^t, L = Cl, THF;[293] R^1 = 2,6-$Cl_2C_6H_3$, R^2 = Me, L = Cl, $N(SiMe_3)_2$ (see Ref. 297)], manganese [R^1 = 2,6-$Pr^i_2C_6H_3$, R^2 = Me, L = $N(SiMe_3)_2$ (see Ref. 294)], copper [R^1 = Mes, R^2 = H, L = OAc;[298] R^1 = 2,6-$Pr^i_2C_6H_3$, R^2 = Me, L = $SCPh_3$, Py (see Ref. 299)] and zinc [R^1 = 2,6-$Pr^i_2C_6H_3$, R^2 = Me, L = NPr_2, OBu^t (see Ref. 300)] complexes and tetracoordinated nickel (Dipp)NiR(2,4-Lut) (Dipp = CH[CMeN(2,6-$C_6H_3Pr^i_2$)]$_2$, 2,4-Lut = 2,4-lutidine, R = Me, Et, Pr),[301] zinc (Dipp)Zn($OSiPh_3$)(THF) [300] and magnesium (Dipp)Mg(NPr^i_2)(THF) and (Dipp)Mg(OBu^t)(THF) [300] complexes.

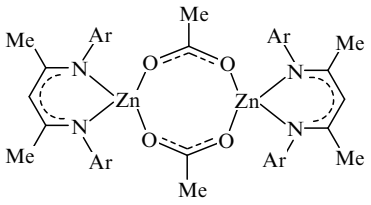
Compounds **174** can form binuclear complexes **175** containing two monoatomic bridges Z [Z = H,[302] Hal,[297, 301 – 304] O,[305] OR (R = H, Alk, Ac),[303, 305 – 308] NR_2, *etc.*]. For instance, monochelate zinc β-aminovinyliminates with the composition (BDI)ZnL [BDI: R^1 = 2,6-$Pr^i_2C_6H_3$, R^2 = H or R^1 = 2,6-$Et_2C_6H_3$, R^2 = H; L = Br, Cl, Et, $N(SiMe_3)_2$, OH, OMe, OPr^i, OAc] were studied.[303] It was established that all these complexes except for ones with L = Et and $N(SiMe_3)_2$ exist in the dimeric form $(BDI)Zn(\mu\text{-}L)_2Zn(BDI)$.

Furthermore, other binuclear chelates with longer bridges are known. In particular, two monochelate fragments are linked through one diatomic bridge N_2 in the iron complex **178**,[309] through two triatomic bridges O---C(Me)---O in the zinc complex **179** [310] and through one triatomic and one monoatomic bridge in complex **180**.[311]



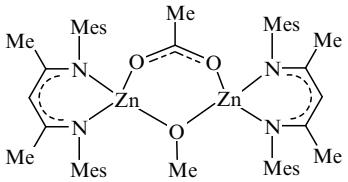
178

Ar = $C_6H_3Pr^i_2$-2,6.



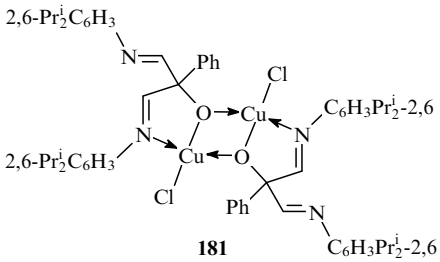
179

Ar = $C_6H_3Et_2$-2,6.



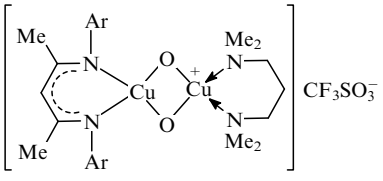
180

Complexes with unusual structures were obtained instead of the expected β-aminovinyliminates in the reaction of 1,3-bis(2,6-diisopropylphenylimido)-2-phenylpropane with Cu^{2+} salts in methanol or ethanol. In particular, copper bis-β-diketonate and the dimer **181** were obtained from $Cu(ClO_4)_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$, respectively; the structure of the latter was established using X-ray diffraction.[312]

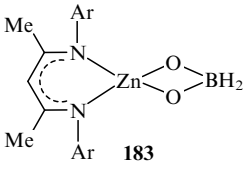


181

Yet another large class of binuclear metal complexes with β-aminovinyl imines as ligands is represented by compounds where two metal atoms linked through a bridge have different ligand environments. For example, complexes **182** – **185** [313, 314] fall into this class.

