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Various types of metal complexes based on chelating β-diketones and their structural analogues

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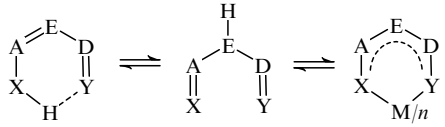
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Abstract. Data on the synthesis and structures of β-diketonates and their N,P-containing structural analogues are generalised and described systematically. The possibility of creating diverse metal complexes with various modes of coordination of typical chelating ligands is discussed. The bibliography includes 200 references.

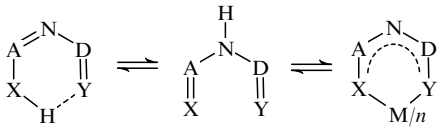
I. Introduction

Chelating systems **1**, which form, most often, six-membered metal-containing rings **2**, are among the most widely used ligands in modern coordination chemistry.[1–3]



1a **1b** **2**

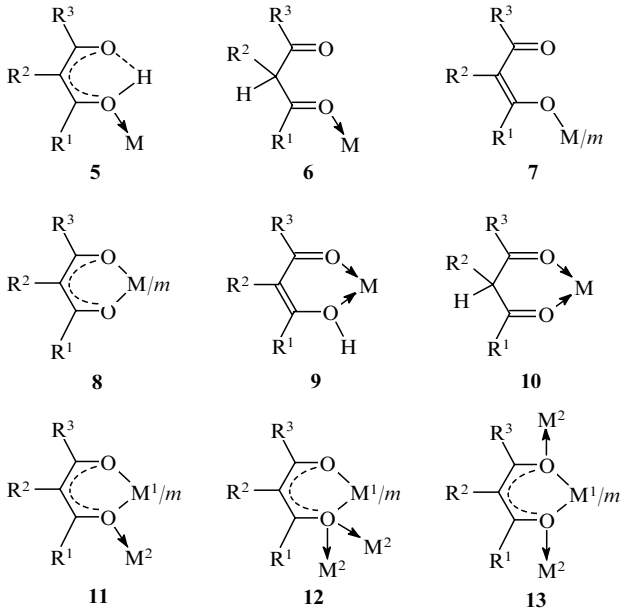
The metal complexes **2** formed by ligands **1** are mainly represented by β-diketonates (X = Y = O; A, D, E = CR, where R = H, Alk, Ar, Het),[4–9] their aza analogues (X = O, NR; Y = NR; A, D = CR, N; E = CR, where R = H, Alk, Ar)[10,11] and hetero analogues (X, Y = O, S, Se; A = CR, PR_2; D = PR_2; E = CR, where R = H, Alk, Ar).[2,3,12,13] Other examples of these ligands are compounds **3**, which are used to prepare metal chelates **4** (X, Y = O, S, Se; A = CR^1, PR^1_2; D = PR^1_2, where R^1 = H, Alk, Ar, NR^2_2, OR^2; R^2 = H, Alk, Ar, ArAlk).[14,15]



3a **3b** **4**

Although metal chelates **2** and **4** arouse the steady interest of researchers, equally important are other coordination capabilities of ligands **1** and **3**, which are not limited to the formation of chelates (intracomplex compounds†) containing the ligand as a bidentate X,Y-donor anion. This aspect of the chemistry of metal complexes of these ligands has been considered in detail only for β-diketonates **2** (X = Y = O; A = D = E = CR). The possible modes of coordination in mono-, di- and polynuclear β-diketonate complexes can be illustrated by structures **5** – **27**.[5,9,16–24]

O- and O,O-coordination



5 **6** **7**

8 **9** **10**

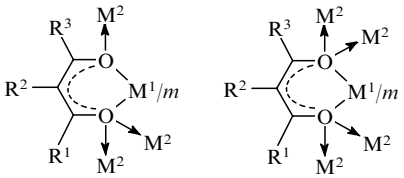
11 **12** **13**

† The notion 'intracomplex compound' taken from early publications (see, for example, Refs 8 and 14) is used in Russian and German literature to emphasise the fact that these compounds have been obtained from ring-forming ligands with an intramolecular H-bond, for example, from acetylacetone. More generally, the complexes with metal-containing rings are called chelates.[2]

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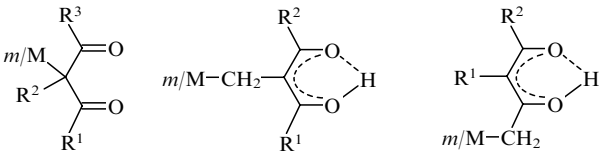
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O- and O,O-coordination

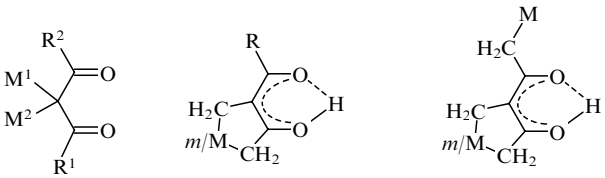


14 **15**

C-, C,C- and C,C,C-coordination

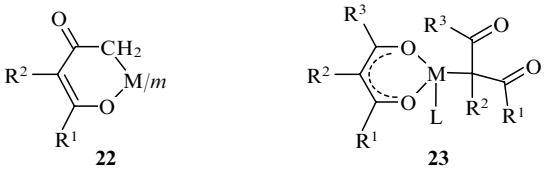


16 **17** **18**

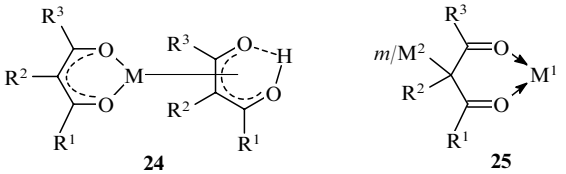


19 **20** **21**

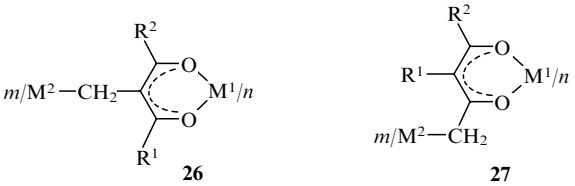
C,O- and C,O,O-coordination



22 **23**



24 **25**



26 **27**

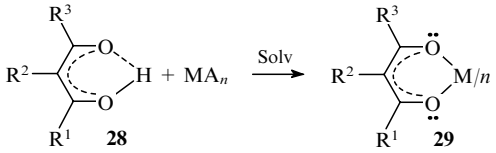
Study of the coordination modes of typical chelating ligands is important for the understanding of their ambident properties.[20–24] Therefore, this review surveys the published data (obtained mainly during the last 10 years) concerned with the ability of ligands **1** and **3** to form metal complexes in which the coordination bonds can be localised in different ways.

II. Metal complexes of β-diketones

Coordination compounds of β-diketones are prepared either by classical methods (by reactions of various compounds, most often salts, of complexing metals with β-diketonate ligands) or by specific reactions (gas-phase synthesis and electrosynthesis[2–5]). The type of the metal complex to be formed plays an important role in the transformations considered below.

1. Chelates formed by β-diketones

The chelates of β-diketones (β-diketonates) containing the monodeprotonated O,O′-anion of the ligand[25] are synthesised most often by the reactions of ligand systems **28** with metal salts in water, aqueous organic solvents, or in solvent mixtures.

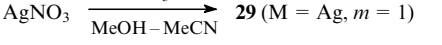


28 **29**

Solv is solvent.

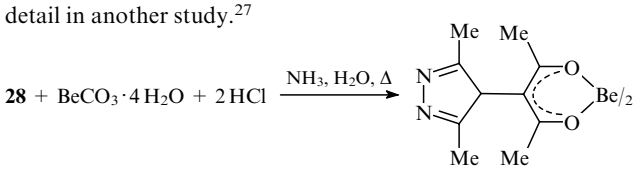
β-Diketonates **29** for metals of virtually all Groups of the Periodic Table have been prepared in this way. Due to the enormous number of publications on this topic, only some examples of such syntheses are cited in this review.‡

Silver(I) β-diketonates **29** are formed in 20%–66% yields upon the reaction[26]



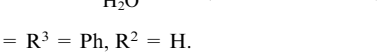
28, **29**: $R^1 = Bu^t$, $R^2 = H$, $R^3 = Bu^t$, $SiMe_3$.

The data on the syntheses of β-diketonates of Group II elements (Be, Ca, Mg, Ba, Sr) are summarised in a recent review.[9] The synthesis of beryllium β-diketonate **30** is described in more detail in another study.[27]



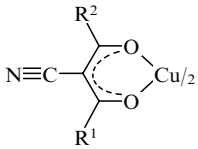
30

β-Diketonates of Group III metals are prepared using metal halides. In particular, aluminium and indium chelates have been obtained in this way.[28]

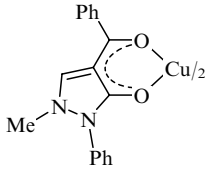


8, **28**: $R^1 = R^3 = Ph$, $R^2 = H$.

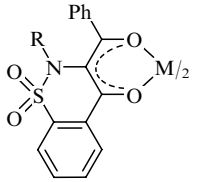
An enormous number of coordination compounds of transition metals have been synthesised on the basis of aliphatic and aromatic β-diketones.[1–8] It should be emphasised that chelates **31**–**34**, similar in structure to chelate **8**, have also been synthesised by reactions of 3d-metal salts with β-diketones containing nitrile,[29] pyrazole,[30] 1,2-benzothiazine 1,1-dioxide[31] and ferrocenyl[32] substituents, respectively.



