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Review

Coordination modes of 5-pyrazolones: A solid-state overview

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Contents

Abstract

The coordination modes of 5-pyrazolones are reviewed in light of the available X-ray diffraction studies of their complexes. This structural analysis firstly concerns the coordination behaviour of the molecules without any donor atoms other than those associated with the pyrazolone ring, and then deals with substituted pyrazolones in which the substituent provides additional donor atoms. Although the C4-substituted molecules are the most widely explored because they are very versatile ligands, interest in the *N*(1)-substituted derivatives and in the bis- and poly-5-pyrazolones has been growing steadily in recent years.

Keywords: 5-Pyrazolone ligands; Metal complexes; X-ray studies; Coordination chemistry

1. Introduction

Pyrazolones constitute a group of organic compounds that have been extensively studied due to their properties and applications. Since the synthesis of antipyrine (2,3-dimethyl-1-phenyl-5-pyrazolone) by Knorr [1,2] in 1883, a great deal of attention has been paid to the analgesic and antipyretic properties of these compounds. The discovery of these properties prompted

Abbreviations: bbpa, bis((2-benzimidazolylmethyl)-(2-pyridylmethyl)-amine); CN, coordination number; dmamp, *o*-(dimethylamino)methylphenyl; DMF, dimethylformamide; DMSO, dimethylsulfoxide; $HB(pz)_3$, tris(3,5-dimethylpyrazol-1-yl)hydroborate; Hpiv, pivalic acid; Meac, α-methylacrylate; Ph_5Cp, pentaphenylcyclopentadienyl; py, pyridine; bipy, bipyridine

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the search for other pyrazolones with similar behaviour but with a better therapeutic action. As a result of this interest, aminoantipyrine (the 4-amino-antipyrine) was synthesized [3] and incorporated into the pharmacopoeia as an antipyretic and, later on, as an analgesic and anti-inflammatory agent. Nevertheless, the use of these compounds in the treatment of humans declined significantly after their toxicity for bone marrow was discovered. A new advance in this field occurred in 1949 when H. Stenzl synthesized phenylbutazone [4], a product for the treatment of rheumatoid arthritis. Once again, the high toxicity of these compounds in human beings has restricted their use, which is currently limited to the veterinary field. Since these first historical moments, the synthesis of pyrazolones has remained to a large extent focused on the search for less toxic new anti-inflammatory drugs [5] or the preparation of new compounds with antifungal [6], antitumor [7] and antihyperglycemic [8] activities.

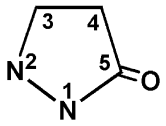
Although the use of pyrazolones as drugs has warranted significant attention, many more applications have been devised for this group of molecules outside the pharmaceutical field. For example, they have been applied to the solvent extraction of metal ions [9], for analytical purposes [10], in the preparation of azo colorants [11], as ligands in complexes with catalytic activity [12] and in the synthesis of rare earth metal complexes with interesting photophysical properties [13].

2. 5-Pyrazolones as ligands in metal complexes

The research outlined above, which is mainly related with the applications of pyrazolones, has also been accompanied by a notable and parallel effort directed at unveiling the coordination chemistry of these molecules. Many complexes have been prepared and their structures explored using X-ray diffraction or spectroscopic methods. Although this information is rather valuable, to the best of our knowledge there has not been a general review of this field until the recent publication by Marchetti et al., which specifically refers to 4-acyl-5-pyrazolones [14].

A certain amount of information about the synthesis of ligands and complexes is included in this review, but this publication is focused mainly on the X-ray analysis of the coordination modes of all types of 5-pyrazolones rather than the properties of their complexes. Furthermore, in an effort to avoid overlap with the review of Marchetti et al., emphasis here is placed on 5-pyrazolones other than the acyl derivatives—although these are also briefly discussed. The experimental information used in the present work was obtained, when available, from the Cambridge Structural Data Base (CSD) [15] or, in some cases, from the corresponding paper. The complexes included are identified, where possible, by their CSD code. The molecular graphics were obtained using MERCURY [16].

The review has been ordered in terms of the positions of the substituents on the pyrazolone ring (i.e., on the C4, N1 or N2 atoms, see Scheme 1) when they have potential donor atom(s), and to the nature of this (or these) atom(s) because they usually determine the final denticity of the pyrazolone ligand. In each section, the complexes formed by each ligand are ordered by metal according to the periodic table. The complexes that include bis- and poly-5-pyrazolones are treated together in the last section.



Scheme 1. Numbering adopted for the pyrazolone ring.

The nomenclature for this type of molecule is not always consistent in the literature, particularly when they are substituted. In order to avoid any confusion, we have adopted for the pyrazolone ring the numbering in Scheme 1, regardless of the criteria used by the authors in a cited paper, and consider that they are all 5-pyrazolones. Finally, it is worth noting that these molecules can adopt different tautomeric forms [17] and only one (not necessarily the most abundant) will be used to represent schematically the molecule in question in each case.

2.1. 5-Pyrazolones without additional donor atoms

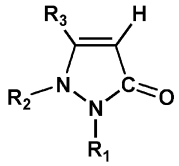
The methods of synthesis for these pyrazolones are diverse, but frequently the preparation involves the condensation of a β-keto aldehyde or a β-keto ester with a hydrazine [18]. In solution these compounds exist in different tautomeric forms, the relative abundance of which depends on the structure of the compound (number and position of the substituents), the concentration, the nature of the solvent and the temperature [19,20].

From a coordinative point of view this is the simplest case, since the only atoms available for coordination are the nitrogen atoms of the pyrazole ring and the oxygen atom of the carbonyl group (see Scheme 1). All complexes of this type studied by X-ray diffraction are listed in Table 1 and the ligands involved are shown in Scheme 2.

The ligand L^1 (antipyrine), in which both nitrogen atoms are blocked by substitution, shows the same coordination mode in all of its complexes [21–34], binding to the metal through the only donor atom available (the O atom), as one would expect (Fig. 1).

Antipyrine does not carry a charge and, as a result, coordination to a metal ion requires the presence of anions (e.g., X^-, NO_3^-, ClO_4^-) to ensure neutrality in the complexes. The anion may be within (as in $[Co(NO_3)_2(L^1)_2]$ [21], Fig. 2) or outside (as in $[Cd(L^1)_6](ClO_4)_2$ [27], Fig. 3) the coordination sphere of the metal.

All of the antipyrine complexes are mononuclear apart from the copper complex $[Cu_2(Meac)_4(L^1)_2]$ [22] (Fig. 4) (Meac = α-



L^1 (antipyrine), R_1 = Ph, R_2 = R_3 = Me
HL^2, R_1 = R_2 = H, R_3 = Me
HL^3, R_1 = R_2 = H, R_3 = -CF_3
HL^4, R_1 = R_2 = H, R_3 = Ph
HL^5, R_1 = R_2 = H, R_3 = Et

Scheme 2.

Table 1
Complexes of 5-pyrazolones without additional donor atoms

Ligand	Complex	CSD code	Pyrazolone donor atoms	Reference
L^1	$[Co(NO_3)_2(L^1)_2]$	NTAPCO	O	[21]
	$[Cu_2(Meac)_4(L^1)_2]$	ECEBAP	O	[22]
	$[Cu(NO_3)_2(L^1)]$	NTAPYC	O	[23]
	$[ZnCl_2(L^1)_2]$	ANTPZN	O	[24]
	$[ZnBr_2(L^1)_2]$	LORHUV	O	[25]
	$[Zn(NO_3)_2(L^1)_2]$	[a]	O	[26]
	$[Cd(L^1)_6](ClO_4)_2$	DAMHAA	O	[27]
	$[Pb(L^1)_6](ClO_4)_2$	PBAPYR	O	[28]
	$[Y(bbpa)(L^1)_3](ClO_4)_3\cdot H_2O$	LUQDAC	O	[29]
	$[Y(HL^1)_6]I_3$	YTANPY10	O	[30]
	$[Pr(bbpa)(L^1)_3](ClO_4)_3\cdot H_2O$	LUQCUV	O	[29]
	$[Nd(NO_3)_3(L^1)_3]$	ANTNND10	O	[31]
	$[EuCl(bbpa)(L^1)(H_2O)_2]Cl_2\cdot 2H_2O$	LUQDEG	O	[29]
	$[Tb(L^1)_6]I_3$	VAPTEL	O	[32]
		VAPTEL01		[33]
	$[Tb(L^1)6](ClO_4)_3$	COLQAV	O	[34]

Ligand	Complex	CSD code	Coordination mode[b]	Reference
HL^2	$[CoCl_2(HL^2)_4]$	MASNAW	(a)	[35]
	$[Ni_4Na_4(L^2)_4(piv)_8(Hpiv)_6]$	[a]	(d)	[36]
	$[Ni_5Na_4(OH)_2(L^2)_4(piv)_8(Hpiv)_2(MeCN)_2]$	EKIYIG	(d)	[36]
	$[Ni_8(OH)_4(L^2)_2(PhCH_2CO_2)_{10}(HL^2)_8]$	EKIYUS	(a) (HL^2) (c) (L^2)	[36]
	$[Ni_{24}(OH)_8(L^2)_{16}(MeCO_2)_{24}(HL^2)_{16}]$	[a]	(a) (HL^2) (c) (L^2)	[37]
	$Na[Ni_8Na(OH)_2F_8(^tBuPhCO_2)_8(HL^2)_8]$	SARZIV	(a)	[38]
	$[Ni_8Na_2(N_3)_{12}(PhCO_2)_2(L^2)_4(HL^2)_6(EtOAc)_6]$	SARZOB	(a) (HL^2) (b) (L^2)	[38]
HL^3	$[Ni_4Na_4(L^3)_4(piv)_8(Hpiv)_8]$	EKIYEC	(d)	[36]
	$[Ni_5Li_6(OH)_2(L^3)_2(piv)_{12}(Hpiv)_4]$	EKIZAZ	(d)	[36]
HL^4	$[Mn_{14}O_2(OH)_4(L^4)_{18}(HL^4)_4(NO_3)_4(MeCN)_4]\cdot Et_2O\cdot 3.5MeCN$	XOTKAS	(a) (HL^4) (b), (c), (d) (L^4)	[39]
	$[Ni_5Na_4(OH)_2(L^4)_4(piv)_8(Hpiv)_2(EtOAc)_2]$	ALOWON	(d)	[36]
	$[Ni_8K_2(OH)_4(L^4)_4(piv)_{10}(HL^4)_2(Hpiv)_2(MeCN)_2]$	EKIYOM	(a) (HL^4) (b), (c), (d) (L^4)	[36]
	$[Ni_8Cs_2(OH)_4(L^4)_4(piv)_{10}(HL^4)_2(Hpiv)_2(MeCN)_2]\cdot MeCN$	EKIZED	(a) (HL^4) (c), (d) (L^4)	[36]
	$[Ni_8Rb_2(OH)_4(L^4)_4(piv)_{10}(HL^4)_2(Hpiv)_2(MeCN)_2]$	EKIZIH	(a) (HL^4) (c), (d) (L^4)	[36]
	$[Ni_6Mg_2(OH)_2(L^4)_4(piv)_{10}(HL^4)_4(MeOH)_2]$	ILEQIZ	(a) (HL^4) (c), (d) (L^4)	[40]
	$[Ni_8Sr(OH)_2(L^4)_6(piv)_{10}(HL^4)_5(Hpiv)_2(MeCN)]$	ILEQOF	(a), (b) (HL^4) (b), (c) (L^4)	[40]
	$[Ni_8Ba(OH)_2(L^4)_6(piv)_{10}(HL^4)_{5.3}(Hpiv)_{0.7}(MeCN)_2]$	ILEQUL	(a), (b) (HL^4) (b), (c) (L^4)	[40]
HL^5	$[Ni_4Na_4(L^5)_4(piv)_8(Hpiv)_5]$	[a]	(d)	[36]
	$[Ni_5Na_4(OH)_2(L^5)_4(piv)_8(MeCN)_4]$	[a]	(d)	[36]
	$[Ni_8K_2(OH)_4(L^5)_4(piv)_{10}(HL^5)_4(MeCN)_2]$	[a]	(a) (HL^5) (c), (d) (L^5)	[36]
	$[Ni_8Rb_2(OH)_4(L^5)_4(piv)_{10}(HL^5)_4(MeCN)_2]$	[a]	(a) (HL^5) (c), (d) (L^5)	[36]
	$[Ni_8Cs_2(OH)_4(L^5)_4(piv)_{10}(HL^5)_2(Hpiv)_2(MeCN)_2]$	[a]	(a) (HL^5) (c), (d) (L^5)	[36]

[a] Structure not deposited or not available in the CSD.
[b] See Fig. 5.

methylacrylate), in which two Cu(II) atoms are bridged by four α-methylacrylate groups and additionally coordinated by a pyrazolone ligand, which occupies the axial position in the distorted square pyramidal coordination sphere.

The pyrazolone ligands HL^2–HL^5, which are all substituted on C3, form metal complexes [35–40] in their neutral and deprotonated forms (see Table 1), both coexisting in many complexes. The neutral form usually coordinates to the metal through the N1 atom (Figs. 5(a) and 6), although in the complexes $[Ni_8Sr(OH)_2(L^4)_6(piv)_{10}(HL^4)_5(Hpiv)_2(MeCN)]$ and $[Ni_8Ba(OH)_2(L^4)_6(piv)_{10}(HL^4)_{5.3}(Hpiv)_{0.7}(MeCN)_2]$, coordination of HL^4 through the N1 and O atoms (see Fig. 5(b)) has been proposed [40]. Curiously, in the CSD [15] interpretation of the preceding structures, the putative bidentate HL^4 ligands are considered as deprotonated (L^4) ligands.

When ligands HL^2–HL^5 are deprotonated they coordinate in the (b), (c) or (d) modes (Fig. 5), binding two, three or four metal atoms, respectively.

The capacity of these ligands to bridge a large number of metal atoms makes their deprotonated forms very useful in the preparation of polynuclear transition metal clusters (cages, wheels, etc.). Indeed, as can be seen from Table 1, complexes of L^2–L^5 are polynuclear and have very complicated structures. All of these complexes, apart from $[Mn_{14}O_2(OH)_4(L^4)_{18}(HL^4)_4(NO_3)_4(MeCN)_4]\cdot Et_2O\cdot 3.5MeCN$ [39], are homo-{$[Ni_8(OH)_4(L^2)_2(PhCH_2CO_2)_{10}(HL^2)_8]$ [36]

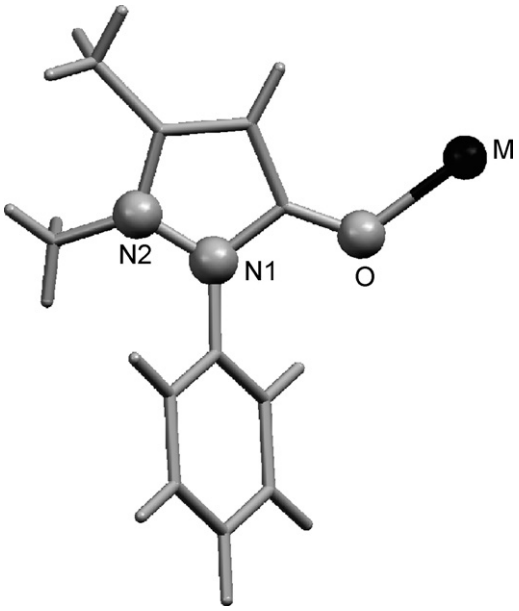


Fig. 1. Coordination mode for ligand L^1 (antipyrine).

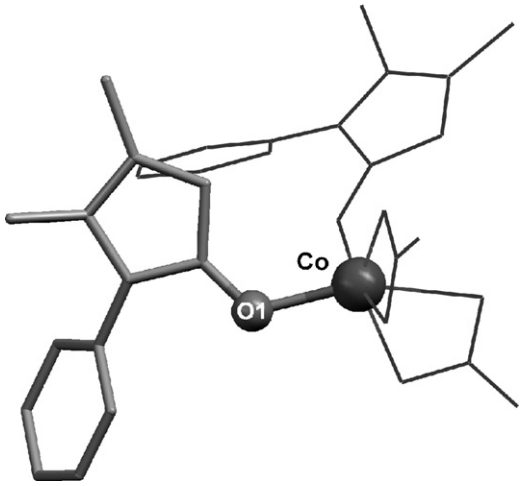


Fig. 2. Coordination mode of the ligand in $[Co(NO_3)_2(L^1)_2]$ (NTAPCO) [21].

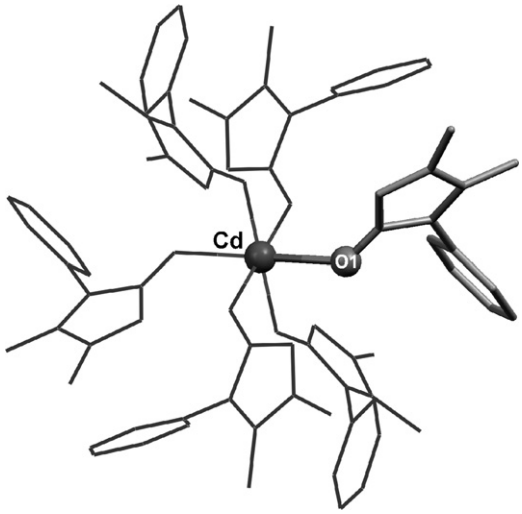


Fig. 3. Coordination mode of the ligand in $[Cd(L^1)_6](ClO_4)_2$ (DAMHAA) [27].

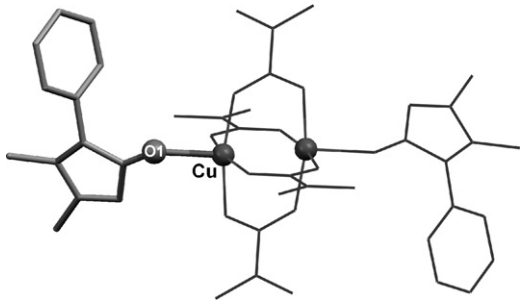


Fig. 4. Coordination mode of the ligand in $[Cu_2(Meac)_4(L^1)_2]$ (ECEBAP) [22].

and $[Ni_{24}(OH)_8(L^2)_{16}(MeCO_2)_{24}(HL^2)_{16}]$ [37]} or heteronuclear Ni(II) complexes that contain, in the latter case, different metal aggregates $[Ni_xM_y]$ (M = Li [36], Na [36,38], K [36], Rb [36], Cs [36], Mg [40], Sr [40], Ba [40]). In these compounds other bridging ligands (such as carboxylate, β-diketonate, hydroxo or oxo) contribute, along with the pyrazolone ligands, to the formation of polynuclear structures. Much of the current interest in these types of compounds is based on their magnetic properties.

The aforementioned Mn complex [39] is a tetradecanuclear manganese(II)/(III) cage obtained by the reaction of HL^4 and hydrated $Mn(NO_3)_2$ in MeOH/MeCN using NBu_4OH as a deprotonating agent. Diffusion of Et_2O into the resulting solution afforded crystals that were suitable for X-ray studies. In this compound the neutral HL^4 ligand coordinates the metal in the (a) mode, while the deprotonated ligands coordinate in the (b)–(d) modes (Fig. 7).

The homometallic Ni compounds both include the pyrazolone HL^2/L^2 ligands. The nickel wheel $[Ni_{24}(OH)_8(L^2)_{16}(MeCO_2)_{24}(HL^2)_{16}]$ [37] was synthesized by reacting HL^2 and hydrated nickel acetate in MeOH. After the solid had been removed, the mother liquor was evaporated to dryness and the resulting powder was re-dissolved in MeCN. The acetonitrile solution finally afforded crystals suitable for an X-ray study. In turn, $[Ni_8(OH)_4(L^2)_2(PhCH_2CO_2)_{10}(HL^2)_8]$ [36] was prepared by stirring a mixture of $Ni(NO_3)_2{\cdot}4H_2O$, NaL^2 and $Na(PhCH_2CO_2)$ in MeOH. The mixture was evaporated to dryness and the crude solid was extracted with EtOAc. Evaporation of the extract led to a crystalline solid. The two Ni cages include the pyrazolone ligand in both the neutral and deprotonated forms. The neutral form coordinates the metal as usual in the (a) mode, while the deprotonated form coordinates in the (c) mode (see Fig. 8 for the Ni_8 cage).

The heteronuclear $[Ni_xM_y]$ (M = alkaline or alkaline earth metal) cage complexes were mostly prepared in a similar manner. Thus, compounds that include the pivalate ligand (piv) [36,40] were all prepared by reacting $[Ni_2(H_2O)(piv)_4(Hpiv)_4]$ with a solution of the corresponding pyrazolone (HL^2–HL^5) and a base (the hydroxide or alkoxide of an alkaline or alkaline earth metal) in MeOH. The mixture was stirred overnight and the solvent removed under reduced pressure. Extraction of the crude products with MeCN (or EtOAc) and slow evaporation of the solvents afforded crystalline solids in a few days. The $[Ni_8Na]$ cage [38] was prepared by reac-

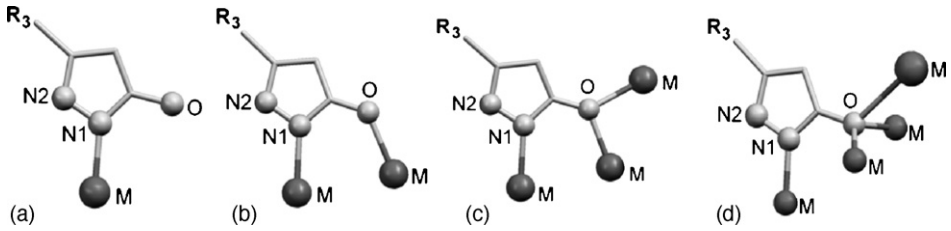


Fig. 5. Coordination modes in ligands HL^2–HL^5.

tion of an aqueous solution of nickel tetrafluoroborate with a methanolic solution of the pyrazolone (HL^2) and *tert*-butylbenzoic acid. After stirring the mixture briefly, a solution of NaOMe in MeOH was added and the solution was heated under reflux for 24 h. The solvent was then removed and the crude product was extracted with ethyl acetate. Crystals of $Na[Ni_8Na(OH)_2F_8(^tBuPhCO_2)_8(HL^2)_8]$ [38] grew in 10 days. $[Ni_8Na_2(N_3)_{12}(PhCO_2)_2(L^2)_4(HL^2)_6(EtOAc)_6]$ [38] was obtained in a similar way using benzoic acid instead of *tert*-butylbenzoic acid and adding an excess of NaN_3 after the addition of NaOMe.