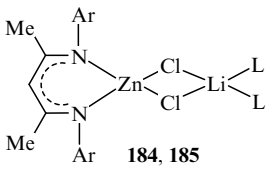


182



183

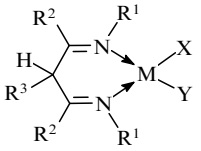
Ar = $C_6H_3Pr^i_2$-2,6.



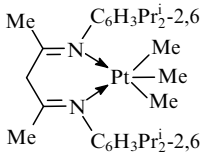
184, **185**

L = OEt (**184**), THF (**185**);
Ar = $C_6H_3Pr^i_2$-2,6.

The complexes considered above contain a β-aminovinylimine ligand in the deprotonated form. In addition, complexes are known with the ligands in neutral form; coordination with a metal stabilises the diimine tautomeric form **172**, which is not typical of free enamino imines.[288] This form of the ligand was found both in mononuclear (**186**–**192** [315–321]) and binuclear (**193** [317] and **194** [286, 322]) complexes.

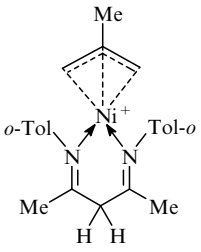


186–**188**

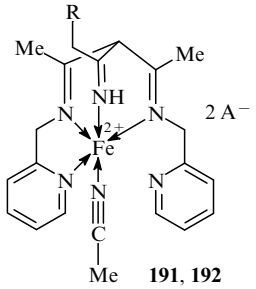


189

186: M = Ir, X = CO, Y = PPh_3, R^1 = H, R^2 = CF_3, R^3 = Allyl;[315]
187: M = Rh^+, X = Y = CO, R^1 = R^3 = H, R^2 = Me;[316]
188: M = Ni, X = Y = Br, R^1 = $C_6H_3Pr^i_2$-2,6, R^2 = Me, R^3 = H.[317]

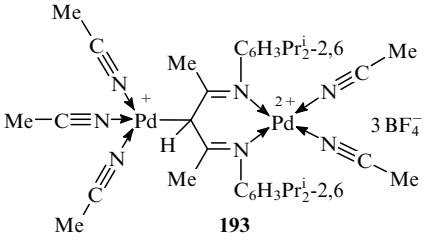


190

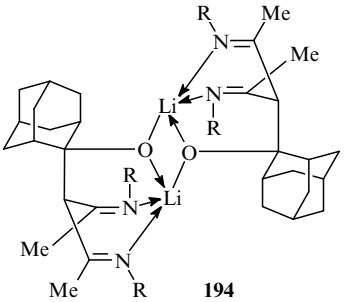


191, **192**

R = Me (**191**), Ph (**192**);
A = ClO_4^-, PF_6^-.



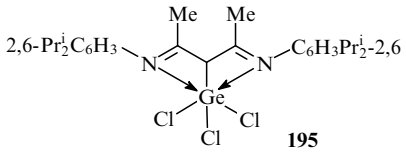
193



194

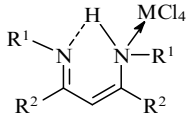
R = $C_6H_3Pr^i_2$-2,6.

Apparently, this form of the ligand is also typical of complex **195**, where the β-aminovinylimine ligand is tridentate.[323]

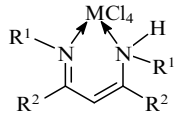


195

The structures of adducts of β-aminovinyl imines with MCl_4 (M = Sn, Ti) [263] are of interest. Although formation of the M–N-coordinated forms **A** or **B** was suggested for them, the question remains open due to a lack of X-ray diffraction data.