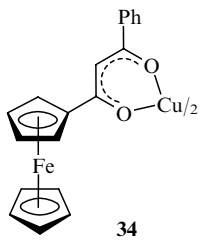
31: $R^1 = R^2 = Me, Bu^t$



32



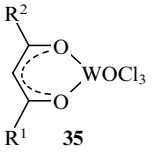
33: R = H, Me;
M = Co, Ni, Cu, Zn



34

‡ The Cambridge Structural Data Base contains structures of more than 1500 β-diketonates and related fragments as parts of monomeric and polymeric coordination compounds.

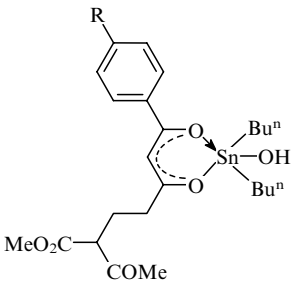
The relatively simple transformations considered above can be complicated by solvolysis, resulting in the formation of adducts and decomposition of complexes (especially, in the case of hydrolysis). Therefore, these syntheses are carried out using anhydrous organic solvents; for example, β-diketonate **35** was synthesised in anhydrous benzene.[33]



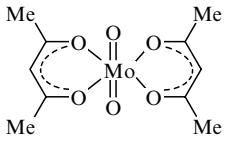
35

R^1, R^2 = Me, Ph, 4-$MeOC_6H_4$.

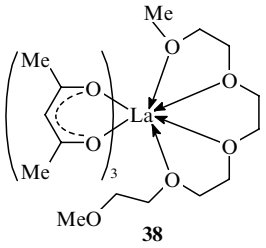
Apart from salts, metal oxides can also be used in complexation reactions.[2–4,9] These syntheses have been long known [34] and still have not lost their significance. For example, complexes **29** ($R^1 = R^3 = CF_3$; R^2 = H; M = Ag; m = 1),[35] **36**,[36] **37** [34] and **38** [37] can be prepared from silver, tin, molybdenum and lanthanum oxides, respectively.



36: R = H, Bu^t, NO_2, Cl



37



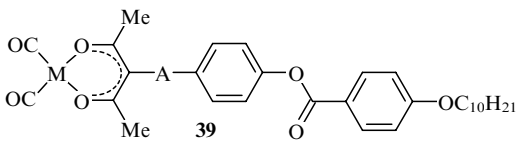
38

The reactions of ligands with metal alkoxides proved to be quite efficient for the synthesis of Group IV metal (Ti, Zr, Hf) β-diketonates.[9]

$$n\,(\beta\text{-diketone}) + M(OR)_4 \xrightarrow{Solv} M(\beta\text{-diketone})_n(OR)_{4-n} + n\,ROH$$

This reaction has been used, in particular,[38] to prepare zirconium and hafnium complexes with 2,2,6,6-tetramethylheptane-3,5-dione (LH), with the composition $M(OPr)_2L_2$, ML_4 and $M_2(OPr)_6L_2$, the synthesis being carried out in hexane.

Metal exchange reactions are often used to prepare β-diketonates **8**.[4,9] β-Diketonates of Group I metals are usually employed as the starting compounds for the exchange with d or f elements. Recently, this method has been used to synthesise mono-β-diketonates of rhodium(I) and iridium(I) **39** dicarbonyls having liquid-crystalline and nonlinear-optical properties. These complexes were prepared by replacement of potassium or sodium in acetylacetonates by platinum metals.[39]

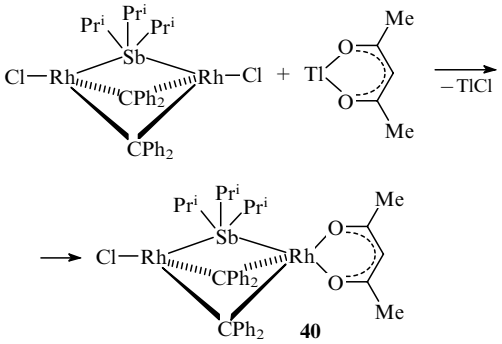


39

M = Rh^I, Ir^I; A = CH_2, CO_2, OOC.

The syntheses of mixed-ligand complexes of lanthanides (La, Sm, Er) described as $LaL_3(bipy)_2$, $[SmL_3(bipy)]bipy$, $ErL_3(phen)$ (bipy is 1,1′ -bipyridyl, phen is *o*-phenanthroline) proceed through the preliminary formation of the caesium salt of 1,1,1,5,5,5-hexafluoropentane-2,4-dione (LH).[40]

Thallium acetylacetonate has been used to prepare rhodium complex **40**.[41]



40

It is noteworthy that in some cases, reactions of β-diketone salts give products absolutely different from those formed in the syntheses from free ligands. In particular,[42] the reaction of gadolinium trichloride with the sodium salt of β-diketone (LNa) gave tetramer **41**, whereas a similar reaction of LH affords mononuclear complex **42**.

$$4\,GdCl_3 + 12\,LNa + 10\,H_2O \xrightarrow{H_2O-EtOH} Gd_4(OH)_4L_8(H_2O)_6 + 4\,LH + 12\,NaCl$$

41

$$GdCl_3 + 3\,LH \xrightarrow[-3\,HCl]{Me_2CO} GdL_3(Me_2CO)_2 \xrightarrow[-Me_2CO]{H_2O} GdL_3(Me_2CO)(H_2O)$$

42

The solid-state syntheses of β-diketonates **43** from salts of complex-forming elements and alkali metal β-diketonates deserve attention.[43–46]

$$PrCl_3 + 3\,M(acac) \longrightarrow Pr(acac)_3 + 3\,MCl$$

43

M = Li, Na; acac is acetylacetonate.

Numerous β-diketonates similar in structure to complex **8** have been prepared by ligand exchange.[4,5] In particular, metal complexes **44** were synthesised in this way.[47]

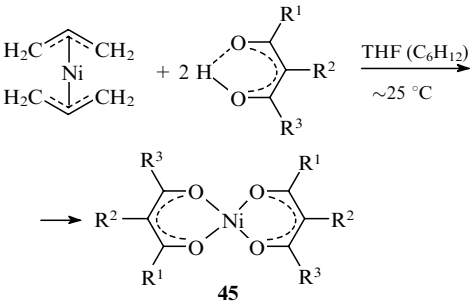
$$[M(OEt)_2(EtOH)_4]_n + 2n\,LH \longrightarrow [ML_2]_n + EtOH$$

44

M = Ca, Ba,Sr; LH = **28**: $R^1 = R^3$ = Me, Bu^t, Ph, CF_3; R^2 = H.

In addition to the above-mentioned polymeric complexes, this transformation carried out in the presence of triglyme (TG) and tetraglyme (TeG) furnished monomeric products, $BaL_2(TeG)$, $SrL_2(TG)$ and $SrL_2(TeG)$.[47]

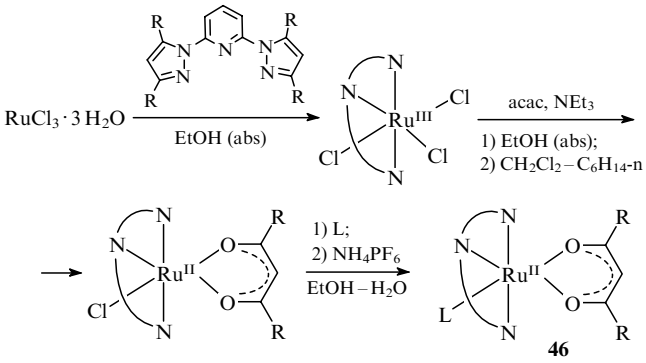
Nickel β-diketonates **45** have been synthesised by the reaction of bis(η^3-allyl)nickel with β-diketones.[48]



45

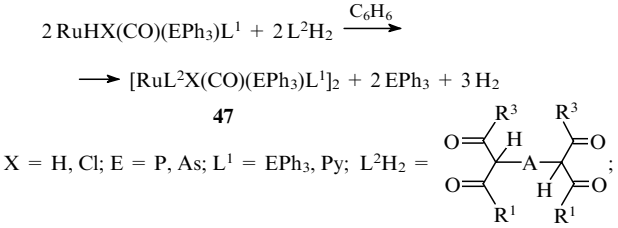
$R^1 = R^3$ = Me; R^2 = Me, Ph, Bn, $H_2C{=}CHR^4$ (R^4 = C_6H_8, C_6H_{12}, $C_{12}H_{24}$).

Mixed-ligand ruthenium(II) acetylacetonates **46** have been prepared by chlorine exchange reaction in ruthenium(III) complexes with 2,6-bis(pyrazolyl)pyridines.[49]



R = Me, Ph, CF_3; L = 4,4′-bipy, MeCN, Py, imidazole, pyrazine.

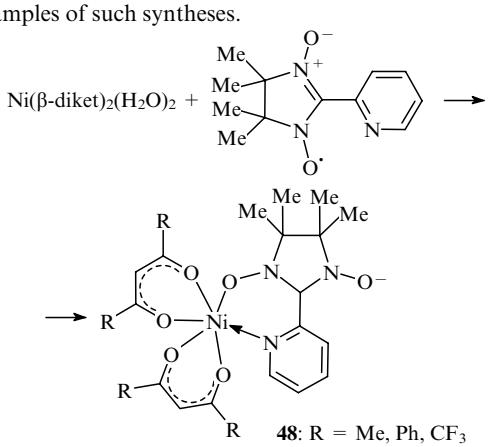
This approach has also been used for the synthesis of ruthenium(II) binuclear complexes with bridging bis-diketonate ligands.[50, 51] On refluxing for 6 h, these ligands replace H^- in the carbonyl hydride complexes of ruthenium to give coordination compounds **47**.



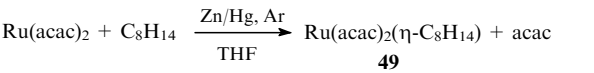
X = H, Cl; E = P, As; L^1 = EPh_3, Py; L^2H_2 = ;

A = CR^2R^4 (R^2, R^4 = H, Ph), S; R^1, R^3 = Me, Ph.