In one of these heteronuclear cages, $Na[Ni_8Na(OH)_2F_8(^tBuPhCO_2)_8(HL^2)_8]$ [38] (Fig. 9), the ligand in the neutral form (HL^2) is coordinated to the metal through the N1 atom [(a) mode].

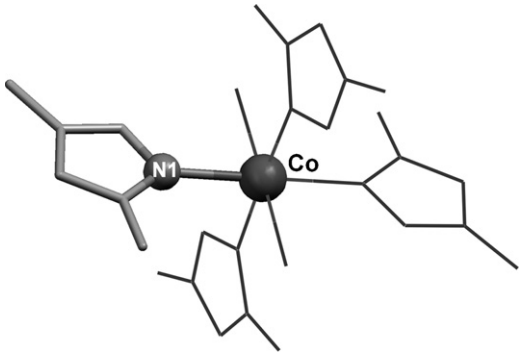


Fig. 6. Coordination mode of the ligand in $[CoCl_2(HL^2)_4]$ (MASNAW) [35].

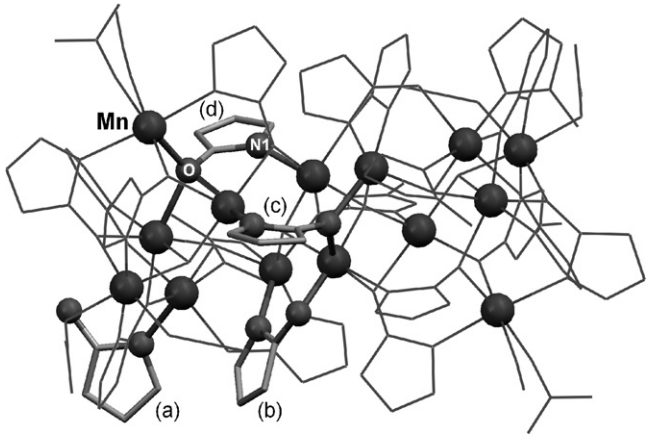


Fig. 7. Coordination modes of the ligands in $[Mn_{14}O_2(OH)_4(L^4)_{18}(HL^4)_4(NO_3)_4(MeCN)_4]\cdot Et_2O\cdot 3.5MeCN$ (XOTKAS) [39].

In another seven cages [36], the pyrazolones are deprotonated ($L^{2–5}$) and all coordinate to the metal in the (d) mode (see Fig. 10 for $[Ni_4Na_4(L^3)_4(piv)_8(Hpiv)_8]$ [36]).

Finally, in the remaining 10 cages, both neutral and deprotonated forms coexist [36,38,40] and these compounds can be classified into three groups according to the coordination mode

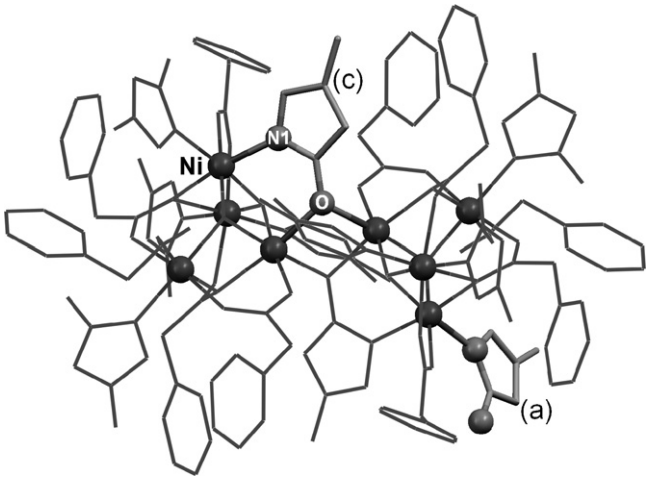


Fig. 8. Coordination modes of the ligands in $[Ni_8(OH)_4(L^2)_2(PhCH_2CO_2)_{10}(HL^2)_8]$ (EKIYUS) [36].

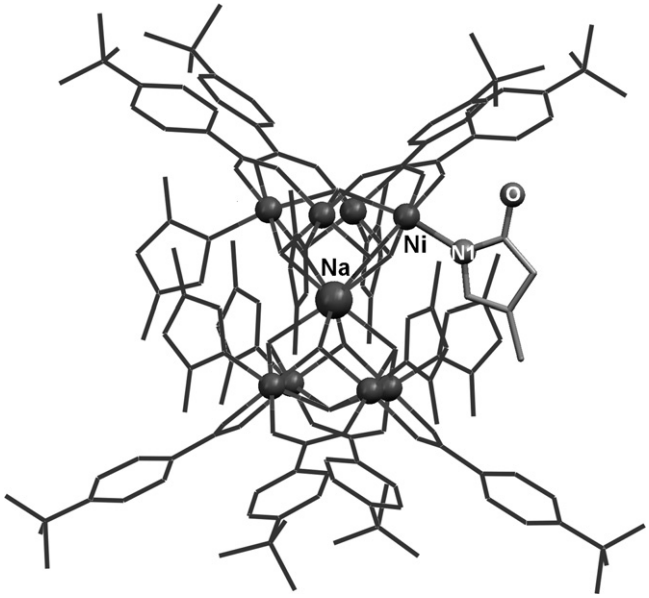


Fig. 9. Coordination mode of the ligand in $Na[Ni_8Na(OH)_2F_8(^tBuPhCO_2)_8(HL^2)_8]$ (SARZIV) [38].

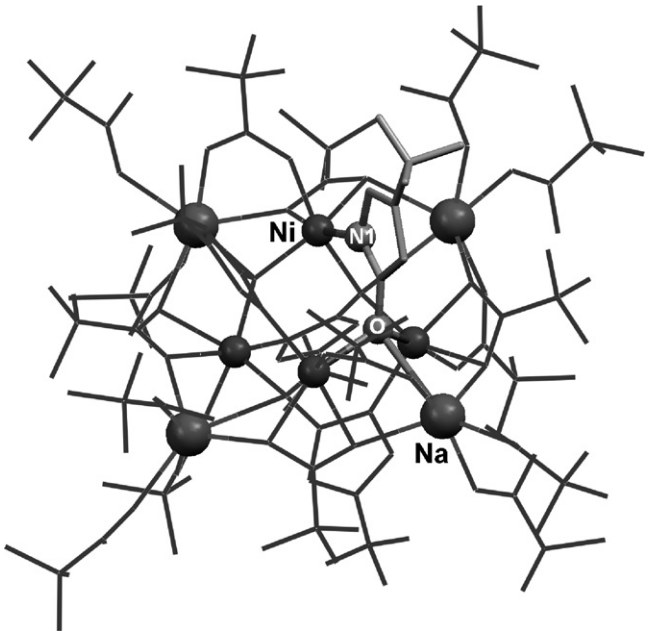


Fig. 10. Coordination mode of the ligand in $[Ni_4Na_4(L^3)_4(piv)_8(Hpiv)_8]$ (EKIYEC) [36].

adopted by the ligand: one group of complexes includes ligands with coordination modes (a) and (b) (see Table 1 and Fig. 11 for $[Ni_8Na_2(N_3)_{12}(PhCO_2)_2(L^2)_4(HL^2)_6(EtOAc)_6]$ [38]), a second group consists of compounds in which the cages contain pyrazolones coordinated in the (a)–(c) modes (see Table 1 and Fig. 12 for $[Ni_8Sr(OH)_2(L^4)_6(piv)_{10}(HL^4)_5(Hpiv)_2(MeCN)]$ [40]) and, finally, there are complexes in which the HL^n/L^n ligands are coordinated in the (a), (c) and (d) modes (see Table 1 and Fig. 13 for $[Ni_8Rb_2(OH)_4(L^4)_4(piv)_{10}(HL^4)_2(Hpiv)_2(MeCN)_2]$ [36]).

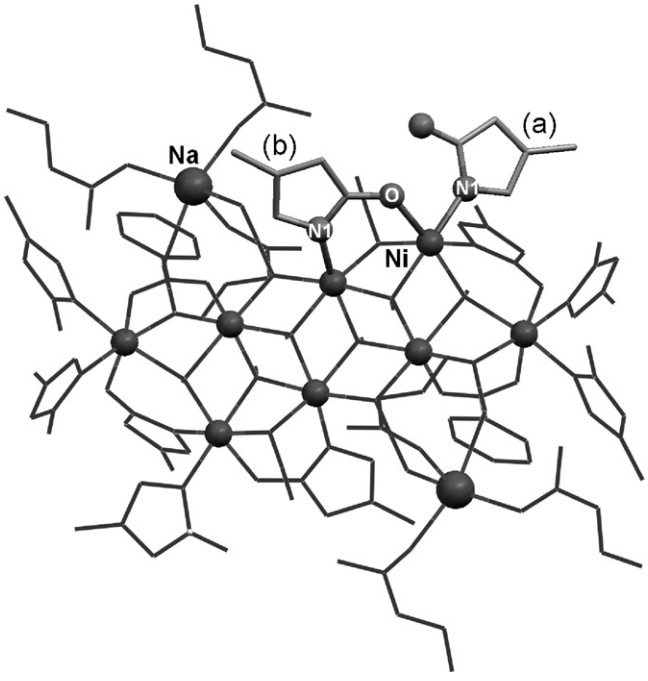


Fig. 11. Coordination modes (a) and (b) for the ligands in $[Ni_8Na_2(N_3)_{12}(PhCO_2)_2(L^2)_4(HL^2)_6(EtOAc)_6]$ (SARZOB) [38].

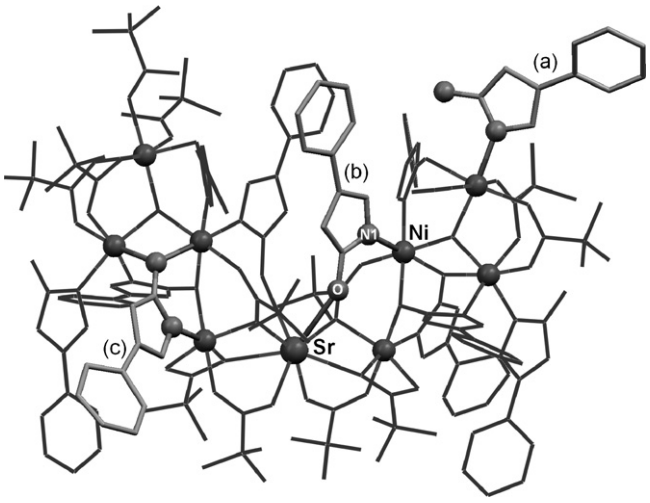


Fig. 12. Coordination modes (a)–(c) for the ligands in $[Ni_8Sr(OH)_2(L^4)_6(piv)_{10}(HL^4)_5(Hpiv)_2(MeCN)]$ (ILEQOF) [40].

2.2. 5-Pyrazolones with C4-substituents bearing additional donor atoms

2.2.1. 4-Amino (or 4-imino)-5-pyrazolones (–C4–N–C– fragment)

The known ligands of this type are included in Scheme 3 and their complexes are listed in Table 2. These compounds are derivatives of 4-aminoantipyrine, a compound that can be prepared by the nitrosation [41] and subsequent reduction [42] of antipyrine (see L^1, Fig. 1). Thus, L^6 was synthesized by methyla-

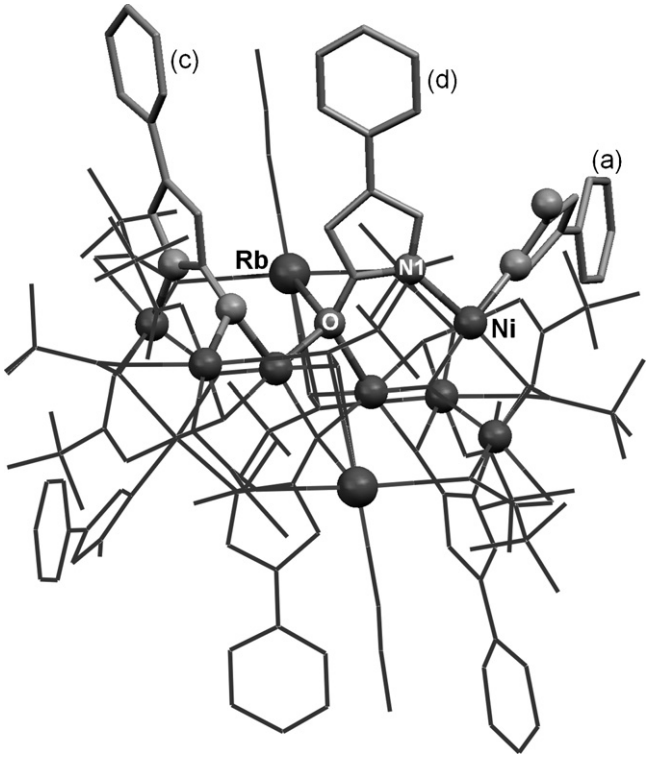
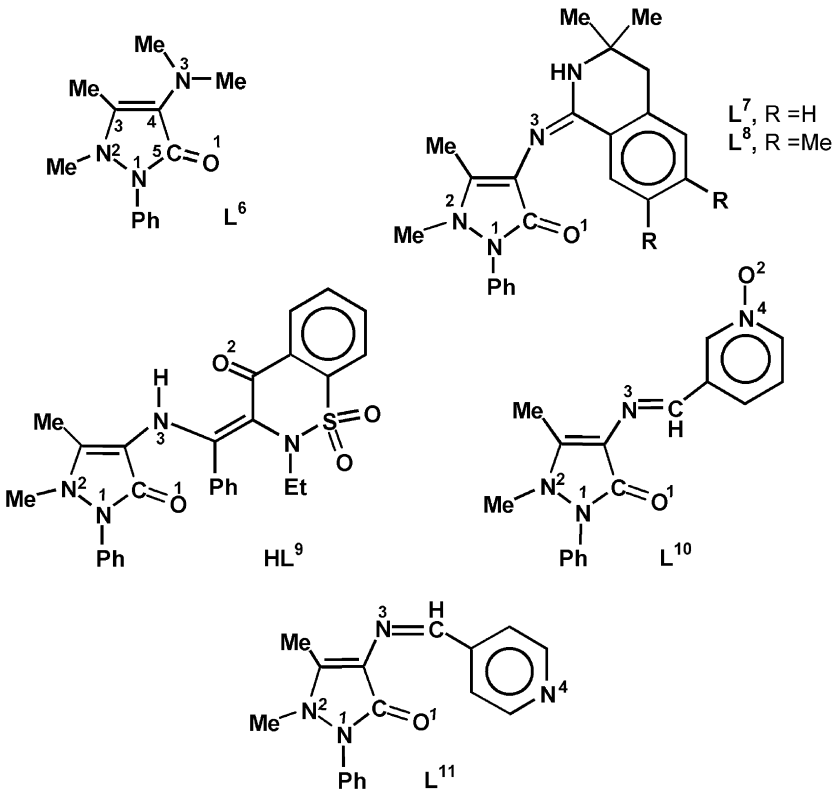


Fig. 13. Coordination modes (a), (c) and (d) for the ligands in $[Ni_8Rb_2(OH)_4(L^4)_4(piv)_{10}(HL^4)_2(Hpiv)_2(MeCN)_2]$ (EKIZIH) [36].



Scheme 3.

tion of 4-aminoantipyrine with CH_2O/HCOOH [43], L^7 and L^8 were prepared from the corresponding 1-methylthioisoquinoline and 4-aminoantipyrine [44] and HL^9, L^{10} and L^{11} were obtained by condensing 4-aminoantipyrine with the corresponding aldehyde or ketone [44,45].

The complete substitution of the pyrazolone ring and the presence in these ligands of an additional donor atom on C4 significantly modifies their coordination behaviour in comparison to the systems described in Section 2.1. In some cases these changes lead to compounds such as $[Cu(L^9)2]$ [45,46] and $[Ni(NO_3)_2(L^{11})_2(H_2O)]$ [47], in which only the donor atoms on the C4-substituent are bound to the metal (vide infra).

The two complexes of L^6, $[Co(NCS)_2(L^6)_2]$ [48] and $[Gd(NO_3)_3(L^6)_2(H_2O)]\cdot MeCN$ [49] (Figs. 14 and 15), show a different coordination mode for the pyrazolone ligand. In the Co(II) derivative [48], prepared by reacting $CoCl_2$ with NaSCN and L^6, the pyrazolone is bound to the metal through O1 and the amino nitrogen N3 atom (see Scheme 3). In $[Gd(NO_3)_3(L^6)_2(H_2O)]$ [49], L^6 is only O1-bound. A similar O1-coordination is observed in the Co(II) complexes of L^7 and L^8 [50,51] (see Fig. 16 for $[CoCl_3(HL^7)]\cdot Me_2CO$ [50]), in which the pyrazolone is protonated at N3 and thus bears a positive charge.

In $[Cu(L^9)_2]$ [45,46] (Fig. 17), a complex obtained by reaction of the ligand and hydrated copper acetate, only the N3 and O2 atoms from the substituent on C^4 bind to the metal. Although the oxygen atom of one antipyrine ring is oriented toward the metal centre, the distance Cu···O (3.41 Å) rules out the formation of a significant bonding interaction between the two atoms.

$[Cu(L^{10})(EtOH)_2]_2(ClO_4)_4$ [52] (Fig. 18) was prepared by the reaction of L^{10} and $Cu(ClO_4)_2\cdot 6H_2O$ in EtOH. In this complex the pyrazolone, which shows the highest denticity observed in this group of ligands, is tridentate and binds the

Table 2
Complexes of 4-amino (or 4-imino)-5-pyrazolones

Ligand	Complex	CSD code	Pyrazolone donor atoms	Reference
L^6	$[Co(NCS)_2(L^6)_2]$	SANNUR	O1, N3	[48]
	$[Gd(NO_3)_3(L^6)_2(H_2O)]\cdot MeCN$	NAVWIQ	O1	[49]
L^7	$[CoCl_3(HL^7)]\cdot Me_2CO$	GISVAF	O1	[50]
L^8	$[CoCl_3(L^8)]$	ACASUS	O1	[51]
HL^9	$[Cu(L^9)_2]$	AZATAW	N3, O2	[46]
		AZATAW01		[45]
L^{10}	$[Cu(L^{10})(EtOH)_2]_2(ClO_4)_4$	XODMEI	O1, N3, O2	[52]
L^{11}	$[Ni(NO_3)_2(L^{11})_2(H_2O)]$	ETESIF	N4	[47]

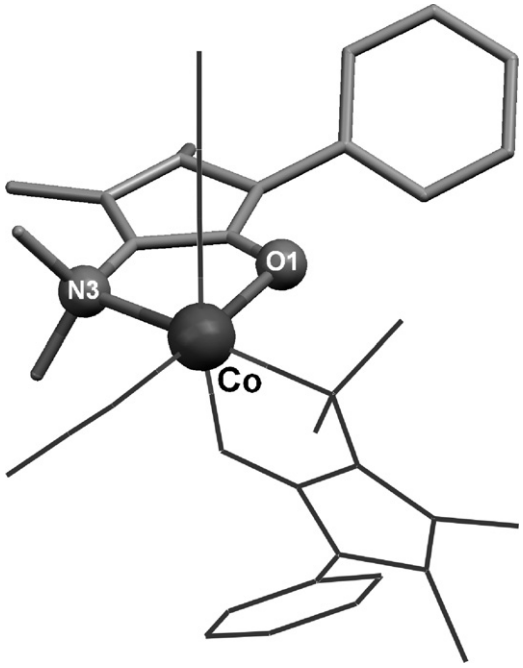


Fig. 14. Coordination mode of the ligand in $[Co(NCS)_2(L^6)_2]$ (SANNUR) [48].

metal through the O1, N3 and O2 atoms to form two chelate rings.

Reaction of L^{11} and $Ni(NO_3)_2{\cdot}6H_2O$ in a sealed tube at 383 K afforded crystals of $[Ni(NO_3)_2(L^{11})_2(H_2O)]$ [47] (Fig. 19).

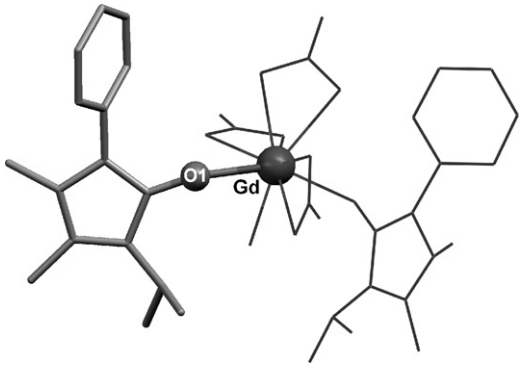


Fig. 15. Coordination mode of the ligand in $[Gd(NO_3)_3(L^6)_2(H_2O)]{\cdot}MeCN$ (NAVWIQ) [49].

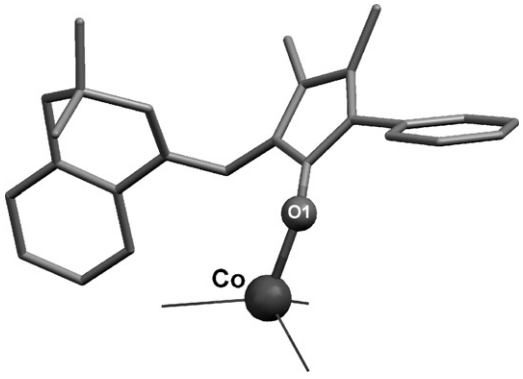


Fig. 16. Coordination mode of the ligand in $[CoCl_3(HL^7)]{\cdot}Me_2CO$ (GISVAF) [50].

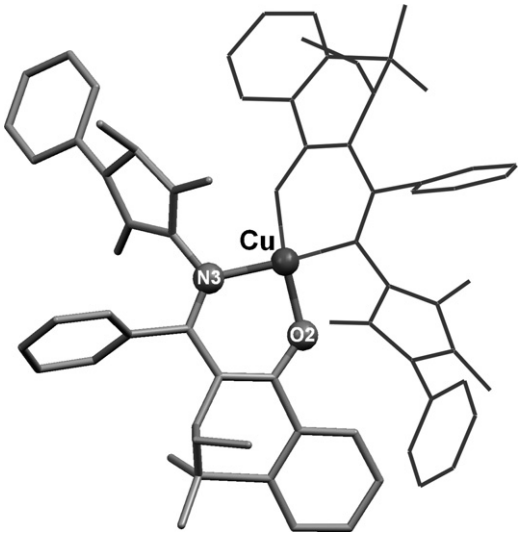


Fig. 17. Coordination mode of the ligand in $[Cu(L^9)_2]$ (AZATAW and AZATAW01) [45,46].