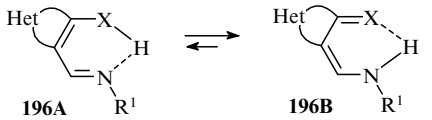
A



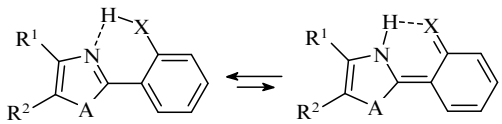
B

V. Heterocyclic azomethines and their complexes

Amino-, hydroxy(oxo)- and thio-substituted heterocyclic azomethines can be subdivided into two groups depending on the type of imine bond, *viz*., compounds with exo- (**196**) and endocyclic (**197**) C=N bonds.[6, 8, 11, 38, 55, 56, 324–327]



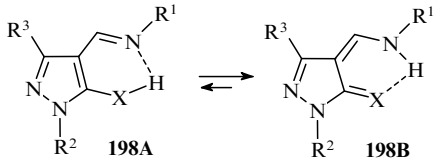
196A **196B** (8)



197A **197B** (9)

X, A = NR^3, O, S.

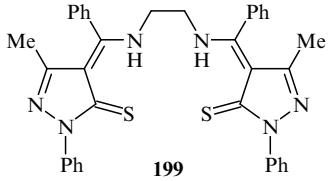
The best studied class of chelating ligands of type **196** is the pyrazole derivatives **198**. Compounds with X = NR^3 exist exclusively in the imine form **A**, whereas those with X = O and S exist in the amine form **B** [equilibrium (10)].



198A **198B** (10)

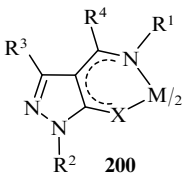
X = NR^4, O, S; R^1 = H, Alk, Ar, Het; R^2, R^3, R^4 = H, Alk, Ar.

The latter form is realised in both solution and the crystalline phase, as evidenced by X-ray diffraction data. For instance, this form was found in a series of hydroxypyrazoles **198** (X = O) with coordinatively active substituents R^1 (R^1 = C_6H_4SMe-2,[328] $COCH_2Cl$,[329] 8-quinolyl,[330] $C_6H_4NH_2$-2,[331] C_6H_4OH-2 [332] and antipyryl [333]) and for pyrazolethione **199** derivatives.[334]



199

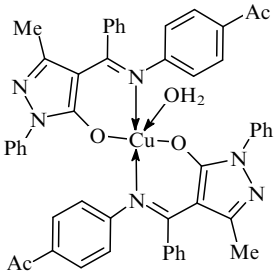
Complex compounds synthesised based on compounds **198** include exclusively chelates **200** with anionic ligands [6, 8, 58, 324, 326, 335] that are characterised by virtually delocalised intrachelate bonds.



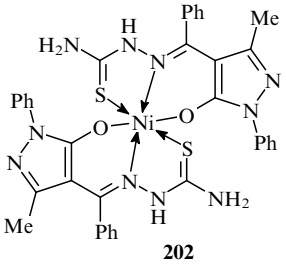
200

X = O, S; M = Ni, Pd, Cu, Zn, Cd, Hg;
R^1, R^2, R^3 = Alk, Ar; R^4 = H, Alk.

Only a few metal complexes with hydroxypyrazole ligands (X = O) have been studied (*e.g.*, compounds **201** [336] and **202** [337]).

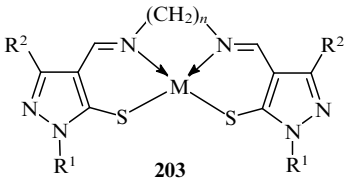


201



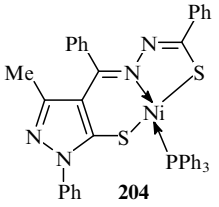
202

Meanwhile, mercaptopyrazole complexes are quite numerous.[8, 158, 264, 338–353] These include bischelate structures **200** (R^1 = Alk, Ar, Ph, cyclo-C_6H_{11}, pyridyl, crown-ether substituent), tricyclic chelates **203** with ethylene,[8, 349, 350] trimethylene [8, 349] or tetramethylene [8] bridges, bicyclic complexes **204** formed due to additional coordination of the metal atom with a coordinatively active substituent R^1 and heteronuclear structures **205**.[352, 353]