It appears of interest to use this approach to replace the ligands in β-diketonate complexes by other chelating compounds. The transformations [52, 53] giving rise to complexes **48** and **49** are examples of such syntheses.



48: R = Me, Ph, CF_3

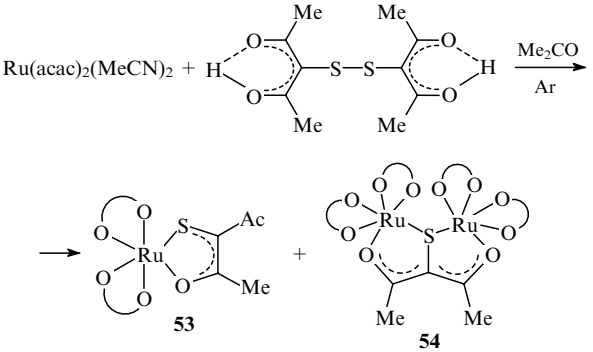


C_8H_{14} is cyclooctene.

By replacing the cyclooctene ligand by other ligands, acetylacetonate **49** has been converted [53] into a series of different-ligand complexes: $Ru(acac)_2Py_2$, $Ru(acac)_2$(bipy), $Ru(acac)_2(NCBu^t)_2$, $Ru(acac)_2(\eta^2\text{-}C_8H_{14})_2(NCMe)$, $Ru(acac)_2(NMe_3)_2$, $Ru(acac)_2(PPh_3)_2$, $Ru(acac)_2(PMePh_2)_2$, $Ru(acac)_2(PAlk_3)_2$, $Ru(acac)_2[P(OMe)_3]_2$; $Ru(acac)_2$ $[P(OPh)_3]_2$, $Ru(acac)_2[Ph_2P(CH_2)_mPPh_2]$ (m = 1–3), $Ru(acac)_2(\eta^2\text{-}C_8H_{14})_2(SbPh_3)$, $Ru(acac)_2(SbPh_3)_2$, $Ru(acac)_2$. .$(CO)(NMe_3)$, $Ru(acac)_2(CO)(PPh_3)$ and $Ru(acac)_2(CO)(AsPh_3)$.

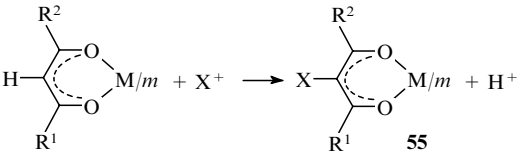
The ligand exchange reactions yielding monoacetylacetonate binuclear rhodium complexes **50**–**52** are shown in Scheme 1.[54]

Ruthenium mono- (**53**) and binuclear (**54**) tris-chelates were prepared in a similar way.[55]



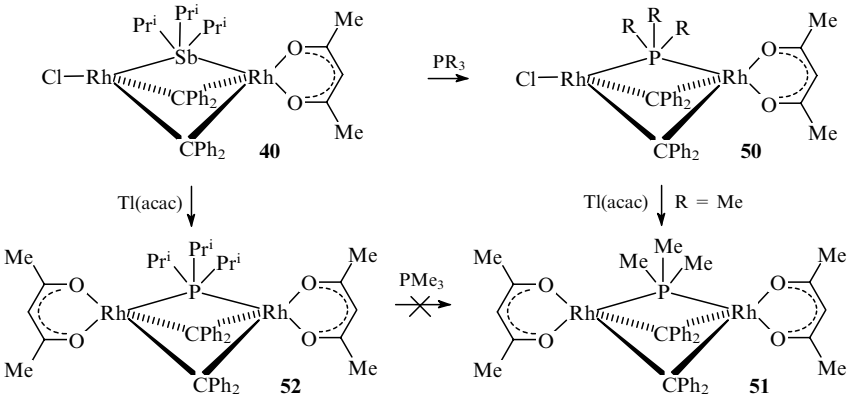
The acetylacetonate ligands can be rather easily completely replaced. This underlies the acetylacetonate method for the synthesis of metal complexes with diverse ligands,[56, 57] widely used in the coordination chemistry of gold.[57]

To our knowledge, no classical template syntheses of β-diketonates in which the β-diketonate ligand system is constructed from components on a metal template (*cf.* the studies [2, 3, 58–60]) have been reported. However, template syntheses of the second type, *i.e.*, the reactions of coordinated ligands (modification of ligand systems), [2, 3, 61–63] are represented rather extensively in the chemistry of metal complexes of β-diketones.[2–5] This is attributable to the ability of β-diketonates **8** devoid of substituents at the C(3) atom of the quasi-aromatic ligand system to undergo electrophilic substitution at this atom.[4, 5, 9]

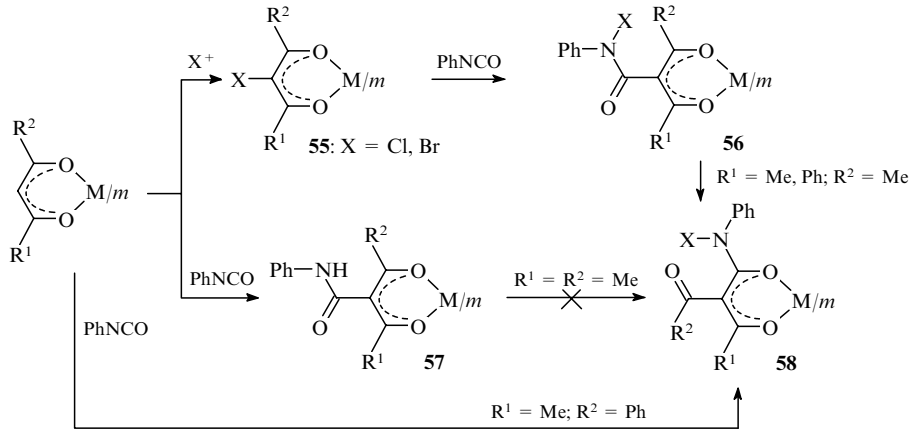


The halogenation, formylation, acylation and Mannich reactions and the introduction of thiocyanate and chlorosulfenyl

Scheme 1

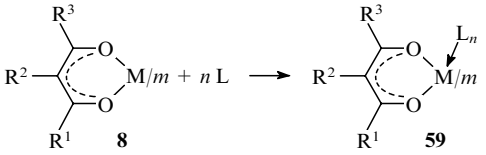


Scheme 2



groups occur according to this route.[5] Nitrile[29] and phenyl isothiocyanate[64] fragments can be introduced in the ligand system in a similar way. The presence of a substituent X in complex **55** also allows one to modify β-diketone ligand systems. Scheme 2 shows transformations of this type, resulting in complexes **56**–**58**.[64]

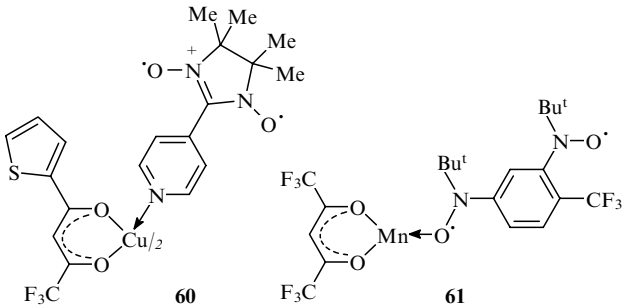
An important role in the modification of the coordination sphere belongs to the reactions of β-diketonates with N-, P-, O- and S-donors involving a coordinatively unsaturated complexing metal, giving rise to adducts **59**.



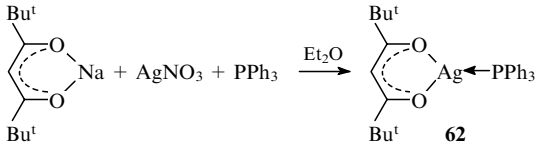
m = 1–3; *n* = 1, 2.

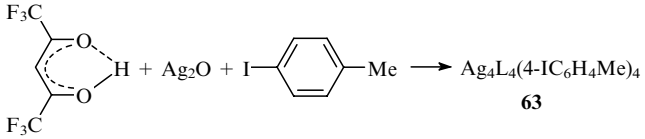
These reactions have been used to prepare adducts of silver(I) β-diketonates with tributyl- and triphenylphosphines,[26] cobalt(II) with pyrazine and 4,4′-bipyridyl,[65] rhodium(I) with cyclooctadiene[32] and iridium(II) with triallylphosphines and -stibines.[66]

In recent years, the interest in β-diketonate adducts with biradical bases such as complexes **60**[67] and **61**[68] has grown due to the development of new molecular magnets.

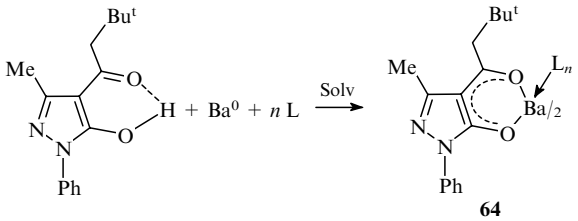


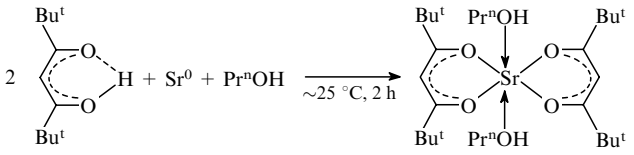
Adducts similar to compound **59** (in particular, complexes **62**[26] and **63**[69]), can also be formed in template reactions.