As in $[Cu(L^9)_2]$ [45,46], none of the donor atoms of the antipyrine fragment is involved in the coordination to the metal, with L^{11} only bound through the N atom of the pyridine ring.

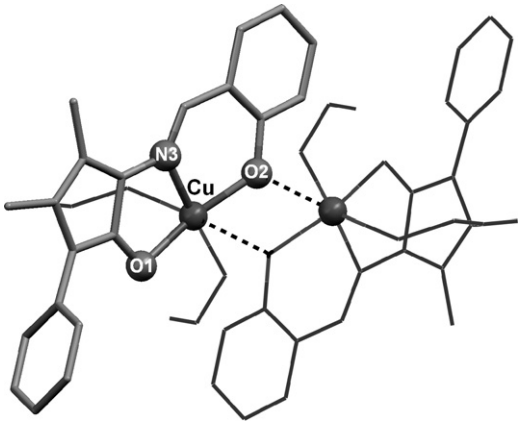


Fig. 18. Coordination mode of the ligand in $[Cu(L^{10})(EtOH)_2]_2(ClO_4)_4$ (XODMEI) [52].

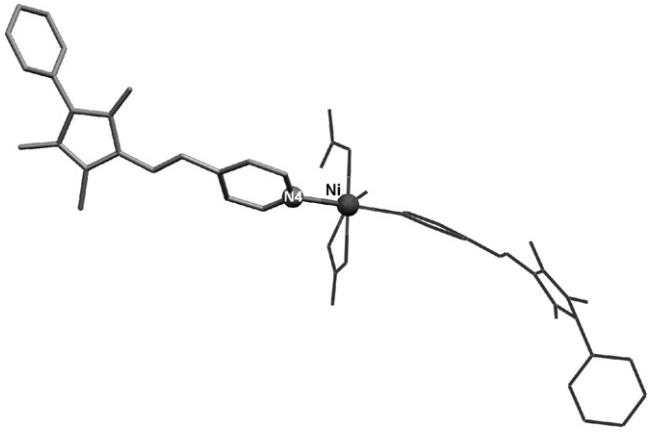
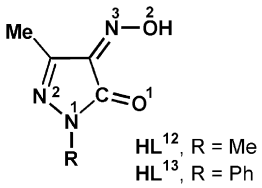


Fig. 19. Coordination mode of the ligand in $[Ni(NO_3)_2(L^{11})_2(H_2O)]$ (ETESIF) [47].



Scheme 4.

2.2.2. 4-Oxime-5-pyrazolones (–C4=N–OH fragment)

Ligands of this type are shown in Scheme 4 and the complexes are listed in Table 3. The ligands are prepared by nitrosation of the 5-pyrazolone with $NaNO_2$ in acidic media [53].

Only two complexes with this type of ligand have been structurally studied [54] and both were obtained by reaction of $HL^{12,13}$ with the corresponding metal acetate. In these complexes the deprotonated pyrazolone-oximato ligand coordinates to the metal through the oxygen atoms of the carbonyl (O1) and oximato (O2) groups (see Fig. 20 for $[Mn(L^{13})_2(py)_2]$), which occupy the equatorial positions in a distorted octahedral structure.

2.2.3. 4-Diazo-5-pyrazolones (–C4–N=N– fragment)

The diazopyrazolones whose complexes have been structurally identified by X-ray diffraction are those shown in Scheme 5 and the complexes are listed in Table 4.

The ligands HL^{14}–HL^{17} can be prepared by coupling the appropriate pyrazolone and the diazonium salt derived from the corresponding substituted aniline [55]. These molecules are represented in Scheme 5 in their diazapyrazolone form but they can adopt other tautomeric forms such as the hydrazone and the hydroxydiazopyrazole forms. The cationic ligand L^{18} was obtained (in the form of tetrafluoroborate salt) by reacting 4-aminoantipyrine and ethyl nitrite in fluoroboric acid and EtOH [56]. All these pyrazolones are highly coloured and have been used extensively in the dyestuffs industry [57].

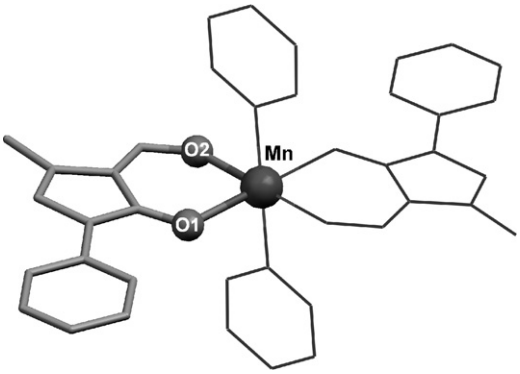
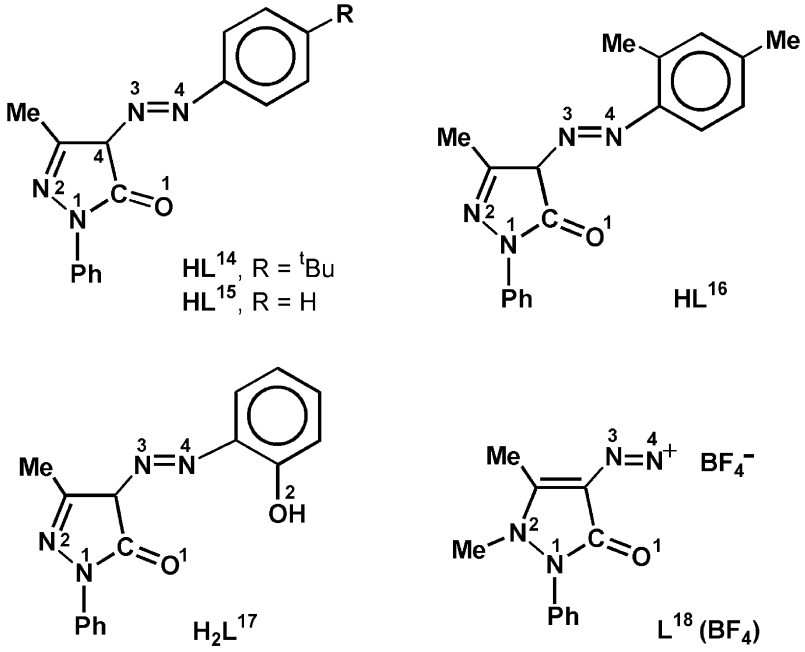


Fig. 20. Coordination mode of the ligand in $[Mn(L^{13})_2(py)_2]$ (ZUDMAM) [54].

The complexes of HL^{14}–HL^{16} [55,58] were prepared by reacting these ligands with the corresponding metal acetate, except for $[Cu(L^{14})_2]$ [55] which was obtained from the nitrate. The syntheses were carried out in MeOH for HL^{14} and HL^{15}

Table 3
Complexes of 4-oxime-5-pyrazolones

Ligand	Complex	CSD code	Pyrazolone donor atoms	Reference
HL^{12}	$[Zn(L^{12})_2(H_2O)_2]$	ZUDLUF	O1, O2	[54]
HL^{13}	$[Mn(L^{13})_2(py)_2]$	ZUDMAM	O1, O2	[54]



Scheme 5.

Table 4
Complexes of 4-diazo-5-pyrazolones

Ligand	Complex	CSD code	Pyrazolone donor atoms	Reference
HL^{14}	$[Co(L^{14})_3]\cdot 3MeOH$	QIRYEV	O1, N4	[55]
	$[Ni(L^{14})_2(MeOH)_2]\cdot 2MeOH$	QIRYIZ	O1, N4	[55]
	$[Cu(L^{14})_2]$	QIRXUK	O1, N4	[55]
	$[Zn(L^{14})_2]$	QIRYAR	O1, N4	[55]
HL^{15}	$[Cu(L^{15})_2]$	QIRYOF	O1, N4	[55]
HL^{16}	$[Co(L^{16})_2]$	[a]	O1, N4	[58]
	$[Ni(L^{16})_2]$	[a]	O1, N4	[58]
	$[Cu(L^{16})_2]$	[a]	O1, N4	[58]
H_2L^{17}	$[Sn(L^{17})_2]$	TOYNUQ	O1, O2, N4	[59]
L^{18}	$[Mo\{HB(pz)_3\}(L^{18})(CO)_2]$	ZESKUD	N4	[60]

[a] Structure not deposited or not available in the CSD.

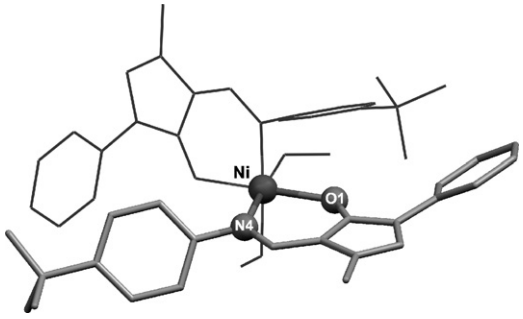


Fig. 21. Coordination mode of the ligand in $[Ni(L^{14})_2(MeOH)_2]\cdot 2MeOH$ (QIRYIZ) [55].

and in DMF or dioxane for HL^{16}. All these complexes, except $[Ni(L^{14})_2(MeOH)_2]\cdot 2MeOH$ [55] (Fig. 21), are homoleptic and in all cases the monodeprotonated azapyrazolones chelate the metal through the O1 and N4 atoms.

The additional hydroxyl group in H_2L^{17} allows this molecule, once deprotonated, to act as a dianionic tridentate ligand in the Sn(IV) complex $[Sn(L^{17})_2]$ (Fig. 22) [59], which was obtained by reacting H_2L^{17}, $Sn(OAc)_2Cl_2$ and triethylamine in MeOH. As shown in Fig. 22, the two *N*,*O*,*O*-tridentate pyrazolonate ligands gives rise to a coordination number of six for the metal.

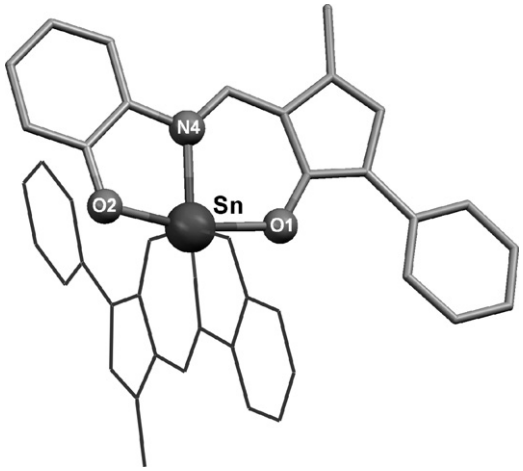


Fig. 22. Coordination mode of the ligand in $[Sn(L^{17})_2]$ (TOYNUQ) [59].

$[Mo\{HB(pz)_3\}(L^{18})(CO)_2]$ [60] (Fig. 23) was prepared by reaction of $[NEt_4][Mo\{HB(pz)_3\}(CO)_3]$ [61] and $L^{18}(BF_4)$ in MeCN. Crystals of this product were obtained by slow evaporation of a saturated solution in a mixture of dichloromethane and hexane. The antipyrin-4-yldiazenide ligand acts as a monodentate system through the N4 atom, probably due to the high steric hindrance of the tris(pyrazolyl)borate ligand.

2.2.4. *4-Alkyl(or aryl)aminomethylidene-5-pyrazolones (–C4=C–N(H)–C– fragment)*

The complexes containing this type of pyrazolone (see Scheme 6) are listed in Table 5.

These ligands are usually prepared by condensation of 4-acyl-5-pyrazolones [14] with substituted amines [62–64]. When free, they can exist in three tautomeric forms; imine-one, imine-ol and amine-ol, with the latter usually found in the solid state [64]. In their complexes, these pyrazolones usually adopt the imine-ol form and chelate the metal through the O1 and N3

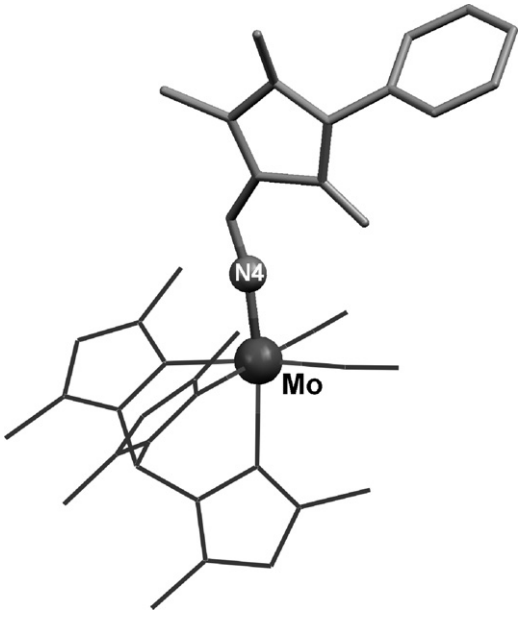


Fig. 23. Coordination mode of the ligand in $[Mo\{HB(pz)_3\}(L^{18})(CO)_2]$ (ZESKUD) [60].

Table 5
Complexes of 4-alkyl(or aryl)aminomethylidene-5-pyrazolones

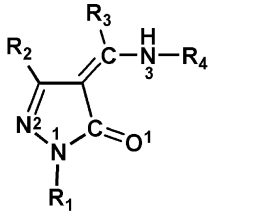
Ligand	Complex	CSD code	Pyrazolone donor atoms	Reference
HL^{19}	$[Co(L^{19})_2(DMF)_2]$	BEQDEH	O1, N3	[65]
	$[Ni(HL^{19})_2(EtOH)_2]$	[a]	O1, N3	[66]
	$[Ag(HL^{19})_2]PF_6$	ASOWIO	N2	[76]
HL^{20}	$[Co(L^{20})_2]$	QAKTIG	O1, N3	[67]
HL^{21}	$[Co(HL^{21})_2(MeOH)_2](NO_3)_2$	XAJRIK	O1, N3	[68]
	$[Ni(L^{21})_2(DMF)_2]$	XAJRAC	O1, N3	[68]
	$[Cu(L^{21})_2(DMF)_2]$	XAJREG	O1, N3	[68]
	$[Zn(L^{21})_2(DMF)_2]$	XAJROQ	O1, N3	[68]
HL^{22}	$[Co(L^{22})_2(EtOH)_2]$	[a]	O1, N3	[69]
	$[Ni(L^{22})_2(EtOH)_2]$	[a]	O1, N3	[66]
	$[Cu(L^{22})_2]$	[a]	O1, N3	[62]
HL^{23}	$[Co(L^{23})_2(EtOH)_2]\cdot EtOH$	[a]	O1, N3	[69]
	$[Cu(L^{23})_2]$	[a]	O1, N3	[62]
HL^{24}	$[Co(L^{24})_2(EtOH)_2]$	HAWVEH	O1, N3	[70]
	$[Ni(L^{24})_2(EtOH)_2]$	HAWVAD	O1, N3	[70]
HL^{25}	$[Cu(L^{25})_2(H_2O)]$	XUYRUE	O1, N3	[63]
HL^{26}	$[Cu(L^{26})_2]$	YASQIT	O1, N3	[71]
HL^{27}	$[Cu(L^{27})_2]$	JAYLIF	O1, N3	[72]
H_2L^{28}	$[Cu2(L^{28})_2]$	TAQJIF	O1, N3, O2	[78]
H_2L^{29}	$[Cu2(L^{29})_2(DMF)_2]$	[a]	O1, N3, O2	[79]
HL^{30}	$[Zn(L^{30})_2]\cdot MeOH$	VUHDOR	O1, N3	[73]
HL^{31}	$[Zn(L^{31})_2]$	LAPWUV	O1, N3	[74]
HL^{32}	$[Ni(L^{32})_2(EtOH)_2]$	[a]	O1, N3	[66]
	$[Cu(L^{32})_2]$	[a]	O1, N3	[62]
HL^{33}	$[Co(L^{33})_2]$	DAYKUK	O1, N3	[75]
HL^{34}	$[Cu(L^{34})_2]\cdot 2HL^{34}$	XULMEW	N2	[77]

[a] Structure not deposited or not available in the CSD.

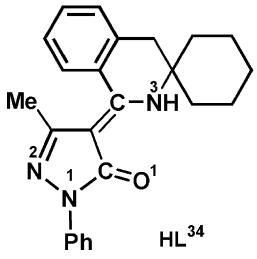
atoms [62,63,65–75] (see Table 5). Less common is monocoordination through N2 [76,77] and three-coordination through O1, N3 and O2 (with O2 being an additional donor atom on R4) [78,79].

Most of these compounds are Cu(II) complexes [62,63,68,71,72,77–79] obtained by reaction of the corresponding pyrazolone with a metal salt (chloride, nitrate, acetate) in the presence, in some cases [72,75], of a deprotonating agent. In these complexes the Cu atom is coordinated to two pyrazolonates and, in some of them, one or two solvent molecules increase the coordination number of the metal to 5 or 6 [63,68,69].

Two examples are dinuclear copper pyrazolonates ($[Cu_2(L^{28})_2]$ [78] (Fig. 24) and $[Cu_2(L^{29})_2(DMF)_2]$ [79])



HL^n/H_2L^n



HL^{34}

Ligand	R_1	R_2	R_3	R_4
HL^{19}	Ph	Me	Ph	naphthyl
HL^{20}	Ph	Me	Ph	*m*-chlorophenyl
HL^{21}	Ph	Me	Ph	-OH
HL^{22}	Ph	Me	Ph	Ph
HL^{23}	Ph	Me	Ph	nitrophenyl
HL^{24}	Ph	Me	Ph	*p*-fluorophenyl
HL^{25}	Ph	Me	Ph	*p*-acetylphenyl
HL^{26}	n-hexyl	Me	Et	Ph
HL^{27}	Ph	Me	Ph	benzyl
H_2L^{28}	Ph	Me	H	*o*-hydroxy(**O2**)phenyl
H_2L^{29}	Ph	Me	H	*o*-hydroxy(**O2**)benzoyl
HL^{30}	Ph	^{i}Pr	H	cyclohexyl
HL^{31}	Ph	Me	H	*p*-^{t}Buphenyl
HL^{32}	Ph	Me	Ph	*o*-tolyl
HL^{33}	Ph	Me	Ph	*p*-tolyl

Scheme 6.

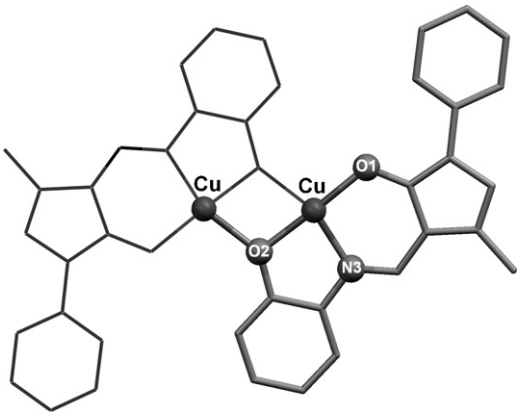


Fig. 24. Coordination mode of the ligand in $[Cu_2(L^{28})_2]$ (TAQJIF) [78].

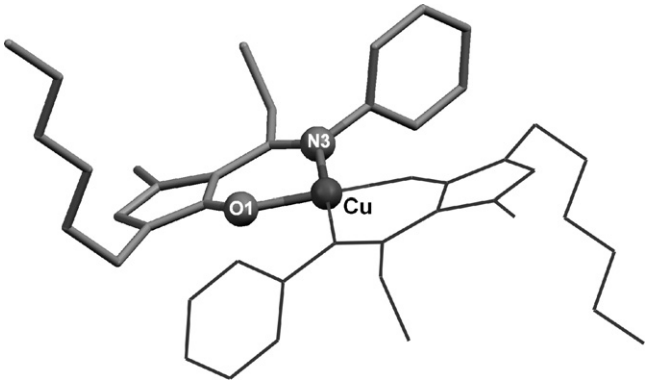


Fig. 25. Coordination mode of the ligand in $[Cu(L^{26})_2]$ (YASQIT) [71].

and these are formed with two ligands that possess an additional hydroxyl group on R4 (see Scheme 6). These ligands lose two protons and coordinate through the atoms O1, N3 and O2. The oxygen atom O2, which belongs to the deprotonated hydroxyl group, bridges between the two metal centres.

In all the mononuclear copper complexes, the pyrazolone ligand coordinates the metal through the O1, N3 donor atoms (see Fig. 25 for $[Cu(L^{26})_2]$ [71])—one exception is $[Cu(L^{34})_2]\cdot 2HL^{34}$ [77], in which the coordination occurs through N2 (Fig. 26).

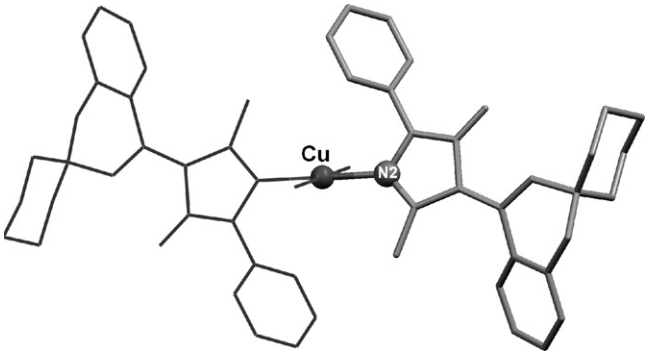


Fig. 26. Coordination mode of the ligand in $[Cu(L^{34})_2]\cdot 2HL^{34}$ (XULMEW) [77].