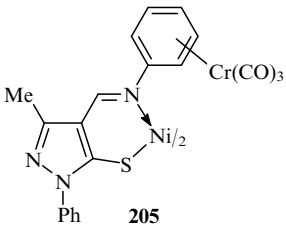


203

M = Ni, Cu; *n* = 2, 3, 4.

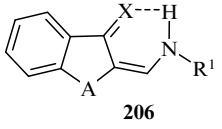


204



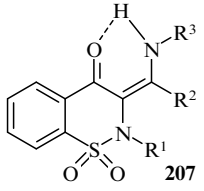
205

Investigations into the tautomeric equilibrium (8) of azomethines of the pyrrole, furan, thiophene, their benzo-analogues [10, 11, 55, 56] (compounds **206**) [354] and benzothiazinone (compounds **207**) [355] series indicate that they predominantly exist in the enaminoketone (thione) tautomeric form.



206

A = NR^2, O, S; X = O, S;
R^1 = H, Alk, Ar.

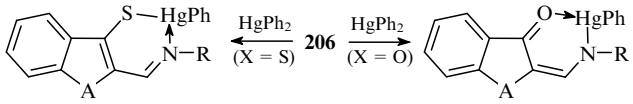


207

R^1, R^2 = Alk, Ar; R^3 = Ar, 8-quinolyl, 4-antipyryl.

This suggestion is supported by the X-ray diffraction data for the respective complexes.[8, 356–360]

The possibility of the coordination-dependent stabilisation of specific tautomeric forms was deduced from the data on the tautomeric equilibrium (elementotropy) [2–4] of organometallic derivatives of ligands of the type **206** (A, X = O, S). It was found [55, 361–363] that the interaction of enaminothione **206** (X = S) with a soft acid (in terms of the Hard and Soft Acids and Bases, or HSAB, principle) [34, 35, 364–366] stabilises the imine form of the ligand (compound **208**), whereas the similar reaction of enamino ketone **206** (X = O) gives rise to the amine form **209**.[55, 56]

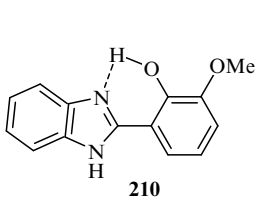


208 **209**

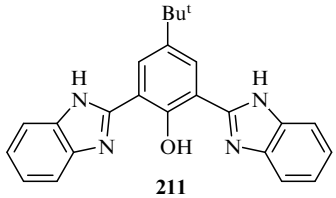
The tautomers formed possess the maximum stability within the HSAB principle.[34, 35, 365]

Ligands of the type **197** manifest photo(thermo)-activated tautomerism [equilibrium (9)] with the tautomeric form **A** prevailing (see reviews [6, 367]). According to X-ray diffraction data, this form is also observed in the crystalline phase.

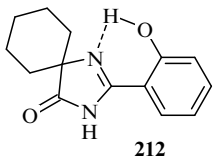
Among compounds **197**, benzoxazole (A = O: R^1–R^2 = benzo),[368] oxazoline [369, 370] and imidazole [A = NH: R^1 = R^2 = H;[371] R^1 = Ph, R^2 = NO_2 (see Ref. 372)] derivatives have been studied using X-ray diffraction. The structures of benzoimidazoles **210** and **211**,[373] spiro- (**212**) [374] and polyheterocyclic (**213a**,**b**) imidazoles [375, 376] have been determnined.



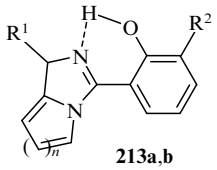
210



211



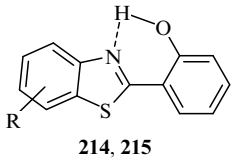
212



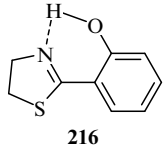
213a,**b**

213a: R^1 = 2-C_5H_4N, R^2 = OMe; *n* = 1;
213b: R^1 = *N*-methylimidazol-2-yl, R^2 = H; *n* = 2.

