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Coordinating ability of ligands derived from phenylenediamines

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Abstract

The preparation of coordinating agents derived from aromatic diamines is of special interest since the use of nitrogen atoms for coordination to a single cation is directly related to their situation in *ortho*, *meta* or *para* positions. In the case of diaminetetramethylenecarboxylic acids or Schiff bases derived from *o*-phenylenediamines, the proximity of the nitrogen atoms permits their simultaneous coordination to the same metal cation, leading mainly to monomer species. Combined with the lesser basicity of the nitrogen atoms of the aromatic diamines, the *o*-phenylenediaminetetramethylene-carboxylic acids are good sequestering agents for some metal ions. Complexes derived from *o*-phenylenediamine Schiff bases provide new and interesting environment for M–C funcionalities. Iron(III) complexes with *o*-phenylenediamine Schiff bases may present spin-crossover. On the other hand, the ligands derived from *m*- or *p*-phenylenediamines can only coordinate one nitrogen atom to any one metal cation. The formation of species with excess of ligand (2:1 ligand:metal ratio), with excess of metal (1:2 ratio), and monomers (1:1 ratio) is now possible. Moreover, the special conformation of the ligands with nitrogen atoms in *meta* or *para* positions on the aromatic ring facilitates the formation of dimer complexes since the ligands act as a bridge. The dinuclear complexes of those ligands with paramagnetic ions may present magnetic coupling. With the nitrogen atoms in *para* position, polymer complexes are also possible since the ligand acts as a bridge.

Keywords: Phenylenediamines; Polyaminecarboxylic acids; Schiff bases; Coordinating ability

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Nomenclature

MeCN	acetonitrile
H_2acen	*N*,*N*′-ethylenebis(acetylacetoneimine)
4-Cl-*o*-PhDTA	4-chloro-*o*-phenylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid
CyDTA	cyclohexanodiamine-*N*,*N*,*N*′,*N*′-tetraacetic acid
dmso	dimethylsulphoxide
DTTA-HP	*N*,*N*′-bis-(3-hydroxy-6-methyl-2-pyridylmethyl)-ethylene-triamine-*N*,*N*′,*N*″-triacetic acid
EDTA	ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid
ENDA-HP	*N*,*N*′-bis-(3-hydroxy-6-methyl-2-pyridylmethyl)-ethylenediamine-*N*,*N*′-diacetic acid
HBED	*N*,*N*-bis(2-hydroxybenzil)-ethylenediamino-*N*,*N*′-diacetic acid
imd	imidazole
mac	generic representation of a macrocyclic ligand
o-PBA	*o*-phenylenebis(oxamato)
m-PDA	*m*-phenylenediamine
o-PDA	*o*-phenylenediamine

p-PDA	*p*-phenylenediamine
m-PhDTA	*m*-phenylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid
o-PhDTA	*o*-phenylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid
p-PhDTA	*p*-phenylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid
py	pyridine
2,5-PyDTA	2,5-pyridinediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid
2,6-PyDTA	2,6-pyridinediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid
H_2salen	*N*,*N*′-ethylenebis(salicylideneimine)
H_2sal-4-Cl-*o*-phen	*N*,*N*′-4-chloro-*o*-phenylenebis(salicylideneimine)
3-F-H_2sal-*o*-phen	*N*,*N*′-*o*-phenylenebis(3-fluor-salicylideneimine)
H_2sal-*o*-phen	*N*,*N*′-*o*-phenylenebis(salicylideneimine)
H_2sal-*m*-phen	*N*,*N*′-*m*-phenylenebis(salicylideneimine)
H_2sal-3,4-toluen	*N*,*N*′-3,4-toluenebis(salicylideneimine)
H_2sal-2,4-toluen	*N*,*N*′-2,4-toluenebis(salicylideneimine)
H_2sal-2,6-toluen	*N*,*N*′-2,6-toluenebis(salicylideneimine)
SB	generic representation of a Schiff base
TCNQ	7, 7, 8, 8-tetracyanoquinodimethane
2,4-TDTA	2,4-toluenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid
2,5-TDTA	2,5-toluenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid
2,6-TDTA	2,6-toluenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid
3,4-TDTA	3,4-toluenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid
tbsal-*o*-phen	*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-*o*-phenylenediamine dianion
thf	tetrahydrofuran
TMPD	tetramethyl-*N*,*N*,*N*′,*N*′-*p*-phenylenediamine
p-TPBD	tetrakis-*N*,*N*,*N*′,*N*′-(2-pyridylmethyl)benzene-*p*-diamine

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1. Introduction

Compared with ligands derived from aliphatic diamines, the ligands derived from aromatic diamines present a special character:

(a) The type and number of the complex species formed with a metallic cation are directly related to the relative *ortho*, *meta* or *para* positions of the nitrogen atoms. Thus for polyaminecarboxylic acids and Schiff bases derived from *o*-phenylenediamines, the proximity of the nitrogen atoms permits simultaneous coordination of both to the same metal cation, leading mainly to monomer species. On the other hand, ligands derived from *m*- or *p*-phenylenediamines can only coordinate a nitrogen atom to any one metal cation. The formation of species with excess of ligands (2:1 ligand:metal ratio), with excess of metal (1:2 ratio), and monomers (1:1 ratio) is now possible. Moreover, the special conformation of the ligands with nitrogen atoms in *meta* or *para* positions on the aromatic rings facilitates the formation of dimer complexes since the ligand acts as a bridge. With the nitrogen atoms in *para* position, polymer complexes are also possible (since the ligand acts as a bridge).