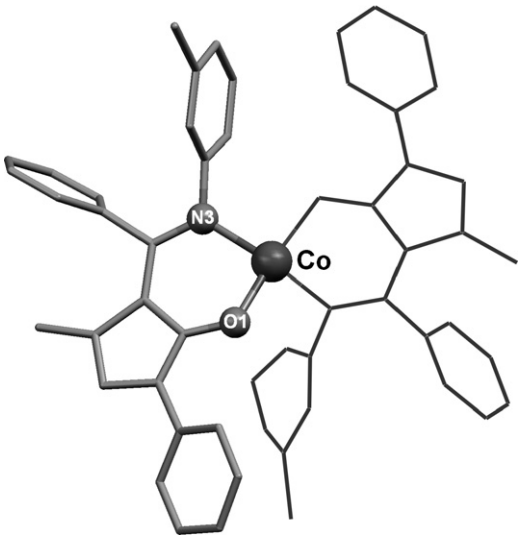


Fig. 27. Coordination mode of the ligand in $[Co(L^{20})_2]$ (QAKTIG) [67].

The complexes of Co(II), Ni(II) and Zn(II) with this type of pyrazolone were prepared in a similar way to the Cu(II) complexes and they are all mononuclear with $[M(L^n)_2]$ or $[M(L^n)_2(solvent)_2]$ stoichiometries [65–70,73–75]. As in most of the copper derivatives, the compounds $[M(L^n)_2]$ have two deprotonated O1, N3-bidentate pyrazolonates forming a tetrahedral coordination sphere, as occurs in $[Co(L^{20})_2]$ [67] (Fig. 27), $[Co(L^{33})_2]$ [75] and $[Zn(L^{30})_2]\cdot MeOH$ (Fig. 28). In the compounds $[M(L^n)_2(solvent)_2]$ and $[Co(HL^{21})_2(MeOH)_2](NO_3)_2$ [68], the presence of two additional coordinated molecules of solvent increases the coordination number to six and leads to octahedral geometries (see Fig. 29 for $[Ni(L^{21})_2(DMF)_2]$ [68]).

Many of these Cu(II), Co(II) and Ni(II) complexes can act as catalyst precursors for styrene and norbornene polymerization with activation by methylaluminoxane [62,66,70].

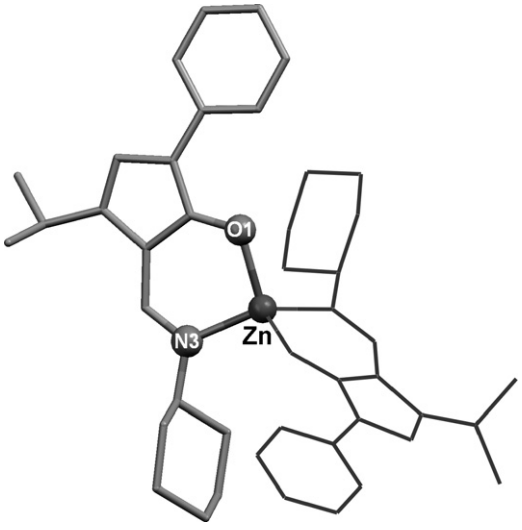


Fig. 28. Coordination mode of the ligand in $[Zn(L^{30})_2]\cdot MeOH$ (VUHDOR) [73].

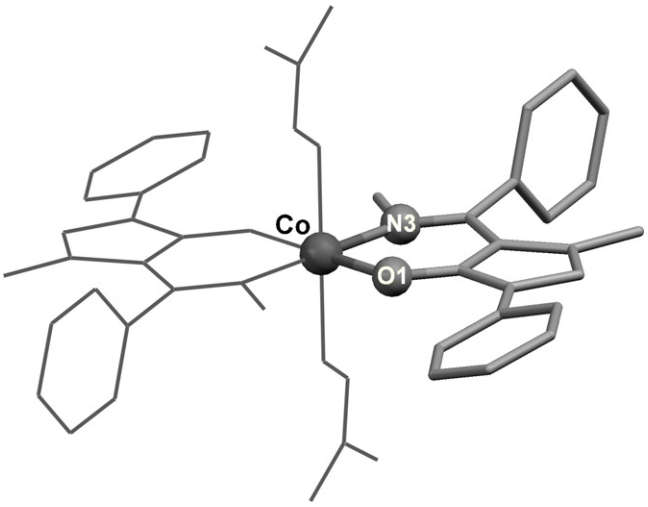


Fig. 29. Coordination mode of the ligand in $[Ni(L^{21})_2(DMF)_2]$ (XAJRAC) [68].

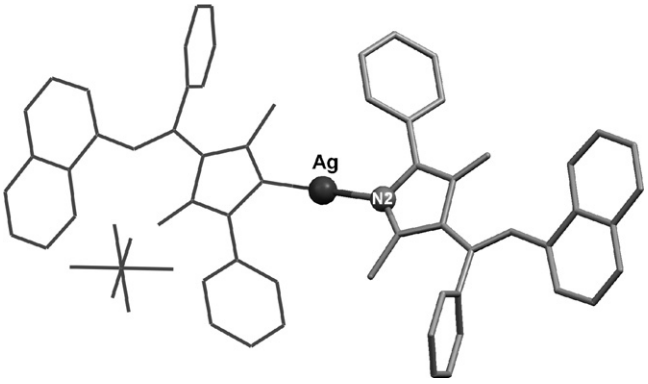


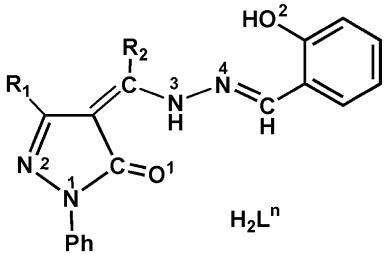
Fig. 30. Coordination mode of the ligand in $[Ag(HL^{19})_2]PF_6$ (ASOWIO) [76].

In the Ag(I) complex $[Ag(HL^{19})_2]PF_6$ [76] (Fig. 30), obtained by reaction of HL^{19} and silver hexafluorophosphate, two neutral pyrazolone ligands coordinate the metal through the N2 atoms to give a linear geometry.

2.2.5. 4-Hydrazone-5-pyrazolones (–C4–C=N–N–C– fragment)

2.2.5.1. Salicylidenehydrazones. The complexes identified with this type of ligand (see Scheme 7) are listed in Table 6.

$H_2L^{35–37}$ can be prepared by reaction of 4-acyl-5-pyrazolones and salicylidene hydrazone in anhydrous ethanol, using a few drops of glacial acetic acid as a catalyst [80,81]. In these compounds the occurrence of keto-enol tautomerism is possible, although an X-ray study of H_2L^{37} [81] indicates that it mainly exists in the keto form in the solid state.



Ligand	R_1	R_2
H_2L^{35}	Me	Ph
H_2L^{36}	Ph	Ph
H_2L^{37}	Ph	-CH_2Ph

Scheme 7.

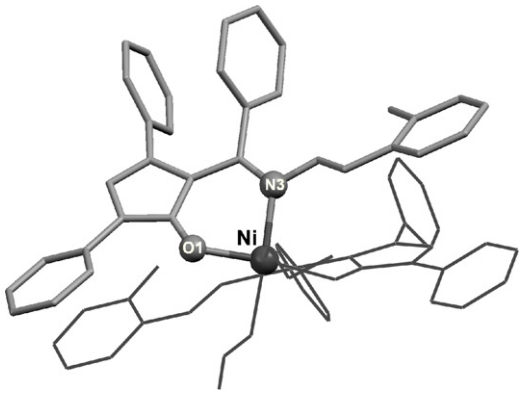


Fig. 31. Coordination mode of the ligand in $[Ni(HL^{36})_2(EtOH)_2]$ (FETDOY) [82].

These ligands, due to their multidentate nature and the location of the donor atoms, can easily bridge between two or more metal ions to give polynuclear complexes. In fact, of the complexes reviewed here, only $[Ni(HL^{36})_2(EtOH)_2]$ – obtained by reaction of H_2L^{36} and $Ni(OAc)_2$ – is mononuclear [82] (Fig. 31). The hydrazone–pyrazolone is singly charged (after losing the proton from the N3–H group) and coordinates to the metal through the O1, N3 atoms.

The dinuclear Cu(II) complex $[Cu_2(L^{37})_2]\cdot 0.5H_2O$ [81] (Fig. 32) was obtained by reacting a solution of $Cu(OAc)_2\cdot H_2O$ in ethanol with a methanolic solution of the ligand (prepared after the addition of aqueous NaOH). The tetradentate ligand is bideprotonated to form two chelating moieties: the first involves the oxygen atom at the 5-position of the pyrazolone (O1) and one of the hydrazone nitrogen atoms (N3) and the other comprises the oxygen of the hydroxyl group (O2) and the other hydrazone nitrogen (N4) (see Fig. 32). Each moiety chelates to a different copper atom, meaning that each copper is coordinated to O1, N3, N4 and O2 atoms in a distorted square planar geometry.

The tetranuclear Zn(II) complexes $[Zn_4(L^{35})_4]\cdot CH_3COOC_2H_5\cdot EtOH\cdot H_2O$ [80] and $[Zn_4(L^{37})_4]$ [81] (Fig. 33) are very similar. Both are obtained by a similar procedure to that previously

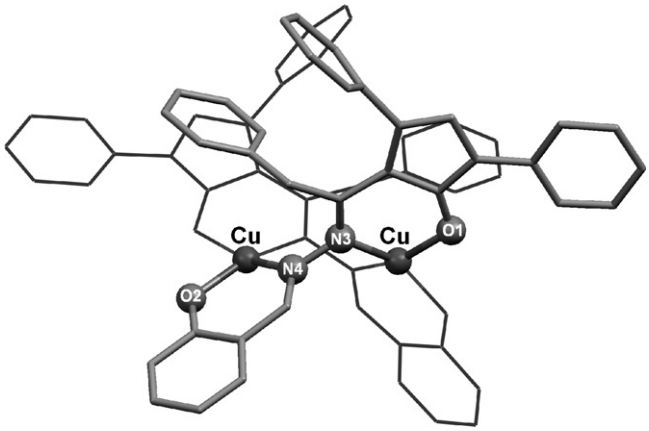


Fig. 32. Coordination mode of the ligand in $[Cu_2(L^{37})_2]\cdot 0.5H_2O$ (FAKPEN) [81].

Table 6
Complexes of 4-salicylidenehydrazone-5-pyrazolones

Ligand	Complex	CSD code	Pyrazolone donor atoms	Reference
H_2L^{35}	$[Zn_4(L^{35})_4]\cdot CH_3COOC_2H_5\cdot EtOH\cdot H_2O$	PAVXUG	O1, N3, N4, O2	[80]
H_2L^{36}	$[Ni(HL^{36})_2(EtOH)_2]$	FETDOY	O1, N3	[82]
H_2L^{37}	$[Cu_2(L^{37})_2]\cdot 0.5H_2O$	FAKPEN	O1, N3, N4, O2	[81]
	$[Zn_4(L^{37})_4]$	FAKPAJ	O1, N3, N4, O2	[81]

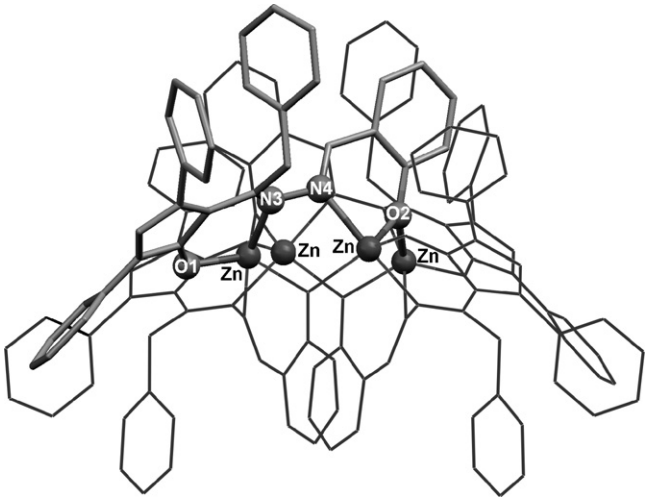


Fig. 33. Coordination mode of the ligand in $[Zn_4(L^{37})_4]$ (FAKPAJ) [81].

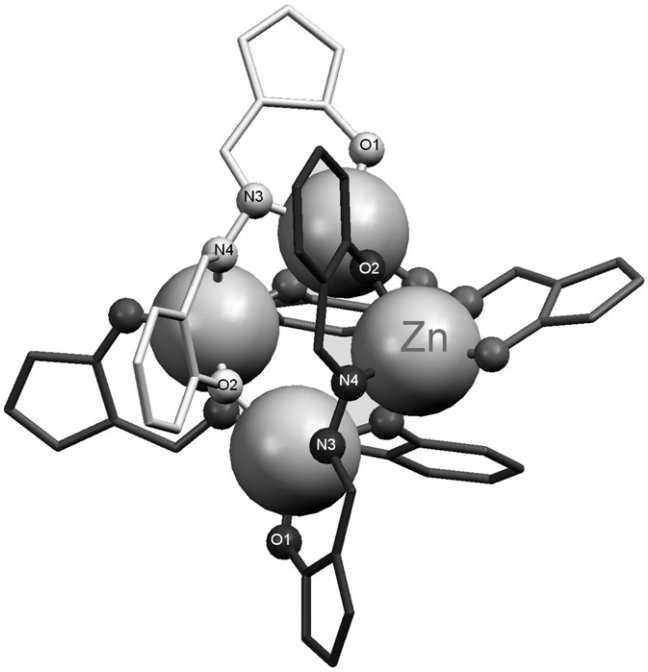


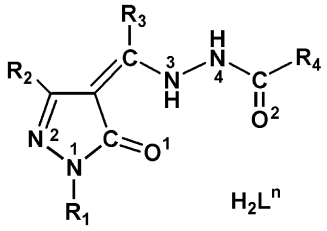
Fig. 34. The tetranuclear core of $[Zn_4(L^{37})_4]$ (FAKPAJ) [81].

described for the Cu(II) complex using $Zn(OAc)_2\cdot 2H_2O$ instead of $Cu(OAc)_2\cdot H_2O$. The bridging bideprotonated pyrazolonates are coordinated to three Zn(II) cations, one through the O1, N3 donor atoms, another through the N4, O2 atoms and the third through O2. In this way, the hydroxyl O2 atom bridges between two metal centres. Each of these centres is pentacoordinated and has a trigonal bipyramidal coordination sphere formed by O1, N3 (from one ligand), N4, O2 (from another) and O2 (from a third ligand). The tetranuclear core of these complexes is practically square planar (Fig. 34) with a Zn···Zn distance of 3.411 Å.

2.2.5.2. Acylhydrazones. The 4-acylhydrazone-5-pyrazolones studied so far in the present context are shown in Scheme 8 and their complexes in Table 7.

These ligands can be synthesized by condensation of equimolar quantities of 4-acyl-5-pyrazolones (see Section 2.2.6) and acylhydrazides in methanol or ethanol under reflux. A few drops of acetic acid are normally used as a catalyst [83–85]. The X-ray studies on H_2L^{38} [83] and H_2L^{41} [86] showed that these molecules are in the keto form in the solid state.

$[ReO(L^{38})(HL^{38})]\cdot CH_2Cl_2$ [83] (Fig. 35) was prepared by reacting H_2L^{38} and triethylamine in ethanol with a solution of $ReOCl_3(PPh_3)$ in boiling chloroform. After heating under reflux, the solution was partially evaporated and the crude product was purified by column chromatography using CH_2Cl_2 as eluent. Crystals were obtained when the residue was recrystallized from dichloromethane/hexane. In the complex, two acylhydrazone–pyrazolone ligands, one monodeprotonated and the other bideprotonated, coordinate the metal. The monodeprotonated ligand is bidentate and binds the rhenium through the N3 and O2 atoms (Fig. 35), whereas the bideprotonated ligand is tridentate and binds through the O1, N3 and O2 atoms.



Ligand	R_1	R_2	R_3	R_4
H_2L^{38}	Ph	Me	Ph	Ph
H_2L^{39}	Ph	Ph	Me	2-hydroxyphenyl
H_2L^{40}	Ph	Me	Ph	2-hydroxyphenyl
H_2L^{41}	Ph	Me	Ph	4-nitrophenyl
H_2L^{42}	Ph	Me	Ph	4-pyridyl

Scheme 8.

Table 7
Complexes of 4-acylhydrazone-5-pyrazolones

Ligand	Complex	CSD code	Pyrazolone donor atoms	Reference
H_2L^{38}	$[ReO(L^{38})(HL^{38})]\cdot CH_2Cl_2$	WIVPEW	L^{38}: O1, N3, O2; HL^{38}: N2, O2	[83]
H_2L^{39}	$[Ni(L^{39})(bipy)(CH_3OH)]$	HEBBEW	O1, N3, O2	[84]
	$[Cu(L^{39})(bipy)]\cdot 2CH_2Cl_2$	HEBBOG	O1, N3, O2	[84]
	$[Zn(L^{39})(bipy)(CH_3OH)]$	HEBBIA	O1, N3, O2	[84]
H_2L^{40}	$[Ni(L^{40})(py)]$	UKEWEM	O1, N3, O2	[87]
H_2L^{41}	$[Ni(L^{41})(py)_3]$	NACBID	O1, N3, O2	[88]
	$[Cu(L^{41})(py)]$	CAVDEJ	O1, N3, O2	[89]
H_2L^{42}	$[Eu(HL^{42})_3]\cdot 3.5H_2O\cdot 0.5MeOH$	QIGJAR	O1, N3, O2	[85]

$[M(L^{39})(bipy)(CH_3OH)]$ (M = Ni, Zn) and $[Cu(L^{39})(bipy)]\cdot 2CH_2Cl_2$ [84] were prepared by reacting the corresponding $M(OAc)_2\cdot nH_2O$ with the ligand H_2L^{39} and 2,2′-bipyridine in MeOH at 70 °C. In all of these complexes the bideprotonated pyrazolone (only the phenolic proton on R4 remains) coordinates the metal through the O1, N3 and O2 atoms (Fig. 36). The same coordination mode occurs in $[Ni(L^{40})(py)]$ [87], which was prepared by a similar procedure.

The complexes of H_2L^{41}, i.e. $[Ni(L^{41})(py)_3]$ [88] and $[Cu(L^{41})(py)]$ [89], were both obtained as follows. Equimolar mixtures of H_2L^{41} and $M(OAc)_2\cdot H_2O$ were ground and dissolved in MeOH. The clear solution was then placed in a Teflon bomb and 1 mL of CH_3CN and 1 mL of pyridine were added to the mixture, which was heated to 120 °C for 2 days. Slow cooling to room temperature afforded crystals in both cases. In these complexes the ligand loses two protons from its enol form and behaves in a tridentate manner through the N3, O1 and O2 atoms (see Fig. 37 for $[Cu(L^{41})(py)]$ [89]). Three pyridine molecules in the Ni(II) complex and one in the Cu(II) complex completed an octahedral and a square planar coordination sphere, respectively.

$[Eu(HL^{42})_3]\cdot 3.5H_2O\cdot 0.5MeOH$ [85] (Fig. 38), prepared by reaction of an aqueous solution of H_2L^{42} at pH 7 with an aqueous solution of $EuCl_3\cdot 6H_2O$, was studied by X-ray diffraction after recrystallization from MeOH/EtOH (1:2). The coordination polyhedron is a tricapped trigonal prism defined by three N atoms (N3) and six O atoms (three O1 and three O2) from three monodeprotonated tridentate pyrazolonates.

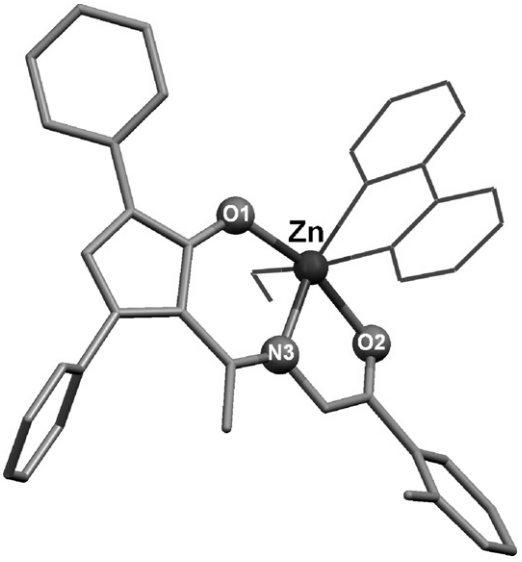


Fig. 36. Coordination mode of the ligand in $[Zn(L^{39})(bipy)(CH_3OH)]$ (HEBBIA) [84].

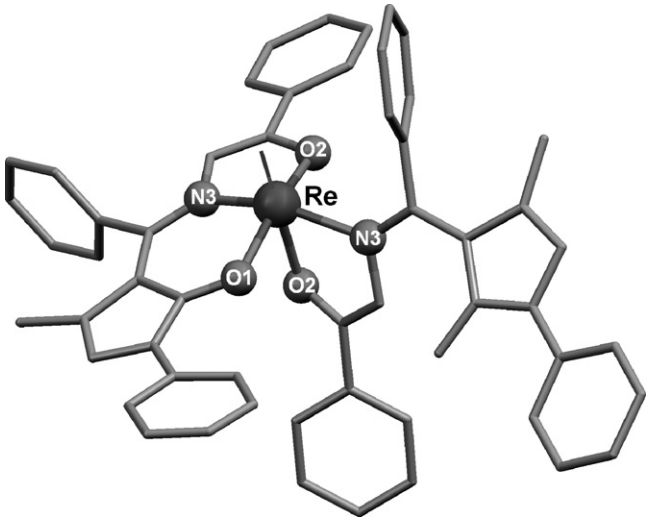


Fig. 35. Coordination mode of the ligand in $[ReO(L^{38})(HL^{38})]\cdot CH_2Cl_2$ (WIVPEW) [83].

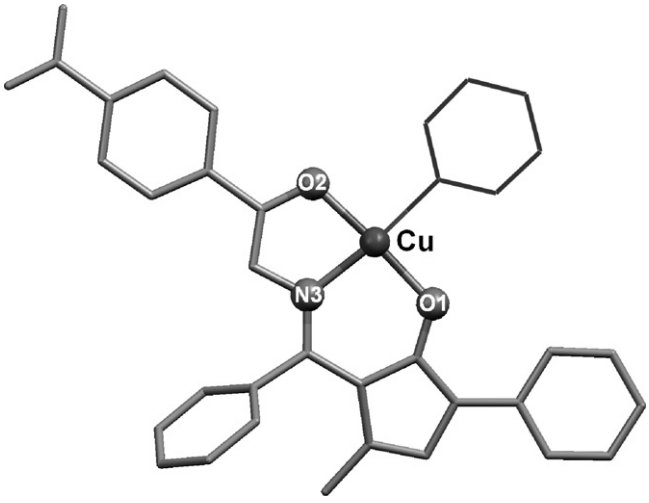


Fig. 37. Coordination mode of the ligand in $[Cu(L^{41})(py)]$ (CAVDEJ) [89].