The tautomeric form **A** is also typical of benzothiazoles **214**,[377] **215** [378] and thiazolines **216**.[379]



214, **215**

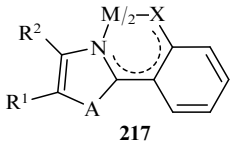


216

R = H (**214**); 5,6-benzo (**215**).

Ligand systems of the type **197** form chelates **217** with delocalised chelate bonds in nearly all cases; this prevents an analysis of the tautomeric forms of the ligands, as in the systems discussed above. The first complexes of this type [380] were synthesised based on 2-tosylaminophenylbenzoimid(ox)azole.[381]

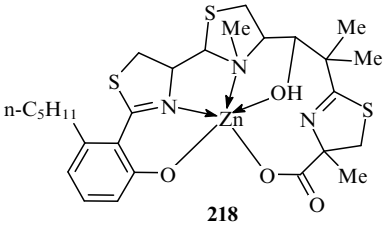
Structural data on complexes **217** (X = NTs) with the coordination core MN_4 are rather scarce.[369, 370, 382]



217

A, X = NTs, O, S, Se.

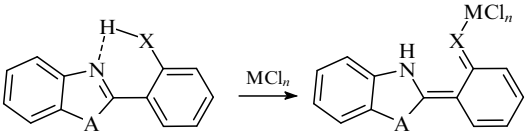
Complexes based on 2-hydroxyphenylazole systems similar to **217** (X = O) are more numerous. These include chelates **217** with A = NH, M = Cu, Co, $R^1 = R^2$ = Ph;[383] A = NH, M = Cu, Co, $R^1 - R^2$ = benzo;[384, 385] A = O, M = Cu, Co, Ni, Zn, R^1 = H, R^2 = H, Me, Ph;[386–388] A = O, M = Cu, $R^1 - R^2$ = benzo;[389, 390] A = S, M = Cu, $R^1 - R^2$ = benzo[391, 392] and the thiazoline complex **218**.[393]



218

Several complexes based on mercaptophenylazoles (**217**, X = S, M = Zn, A = O, R^1 = H, R^2 = Me)[394] and their hydroseleno-derivatives (**217**, X = Se, M = Zn, A = O, R^1 = H, R^2 = Me)[395] have been reported.

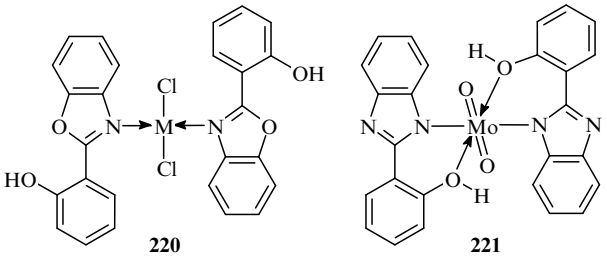
IR spectroscopic studies of molecular complexes of metal halides **219** produced in the following reaction:[6, 396, 397]



219

A = NH, O; X = NTs, O; M = Sn, Ti, Co, Cu, Zn; *n* = 2, 4.

suggest stabilisation of the non-typical quinoid form **197B** due to coordination. However, this suggestion requires more reliable X-ray diffraction confirmation, since the enol form of the ligand was shown to be retained in analogous structurally characterised complexes **220** and **221** with N- (**220**)[398, 399] or N,O-coordination (**221**).[400]

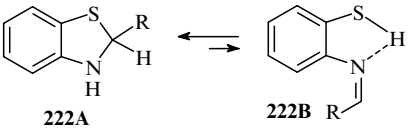


220 **221**

M = Pd, Pt.

The structure of compound **221** is of note; the metal atom therein replaces the hydrogen atom at the endocyclic nitrogen atom rather than the exocyclic phenolic proton.