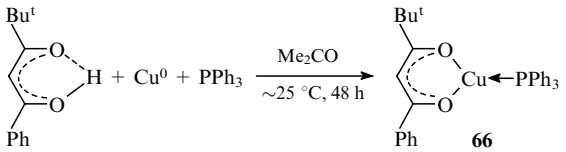


The direct method for the synthesis of β-diketones from ligands and zerovalent metals[2,3,4,9] is mainly applied for Group IA and IIA elements of the Periodic Table. This technique was used to prepare magnesium, calcium, barium and strontium β-diketonates (see the review[9] and references cited therein). Among more recent publications, noteworthy are papers devoted to the syntheses and structural studies of mononuclear chelates of barium **64**[70] and strontium **65**.[71]





Some transition metals (Co, Fe, Ni, Cu) can also directly react with β-diketones. In these syntheses, iron is activated by atmospheric oxygen, whereas cobalt, copper and nickel are activated by the addition of N- or P-bases into the reaction mixture.[72–74] This method has been used to prepare[74] the β-diketonate complex of monovalent copper **66**, which has been structurally characterised.



Direct one-step syntheses of β-diketonates from zerovalent metals in the gas phase[2,3,72,73,75–78] and under conditions of electrolysis[2,3,72,73,76,79] are especially efficient.

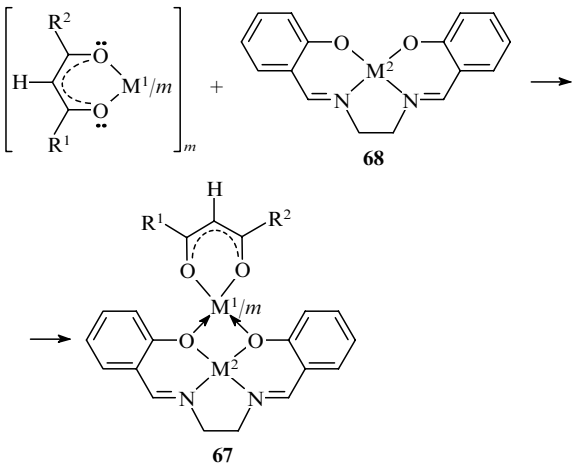
Gas-phase syntheses of β-diketonates have been developed for both non-transition and transition metals (M = Al, Sn, Pb, Ti, Zr, Hf, Co, Mn, Cr, Fe, Ni, Pd, Cu, Dy, Ho, Eu) which are evaporated *in vacuo* at 1000–2500 °C (see Refs 72, 73 and 78). A special setup for the gas-phase synthesis of β-diketonates has been designed.[73,80] Using this setup, chelates **8** of some metals (Ti, Zr, Hf, Co, Cr, Ni, Cu) can be obtained in almost quantitative yields (~90%–100%). The gas-phase syntheses of β-diketonates have been reported,[75,80] the latter publication being devoted to the synthesis of mononuclear calcium, strontium and barium trifluoro- and hexafluoroacetylacetonates (**8**: R^1 = H, CF_3;

R^2 = H; R^3 = CF_3; M = Ca, Sr, Ba; m = 2) from metals, metal oxides or fluorides.

The electrochemical method for the synthesis of β-diketonates implies anodic dissolution of the complexing metal in organic or aqueous–organic solvents containing the corresponding β-diketones (LH) and conductive additives.[2, 3, 72, 73, 75, 79–88] Graphite, platinum or some other metals, for example, nickel, are suitable as the cathode.[85–88] A systematic study of the electrochemical synthesis of β-diketonates has been reported.[75] The syntheses were carried out in 15%–20% solutions of ligands in aqueous (60%) methanol or ethanol, acetonitrile or DMF in the presence of LiCl, LiBr, NH_4Cl or Bu_4NBF_3. This gave β-diketonates ML_2 (M = Co, Mn, Ni), ML_3 (M = Al, In, Ga, Co, Fe), ML_4 (M = Zr, Hf), ML_2Solv (M = Ni, Fe), ML_3Cl (M = Ti, Zr), $TiL_3(OMe)$ and $ZrL_3(OMe)$ in yields of 60% to 90%. Several other publications [85–88] describe cobalt,[88] uranium [86] and dysprosium [85, 87] complexes obtained in an undivided electrolytic cell in ethanol. A synthesis carried out under an inert atmosphere (Ar, He) yields uranium β-diketonates UL_4, whereas in the presence of oxygen, the reaction gives UO_2L_2 (LH is acetyl- or benzoylacetone). The resulting cobalt and dysprosium β-diketonates are described as $CoL_2(EtOH)$ and Dy_3L_n (n = 1, 0.5). The use of the electrochemical method together with the chemical method (platinum cathode, methanol, Et_4NClO_4) furnishes chelates **32** (M = Co, Ni, Cu, Zn) in 17%–85% yields.[31] A promising approach is the use, in the electrochemical synthesis, of alkali metal β-diketonates in acetonitrile without any other conductive additives.[89] In this case, sodium β-diketonates can be obtained in the first stage and, subsequently, electrochemical replacement of sodium by a transition metal takes place.

β-Diketonates **8** can also be synthesised under boundary friction conditions (tribochemical mechanosynthesis);[72, 73] however, the preparative value of this method (see, for example, Ref. 90) is still obscure.

Since coordinatively unsaturated β-diketonates **8** are able to form adducts **59**–**66** with bases (see also a number of publications [91–95]), it appears of interest to convert them into heteronuclear complexes **67** .[96–99]



68

67

R^1 = Me, CF_3, Bu^t; R^2 = Me, CF_3;
M^1 = Mg, Ba, La, Y, Gd; M^2 = Cu, Ni; m = 2, 3.

In this reaction, *o*-hydroxyazomethine chelates **68** act as ligands.[10, 99, 100]

Similar procedures have been used to prepare bi- [101, 102] and trinuclear [103] complexes based on lanthanide (La, Gd) β-diketonates and transition metal *N*,*N*′-bisacetylacetone iminates.

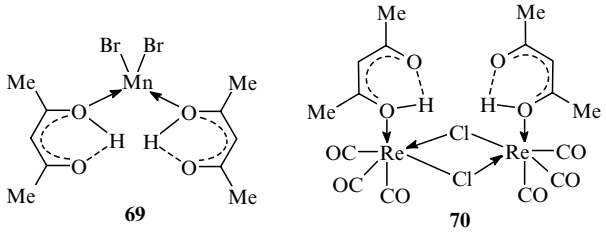
The heteronuclear complexes in question were characterised by X-ray diffraction; they present considerable interest as molecular ferromagnets [96] and as precursors for the production of films and coatings by vapour deposition of heterometallic materials.[97–99, 101–103]

Note that fragment **8** can be incorporated in more complex structures (see, for example, Ref. 9).

2. Complexes with neutral β-diketonate ligands

Complexes of this type are few; they have been studied by X-ray diffraction.[2, 3, 16–18, 21]

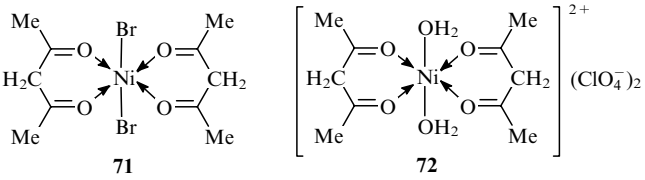
The mononuclear complex $MnBr_2(LH)_2$ (**69**) [104, 105] and the binuclear complex $[ReCl(CO)_3(L'H)]_2$ (**70**) [106, 107] correspond to structure **5**. Complexes with monodentate O-coordination corresponding to structure **7** have been discussed in the literature.[17, 18]



69 **70**

Compound **69** was synthesised without a solvent,[105] while compound **70** was prepared in benzene.[107] Apparently, the enol tautomer of the ligand is stabilised in these complexes.[104, 106]

It was found that the complexes $NiBr_2(LH)_2$ (**71**) [108] and $Ni(LH)_2(ClO_4)_2(H_2O)_2$ (**72**) have the same structure as chelate **10**.[109, 110]



71 **72**

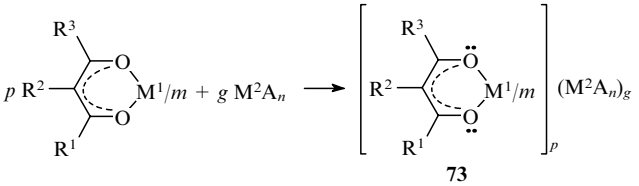
It should be emphasised that all hydrogen atoms in the structure of **72** have been located and the presence of a CH_2 group has been proven reliably. This indicates that the ligand exists in the keto form.

The data concerning other molecular complexes of β-diketones with mercury, tin, titanium, zirconium, manganese, cobalt, vanadium, rhenium, chromium, nickel, platinum, uranyl and europium halides and acetates are summarised in reviews.[17, 18] Only the results of elemental analysis (the composition was established to be MA_2L) and IR spectra were reported for these complexes, which precludes exact determination of their structures, in particular, distinguishing between the structures **9** and **10**.

3. Polynuclear complexes of O,O-coordinated β-diketones

The greatest number of structures of the type **11**–**15** is known among β-diketonates of Group IIA elements (Ca, Mg, Sr, Ba).[2, 3, 9, 21] In addition, worth mentioning are the dimer $[Ba_2L_4(NH_3)_4]$,[111] the trimer $[CaL_2]_3$,[112] the tetramer $[BaL_2]_4$,[9, 113–115] and the pentanuclear $Ba_5L_9Cl(H_2O)_7$ [116] and hexanuclear $Ba_6L_{10}(O_2)(H_2O)_6$ [117] complexes, which contain simultaneously structural elements of **8** and fragments of chelates **11**.

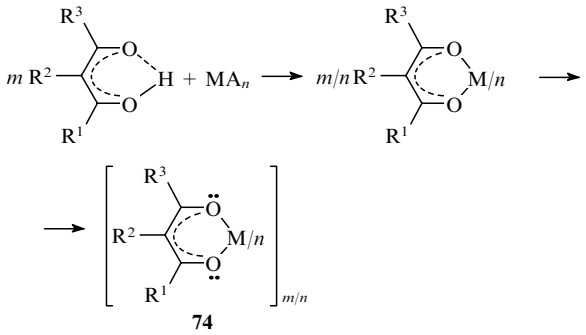
The syntheses of these polynuclear complexes are based on the ability of β-diketones to behave not only as Lewis acids but also as bases due to the oxygen electron pairs not involved in the coordination.[9, 113–120]



73

A is anion.