(b) The aromatic amines are less basic than the aliphatic amines due to the delocalization of the electron-pair on the nitrogen atom towards the orbitals of the aromatic ring, the electron-density on the nitrogen atom available for bond formation being lower [1]. Thus, the protonation constants and the stability constants of the ligands derived from aliphatic diamines are greater than those of similar ligands derived from aromatic diamines. However, the lesser basicity of ligands derived from aromatic diamines has several advantages:

1. It is well known that EDTA and similar ligands derived from aliphatic diamines are relatively ineffective as selective chelating agents for Fe(III) because they do not prevent the precipitation of ferric hydroxide in the weakly alkaline range (pH 8–9) [2–5], whereas similar ligands derived from *o*-phenylenediamines such as *o*-PhDTA and 3,4-TDTA are better sequestering agents [6]. Moreover, EDTA and similar ligands are not good sequestering agents for Be(II), another cation with strong hydrolysis, whereas *o*-PhDTA and 3,4-TDTA are better sequestering agents: the lesser basicity of the nitrogen atoms allows Be(II) to compete favourably with H^+, to form the complex BeL^{2-} (ligand H_4L) at $pH < 4$, hindering the formation of the hydrolytic species of Be(II) [7–9].
2. The Schiff bases derived from aliphatic diamines, such as H_2salen, are unstable in acid aqueous solution because of their hydrolytic decomposition to yield aldehyde and primary amine. The salen–Fe(III) complex undergoes similar hydrolytic decomposition. However, the Schiff base H_2sal-*o*-phen, derived from *o*-phenylenediamine, and the sal-*o*-phen-Fe(III) complex are completely stable in acid medium and do not undergo any decomposition due to the less basic character of the *o*-PDA which remains unprotonated in the media where the ethylenediamine is completely protonated [10,11]. This allows the thermodynamic studies in the mixed solvent dmso:water (80:20 wt./wt.), in which H_2sal-*o*-phen and its complexes are soluble and stable [12,13].
3. Schiff base ligands provide new and interesting environments for M–C functionalities [14]. The reduction of cobalt–Schiff base complexes was explored as a function of the nature of the ligand [15]: in the case of substituted salen complexes, reduction occurred at the metal with the formation of bifunctional Co(I)–Na complexes, while for sal-*o*-phen derivatives the reductive coupling of two imino groups, which in turn leads to C–C bond bridging of the two Schiff base units, was observed. The reduction does not affect the oxidation state of the Co(II) but, rather, the ligand. Alkylation at the cobalt was observed with the formation of a Co(III)–C bond in [Co(sal-*o*-phen)(CH_3)] complex [15].
4. The octahedral structure is quite common in metal complexes of potentially hexadentate polyaminecarboxylates such as EDTA. This is, however, not the case for the complexes of *o*-PhDTA and 3,4-TDTA acids, since the substitution of the ethylenic (EDTA) for the phenylene (*o*-PhDTA) [16–22] or toluene

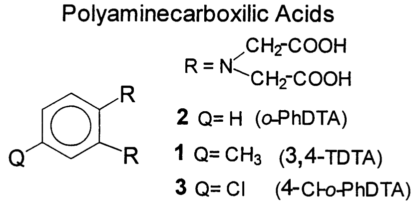
(3,4-TDTA) [23,24] backbone imposes a planar configuration on the diamine chelate ring and the coordination geometries are antiprismatic, twisted toward the trigonal prismatic. In the Schiff base complex [Zr(sal-*o*-phen)Cl_2(THF)], due to the presence of a very rigid tetradentate ligand, the two chlorine atoms are forced to be *trans*, while for less rigid tetradentate ligands, i.e. acen, both the *cis*- and *trans*- isomers have been observed [14].

So far, the most studied ligands derived from phenylenediamines are polyaminecarboxylic acids and Schiff bases, especially those derived from *o*-phenylenediamines. Both types of ligands are the object of this review.

2. Polyaminecarboxylic acids derived from phenylenediamines

2.1. *o*-Phenylenediamine derivatives

The synthesis of tetramethylenecarboxylic ligands consists of the reaction of the aromatic diamine with sodium or potassium chloroacetate [25] or bromoacetate [16]. Due to the formation of HCl or HBr it was observed that the yield was dramatically increased when a strict control of the pH and the temperature was maintained [16,26a,b,27]. Under this control yields around 70% were obtained for 3,4-TDTA (**1**) [26a], *o*-PhDTA (**2**) [26a,27] and 4-Cl-*o*-PhDTA (**3**) [26b]. When the pH is out of control in the preparation of the acids *o*-PhDTA, 3,4-TDTA and 4-Cl-*o*-PhDTA, an internal cyclization of a methylcarboxylic group is produced forming carboxylic acids with quinoxalinic structure [26b,28].