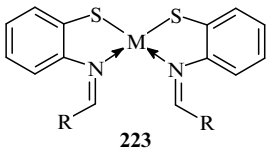
The stabilisation of specific tautomeric forms of azomethine ligands can be achieved not only for proto- and elementotropic tautomerism but for the ring-chain tautomerism of azole ligand systems **222**[6, 401–403] as well.



222A **222B**

R = Ar, Het.

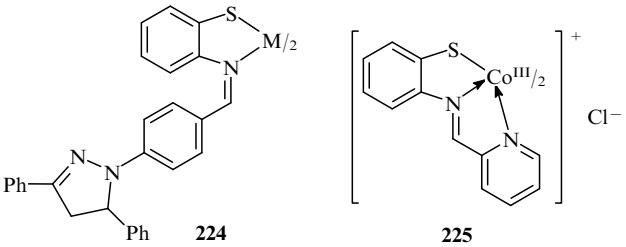
Compound **222** in the free state (in both solution and the crystalline phase) exists predominantly in the closed tautomeric form **A**. Coordination stabilises form **B** (complex **223**).[6, 8, 34, 35, 58, 157]



223

M = Ni, Pd, Pt; R = Ar, Het.

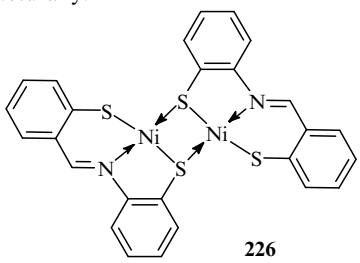
Recently, five-membered chelates with the coordination core MN_2S_2 [compounds **223** (R = Ar),[404–406] **224**[407] and **225**[408]] have been synthesised based on benzothiazolines.



224 **225**

M = Co, Ni, Zn, Cd.

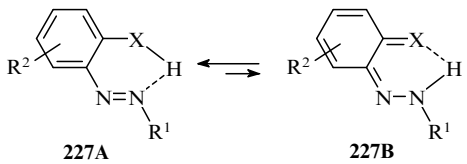
One binuclear mercaptoazomethine chelate **226** with an S-bridge and the coordination core MNS_3 has been characterised structurally.[409]



226

VI. Hydroxy(mercapto)azo-compounds and metal chelates based on them

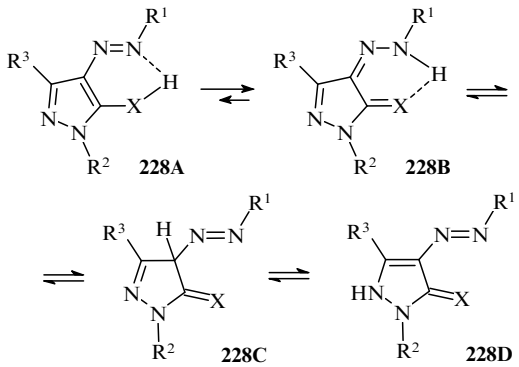
Tautomeric transformations occur also in diazo-analogues of azomethines, *viz.*, hydroxy(mercapto)-derivatives of aromatic **227** and heterocyclic **228** azo-compounds.[6, 34, 35, 410, 411]



(11)

227A **227B**

R^1 = Ar, Het; R^2 = benzo, OAlk, Hal, NO_2;
X = O, NR^3 (R^3 = Alk, Ts).



(12)

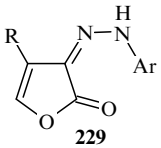
228A **228B** **228C** **228D**

X = NR^4, O, S, Se; R^1 = Ar, Het; $R^2 = R^3 = R^4$ = H, Alk, Ar.