The formation of structures **73** can in principle be regarded as a sort of oligomerisation of metal β-diketonate monomers through M—O coordination, as in complex **74**.



74

This transformation underlies the synthesis of a series of heterometallic complexes, for example, β-diketonates and other metal chelates **75** (metal exchange in the β-diketonate fragment and the transformation of the heterocyclic ligand system)[121] or alkoxides **76**[122] as well as the template reaction giving rise to complex **77**.[123]

$$2\,CuL^1_2 + 2\,CdL^2_2(phen) \xrightarrow[\Delta,\ 1\ h]{MeCN} (Cd_2L^1_2)(\mu^3\text{-}L^3_2)[Cu_2(phen)]_2$$

75

L^1H is 1,1,1,5,5,5-hexafluoroacetylacetone, L^2H is pyridine-2-thione, L^3H is 1,3,5-tris(trifluoromethyl)-1,3,5-trioxycyclohexane trianion;

$$BaL_4 + Bi(OEt)_3 \xrightarrow[\sim 25\ ^\circ C]{C_6H_5Me} Bi_4Ba_4(\mu^4\text{-}O_2)_2(\mu^3\text{-}OEt)_8(\mu\text{-}OEt)_4(\eta^2\text{-}L)_4$$

76

LH is 2,2,6,6-tetramethylheptane-3,5-dione;

$$Cu(OMe)_3 + H_2L^1 + BaL^2_2 \xrightarrow[25\ ^\circ C,\ 4\ h]{CH_2Cl_2} Ba_2Cu_2L^1_4L^2_4$$

77

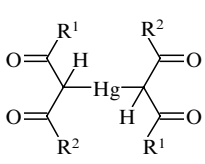
H_2L^1 is 2,2-thiodiethanol, L^2H is 1,1,1,5,5,5-hexafluoroacetylacetone.

The complex $(Pr_2CuL^1_3)HL^2_2(L^3_4)(\mu^6\text{-}O)$ was synthesised under similar conditions.

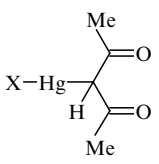
4. β-Diketonates with M—C- and M—C,O-coordination

β-Diketonate complexes of these types are represented by structures **16**, **18** and **23** studied by X-ray diffraction and reported in monographs[2–4, 16, 18, 124] and reviews.[5, 17, 20–24] Therefore, we will consider only the synthetic aspect of the design of this type of complex with unusual localisation of the coordination bonds.

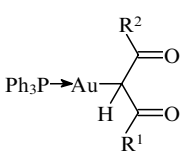
As emphasised in a monograph,[124] the M—C-coordination, which is found, for example, in compound **16**, is observed in the complexes of β-diketones with Mn^I, Rh^I, Au^I, Pt^{II}, Pt^{III}, *i.e.*, with soft metals, which is consistent with Pearson's hard–soft acid–base (HSAB) principle.[2, 3, 125, 126] Examples of such compounds are mercury(II) complexes **78**[127, 128] and **79**[129, 130] and gold(I) complex **80**.[131–135]



78: R^1, R^2 = Me, Bu^t

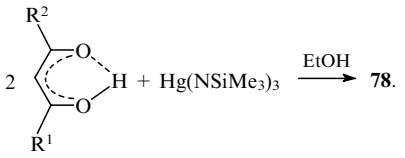


79: X = $MeCO_2$, Cl



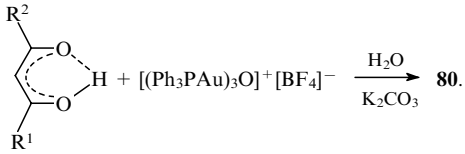
80: R^1 = Me, Bu^t, Ph; R^2 = Me, Bu^t, Ph, Fc (Fc is ferrocenyl)

Compound **78** was prepared in a quantitative yield by the following reaction:[127]



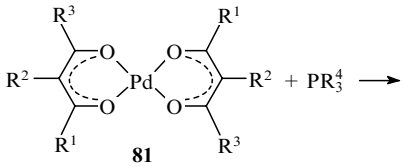
Subsequently,[128] complex **78** (R^1 = Bu^t; R^2 = n-C_3F_7) has been prepared using mercury(II) acetate. The structure of the resulting complex was studied by ^1H NMR spectroscopy and mass spectrometry, demonstrating the presence of keto–enol tautomerism (acetone, −60 to 40 °C).

Compounds **80** have been prepared in 46%–100% yields[135] upon the following transformation:

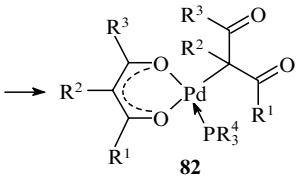


Other complexes with the structure of compound **16** have been discussed in reviews.[16–18, 136] Complexes with the structure of chelate **18** have been reported.[17, 18, 137]

The general method for the synthesis of complexes with the structure of chelate **23** is based on the reactions of β-diketonates **8** (M = Pt, Pd, Au) with organic amines and phosphines.[2, 3, 17, 18, 138, 139] This approach has received the most study in relation to the transformation of palladium diketonate **81** into complex **82**.[139–144]



81

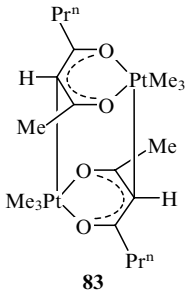


82

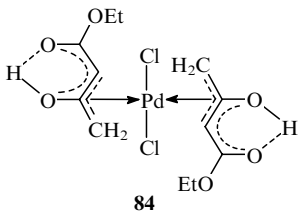
R^1–R^4 = H, Alk, Ar.

The M—C coordinated β-diketonate fragment is a part of trinuclear complexes $M[PtCl(acac)(acac\text{-}C^3)]_2$ where M = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Pd^{II}, Cu^{II}, Zn^{II}, Cd^{II}, VO and UO_2.[17, 18]

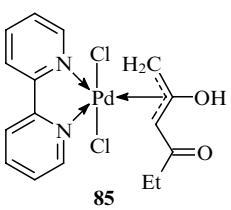
Other possible modes of coordination of β-diketone ligands have been confirmed experimentally,[16–18, 124] namely, C—O coordination as in chelate **22**; η^2(C,C′)- and μ^1(C)-coordinations in complex **83**; η-allylic coordination in complexes **84** and **85**; η^3(O,O′)-bridging coordination in complex **86**; and η^3(C,O)-bridging coordination in complex **87**.



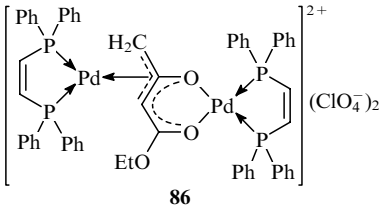
83



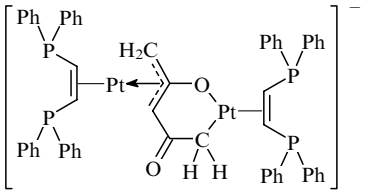
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85

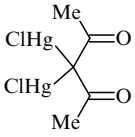


86



87

Binuclear compound **88** with the C—M-coordination, as in structure **19**, has been described and structurally characterised.[145]



88

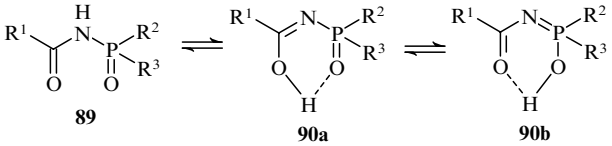
The compound **88** is the only example of a binuclear C-coordinated complex of β-diketone.

III. Modified β-diketonates

β-Diketone ligands are modified by altering the C—C—C fragment or replacing the oxygen atoms by N-, P-, S- and Se-donor centres. This gives rise to diverse ambident ligand systems. N,P-Containing analogues of β-diketones and chalcogen-substituted derivatives **3** (A = CR, D = PR^1R^2; X, Y = O, S) have been studied during the last decade.

1. N,P-Substituted β-diketonates

Among the potential polydentate ligands with N,O-donor centres, noteworthy are *N*-carbacylphosphoramidates (CAPh) **3** (A = CR, D = PR_2, X = Y = O), which have become readily available owing to the phosphazo reaction developed by Academician Kirsanov and co-workers.[146] Since CAPh are weak NH-(compound **89**) or OH-acids (compound **90**), they are able, similarly to β-diketones, to enter into the metal coordination sphere in either the deprotonated or the neutral form.[147]



89 **90a** **90b**

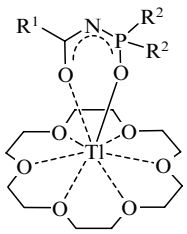
R^1, R^2, R^3 = Alk, Ar, Het.

The complexes with CAPh, like β-diketonates, exist most often as structure **4** (A = CR, D = PR^1R^2, X = Y = O). This structure was proved for thallium complex **91** prepared by the following transformation (the crown ether was used to restrict the susceptibility of Tl^+ complexes to di- and polymerisation).[148]

$$Tl_2CO_3 + 2\,HL + 2\,(18\text{-crown-}6) \longrightarrow$$

$$\longrightarrow 2\,Tl(18\text{-crown-}6)L + CO_2\uparrow + H_2O$$

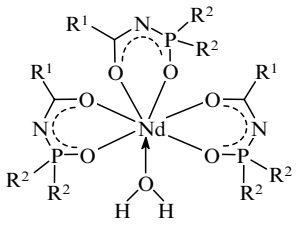
91



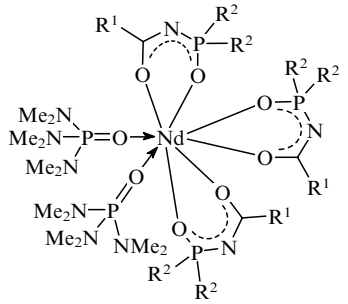
91: $R^1 = CCl_3$, $R^2 = OMe$

Structures of this type are widely represented in the series of lanthanide complexes.