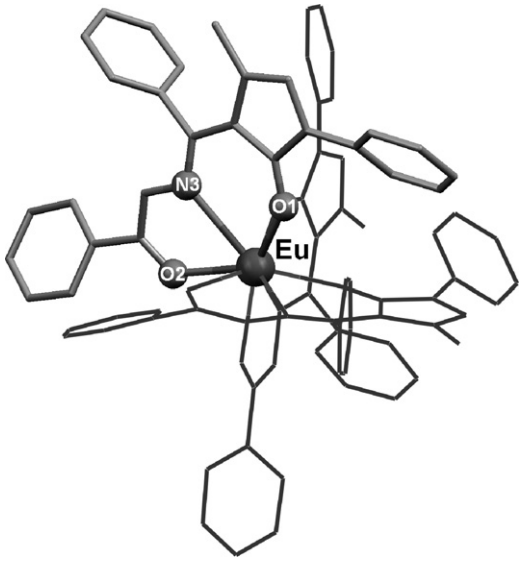


Fig. 38. Coordination mode of the ligand in $[Eu(HL^{42})_3]\cdot 3.5H_2O\cdot 0.5MeOH$ (QIGJAR) [85].

2.2.5.3. Thiosemicarbazones. The 4-thiosemicarbazone-5-pyrazolones are indicated in Scheme 9 and their complexes are listed in Table 8.

These ligands can be easily prepared by condensation of the corresponding 4-acyl-5-pyrazolone [14] and the desired thiosemicarbazide in MeOH or EtOH. Yields can be improved by the addition of a few drops of an acid (AcOH or H_2SO_4) as a catalyst [90,91]. In the solid state these ligands exist in the keto-thione form [92,93].

$[Co(HL^{43})_2]\cdot 2H_2O\cdot 2DMF$ [90] (Fig. 39) was synthesized by reacting $Co(OAc)_2$ with HL^{43} in H_2O/EtOH and the product was recrystallized from DMF. Both monodeprotonated ligands coordinate the metal through the O, N3 and S atoms, giving rise to a distorted octahedral coordination sphere.

In $[Ni(L^{43})(H_2L^{43})]\cdot 2H_2O\cdot EtOH$ [92], although the metal environment is similar to that in the Co(II) complex and the pyrazolones are also O, N3, S-tridentate, one ligand is neutral and the other bideprotonated.

The Co(III) derivative $[Co(L^{44})_2]BF_4$ [94] was obtained during crystallization of the corresponding Co(II) complex $[Co(HL^{44})_2](BF_4)_2$ (prepared by reacting H_2L^{44} and $Co(BF_4)_2$ in MeOH under reflux [95]). In a similar way to previous compounds, the monodeprotonated ligands coordinate the metal through the O, N3 and S atoms.

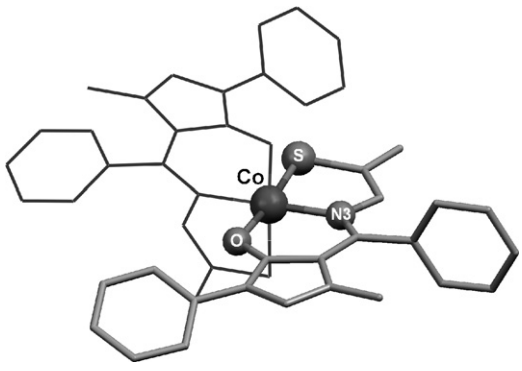


Fig. 39. Coordination mode of the ligand in $[Co(HL^{43})_2]\cdot 2H_2O\cdot 2DMF$ (FASKEQ) [90].

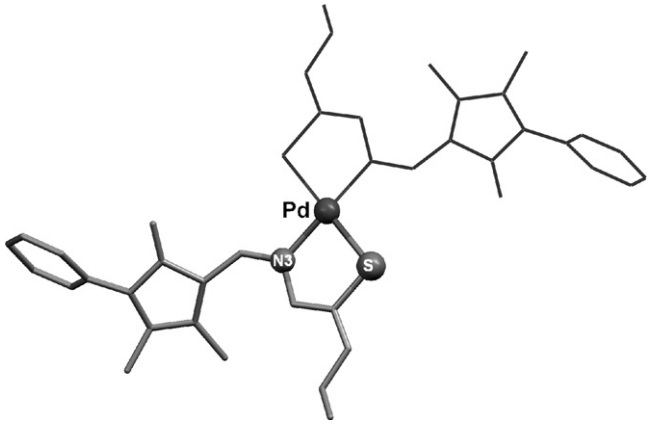


Fig. 40. Coordination mode of the ligand in $[Pd(L^{45})_2]$ (UJELOK) [96].

When K_2PdCl_4 and HL^{45} were reacted in water (pH 8–9, adjusted with aqueous 1.0 M NH_3) and the isolated solid was recrystallized from MeCN/MeOH, the Pd(II) complex $[Pd(L^{45})_2]$ [96] (Fig. 40) was obtained. In this case the deprotonated thiosemicarbazone-5-pyrazolone ligands are N3, S-coordinated and the Pd(II) has a *trans*-N2,S2 square planar environment.

2.2.5.4. Dithiocarbazates. HL^{46} (Scheme 10) was prepared by condensation of 3-methyl-1-phenyl-4-benzoylpyrazol-5-one [14] and *S*-methylthiosemicarbazate [97] in MeOH. This ligand exhibits solid-state photochromism due to photoisomerization from the enol to the keto form through an intermolecular proton transfer.

The complex $[Co(L^{46})_2]\cdot 2H_2O$ [98] (Fig. 41) was prepared by reaction of HL^{46} and $Co(OAc)_2\cdot 4H_2O$ in EtOH/H_2O.

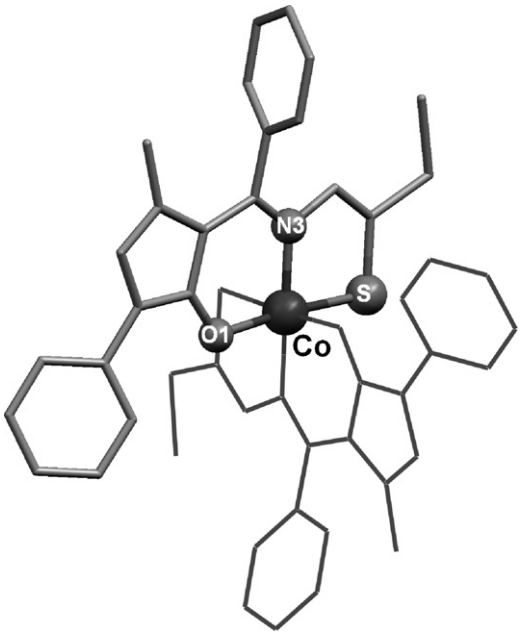
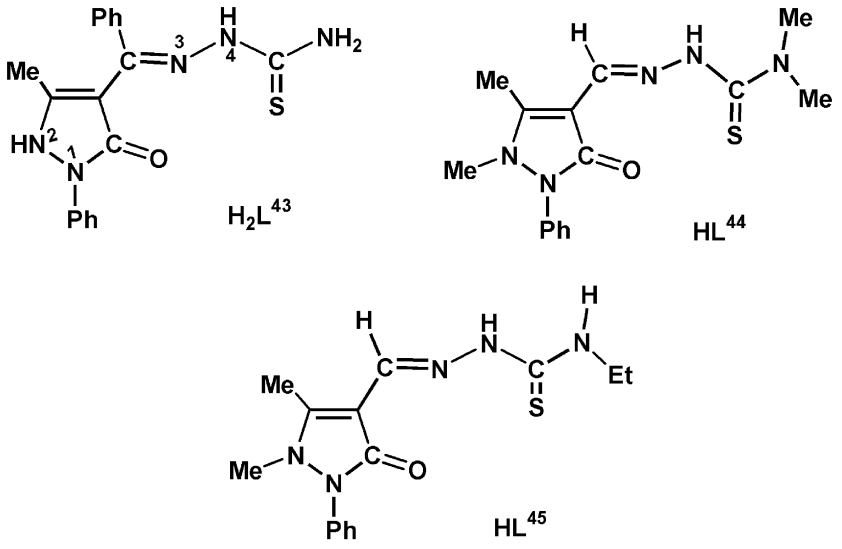
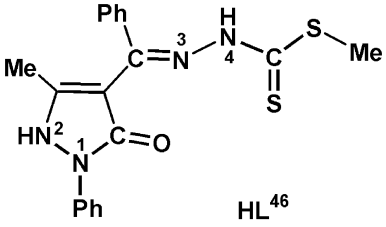


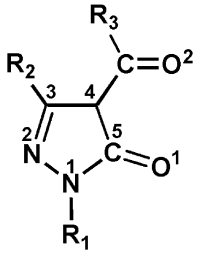
Fig. 41. Coordination mode of the ligand in $[Co(L^{46})_2]\cdot 2H_2O$ (IWETEJ) [98].



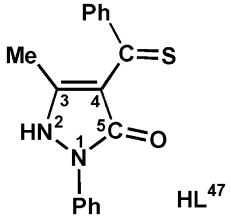
Scheme 9.



Scheme 10.



Scheme 11.



Scheme 12.

Crystals suitable for the X-ray study were obtained from ethanol/acetone. The ligand is in its tautomeric thiol form and coordinates the metal through the thiolato sulphur (S), the azomethine nitrogen (N3) and the pyrazolone oxygen (O) atoms. The coordination geometry around the metal is described as a slightly distorted octahedron.

2.2.6. 4-Acyl-5-pyrazolones (–C4–C(O)–C– fragment)

As mentioned previously, the synthesis, structure, coordination behaviour and applications of 4-acyl-5-pyrazolones (see Scheme 11) were extensively reviewed by Marchetti et al. [14]. According to this review the coordination modes for these ligands are those summarized in Fig. 42.

2.2.7. 4-Thioacyl-5-pyrazolones (–C4–C(S)–C– fragment)

The 4-thioacyl-5-pyrazolone HL^{47} (Scheme 12) was prepared by reacting a solution of 3-methyl-1-phenyl-5-pyrazolone and thiobenzoylthioglycolic acid in 50% MeOH containing sodium hydroxide. After heating the mixture under reflux, the solution was allowed to cool and then acidified with acetic acid [99].

In the only complex of this ligand studied to date by X-ray diffraction, i.e. $[Cu(L^{47})_2]$ [100] (Fig. 43), the monodeprotonated ligands coordinate the metal through the O and S atoms, giving rise to a very distorted square planar geometry.

Table 8
Complexes of 4-thiosemicarbazone-5-pyrazolones

Ligand	Complex	CSD code	Pyrazolone donor atoms	Reference
H_2L^{43}	$[Co(HL^{43})_2]\cdot 2H_2O\cdot 2DMF$	FASKEQ	N3, O, S	[90]
	$[Ni(L^{43})(H_2L^{43})_2]\cdot 2H_2O\cdot EtOH$	IFENOW	N3, O, S	[92]
HL^{44}	$[Co(L^{44})_2]BF_4$	NATFOE	N3, O, S	[94]
HL^{45}	$[Pd(L^{45})_2]$	UJELOK	N3, S	[96]

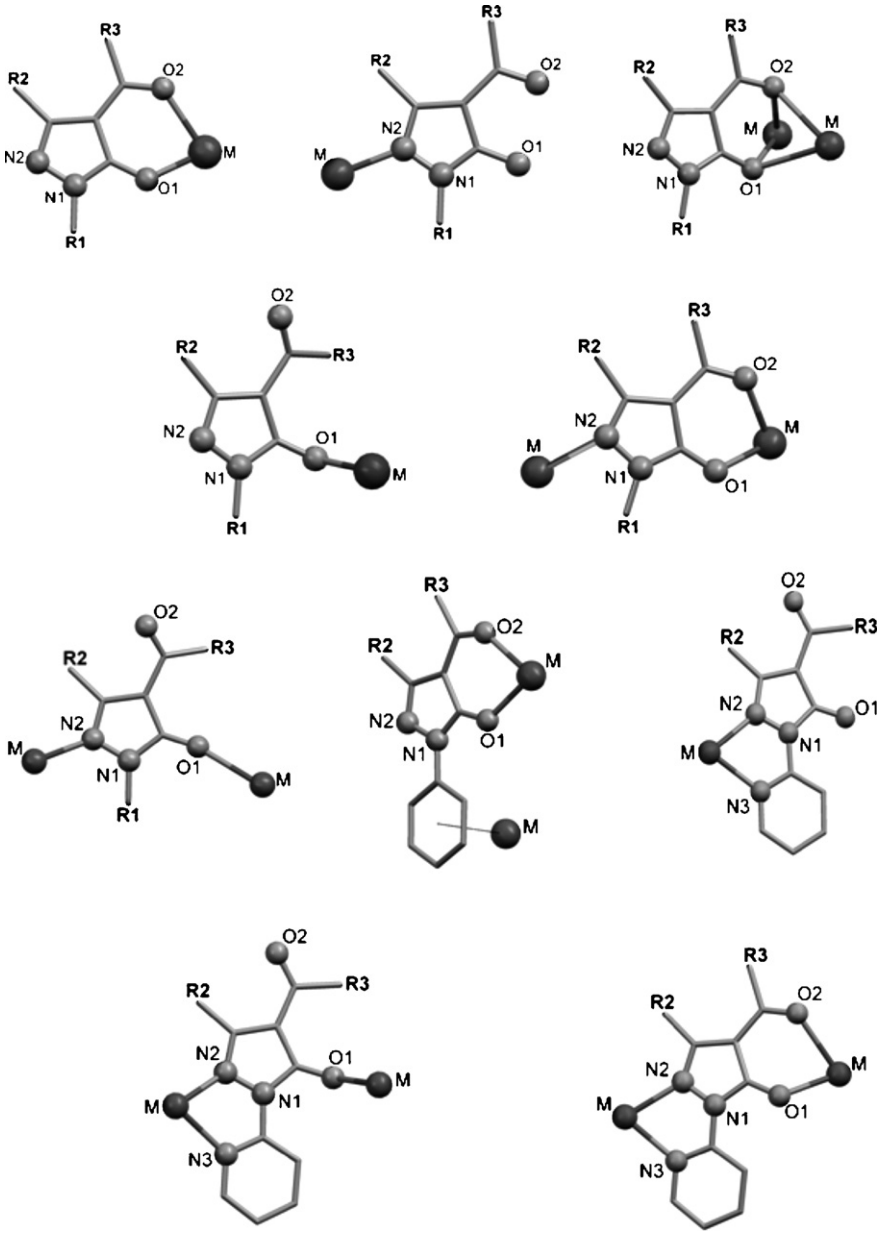


Fig. 42. Coordination modes for 4-acyl-5-pyrazolones [14].

2.2.8. 4-Phosphino (phosphoryl or phosphoranylidene)-5-pyrazolones (–C4–P–C– fragment)

Some 5-pyrazolones with a P atom on C^4 have been prepared (Scheme 13) and their complexes are included in Table 9.

NaL^{48} was obtained by reacting 3-methyl-1-phenyl-5-pyrazolone first with sodium hydride in THF at 0 °C and then with Ph_2PCl [101]. The reaction of 4-diphenylphosphine-5-ethoxy-3-methyl-1-phenyl-l-pyrazole with Cl_2 in benzene afforded a chloro ylide that was then reacted with aqueous sodium carbonate to give HL^{49} [102]. The ligand L^{50} was prepared by mixing the corresponding 4-bromo-5-pyrazolone [103] with triphenylphosphine in toluene at 90 °C to give the phosphonium salt, which was then deprotonated with NaH/THF [104].

The reactions of NaL^{48} with the Ni(II) organometallic derivatives [Ni(Ph_5Cp)(CO)Br] and [Ni(Ph)Cl(PPh_3)] afforded the complexes [Ni(Ph_5Cp)(L^{48})] [105] and [Ni(Ph)(L^{48})(PPh_3)]·$PhCH_3$ [106] (Fig. 44), respectively. These two Ni(II) compounds show catalytic activity toward ethene polymerization. In both cases the 4-phosphane-5-pyrazolonato unit is linked to the metal through O and P atoms (Fig. 44).

The Pd(II) complexes [Pd(dmamp)(L^{48})] [107] and [Pd(L^{48})$_2$] [101] (Fig. 45) were prepared by reacting NaL^{48} with [PdCl(dmamp)]$_2$ in dry THF or Pd(OAc)$_2$ in CH_2Cl_2, respectively. In both compounds the metal atom is in a square planar environment and the pyrazolonate is again bound through the O and P atoms.

[Fe(L^{49})$_3$] [108] was isolated by adding a solution of the ligand in dichloromethane to an aqueous solution of Fe(NO_3)$_3$ (M:L molar ratio 10:1). The crystals used in the X-ray study were obtained by diffusion of pentane into a THF solution of the complex. It can be seen from Fig. 46 that the three deprotonated ligands bind the metal through the two donor O atoms, O1 and O2.

Table 9
Complexes of 4-phosphanyl (phosphonate or phosphoranylidene)-5-pyrazolones

Ligand	Complex	CSD code	Pyrazolone donor atoms	Reference
NaL^{48}	$[Ni(Ph_5Cp)(L^{48})]$	YOGKAG	O, P	[105]
	$[Ni(Ph)(L^{48})(PPh_3)]\cdot PhCH_3$	WALTOT	O, P	[106]
	$[Pd(dmamp)(L^{48})]\cdot C_6H_6$	HATRAV	O, P	[107]
	$[Pd(L^{48})_2]$	LATJAR	O, P	[101]
HL^{49}	$[Fe(L^{49})_3]$	JOSRUE	O1, O2	[108]
L^{50}	$[PdCl_2(L^{50})_2]\cdot 4CHCl_3$	HAVHIW	N2	[104]
	$[PdCl(L^{50})(dmamp)]$	HAVHES	N2	[104]

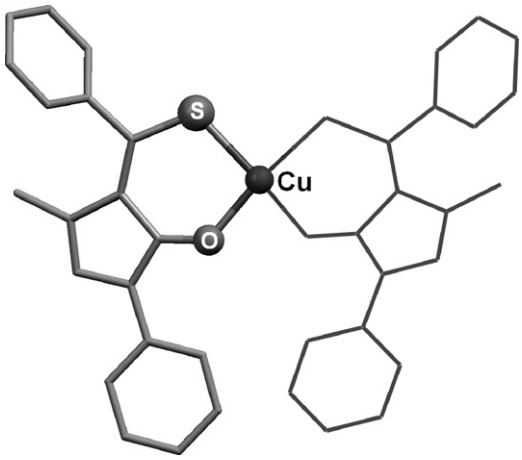


Fig. 43. Coordination mode of the ligand in $[Cu(L^{47})_2]$ (OCEFUY) [100].

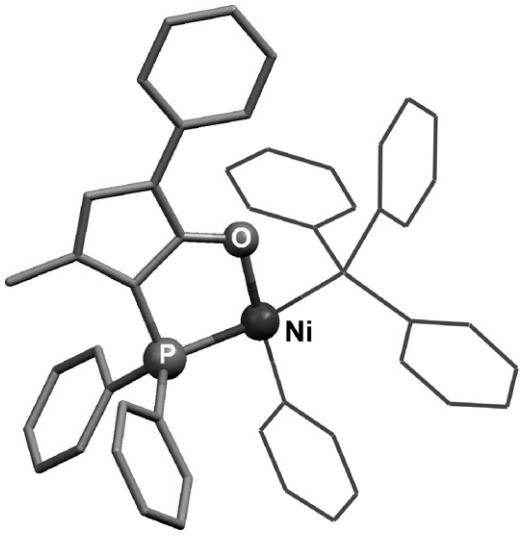


Fig. 44. Coordination mode of the ligand in $[Ni(Ph)(L^{48})(PPh_3)]\cdot PhCH_3$ (WALTOT) [106].

The Pd(II) complexes of L^{50}, $[PdCl_2(L^{50})_2]\cdot 4CHCl_3$ [104] (Fig. 47) and $[PdCl(L^{50})(dmamp)]$ [104], were prepared by mixing a solution of the ligand in chloroform or toluene with a solution of $[PdCl_2(PhCN)_2]$ in chloroform or $[Pd(dmamp)Cl]_2$ in toluene, respectively. Crystals of these compounds were grown by slow evaporation of chloroform or dichloromethane solutions. In both complexes L^{50} coordinates the metal in a similar way through the N2 atom and the metal atoms have an almost ideal square planar environment.

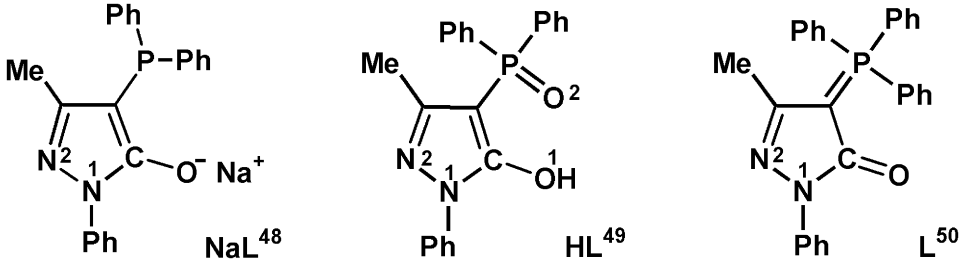
2.3. 5-Pyrazolones with additional donor atoms on N1

The ligands of this type that have been prepared to date are all N^1-carbothioamide-5-pyrazolones (see Scheme 14) and their complexes are listed in Table 10.

All these carbothioamide-5-pyrazolones were obtained by elimination-cyclization processes involving β-keto ester or β-keto amide thiosemicarbazones (HβTSCs) in the presence of a metal cation (although other factors such as pH, temperature and the nature of the solvent may influence the process) [109–114] (see Scheme 15).

When reacted with aqueous trifluoroacetic acid, these complexes release the free pyrazolone, which is then easily isolated [111]. In their free form all of these ligands adopt the keto-thione form in the solid state [111,115].

The interesting coordination possibilities of these molecules are well illustrated by the related rhenium coordination chemistry developed in recent years. The reaction of $[ReBr(CO)_5]$



Scheme 13.