Ligands **227** and **228** manifest the azo – hydrazone tautomerism [equilibrium (11)]. The equilibrium is shifted towards the azo-tautomer **A** in the case of aromatic amino- (**227**, X = NR^3, R^1 = Ar) and hydroxyazo-compounds (**227**, X = O, R^1 = Ar) **A**.[411–414] Pyrazole compounds **228**[6,34,35,38,411,415] exhibit a more complex equilibrium (12) with the tautomer **B**[6,38,411,412] prevailing. According to a combined ^{15}N NMR (in $CDCl_3$) and X-ray diffraction study,[416] complexs **227** exist predominantly in the azophenol form (**227A**), whereas compound **228** exists in the oxohydrazone (**228B**) tautomeric form. A similar situation is observed in the crystalline phases of compounds **227** and **228**.

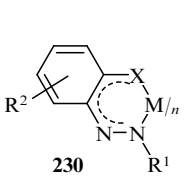
In particular, compounds **228** (X = O) exist in the solid phase exclusively in the form **228B** (R^1 = $C_6H_3Me_2$-2,4, R^2 = Ph, R^3 = Me;[417,418] R^1 = $C_6H_4NO_2$-4, R^2 = Ph, R^3 = Me;[419] R^1 = C_6H_4Cl-4, R^2 = Ph, R^3 = Me;[420] R^1 = $C_6H_3Cl_2$-2,4, R^2 = Ph, R^3 = Me;[421] R^1 = R^2 = Ph, R^3 = $COOPr^i$;[422] R^1 = R^2 = C_6H_4OMe-4, R^3 = CO_2Et[423]); the same form is typical of mercaptopyrazole derivatives (X = S, R^1 = R^2 = Ph, R^3 = Me).[424] Meanwhile, amino-derivatives exist in the azo-form (**228A**, X = NR^4).[6,425]

The oxohydrazone tautomeric form is also typical of hydroxy-azo-derivatives of isoxazole **229**.[426]

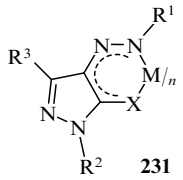


229

A large number of metal complexes of the types **230** and **231** with hydroxy(mercapto)azo-ligands have been reported, which are characterised by virtually delocalised intrachelate bonds.



230

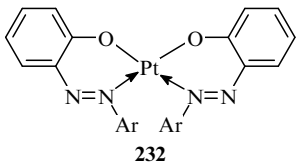


231

X = NR^4, O, S; n = 2, 3; R^1 = Ar, Het; R^2, R^3, R^4 = H, Alk, Ar.

According to a suggestion by Price,[427] two five-membered metallacycles are realised in a newly synthesised cobalt complex **230** (X = NH, R^1 = Ph, R^2 = H, M = Co). This suggestion needs to be verified, since it was two six-membered metallacycles that were revealed in a similar nickel complex using X-ray diffraction,[428] while five- and a six-membered metallacycles were shown to co-exist in a chelate with X = NTs.[429] Six-membered metallacyclic structures are also realised in coordination compounds based on hydroxyaromatic azo-compounds **230** (X = O, M = Ni,[430] Cu,[431] Pt[432]).

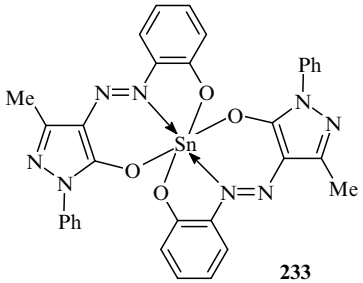
Typically, complexes **230** have *trans*-planar structures; however, in the case of a Pt-complex it was possible to isolate and determine the structure of the *cis*-isomer **232**.[432]



232

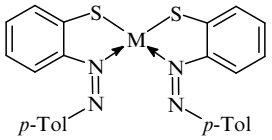
The formation of six-membered chelate structures is also typical of nickel complexes with aminoazo-ligands of the pyrazole series **231** (X = NR^4, M = Ni).[425,433]

According to the ^1H NMR data and measurements of the dipole and magnetic moments, nickel pyrazole complexes (**231**, X = O, R^1, R^2, R^3 = Alk, Ar) adopt tetrahedral structures in solution and the crystalline state.[434] According to X-ray diffraction data, the copper complex **231** (M = Cu, n = 2, R^1 = R^2 = Ph, R^3 = Me) is characterised[435] by planar structure, whereas the corresponding zinc complex is pseudotetrahedral; octahedral structures are observed for cobalt and nickel complexes ($[CoL_3]\cdot 3\,MeOH$, $[NiL_2]\cdot 2\,MeOH$; LH is the ligand **220**). The octahedral structure is also realised in the chelate **233**.[436]