In most lanthanide complexes, CAPh in the acid form is coordinated in the O,O′-bidentate mode (structures of chelates **4**, **8**). This was shown by X-ray diffraction[147] for neodymium complexes **92** and **93**.

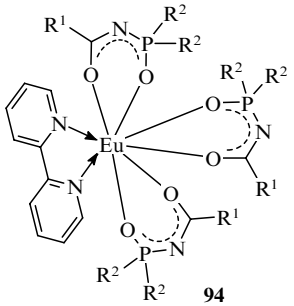


92: $R^1 = CCl_3$, $R^2 = N(C_2H_4)_2O$

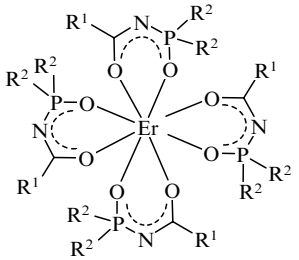


93: $R^1 = CCl_3$, $R^2 = OMe$

Complexes $LnL_3 \cdot Q$ with CAPh ligands, for example, **94** [$R^1 = CCl_3$; $R^2 = N(C_2H_4)_2O$, OPh, OMe; Q is α,α′-bipyridyl or 1,10-phenanthroline] have been prepared and structurally characterised.[149, 150]



94



95

In the anionic complex of erbium **95**, the ligands are also coordinated in the bidentate chelating mode through the oxygen atoms of the phosphoryl and carbonyl groups.[151–153]

The homoligand anionic tetrakis-complexes M[LnL_4] with the ester type CAPh ligands have been synthesised from methanolic solutions in the following way:[151]

$$LnA_3 + 4\,NaL \longrightarrow Na[LnL_4] + 3\,NaA$$

A = Cl^-, NO_3^-.

Heteroligand cationic complexes of lanthanides have been prepared by metal exchange[2,3] from the sodium salt of *N*,*N*′-tetraethyl-*N*″-trichloroacetylphosphortriamide (NaL):[154]

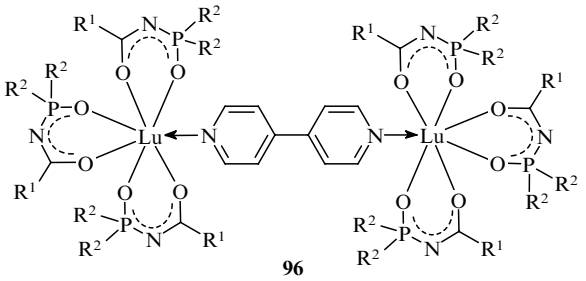
$$Ln(NO_3)_3 + (3-n)\,NaL + m\,HMPA + n\,NaBPh_4 \longrightarrow$$

$$\longrightarrow [LnL_{3-n}(HMPA)_m](BPh_4)_n + 3\,NaNO_3\downarrow$$

$m = 2, 4$; $n = 1, 2$.

The synthesis was carried out in isopropyl alcohol in the presence of a dehydrating agent, ethyl orthoformate. According to electronic spectroscopy, the coordination polyhedron is a distorted octahedron.

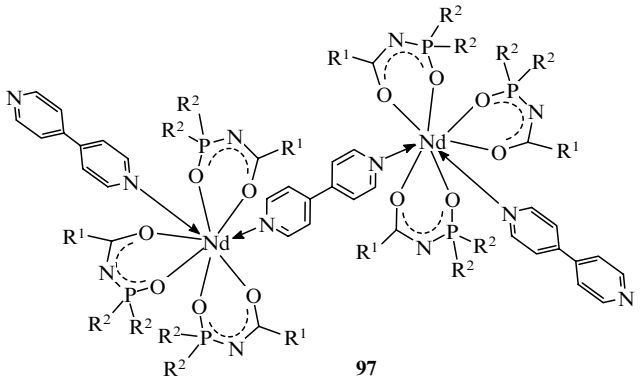
The deliberate synthesis of binuclear complexes of lanthanides proceeds successfully when coordinatively unsaturated tris-complexes are used as structural elements and potential bridging ligands. For example, in the case of γ,γ′-bipyridyl, compounds of the type $(CAPh)_3Ln(\gamma,\gamma'\text{-bipy})Ln(CAPh)_3$ (**96**) were obtained;[155] in these products, the central atom is heptacoordinated, being O,O′-chelated by the ligand (structure **4**).



96

$R^1 = CCl_3$, $R^2 = OMe$.

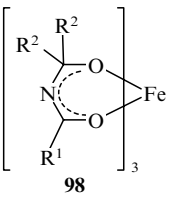
The influence of the nature of the central lanthanide atom on the composition and structure of its complexes with these ligands was demonstrated in relation to $Nd_2(CAPh)_6(\gamma,\gamma'\text{-bipy})_3$ (**97**).[147] In this case, neodymium is octacoordinated.



97

$R^1 = CCl_3$, $R^2 = NEt_2$.

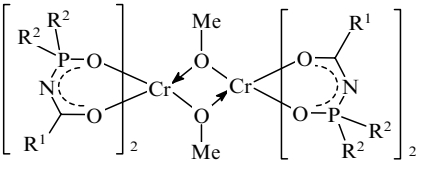
The structure of chelate **4** (or **8**) is characteristic of CAPh complexes with transition metals, for example, the complex with iron(III) (**98**).[156]



98

$R^1 = CCl_3$, $R^2 = NEt_2$, $N(C_2H_4)_2O$.

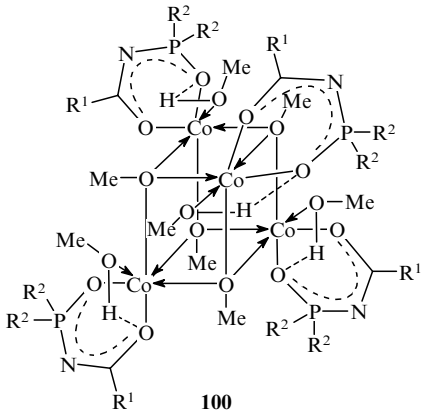
These compounds are known as not only monomeric (**98**) but also bi- and oligonuclear structures. Oligomerisation of the coordination polyhedra can take place by coordination of simple fragments such as alkoxy groups by the metal. For example, in the structure of dimeric chromium(III) complex (**99**), deprotonated CAPh ligands are coordinated in the bidentate chelating mode, the bridging functions being performed by two alkoxyl groups.[157]



99

$R^1 = CCl_3$, $R^2 = OMe$.

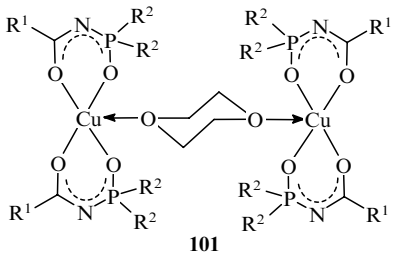
Cobalt and nickel complexes crystallise as tetramers **100** with the composition $Me_4L_4(OMe)_4(HOMe)_4$ in which the tetramer core is formed by four Co atoms and by four O atoms of the methoxy groups.[147]



100

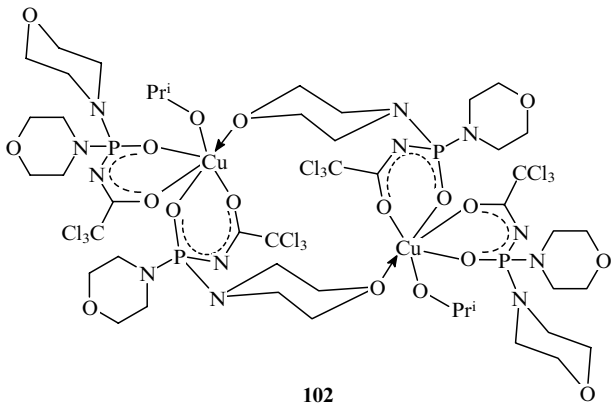
$R^1 = Ph$, $R^2 = NEt_2$.

Dioxane molecules and morpholine substituents can also function as bridges; this gives rise to dimeric copper(II) complexes **101** and **102** and polymeric complexes **103**.[158]

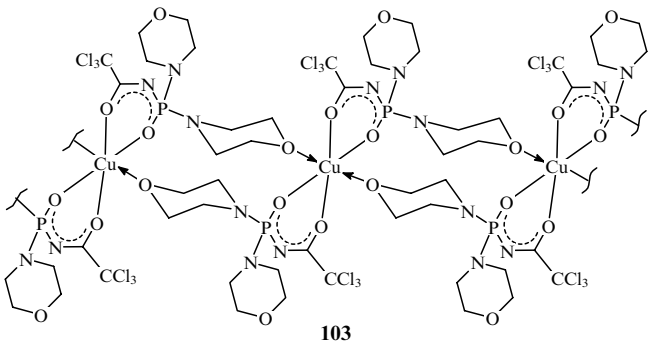


101

$R^1 = CCl_3$, $R^2 = NEt_2$.



102



103

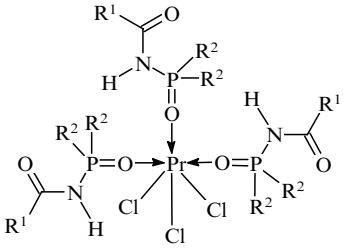
In the complexes of neutral CAPh with lanthanides, the ligand is monodentate, being coordinated through the oxygen atom of the phosphoryl group (similarly to structure **6**). These compounds

are prepared by direct reactions of the ligands (HL = CAPh) with lanthanide salts.[159]

$$LnA_3 \cdot n\,H_2O + 3\,HL \longrightarrow LnA_3(HL)_3 + n\,H_2O$$

A = Cl^-, NO_3^-.