Table 10
Complexes of N^1-carbothioamide-5-pyrazolone ligands

Ligand	Complex	CSD code	Pyrazolone donor atoms	Reference
HL^{51}	$[Re(L^{51})(CO)_3]_4{\cdot}PhCH_3$	ALIBAY	N2, S1, O1	[109]
	$[Zn(L^{51})_2(H_2O)]{\cdot}DMSO$	XIHBAR	N2, S1	[110]
	$[Cd(L^{51})_2(py)]$	HOXLEL	N2, S1	[111]
HL^{52}	$[Zn(L^{52})_2(MeOH)]$	TAYQIU	N2, S1	[112]
HL^{53}	$[Zn(L^{53})_2]{\cdot}MeOH$	TAYQOA	N2, S1	[112]
	$[Cd(L^{53})_2(DMSO)]{\cdot}DMSO$	BEYKOG	L^{53}: N2, S1, O1; L^{53}: N2, S1	[113]
HL^{54}	$[Zn(L^{54})_2]{\cdot}H_2O$	BEYKEW	N2, S1	[113]
HL^{55}	$[ReBr(CO)_3(HL^{55})]$	ALEZOG	N2, S1	[109]
	$[Re(L^{55})(CO)_3(H_2O)]$	ALIBEC	N2, S1	[109]
	$[Zn(L^{55})2(H_2O)]{\cdot}2DMSO$	XIHBEV	N2, S1	[110]
	$[Cd(L^{55})_2(H_2O)]{\cdot}DMSO$	BEYKIA	N2, S1	[113]
HL^{56}	$[Zn(L^{56})_2]$	TAYQUG	N2, S1	[112]
	$[Zn(L^{56})_2]$	TAYQUG01	N2, S1	[112]
HL^{57}	$[Re(L^{57})(CO)_3]_3{\cdot}0.5PhCH_3$	[a]	N2, S1, O1	[114]
HL^{58}	$[Zn(L^{58})_2]$	TAYRAN	N2, S1	[112]
HL^{59}	$[Re(L^{59})(CO)_3]_3$	[a]	N2, S1, O1	[114]
	$[Re(L^{59})(CO)_3]_3{\cdot}2PhCH_3$	[a]	N2, S1, O1	[114]

[a] Structure not deposited or not available in CSD.

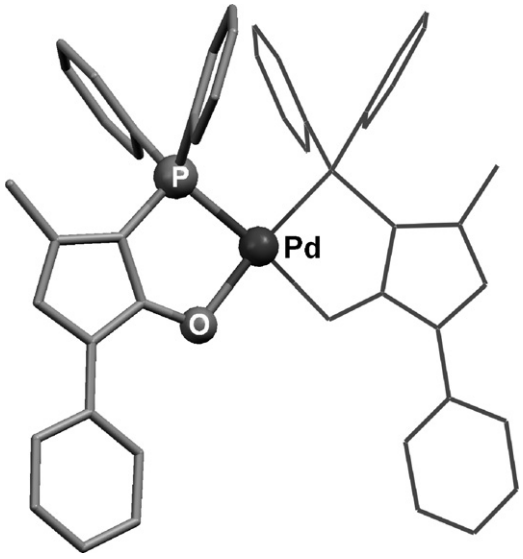
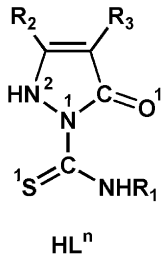


Fig. 45. Coordination mode of the ligand in $[Pd(L^{48})_2]$ (LATJAR) [101].

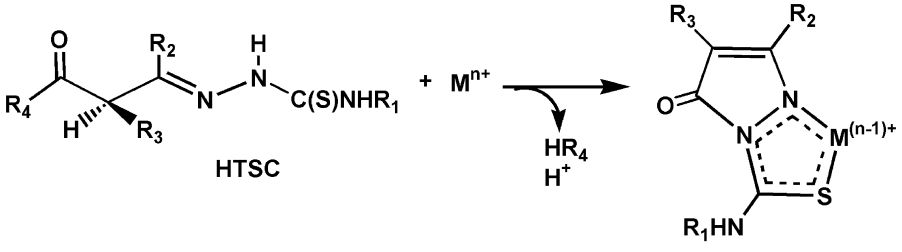


Ligand	R_1	R_2	R_3
HL^{51}	H	Me	H
HL^{52}	H	Et	H
HL^{53}	H	Ph	H
HL^{54}	H	CH_3-O-CH_2-	H
HL^{55}	H	Me	Me
HL^{56}	H	Me	Et
HL^{57}	Me	Me	H
HL^{58}	Et	Me	H
HL^{59}	Ph	Me	H

Scheme 14.

with methyl acetoacetate and ethyl 2-methylacetoacetate thiosemicarbazone in toluene under reflux afforded crystals of $[Re(L^{51})(CO)_3]_4{\cdot}PhCH_3$ and $[ReBr(CO)_3(HL^{55})]$, respectively [109]. In the former case, four *fac*-$Re(CO)_3$ and four bridging pyrazolonates form a tetramer (Fig. 48) in which the pyrazolonate coordinates to one rhenium atom through its S and N2 atoms, forming a five-membered chelate ring, and to a second metal atom through the oxygen atom (O1). However, $[ReBr(CO)_3(HL^{55})]$ is a monomer [109] (Fig. 49) and the neutral pyrazolone is in the enol form and coordinates to the metal through the N2, S atoms.

The same coordination mode, this time for the anionic form of the ligand, occurs in $[Re(L^{55})(CO)_3(H_2O)]$ [109]. This complex was prepared by mixing ethyl 2-methylacetoacetate thiosemicarbazone and $[ReX(CO)_3(CH_3CN)_2]$ (X = Cl,



Scheme 15.

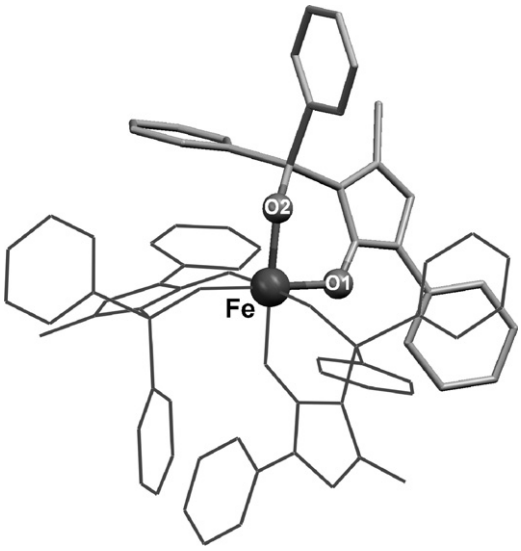


Fig. 46. Coordination mode of the ligand in $[Fe(L^{49})_3]$ (JOSRUE) [108].

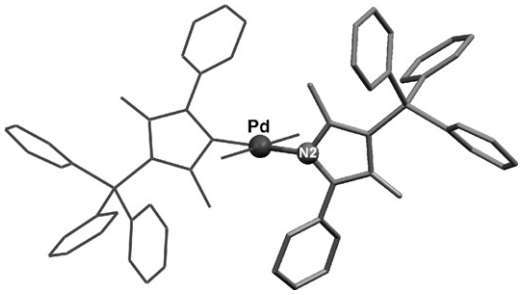


Fig. 47. Coordination mode of the ligand in $[PdCl_2(L^{50})_2]\cdot 4CHCl_3$ (HAVHIW) [104].

Br) in chloroform at room temperature and then reacting the resulting complex {[ReBr(CO)$_3$(HTSC)]} with NaOMe. However, $[Re(L^{57})(CO)_3]_3\cdot 0.5PhCH_3$, $[Re(L^{59})(CO)_3]_3\cdot 2PhCH_3$ and $[Re(L^{59})(CO)_3]_3$ [114], which were isolated from the reaction of $[ReCl(CO)_5]$ with

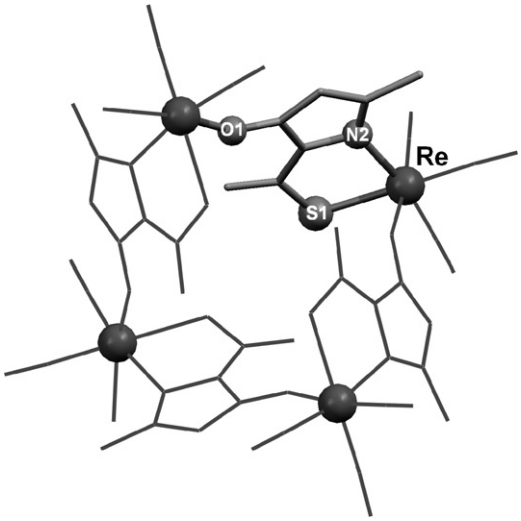


Fig. 48. Coordination mode of the ligand in $[Re(L^{51})(CO)_3]^4\cdot PhCH_3$ (ALIBAY) [109].

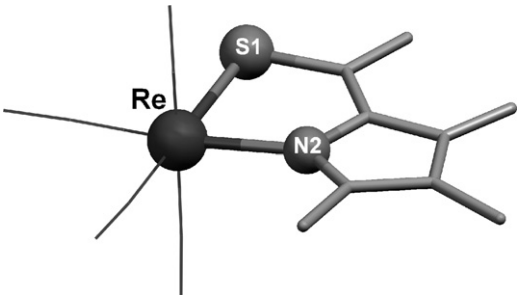


Fig. 49. Coordination mode of the ligand in $[ReBr(CO)_3(HL^{55})]$ (ALEZOG) [109].

methyl acetoacetate-N^3-methylthiosemicarbazone or methyl acetoacetate-N^3-phenylthiosemicarbazone, are all trimers, with the pyrazolonate ligands bridging two [Re(CO)$_3$] fragments (see Fig. 50 for $[Re(L^{59})(CO)_3]_3$ [114]) in a similar way to L^{51} in the previously described tetramer.

Zn(II) complexes with the general formulae $[Zn(L^n)_2]$ (n = 53, 54, 56, 58) [112,113] and $[Zn(L^n)_2(Solv)]$ (n = 51, Solv = H_2O; n = 52, Solv = MeOH; n = 55, Solv = H_2O) [110,112] have also been prepared, as was indicated in Scheme 15, by reaction of $Zn(OAc)_2$ and the corresponding thiosemicarbazone ligand in MeOH (at room temperature or under reflux). These complexes contain monodeprotonated N2, S-bound pyrazolonate ligands and the complexes $[Zn(L^n)_2]$ have a distorted tetrahedral geometry (see Fig. 51 for $[Zn(L^{53})_2]\cdot$MeOH [112]), whereas those with $[Zn(L^n)_2(Solv)]$ stoichiometry possess distorted trigonal bipyramidal coordination spheres (see Fig. 52 for $[Zn(L^{52})_2(MeOH)]$ [112]). Curiously, the potentially polymeric $[Zn(L^n\text{-H})]$ complexes have also been isolated but their X-ray structures are yet to be determined.

The Cd(II) complexes with the ligands HL^{51} [111], HL^{53} [113] and HL^{55} [113] were synthesized in a similar way to the Zn(II) systems by reacting $Cd(OAc)_2$ with the corresponding thiosemicarbazone. Recrystallization of the complexes from pyridine or DMSO afforded crystals suitable for X-ray

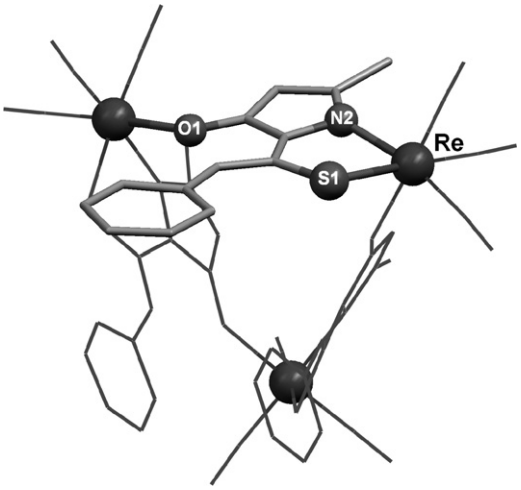


Fig. 50. Coordination mode of the ligand in $[Re(L^{59})(CO)_3]_3$ [114].

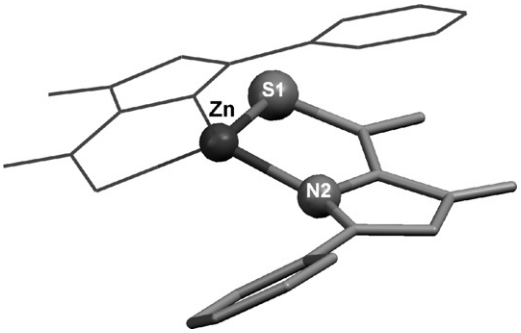


Fig. 51. Coordination mode of the ligand in $[Zn(L^{53})_2]$·MeOH (TAYQOA) [112].

study. As one would expect given the increase in the size of the metal cation, all three complexes have the stoichiometry $[Cd(L^n)_2(Solv)]$ ($n = 51$ Solv = Py, $n = 53$ Solv = DMSO, $n = 55$ Solv = H_2O). In $[Cd(L^{51})_2(Py)]$ [111] and $[Cd(L^{55})_2(H_2O)]$ [113] two monocharged pyrazolonate ligands chelate the metal through the N2, S1 atoms. An additional donor atom (N or O) from the solvent molecule completes the coordination number of five, giving rise to a distorted trigonal bipyramidal coordination geometry (see Fig. 53 for $[Cd(L^{51})_2(Py)]$ [111]).

In $[Cd(L^{53})_2(DMSO)]$·DMSO [113] (Fig. 54) the monodeprotonated pyrazolonates chelate the metal as in the previous complex through the N2, S1 atoms, which is once again consistent with the increase of the size of the Cd(II) ion with respect to that of Zn(II). However, one of the L^{53} ligands is also linked to a second metal atom through O1 to give a chain. This bond,

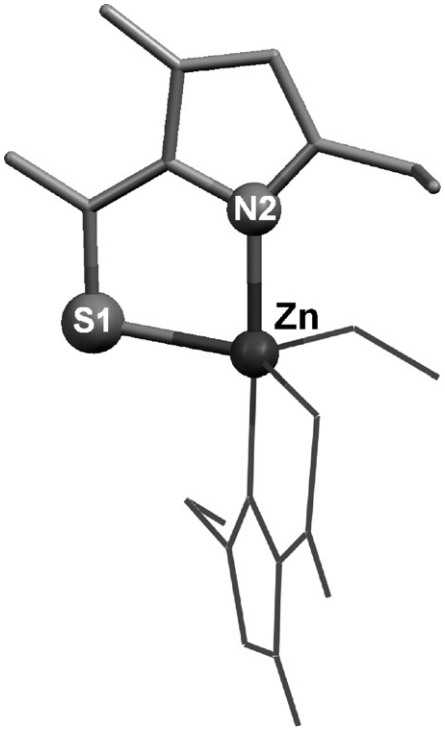


Fig. 52. Coordination mode of the ligand in $[Zn(L^{52})_2(MeOH)]$ (TAYQIU) [112].

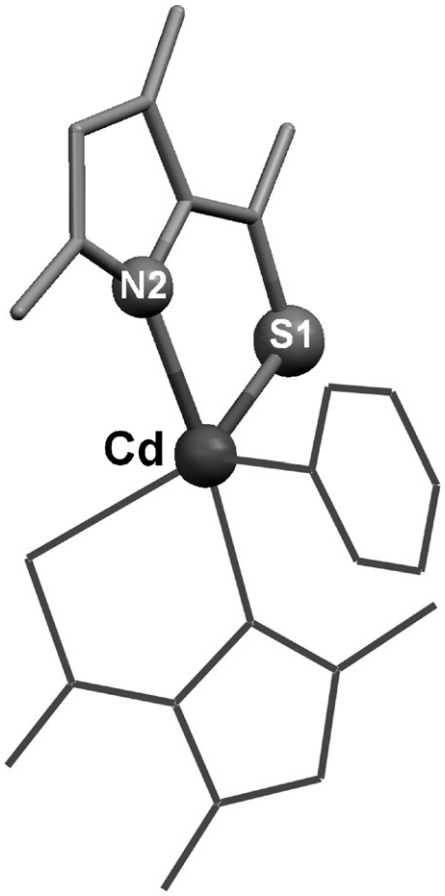


Fig. 53. Coordination mode of the ligand in $[Cd(L^{51})_2(py)]$ (HOXLEL) [111].

together with that of the solvent molecule, increases the CN of cadmium to six and leads to a trigonal prismatic coordination geometry.

2.4. 5-Pyrazolones with additional donor atoms on N2

Only one complex $\{[Mo_2O_5(L^{60})_2]$·2MeCN$\}$ containing an N2-subtituted 5-pyrazolone (see Scheme 16) has been structurally identified (Fig. 55) [116].

HL^{60} was not independently synthesized and isolated but the complex $[Mo_2O_5(L^{60})_2]$·2MeCN was formed during the reaction of $FcTp^{Ph}Li$ [Fc = ferrocenyl, Tp^{Ph} = tris(4-phenylpyrazolyl)borate] with $Mo(CO)_6$ upon treatment with

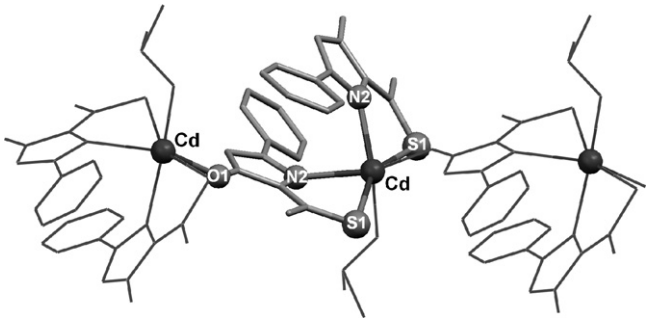
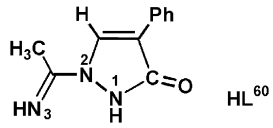


Fig. 54. Coordination mode of the ligand in $[Cd(L^{53})_2(DMSO)]$·DMSO (BEYKOG) [113].



HL^{60}

Scheme 16.

3-bromo-2-methylpropene and subsequent recrystallization of the crude product from CH_3CN/toluene [116]. The *in situ* formation of this pyrazolonate ligand seems to occur via complete breakdown of the initial scorpionate, which is accompanied by the oxidative CH activation at the pyrazolyl moiety and nucleophilic attack on the acetonitrile by a pyrazolyl N atom. The oxidation of molybdenum occurs simultaneously.

In $[Mo_2O_5(L^{60})_2]\cdot 2MeCN$ [116] (Fig. 55) the pyrazolone is tridentate and chelates one metal atom through N1 and N3 and links a second one through the O atom.

2.5. Bis- and tetra-5-pyrazolones

The bis- and tetra-5-pyrazolones discussed in this review are represented in Scheme 17 and their metal complexes are listed in Table 11.

The ligands L^{61} and L^{62} can be prepared by condensation of antipyrine and the corresponding aldehyde (formaldehyde or benzaldehyde) [117,118]. H_2L^{63} was synthesized by reaction of 3-methyl-1-phenyl-5-pyrazolone with phthaloyl chloride [119]. H_2L^{64} to H_2L^{67} are obtained by condensing 4-acyl-5-pyrazolones (Section 2.2.6) and diamines [120,121], while L^{68} and L^{69} were prepared by a Mannich process using antipyrine, formaldehyde and the corresponding diamine (piperazine or ethylenediamine) [122].

The reaction of L^{61} with $TiCl_4$ in a perchloric acid solution afforded crystals of $[Ti(L^{61})_3](ClO_4)_4$ (violet) and $[Ti(L^{61})_3](ClO_4)_4\cdot H_2O$ (orange) [123] and that of L^{62} with a methanolic solution of $Nd(NO_3)_3$ gave $[Nd(NO_3)_3(L^{62})(MeOH)]\cdot MeOH$ [124]. In all of these complexes the bis-pyrazolone chelates the metal through its two available donor atoms, O1 and O1′ (see Fig. 56 for the Nd complex).

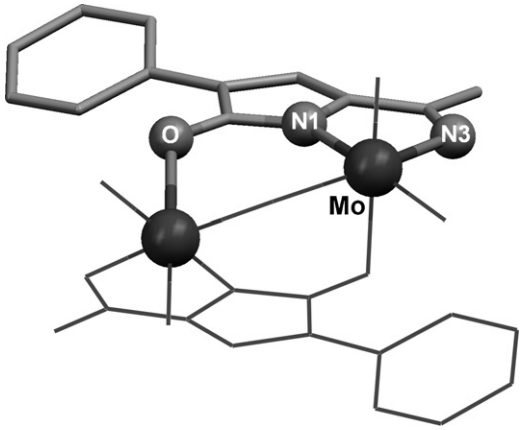


Fig. 55. Coordination mode of the ligand in $[Mo_2O_5(L^{60})_2]\cdot 2MeCN$ (EDALOK) [116].

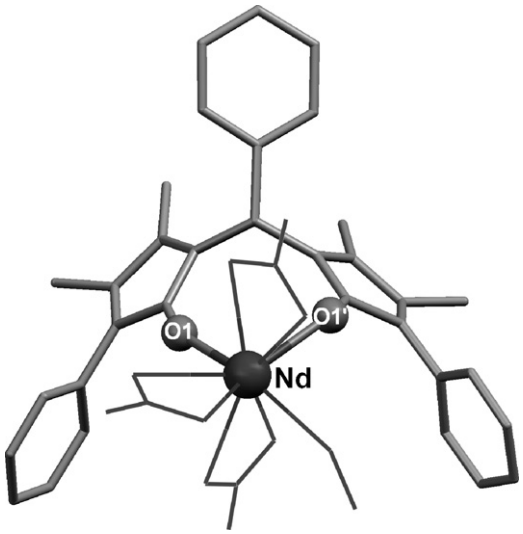


Fig. 56. Coordination mode of the ligand in $[Nd(NO_3)_3(L^{62})(MeOH)]\cdot MeOH$ (LUHSOW) [124].