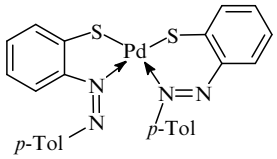


233

Complexes with ligand **227** (X = S) can contain two five-membered metallacycles (compound **234**)[437–441] or a five- and a six-membered (compound **235**)[411,442] metallacycle (intrachelate isomerism).



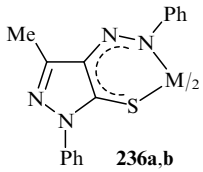
234



235

M = Ni, Zn.

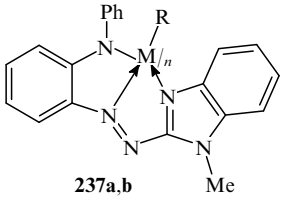
Meanwhile, chelates based on 4-azo-derivatives of pyrazole-5-thione (**228**, X = S) contain only six-membered metallacycles, as in complex **236**.[443,444]



236a,**b**

M = Zn, n = 2 (**a**); M = Ru; n = 3 (**b**).

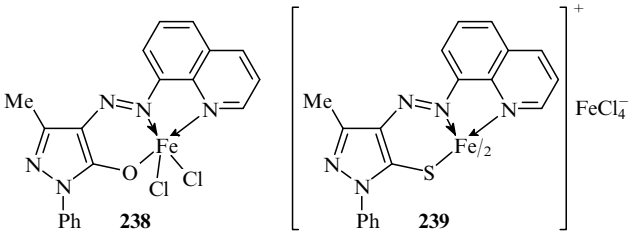
Chelates based on aromatic azo-compounds **227** with coordinatively active substituents (R^1 is a derivative of a nitrogen heterocycle Het) manifest intrachelate isomerism due to the possibility of the closure of metallacycles with different numbers of atoms. For instance, complexes **237a**,**b** synthesised based on aminoazo-ligands of the type **227** contain two five-membered metallacycles **187**,[445,446] as evidenced by X-ray diffraction.



237a,**b**

M = Pd, n = 1, R = OAc (**a**); M = Ni, n = 2, no R (**b**).

Pyrazole aza-ligands of the type **228** (X = O, S; R = 8-quinolyl) form five- and six-membered metallacycles (compounds **238** and **239**)[447] upon coordination with metal atoms.



The structure of complex **239** was confirmed by X-ray diffraction.[447]

VII. Conclusion

The ligand systems discussed in the present review are widely employed in the synthesis of typical metal chelate complexes. These complexes contain the ligands in the deprotonated (L^-) form with delocalised intrachelate bonds. The involvement of the protonated ligand (LH) in coordination with a metal atom gives rise to molecular complexes containing the ligand in a non-standard tautomeric form. The experimental evidence summarised above implies that coordination with a metal represents an efficient means for stabilisation of non-standard tautomeric forms of these chelating ligand systems.[27–30, 58]

To intensify research in the field of coordination-dependent stabilisation of tautomers, it would be desirable to extend the range of prototropic ligand systems under study.[34, 35, 448] In addition to the chelating ligands mentioned in the present review, heterocyclic amino-, hydroxy- and thio-derivatives[6, 28, 326, 327, 449–452] as well as tosylamino-[453] and hydroxyphenylazines[454, 455] can be considered. Taking into account that complex formation can stabilise not only prototropic but other tautomeric forms as well, the range of ligand systems can be extended to include those manifesting elementotropic (see Section III.4), photo- and thermochromic (see Section V), ring–chain (see Section V) and azido–tetrazole[6] tautomerism. Studies of such tautomeric systems are still in the maturation stage.

The competitive coordination (see Ref. 326) and stabilisation of non-classical organometallic structures are worth special attention.

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