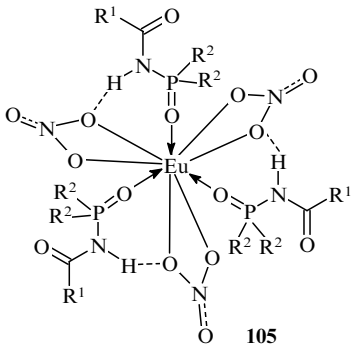
In the case of complex $PrCl_3(HL)_3$, the *fac*-isomer **104** has been isolated; its structure was proved by X-ray diffraction.[160]



104

$R^1 = CCl_3$, $R^2 = NEt_2$.

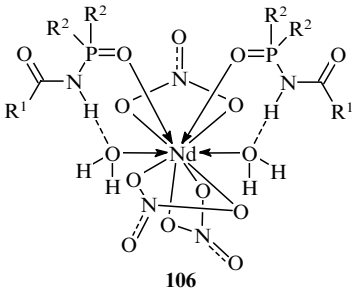
The nitrate groups in the compound $Eu(NO_3)_3(HL)_3$ (**105**), which is similar to complex **6** in structure, are arranged in three mutually perdicular planes due to the directing action of the intramolecular hydrogen bonds.[161, 162]



105

$R^1 = CCl_3$, $R^2 = NEt_2$.

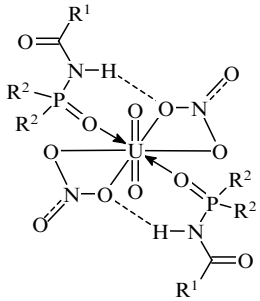
The synthesis of complex $Nd(NO_3)_3(HL)_2(H_2O)_2$ (**106**) can be considered as an example of supramolecular self-organisation,[163, 164] whose driving force is the formation of hydrogen bonds with participation of the NH proton.[165]



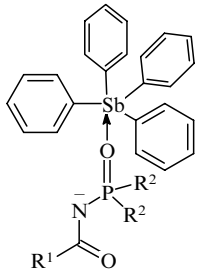
106

$R^1 = CCl_3$, $R^2 = N(C_2H_4)_2O$.

The supramolecular self-organisation typical of complexes formed by neutral CAPh (structure **6**) is manifested in the coordination compounds of uranyl $UO_2(NO_3)_2(HL)_2$ (**107**) in which the coordination polyhedron is a hexagonal bipyramid. The equatorial oxygen atoms are arranged in a virtually ideal plane.[166]



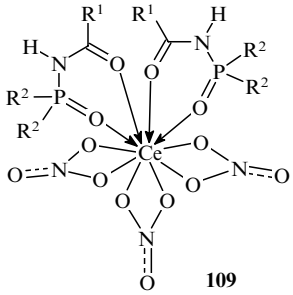
107: $R^1 = CCl_3$, $R^2 = NEt_2$



108: $R^1 = CCl_3$, $R^2 = OMe$

The monodentate coordination with participation of the phosphoryl oxygen atom has been established by X-ray diffraction also for the antimony complex **108**.[147]

The coordination compound $Ce(NO_3)_3(HL)_2$ (**109**) is the first example of bidentate chelating coordination of neutral CAPh (as in chelate **10**) realised through the phosphoryl and carbonyl oxygen atoms.[167]



109

Among the coordination compounds of CAPh, structures with tridentate ligands similar to chelate **11** are represented rather widely. These include, in particular, complexes of Group IA metals.

Compounds of complex-forming alkali metals with some CAPh can be prepared in high yields by direct reaction of the ligands with metal salts in aqueous alcohols, for example:[147]

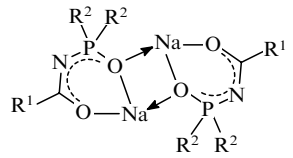
$$2\,HL + M_2CO_3 \longrightarrow 2\,ML + CO_2\uparrow + H_2O$$

M = Na, K, Rb, Cs.

Metal complexes with CAPh are also prepared by the reaction of ligands with the alkoxides of complexing metals in alcohols.[168–174]

$$HL + MOR \longrightarrow ML + HOR$$

The sodium and thallium complexes M_2L_2 crystallise as centrosymmetrical dimers **110**,[147] formed through the bridging oxygen atoms of the phosphoryl groups (the coordination mode is the same as in chelate **11**).



110

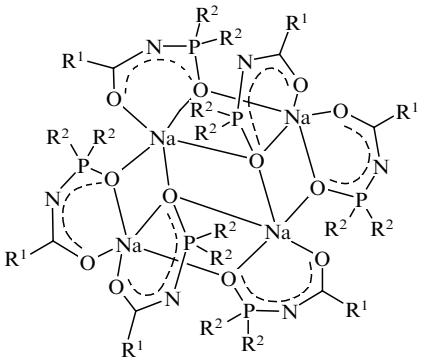
$R^1 = CCl_3$, $R^2 = OMe$.

The tendency of CAPh to form associates has been demonstrated in relation to the synthesis of the anionic $(PPh_4)_2[Na_4L_6]$ (**111**) complex [147] carried out in anhydrous acetonitrile.

$$2\,(PPh_4)Br + 6\,NaL \longrightarrow (PPh_4)_2[Na_4L_6] + 2\,NaBr\downarrow$$

111

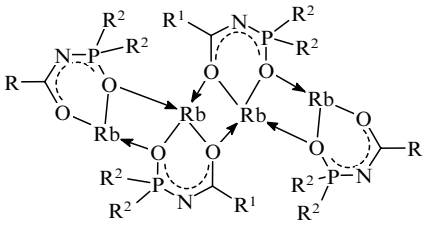
Compound **111** contains two tetraphenylphosphonium cations and the $[Na_4L_6]^{2-}$ anion. The complex anion is composed of four sodium ions connected to one another by bi- and tridentate bridging oxygen atoms of the phosphoryl groups of the ligands (the coordination mode is the same as in chelate **12**).



111

$R^1 = CCl_3$, $R^2 = OMe$.

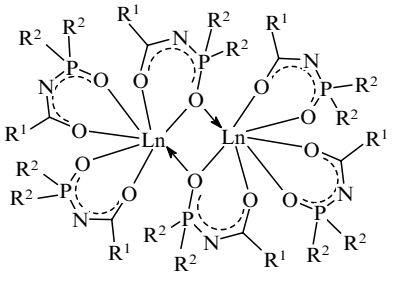
The unit cell of complex Rb_4L_4 (**112**) contains four Rb^+ ions linked by bridging oxygen atoms of the phosphoryl and carbonyl groups,[147] *i.e.*, the mode of coordination is the same as in chelate **11**.



112

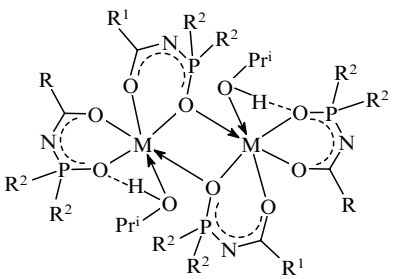
112: $R^1 = CCl_3$, $R^2 = OMe$.

The structures with mixed coordination of the ligands, similar to chelates **4** (or **8**) and **11**, are also encountered [147, 173] both in lanthanide complexes **113** and in cobalt(II) and nickel(II) complexes **114**.[175, 176]



113

$R^1 = CCl_3$, $R^2 = NEt_2$.



114

$R^1 = CCl_3$, $R^2 = OMe$; $M = Co^{2+}$, Ni^{2+}.

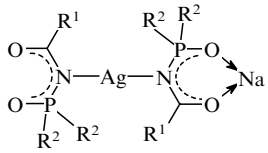
The complexes **113** were prepared in the following way:

$$2\,Ln(NO_3)_3 + 6\,NaL \longrightarrow Ln_2L_6 + 6\,NaNO_3\downarrow$$

Ln = La, Ce – Nd, Sm – Yb, Y.

Only one complex of CAPh with ligand coordination similar to that observed in compound **16** is currently known. The structure of this complex was proved by X-ray diffraction. This is the silver complex $Na[AgL_2]$ (**115**) prepared by metal exchange from acetonitrile solutions.[147]

$$2\,NaL + AgNO_3 \longrightarrow Na[AgL_2] + NaNO_3\downarrow$$



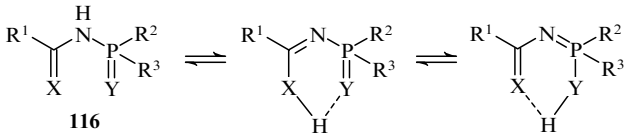
115

115: $R^1 = CCl_3$, $R^2 = OMe$.

The coordination of CAPh in this case can be compared with C-coordination of β-diketones, for example, the coordination found in compound **78**.[2, 3]

2. Metal complexes of N,P-derivatives of thio- and bisthiodiketones

The ligand systems and complexes in which structural analogues of β-diketones containing the XCNPY fragment (X = S, Y = O; X = O, Y = S; X = Y = S; X = O, Y = Se; X = Se, Y = O) are present as ligands in the coordination sphere (**116**, **117**) have been surveyed in sufficient detail.[177, 178]

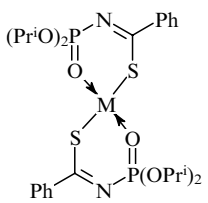


116 **117a** **117b**

X, Y = O, S, Se; R^1, R^2, R^3 = Alk, Ar, Het.