The organotin(IV) derivative $[SnPh_3(HL^{63})]$ [119] was prepared by adding $(SnPh_3)_2O$ to a benzene solution of H_2L^{63} under a N_2 atmosphere and heating the mixture under reflux overnight. After removing the solvent, the addition of diethyl ether afforded the aforementioned complex. The compound was recrystallized from MeOH/Me_2CO to give crystals of $[SnPh_3(H_2O)(HL^{63})]$ $0.5Me_2CO$ [119]. In both derivatives the monoanionic ligand coordinates the Sn atom through the oxygen atom O2 (Fig. 57) of the deprotonated carboxylic acid group (see H_2L^{63} in Scheme 17).

The dinuclear complex $[SnMe_2(L^{63})]_2$ was synthesized when an acetonitrile solution of H_2L^{63} and triethylamine was reacted with $SnMe_2Cl_2$ [119]. Recrystallization ($CHCl_3$/MeOH) of the solid led to the isolation of single crystals of $[SnMe_2(L^{63})]_2\cdot CHCl_3$. In the dimeric structure of this complex, two bideprotonated bis-pyrazolones are bridging between two tin atoms, Sn and Sn′, coordinating one of them through the two oxygen atoms (O1 and O1′) from the pyrazolone fragments and the other one through the carboxylic O2 oxygen (Fig. 58).

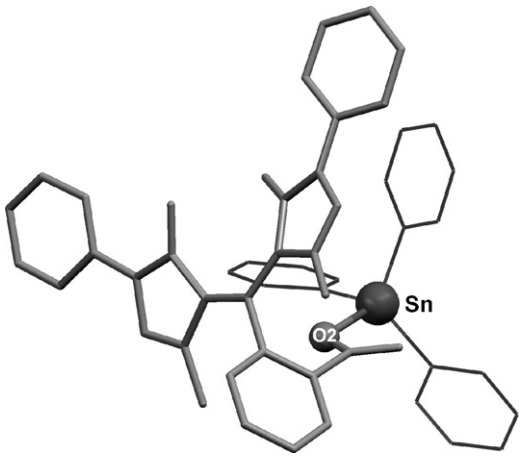
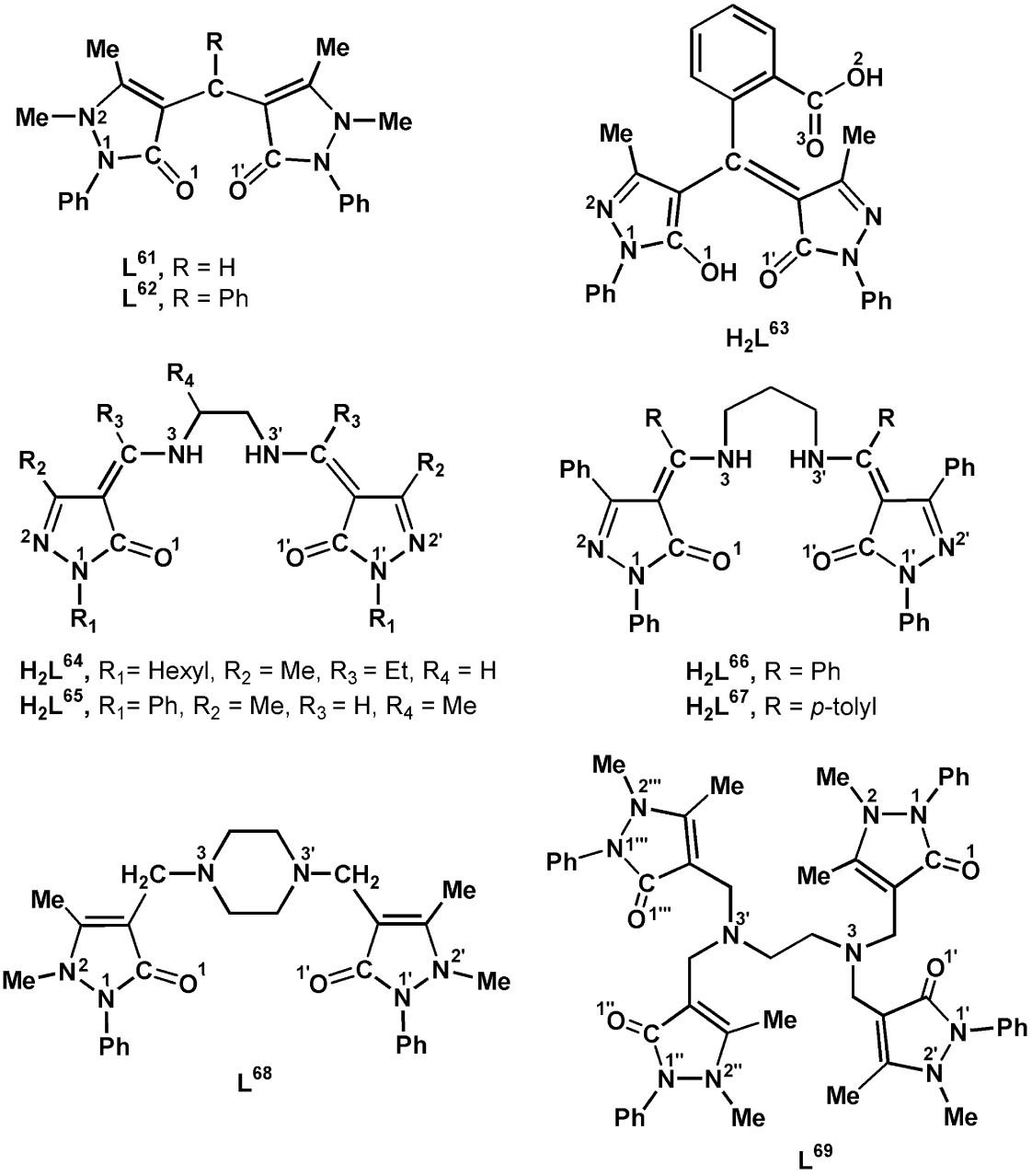


Fig. 57. Coordination mode of the ligand in $[SnPh_3(HL^{63})]$ (QOWYEG) [119].



Scheme 17.

Reaction of H_2L^{64} with $Mn(OAc)_3{\cdot}2H_2O$ and LiCl gives the complex $[Mn(Cl)(L^{64})]$. The reaction of this chloromanganese(III) derivative with aqueous ammonia in a CH_2Cl_2/CH_3OH mixture and subsequent oxidation with NaClO enabled the isolation of the nitridomanganese(V) complex $[Mn(N)(L^{64})]$ from the organic phase [125]. Crystals suitable for an X-ray study were obtained by slow evaporation of a methylene chloride/hexane solution of the crude product. In this complex (Fig. 59) the bideprotonated bis-pyrazolone embraces the cation with its four coordinating atoms (O1, O1′, N3, N3′) defining the square-base of an almost perfect square pyramidal environment. The fifth position is occupied by the nitrido ligand. The ability of this complex to transfer nitrogen to styrene in stoichiometric reactions has been tested.

The Ni(II) complexes with the ligands H_2L^n ($n = 65$, 66, 67) [126,127] were prepared by reacting the pyrazolones and anhydrous $Ni(OAc)_2$ in 2-methoxyethanol under reflux [127]. Crystals of these complexes were isolated by recrystallization from $CHCl_3$, DMSO or mixtures of these two solvents. In all of these Ni(II) derivatives the bis-pyrazolones, which are bideprotonated and tetradentate, show the same coordination behaviour and bind the same metal through four donor atoms (O1, O1′, N3 and N3′). These four atoms are almost in a plane in $[Ni(L^{65})]$ [126] (Fig. 60), giving rise to a planar coordination geometry around the metal, and in $[Ni(L^n)(DMSO)_2]$ ($n = 66$, 67) [127] (see Fig. 61 for $[Ni(L^{67})(DMSO)_2]$), where the metal reaches a pseudo-octahedral environment with the DMSO molecules axial. However, in $[Ni(L^{66})]{\cdot}0.5CHCl_3$ [127] the four donor

Table 11
Complexes of bis- and tetra-5-pyrazolone ligands

Ligand	Complex	CSD code	Pyrazolone donor atoms	Reference
L^{61}	$[Ti(L^{61})_3](ClO_4)_4$		O1, O1′	[123]
	$[Ti(L^{61})_3](ClO_4)_4{\cdot}H_2O$		O1, O1′	[123]
L^{62}	$[Nd(NO_3)_3(L^{62})(MeOH)]{\cdot}MeOH$	LUHSOW	O1, O1′	[124]
H_2L^{63}	$[SnPh_3(HL^{63})]$	QOWYEG	O2	[119]
	$[SnPh_3(HL^{63})(H_2O)]{\cdot}0.5MeCOMe$	QOWYIK	O2	[119]
	$[SnMe_2(L^{63})]_2{\cdot}CHCl_3$	QOWYOQ	O1, O1′ (Sn), O2 (Sn′)	[119]
H_2L^{64}	$[Mn(N)(L^{64})]$	NAHQET	O1, O1′, N3, N3′	[125]
H_2L^{65}	$[Ni(L^{65})]$	NEKFOY	O1, O1′, N3, N3′	[126]
H_2L^{66}	$[Ni(L^{66})]{\cdot}0.5CHCl_3$	TONPAN	O1, O1′, N3, N3′	[127]
	$[Ni(L^{66})(DMSO)_2]$	TONPER	O1, O1′, N3, N3′	[127]
H_2L^{67}	$[Ni(L^{67})(DMSO)_2]$	TONPIV	O1, O1′, N3, N3′	[127]
L^{68}	$[Co_2(L^{68})Cl_4]$	BIFFEC	O1, N3 (Co), O1′, N3′ (Co′)	[128]
	$[Cu(L^{68})](ClO_4)_2$		O1, O1′, N3, N3′	[129]
	$[Cu(L^{68})(H_2O)](ClO_4)_2$	BIFFIG	O1, O1′, N3, N3′	[128]
	$[Cu_2I_3(L^{68})]{\cdot}DMF$	QOBXAG	O1, O1′, N3, N3′	[130]
	$[Cu(L^{68})(DMSO)][Zn(NCS)_4]$	DAXBIO	O1, O1′, N3, N3′	[131]
L^{69}	$[Cu(L^{69})](ClO_4)_2{\cdot}H_2O{\cdot}DMF$	NAXXEQ	O1, O1′, O1″, O1‴, N3, N3′	[132]

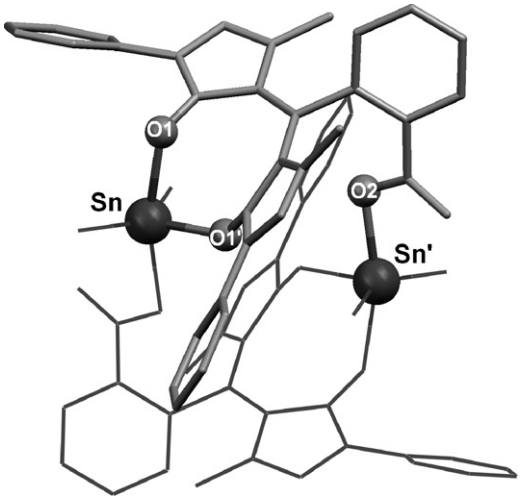


Fig. 58. Coordination mode of the ligand in $[SnMe_2(L^{63})]_2{\cdot}CHCl_3$ (QOWYOQ) [119].

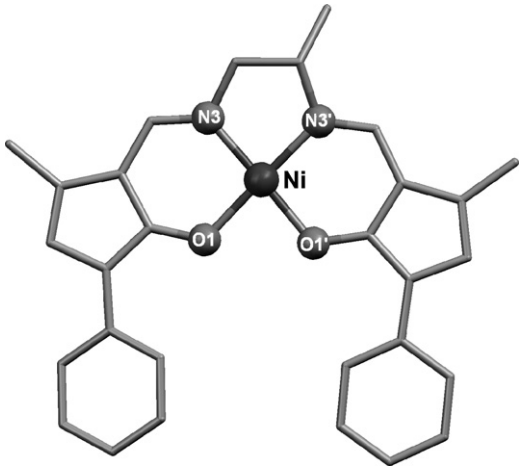


Fig. 60. Coordination mode of the ligand in $[Ni(L^{65})]$ (NEKFOY) [126].

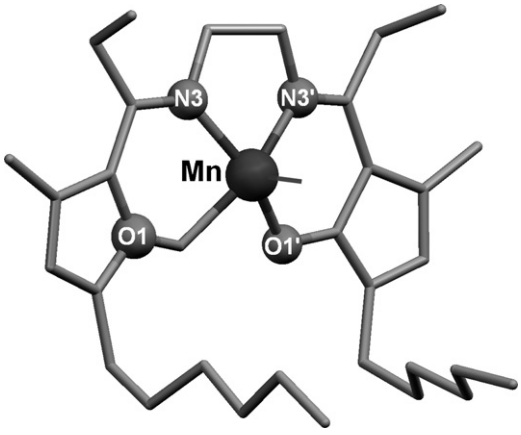


Fig. 59. Coordination mode of the ligand in $[Mn(N)(L^{64})]$ (NAHQET) [125].

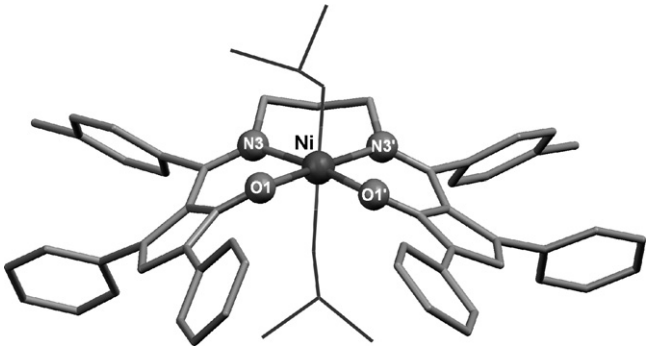


Fig. 61. Coordination mode of the ligand in $[Ni(L^{67})(DMSO)_2]$ (TONPIV) [127].

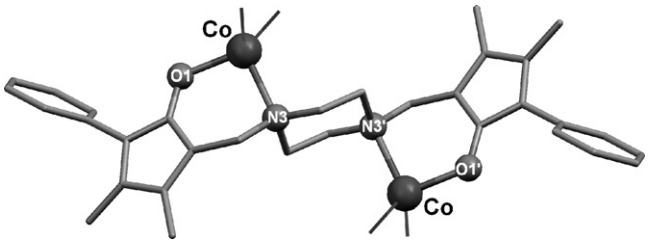


Fig. 62. Coordination mode of the ligand in $[Co_2(L^{68})Cl_4]$ (BIFFEC) [128].

atoms of the bis-pyrazolone are not in a strictly planar environment (the angle between planes N3–Ni–O1 and N3′–Ni–O1′ is 12.7°), leading to a coordination sphere that is described by the authors as pseudo-tetrahedral.

Crystals of the binuclear complex $[Co_2(L^{68})Cl_4]$ [128] (Fig. 62) were isolated when the solid obtained by reaction of L^{68} and $CoCl_2{\cdot}6H_2O$ in EtOH was recrystallized from DMSO. In this complex the bis-bidentate ligand L^{68}, with its piperazine ring in a "chair" conformation, coordinates with two metal ions through its O1, N3 and O1′, N3′ pairs of donor atoms.

The reaction of L^{68} with $Cu(ClO_4)_2$ in EtOH at 40 °C and recrystallization of the resulting solid from EtOH/CH_3CN led to the isolation of crystals of $[Cu(L^{68})](ClO_4)_2$ [129]. Surprisingly, reaction of this complex with $MnCl_2.4H_2O$ in MeOH/H_2O at 35 °C afforded crystals of $[Cu(L^{68})(H_2O)](ClO_4)_2$ [128] (Fig. 63). In both Cu(II) complexes the pyrazolone (with the pyperazine in a boat conformation) is tetradentate and the N_2O_2-donor atoms are essentially located on a distorted plane. In $[Cu(L^{68})](ClO_4)_2$ [129] one of the oxygen atoms also interacts, albeit weakly, with a copper atom from a neighbouring molecule, thus allowing the metal to acquire coordination number 5. This coordination number is achieved in $[Cu(L^{68})(H_2O)](ClO_4)_2$ [128] by the additional bonding of the water molecule.

The dinuclear complex $[Cu_2I_3(L^{68})]$ [130] was synthesized by reaction of $Cu(OAc)_2{\cdot}H_2O$ and L^{68} in EtOH at 50 °C and treatment of the resulting solution with an excess of KI. Recrystallization of the crude product from DMF gave monocrystals of $[Cu_2I_3(L^{68})]{\cdot}$DMF [130] (Fig. 64). In this compound L^{68} coordinates through all of its donor atoms to the same metal centre, giving rise to the same coordination behaviour as in previously

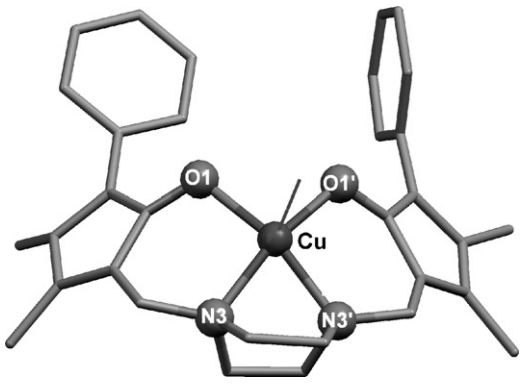


Fig. 63. Coordination mode of the ligand in $[Cu(L^{68})(H_2O)](ClO_4)_2$ (BIFFIG) [128].

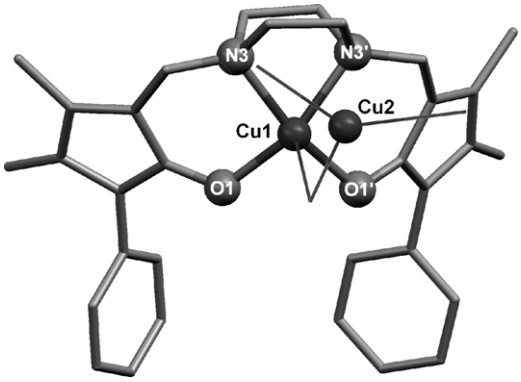


Fig. 64. Coordination mode of the ligand in $[Cu_2I_3(L^{68})]{\cdot}$DMF (QOBXAG) [130].

described Cu(II) complexes. An analogous bonding mode for L^{68} was also found in $[Cu(L^{68})(DMSO)][Zn(NCS)_4]$ [131], a complex that was prepared by reacting L^{68} with $Cu(OAc)_2$ and $Zn(OAc)_2$ in the presence of NH_4SCN, followed by recrystallization of the crude product from DMSO.

$[Cu(L^{69})](ClO_4)_2{\cdot}H_2O{\cdot}$DMF [132] is the only complex of a tetra-pyrazolone that has been studied by X-ray diffraction to date. This complex was obtained by reaction of L^{69} and $Cu(ClO_4)_2{\cdot}6H_2O$ in ethanol at 40 °C and recrystallization of the resulting solid from DMF trichloroethylene. In the $[Cu(L^{69})]^{2+}$ cation (Fig. 65) the ligand with the ethylene bridge in a *gauche* conformation uses all of its donor atoms in coordinating the metal, although these atoms are bound to the metal with different strengths. Thus, four of these atoms (N3, N3′, O1, O1‴, Fig. 65) bind the metal strongly and are located in the equatorial plane of a tetragonally distorted octahedron, while the other two atoms (O1′ and O1″) are weakly bonded in the axial positions—as one would expect in an octahedral Cu(II) derivative.

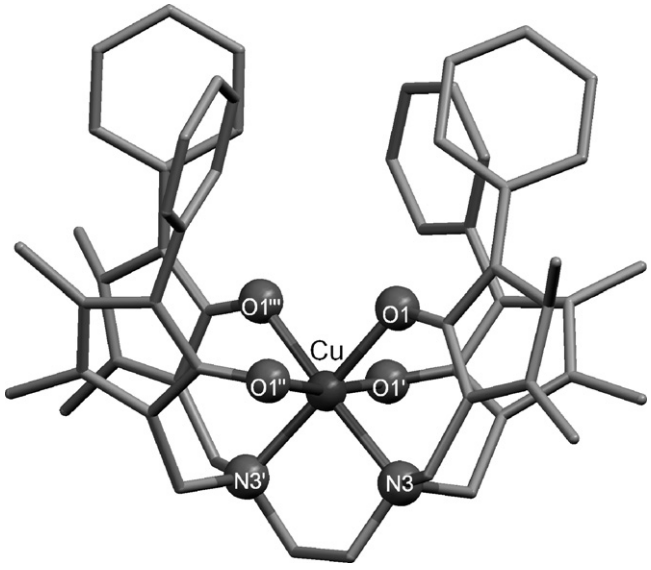


Fig. 65. Coordination mode of the ligand in $[Cu(L^{69})](ClO_4)_2{\cdot}H_2O{\cdot}$DMF (NAXXEQ) [132].

3. Conclusions

On the basis of the structural information described above, 5-pyrazolones have well-documented coordination chemistry. The pyrazolone ring itself can efficiently bind to metal ions through the pyridine-like N atom (N2, see Scheme 1) and the carbonyl O atom. In the latter case, probably due to the keto-enol tautomerism that occurs in this type of heterocycle, this donor atom sometimes shows behaviour that closely resembles that of bridging hydroxyl groups, contributing to the formation of very interesting metal-pyrazolone polynuclear assemblies. However, the most significant aspect of the explored versatility of these molecules as ligands derives from the easy substitution of one hydrogen atom on the C4 carbon by another fragment that can vary in complexity. This allows the incorporation of donor atoms that complement those of the pyrazolone ring and facilitates the preparation of chelating molecules that can be tailored in order to achieve more efficient binding properties with respect to a specific metal cation. Besides the 4-acyl derivatives, the coordination behaviour of which has been extensively explored, the group of compounds bearing 4-hydrazone moieties have also warranted considerable attention in recent years. In these two types of molecule, the presence of a donor atom that is well placed for chelation in the substituent on C4 (the acyl oxygen in the case of the 4-acyl derivatives or one of the hydrazinic nitrogens in the 4-hydrazone compounds) usually leads to six-membered chelate rings that also involve the carbonyl oxygen atom of the 5-pyrazolone.