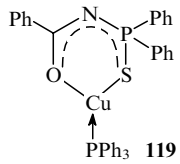
The metal complexes **116** and **117** mainly exist as structures **4** (A = CR; D = PR^1R^2; X, Y = O, S), which are classical for β-diketonates (chelates **8**). The structures of complexes **118** – **126** were confirmed by X-ray diffraction; these compounds are described below.

The synthesis and structure of copper and lead chelates ML_2 (**118**) with *N*-diisopropoxyphosphorylthiobenzamide (the MO_2S_2 coordination unit), characterised by a square planar and tetrahedral environments of the central atom, respectively, have been reported.[179, 180] The Cu^{2+} complexes were obtained from malachite (basic copper carbonate) in solutions of *N*-(thio)phosphorylated thioamides followed by reprecipitation from benzene with hexane. The Pb^{2+} compounds were synthesised by the reactions of alkali metal salts of the ligands dissolved in aqueous alcohols with lead salts or oxides.



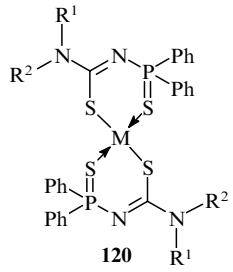
118: M = Cu, Pb

A bidentate O,S-coordination has also been found for copper(I) chelate **119**.[181]



119

A number of studies are devoted to complex compounds containing the MS_4 coordination unit (structure **4**: A = CR, D = PR_2, X = Y = S). The syntheses of cobalt, nickel and palladium chelates with S-donor ligands of the type $R^1C(S)NHP(S)R^2_2$ were first described back in 1969.[182] The conclusions about the structures of the resulting compounds **120** were drawn from data of IR spectroscopy and magnetic chemistry (the square-planar environment for Ni^{2+}, Pd^{2+} and the tetrahedral environment for Co^{2+}).

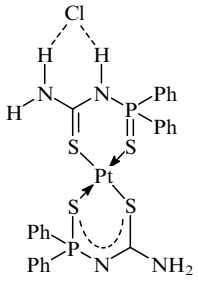


120

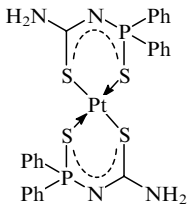
R^1 = Ph, R^2 = H; R^1 = R^2 = Et; M = Co, Ni, Pd.

Later on, data on the structure of an analogous nickel complex with *N*-(diphenylthiophosphoryl)methylthiourea (**120**, M = Ni) were documented.[183]

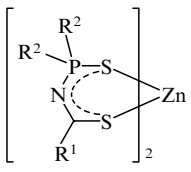
It should be emphasised that the reaction of platinum(II) chloride with diphenylthiophosphorylthiourea in CH_2Cl_2 results in complex **121**, whose coordination sphere contains bidentate chelating ligands coordinated in either deprotonated (structures **4**, **8**) or neutral (structure **10**) form. The exchange reaction of platinum(II) or zinc(II) chloride with the potassium salt of the ligand gives the usual chelates with square planar (**122**) and tetrahedral (**123**) structures, respectively.[181]



121

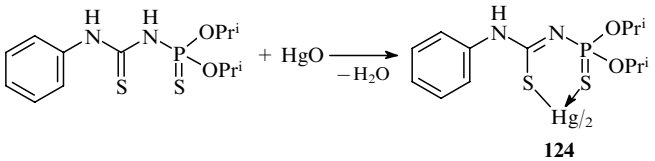


122



123

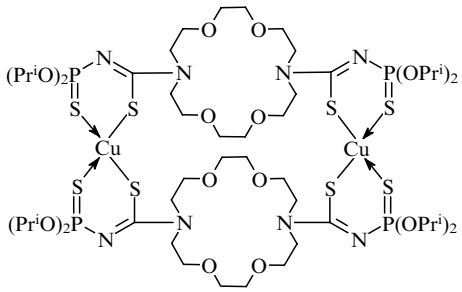
The reaction of *N*-(diisopropoxythiophosphoryl)thiobenzamide with mercury oxide in organic solvents gives mercury chelate **124**.[184]



124

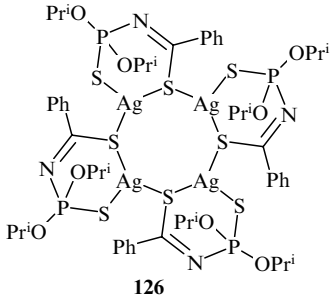
The central mercury atom in complex **124** forms a distorted tetrahedral environment.

On the basis of EPR and electronic spectroscopy studies, structures have been proposed for binuclear copper complexes (**125**); in addition, the electrochemical behaviour of these complexes has been studied.[185, 186]



125

A method for the synthesis has been described and X-ray diffraction analysis has been performed for the tetrameric Ag(I) complex **126** in which the ligands are coordinated in the same way as in structure **11**.[187]

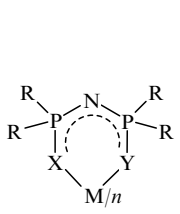


126

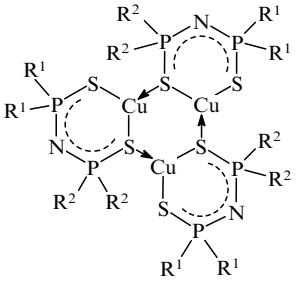
The formation of this tetramer is due to the presence of lone electron pairs at the donor sulfur atoms in mononuclear complexes, for example, in **121**–**123**. This is also quite usual for classical β-diketonates.[21, 188]

3. Coordination compounds of the N,P,P-derivatives of β-diketones and their chalcogen-containing analogues

Like the coordination compounds addressed in the preceding Sections, complexes of azobisphosphorus-containing analogues of β-diketones (their tautomers correspond to structures **89**–**91**, **116**, **117**) are represented, most often, by chelates with structure **4** (A = D = PR_2; X = O, Y = S, Se; X = S, Y = S, Se).[189–199] The structures **127** can be found in the six-membered chelates of indium,[189] palladium,[190, 195] platinum,[190] zinc[190] and cadmium.[190]



127



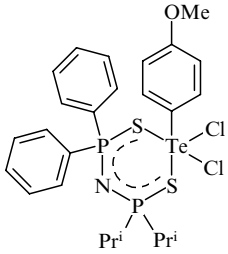
128: R^1 = Pr^i: R^2 = Pr^i, Ph, OPh

Of particular interest is the fact that the indium[189] and palladium[194] complexes were prepared directly from the corresponding zerovalent metals (synthetic strategies of this type are widely used in modern coordination chemistry[2, 3]).

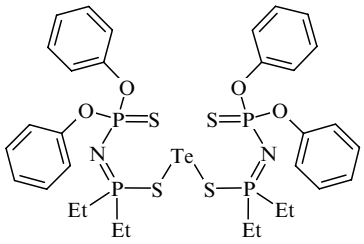
Other modes of coordination are also known for complexes of these ligands. For example, in the case of platinum complexes, in addition to the coordination as in chelate **4** (**127**: X = O, Y = S), a structure with monodentate S-coordination of the metal atom is also formed.[195] A similar structure has been found for the gold complex,[195] which could be expected in terms of Pearson's HSAB principle (in view of the softness of the metals in question).[2, 3, 125, 126]

According to X-ray diffraction data, the trimeric copper complexes synthesised from compound **3** (A = D = PR_2, X = Y = S) and $CuCl_2$ in methanol occur as structure **128**[196] with the same coordination mode of the metal as found in chelate **11** .

In relation to the problem of competitive reactivity of ligands **3**, tellurium complexes are of interest.[197, 198] Not only tellurium complexes with a ligand coordination usual[20–24] for chelates, as in **127** (M = Te; X = S; Y = Se; n = 2) and **129**, have been described, but also complexes with the monodentate ligand bound through the S-donor centre at the phosphorus atom. This type of ligand coordination is embodied in structure **4** (A = D = PEt_2; X = Y = S).



129



130

Complex **129** is of interest due to the fact that, according to X-ray diffraction data, the tellurium central atom is pentacoordinated, whereas in **130**, the same complex-forming element has a coordination number equal to two.

In conclusion, we would like to note that the material covered in this Section can be substantially extended by the data reported in the recent publication.[198]

IV. Conclusion

In writing this review, we have not set ourselves the task of embracing all the possible methods for the preparation of metal complexes of β-diketonates and their analogues. For example, we did not consider the coordination compounds of mono- and disubstituted nitrogen analogues of β-diketones, namely, β-aminovinyl ketones (**1**: A = E = D = CR^1; X = O; Y = NR^2) and β-aminovinylimines (**1**: A = E = D = CR^1; X = Y = NR^2), which have been studied rather comprehensively (see, for example, an exhaustive review [11]). All the complexes described in that review are chelates coordinated in the same manner as in chelate **2** (A = E = D = CR^1; X = O, NR^2; Y = NR^2). Meanwhile, in view of the data [10, 200] attesting to different modes of coordination of Schiff's bases in metal chelates (bidentate N,O-chelation by the anionic form of the ligand) and in molecular complexes (O-monodentate coordination of the neutral ligand), one should expect the formation of various types of complexes also for β-aminovinyl ketones and β-aminovinylimines.

This situation is typical of fairly well-known metal chelates of mono- and dithio-β-diketones (**1**: A = E = D = CR; X = O, Y = S; X = Y = S)[2, 3] and phosphorus-containing analogues of β-diketones (**1**: A = E = CR; D = PR_2; A = D = PR_2, E = CR; X, Y = O, S, Se).[12]

The material outlined in this review indicates that a number of β-diketonate ligands can be coordinated according to different modes. Therefore, metal complexes of different types can be prepared. We hope that further research will bring new data on the complexation of such ligands and will thus contribute to the development of deliberate strategies for the synthesis of complex compounds with specified coordination units on the basis of typical chelating ligands.

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