Substitutions at other positions in the pyrazolone ring that lead to new coordination possibilities are less well documented. As a consequence of the synthetic procedure most commonly used for the preparation of these ligands (condensation of phenylhydrazine and a β-keto ester), the N1 atom is usually blocked by a phenyl group. In a few cases in which this group was substituted by a pyridine fragment, N2,N_{Py}-chelates were isolated. A new strategy for the preparation of 5-pyrazolones by cyclization of thiosemicarbazones in the presence of a metal substrate afforded 1-carbothiamide-5-pyrazolone complexes. It was found that in these derivatives N2,$S_{thioamide}$-chelation is preferred to O,$S_{thioamide}$-chelation. Nevertheless, when the former situation occurs, the oxygen atom of the carbonyl group retains its donor ability and can contribute to form interesting polynuclear assemblies, as occurs in the Re complexes (see Section 2.3). Only one complex containing an N2-subtituted pyrazolone has been studied by X-ray diffraction and this was prepared via a decomposition mechanism that is difficult to rationalise. The product of this reaction was a Mo(VI) complex in which the pyrazolone ring donor atom is N1. Some C3-substituted 5-pyrazolones have been prepared but the substituents did not bear additional donor atoms, meaning that their influence was reduced to their effects on the electron charge distribution over the ring.

Finally, in recent years there has been a rapid growth in the published information available on the coordination behaviour of bis- and poly-5-pyrazolones. The current trends in this emerging field include the inclusion of spacers that connect the rings because they can contribute with their own donor atoms to the coordination of the metal and also tailor the particular arrangement of the pyrazolone donor atoms. It is expected that this area will maintain a high level of interest in the near future.

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References

[1] L. Knorr, Ber. 17 (1883) 2032.
[2] D. Lednicer, L.A. Georg, The Organic Chemistry of Drug Synthesis, vol. 1, John Wiley & Sons, New York, 1977.
[3] A. Goodman Gilman, T.W. Rall, A.S. Nies, P. Taylor, Goodman and Gilman's, The Pharmacological Basis of Therapeutics, 8th ed., Pergamon Press, Oxford, 1996.
[4] H.R. Wiley, P. Wiley, Pyrazolones, Pyrazolidones and Derivatives, Interscience Publishers, 1964.
[5] M.P. Clark, R.G. Bookland, Expert Opin. Ther. Pat. 15 (2005) 1617.
[6] A. Omotowa, M.A. Mesubi, Appl. Organomet. Chem. 11 (1997) 1.
[7] F. Caruso, M. Rossi, J. Tanski, R. Sartori, R. Sariego, S. Moya, S. Diez, E. Navarrete, A. Cingolani, F. Marchetti, C. Pettinari, J. Med. Chem. 43 (2000) 3665.
[8] K.L. Kees, J.J. Fitzgerald Jr., K.E. Steiner, J.F. Mattes, B. Mihan, T. Tosi, D. Mondoro, M.L. McCaleb, J. Med. Chem. 39 (1996) 3928.
[9] R. Bose, D.S.R. Murty, G. Chakrapani, J. Radioanal. Nucl. Chem. 265 (2005) 115.
[10] T. Ito, C. Goto, K. Noguchi, Anal. Chim. Acta 443 (2001) 41.
[11] A. Whitaker, J. Soc. Dyers Colour 111 (1995) 66.
[12] F. Bao, X. Lu, B. Kang, Q. Wu, Eur. Polym. J. 42 (2006) 928.
[13] M. Shi, F. Li, T. Yi, D. Zhang, H. Hu, C. Huang, Inorg. Chem. 44 (2005) 8929.
[14] F. Marchetti, C. Pettinari, R. Pettinari, Coord. Chem. Rev. 249 (2005) 2909.
[15] F.H. Allen, Acta Crystallogr. B 58 (2002) 380.
[16] I.J. Bruno, J.C. Cole, P.R. Edgington, M.K. Kessler, C.F. Macrae, P. McCabe, J. Pearson, R. Taylor, Acta Crystallogr. B 58 (2002) 876.
[17] W. Holzer, C. Kautsch, C. Laggner, R.M. Claramunt, M. Pérez-Torralba, I. Alkorta, J. Elguero, Tetrahedron 60 (2004) 6791.
[18] H.O. Burrus, G. Powell, J. Am. Chem. Soc. 67 (1945) 1468.
[19] L.N. Kurkovskaya, N.N. Shapem'ko, I.Y. Kvimko, Y.N. Koshelev, E.M. Sof'ina, Zh. Org. Khim. 9 (1973) 821.
[20] E. Kleinpeter, A. Koch, J. Phys. Org. Chem. 14 (2001) 566.
[21] C. Brassy, J.P. Mornon, J. Delettre, Acta Crystallogr., Sect. B 30 (1974) 2243.
[22] Y.-Y. Wang, Ch.-Ch. Shi, Q. Shi, Y.-C. Gao, Q.-Zh. Shi, Wuji Huaxue Xuebao 16 (2000) 321.
[23] C. Brassy, A. Renaud, J. Delettre, J.P. Mornon, Acta Crystallogr., Sect. B 30 (1974) 2246.
[24] M.B. Cingi, C. Guastini, A. Musatti, M. Nardelli, Acta Crystallogr., Sect. B 28 (1972) 667.
[25] V. Zelenak, K. Gyoryova, S. Vargova, Main Group Met. Chem. 22 (1999) 179.
[26] C. Brassy, M.Ch. Michaud, J. Delettré, J.P. Mornon, Acta Crystallogr., Sect. B 30 (1974) 2848.
[27] C. Mahadevan, A. Radha, M. Seshasayee, Z. Kristallogr. 169 (1984) 159.
[28] M. Vijayan, M.A. Viswamitra, Acta Crystallogr. 21 (1966) 522.
[29] X.-P. Yang, B.-S. Kang, W.-K. Wong, Ch.-Y. Su, H.-Q. Liu, Inorg. Chem. 42 (2003) 169.
[30] R.W. Baker, J.W. Jeffery, J. Chem. Soc., Dalton Trans. 2 (1974) 229.

[31] K.K. Bhandary, H. Manohar, K. Venkatesan, Acta Crystallogr., Sect. B 32 (1976) 861.
[32] W. Clegg, G. Bourhill, I. Sage, Acta Crystallogr. E 58 (2002) m159.
[33] A.L. Rheingold, W. King, Inorg. Chem. 28 (1989) 1715.
[34] Ch.-Y. Su, X.-P. Yang, A.-W. Xu, Z.-F. Zhang, H.-K. Liu, B.-Sh. Kang, Acta Crystallogr., Sect. C 56 (2000) e82.
[35] R. Winpenny, A. Dearden, S. Parsons, D. Messenger, Private Communication to CSD, 2005.
[36] G. Aromí, A.R. Bell, M. Helliwell, J. Raftery, S.J. Teat, G.A. Timco, O. Roubeau, R.E.P. Winpenny, Chem. Eur. J. 9 (2003) 3024.
[37] A.L. Dearden, S. Parsons, R.E.P. Winpenny, Angew. Chem. Int. Ed. 40 (2001) 151.
[38] A. Bell, G. Aromi, S.J. Teat, W. Wernsdorfer, R.E.P. Winpenny, Chem. Commun. (2005) 2808.
[39] G. Aromí, A. Bell, S.J. Teat, A.G. Whittaker, R.E.P. Winpenny, Chem. Commun. 1896 (2002).
[40] G. Aromí, O. Roubeau, M. Helliwell, S.J. Teat, R.E.P. Winpenny, Dalton Trans. 3436 (2003).
[41] B. Nanda, S. Padmanavan, B. Tripathy, A.S. Mittra, J. Indian Chem. Soc. 52 (1975) 533.
[42] M.A. Toporovskaya, N.V. Anisimova, T.D. Levintova, A.M. Pak, Khim. Farm. Zh. 27 (1993) 51.
[43] H. Moehrle, J. Tenczer, Arch. Pharm. 306 (1973) 419.
[44] V.I. Sokol, M.A. Ryabov, N.Yu. Merkur'eva, V.V. Davydov, Yu.V. Shklyaev, V.S. Sergienko, B.E. Zaitsev, Kristallografiya 41 (1996) 483.
[45] A.D. Garnovskii, B.I. Kharisov, E.L. Anpilova, A.V. Bicherov, O.Yu. Korshunov, A.S. Burlov, M.A. Méndez-Rojas, L.M. Blanco, G.S. Borodkin, I.E. Uflyand, U.O. Méndez, Polyhedron 23 (2004) 1909.
[46] A.D. Garnovskii, A.S. Antsyshkina, E.L. Anpilova, O.Yu. Korshunov, A.V. Bicherov, A.S. Burlov, G.G. Sadikov, V.S. Sergienko, I.E. Uflyand, Zh. Neorg. Khim. 48 (2003) 1992.
[47] H. Liang, X.-W. Wang, Z.-F. Chen, L. Huang, H.-L. Zou, J. Zhou, K.-B. Yu, Acta Crystallogr. E 60 (2004) m294.
[48] T.G. Cherkasova, O.V. Katkova, Zh. Neorg. Khim. 49 (2004) 1274.
[49] M.L. Kuznetsov, Yu.N. Medvedev, B.K. Belĭskii, A.I. Dementĭev, B.E. Zaitsev, Zh. Neorg. Khim. 42 (1997) 1114.
[50] V.I. Sokol, M.A. Ryabov, V.V. Davydov, N.Yu. Merkurĭeva, Yu.V. Shklyaev, V.S. Sergienko, B.E. Zaitsev, Russ. J. Inorg. Chem. 43 (1998) 492.
[51] V.I. Sokol, V.V. Davydov, V.S. Sergienko, N.Yu. Merkurĭeva, M.A. Ryabov, Yu.V. Shklyaev, S.M. Korchevoi, Russ. J. Inorg. Chem. 46 (2001) 226.
[52] H. Liang, Q. Yu, R.-X. Hu, Z.-Y. Zhou, X.-G. Zhou, Transition Met. Chem. 27 (2002) 454.
[53] V. Hovorka, L. Sucha, Coll. Czech. Chem. Commun. 25 (1960) 55.
[54] H. Barjesteh, J. Chakrabarti, J. Charalambous, O. Carugo, C.B. Castellani, Polyhedron 15 (1996) 1323.
[55] L.C. Emeleus, D.C. Cupertino, S.G. Harris, S. Owens, S. Parsons, R.M. Swart, P.A. Tasker, D.J. White, J. Chem. Soc., Dalton Trans. 1239 (2001).
[56] P.J. Robbins, J. Heterocyclic Chem. 14 (1977) 1107.
[57] M. Grayson, D. Eckroth (Eds.), Kirk-Othmer Encyclopaedia of Chemical Technology, vol. 6, 3rd ed., Wiley, NY, 1978, p. 819.
[58] V.A. Zaitseva, B.E. Zaitsev, A.K. Molodkin, A.A. Zhikharev, A.I. Ezhov, Zh. Neorg. Khim. 26 (1981) 1144.
[59] W. Bansse, N. Jager, E. Ludwig, U. Schilde, E. Uhlemann, A. Lehmann, H. Mehner, Z. Naturforsch. 52b (1997) 237.
[60] F.J. Lalor, T.J. Desmond, G.M. Cotter, C.A. Shanahan, G. Ferguson, M. Parvez, B. Ruhl, J. Chem. Soc., Dalton Trans. 1709 (1995).
[61] S. Trofimenko, J. Am. Chem. Soc. 91 (1969) 588.
[62] X.-Q. Lü, F. Bao, B.-Sh. Kang, Q. Wu, H.-Q. Liu, F.-M. Zhu, J. Organomet. Chem. 691 (2006) 821.
[63] J.-L. Wang, F. Ding, F.-M. Miao, Acta Crystallogr. E 59 (2003) m128.
[64] R.N. Jadeja, J.R. Shah, E. Suresh, P. Paul, Polyhedron 23 (2004) 2465.
[65] S.-M. Zhang, P.-F. Li, M. Yu, J.-L. Wang, Wuji Huaxue Xuebao 20 (2004) 439.
[66] F. Bao, R. Ma, X. Lü, G. Gui, Q. Wu, Appl. Organometal. Chem. 20 (2006) 32.
[67] A.-X. Li, Y. Yang, J.-L. Wang, Yingyong Huaxue 21 (2004) 49.
[68] S. Parsons, L. Emeleus. P. Tasker, P. Wood, Private Communication to CSD, 2004.
[69] F. Bao, X.-Q. Lü, H. Gao, G. Gui, Q. Wu, J. Polym. Sci., Part A: Polym. Chem. 43 (2005) 5535.
[70] F. Bao, X. Lü, Y. Qiao, G. Gui, H. Gao, Q. Wu, Appl. Organometal. Chem. 19 (2005) 957.
[71] F.R. Pérez, J. Belmar, C. Jiménez, Y. Moreno, P. Hermosilla, R. Baggio, Acta Crystallogr. C 61 (2005) m318.
[72] F. Bao, J. Feng, S.W. Ng, Acta Crystallogr. E 61 (2005) m2393.
[73] T.G. Takhirov, O.A. Dĭyachenko, D.B. Tagiev, A.L. Nivorozhkin, M.S. Korobov, R.Ya. Olekhnovich, L.E. Nivorozhkin, V.I. Minkin, Koord. Khim. 17 (1991) 711.
[74] P. Tasker, A. Smith, S. Parsons, D. Messenger, Private Communication to CSD, 2005.
[75] R.-M. Ma, S.-F. Sun, S.W. Ng, Acta Crystallogr. E 61 (2005) m2741.
[76] X.Q. Lue, F. Bao, Q. Wu, B.-S. Kang, S.W. Ng, Acta Crystallogr. E 60 (2004) m362.
[77] V.I. Sokol, V.V. Davydov, N.Yu. Merkur'eva, O.A. Al-Saleh, M.A. Ryabov, V.S. Sergienko, Yu.V. Shklyaev, Russ. J. Inorg. Chem. 47 (2002) 353.
[78] P. Tasker, A. Parkin, A. Smith, S. Parsons, D. Messenger, Private Communication to CSD, 2005.
[79] J.-L. Wang, A.-X. Li, Y.-J. Jia, S.-M. Zhang, Huaxue Xuebao 62 (2004) 2329.
[80] G. Xu, L. Liu, L. Zhang, G. Liu, D. Jia, J. Lang, Struct. Chem. 16 (2005) 431.
[81] L. Zhang, L. Liu, D. Jia, G. Xu, K. Yu, Inorg. Chem. Commun. 7 (2004) 1306.
[82] L. Zhang, L. Liu, G.-F. Liu, D.-Z. Jia, K.-B. Yu, Wuji Huaxue Xuebao 21 (2005) 291.
[83] S. Sawusch, N. Jäger, U. Schilde, E. Uhlemann, Struct. Chem. 10 (1999) 105.
[84] X. Hu, L. Zhang, L. Liu, G. Liu, D. Jia, G. Xu, Inorg. Chim. Acta 359 (2006) 633.
[85] Z.-Y. Yang, R.-D. Yang, F.-S. Li, K.-B. Yu, Polyhedron 19 (2000) 2599.
[86] Y.-L. Ji, L. Liu, D.-Z. Jia, K.-B. Yu, Jiegou Huaxue 21 (2002) 553.
[87] Y.-L. Ji, L. Liu, D.-Z. Jia, K.-B. Yu, Wuji Huaxue Xuebao 19 (2003) 345.
[88] L. Zhang, L. Liu, D. Jia, K. Yu, Struct. Chem. 15 (2004) 327.
[89] L. Zhang, L. Liu, G.-F. Liu, G.-Ch. Xu, D.-Z. Jia, J.-P. Lang, J. Chem. Crystallogr. 35 (2005) 583.
[90] L. Liu, D.-Z. Jia, Y.-M. Qiao, K.-B. Yu, Chin. J. Chem. 20 (2002) 286.
[91] A.K. El-Sawaf, D.X. West, F.A. El-Saied, R.M. El-Bahnasawy, Transition Met. Chem. 22 (1997) 360.
[92] K. Liang, D.-Z. Jian, W.-M. Bu, X.-C. Tang, Huaxue Xuebao 59 (2001) 1009.
[93] A.K. El-Sawaf, S. Hernández-Ortega, J. Valdés-Martínez, J.K. Swearingen, D.X. West, J. Chem. Crystallogr. 23 (2003) 105.
[94] J. Valdés-Martínez, S. Hernández-Ortega, D.X. West, A.K. El-Sawaf, R.M. El-Bahanasawy, F.A. El-Saied, Acta Crystallogr. E 61 (2005) m1593.
[95] A.K. El-Sawaf, D.X. West, R.M. El-Bahnasawy, F.A. El-Saied, Transition Met. Chem. 23 (1998) 227.
[96] P.N. Yadav, M.A. Demertzis, D. Kovala-Demertzi, S. Skoulika, D.X. West, Inorg. Chim. Acta 349 (2003) 30.
[97] M. Das, S.E. Livingstone, Inorg. Chim. Acta 19 (1976) 5.
[98] Y. Ji, L. Liu, D. Jia, Y.M. Qiao, K. Yu, J. Chem. Crystallogr. 32 (2002) 505.
[99] P.D. Callaghan, A.J. Elliott, S.S. Gandhi, M.S. Gibson, H. Mastalerz, D.J. Vukov, J. Chem. Soc., Perkin Trans. 11 (1981) 2948.
[100] S. Parsons, D. White, P. Tasker, P. Wood, Private Communication to CSD, 2004.
[101] D. Matt, N. Sutter-Beydoun, J.-P. Brunette, F. Balegroune, D. Grandjean, Inorg. Chem. 32 (1993) 3488.
[102] A.A. Tolmachev, A.I. Konovets, A.N. Kostyuk, A.N. Chernega, A.M. Pinchuk, Heteroat. Chem. 9 (1998) 41.
[103] G. Westöö, Acta Chim. Scand. 6 (1952) 1499.

[104] A.J. Mota, A. Dedieu, P. Kuhn, D. Matt, R. Welter, M. Neuburger, Dalton Trans. 19 (2005) 3155.
[105] D. Matt, M. Huhn, M. Bonnet, J. Tkatchenko, U. Englert, W. Kläui, Inorg. Chem. 34 (1995) 1288.
[106] P. Kuhn, D. Sémeril, C. Jeunesse, D. Matt, P. Lutz, R. Welter, Eur. J. Inorg. Chem. (2005) 1477.
[107] D. Matt, J.-C. Guillemin, R. Ziessel, F. Balegroune, D. Grandjean, Acta Crystallogr. C 50 (1994) 193.
[108] D. Matt, D. Lakkis, D. Grandjean, F. Balegroune, A. Laidoudi, Acta Crystallogr. C 48 (1992) 1408.
[109] R. Carballo, J.S. Casas, E. García-Martínez, G. Pereiras-Gabián, A. Sánchez, J. Sordo, E.M. Vázquez-López, Inorg. Chem. 42 (2003) 6395.
[110] J.S. Casas, M.V. Castaño, E.E. Castellano, J. Ellena, M.S. García-Tasende, A. Gato, A. Sánchez, L.M. Sanjuán, J. Sordo, Inorg. Chem. 41 (2002) 1550.
[111] J.S. Casas, M.V. Castaño, E.E. Castellano, M.S. García-Tasende, A. Sánchez, M.L. Sanjuán, J. Sordo, Eur. J. Inorg. Chem. (2000) 83.
[112] J.S. Casas, M.V. Castaño, M.S. García-Tasende, A. Sánchez, J. Sordo, A. Touceda, Polyhedron 24 (2005) 3057.
[113] J.S. Casas, M.V. Castaño, M.S. García-Tasende, E. Rodríguez-Castellón, A. Sánchez, L.M. Sanjuán, J. Sordo, Dalton Trans. (2004) 2019.
[114] P. Barbazán, R. Carballo, J.S. Casas, E. García-Martínez, G. Pereiras-Gabián, A. Sánchez, E.M. Vázquez-López, Inorg. Chem. 45 (2006) 7323.
[115] R. Carballo, J.S. Casas, E. García-Martínez, G. Pereiras-Gabián, A. Sánchez, J. Sordo, E.M. Vázquez-López, Acta Crystallogr. E 58 (2002) o787.
[116] S.-L. Guo, M. Wagner, M. Bolte, Acta Crystallogr., Sect. E: Struct. Rep. Online 57 (2001) m428.
[117] C. Astre, Bull. Soc. Chim. 17 (1915) 175.
[118] H. Koshima, M. Hamada, J. Heterocycl. Chem. 39 (2002) 1087.
[119] C. Pettinari, F. Marchetti, R. Pettinari, D. Martini, A. Drozdov, S. Troyanov, J. Chem. Soc., Dalton Trans. (2001) 1790.
[120] J. Belmar, J. Alderete, F. Leonardi, G. Leon, M. Parra, C. Zúñiga, Boll. Soc. Chil. Quim. 42 (1997) 355.
[121] L. Henning, G. Mann, Z. Chem. 28 (1988) 364.
[122] C. Mannich, B. Kather, Arch. Pharm. 257 (1919) 18.
[123] A. Yuchi, M. Shiro, H. Wada, G. Nakagawa, Bull. Chem. Soc. Jpn. 64 (1991) 760.
[124] K.A. Lysenko, M.L. Kuznetsov, Yu.N. Medvedev, B.E. Zaitsev, Crystallogr. Rep. 47 (2002) 262.
[125] F.R. Perez, J. Belmar, Y. Moreno, R. Baggio, O. Pena, New J. Chem. 29 (2005) 283.
[126] B. Adhikhari, O.P. Anderson, A. la Cour, R. Hazell, S.M. Miller, C.E. Olsen, H. Toftlund, J. Chem. Soc., Dalton Trans. (1997) 4539.
[127] A. la Cour, M. Findeisen, R. Hazell, L. Henning, C.E. Olsen, O. Simonsen, J. Chem. Soc., Dalton Trans. (1996) 3437.
[128] O. Costisor, I. Pantenburg, R. Tudose, G. Meyer, Z. Anorg. Allg. Chem. 630 (2004) 1645.
[129] O. Costisor, R. Tudose, I. Pantenburg, G. Meyer, Z. Naturforsch. 57b (2002) 1454.
[130] P. Weinberger, O. Costisor, R. Tudose, O. Baumgartner, W. Linert, J. Mol. Struct. 519 (2000) 21.
[131] R. Tudose, I. Pantenburg, G. Meyer, O. Costisor, M. Brezeanu, Rev. Roum. Chim. 49 (2004) 663.
[132] R. Tudose, I. Pantenburg, E.M. Mosoarca, G. Meyer, O. Costisor, Z. Anorg. Allg. Chem. 631 (2005) 2423.