Grimes et al. studied the thermodynamic stability in aqueous solution of the alkaline earth chelates of *o*-PhDTA [29]. The stability constants with this ligand were found to be in the order $K_{\mathrm{MgL}} < K_{\mathrm{CaL}} > K_{\mathrm{SrL}} > K_{\mathrm{BaL}}$, in agreement with the known chelate stability orders for the alkaline earth metals.

The coordinating ability of the *o*-PhDTA ligand has been intensively studied by Nakasuka et al. [22,30–33]. The complex formation with monovalent cations Li(I) and Na(I) [30], divalent cations Be(II) [7], Mg(II) [7], Ca(II), Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) [27], heavy divalent toxic cations Cd(II), Hg(II) and Pb(II) [31] and the trivalents Fe(III) [22] and the lanthanoids(III) (La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) [32] have been studied. The log K values are presented in Table 1. The main studies consisted in the determination of the stability constants in aqueous solution of the complexes formed, and the technique most used is potentiometry [7,27,31,32]. Spectrophotometric studies have been used

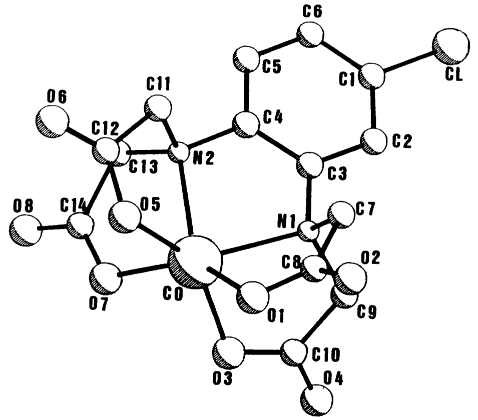


Fig. 1. View of the structure of the anionic complex [Co(4-Cl-*o*-PhDTA)]$^{2-}$. Adapted from Ref. [42].

when potentiometric measurements were not able to establish the values of the stability constants [27,30]. The use of ion-selective electrodes in a ligand buffer has been found to be very useful when studying the formation of very stable complexes [27,31,32]. Proton NMR studies have been performed for La(III) and Lu(III) complexes [32] and ^{17}O-NMR studies for Fe(III) complexes [22]. In all cases the models consisted in mononuclear protonated [MHL], unprotonated [ML] and hydroxocomplexes [M(OH)L]. The Irving-Williams order of complexation is fulfilled. Due to the lesser basicity of the nitrogen atoms in *o*-PhDTA, the complexes are formed at very low pH. This is particularly interesting in the case of Be(II), a cation with very important hydrolysis. The complexation by this ligand at very low pH prevents the hydrolysis and the complexes formed are very stable up to neutral medium. This allows a titrimetric determination of Be(II) with *o*-PhDTA [7], that is not possible with EDTA or CyDTA. Calorimetric [26,30–32] studies have been carried out in order to establish the changes in enthalpy and entropy. In most cases the complex formation was endothermic and the complexes were found to be stable due to the large change in entropy. The crystal structures of many complexes have been solved. Hexacoordination has been observed for Co(II) [16], Zn(II) [21] and Cu(II) [18] ([ML]$^{2-}$) complexes. *o*-PhDTA is a hexadentate ligand but since this ligand is not flexible, considerable distortion from octahedral geometry twisting towards a trigonal prism has been observed (Fig. 1 for Co(II) and 4-Cl-*o*-PhDTA). For Zn(II) also a protonated complex is obtained $H_2[Zn(H_2O)L]$, the protonated species retrieving the octahedral geometry to a considerable extent by dissociation of a carboxyl group from the central metal atom [21] (Fig. 2). Seven-coordination is found for Mg(II) [20], Mn(II) [17] and Fe(III) [22] $[M(OH_2)L]$ complexes (similar to Fe-4-Cl-*o*-PhDTA in Fig. 3). In the Mg(II) complex (Fig. 4), the molecular geometry is close to a water capped trigonal prism and the latter has a roughly pentagonal-bipyramidal shape. The Cd(II) complex (Fig. 5) [19] exhibits octa-coordination, two positions of the coordination sphere of the central atom being occupied by water molecules. In this compound a discrete tetranuclear entity $[Cd(OH_2)_2]_2[Cd(OH_2)L]_2$ is formed.

Table 1
Stability constants (log *K*) at 25°C of the complexes ML for the equilibrium $M+L \rightleftarrows ML$, for the ligands 3,4-TDTA, *o*-PhDTA and 4-Cl-*o*-PhDTA

Ion	3,4-TDTA	*o*-PhDTA	4-Cl-*o*-PhDTA	Reference
H^+	6.80	6.41	5.79	[6][a]
		6.41		[27][b]
Li^+	2.31	2.39		[33][c]
		1.99		[30][d]
Na^+	1.37	1.52		[33][c]
		0.73		[30][d]
K^+		0.28		[33][c]
Be^{2+}	6.88	6.51	5.79	[8][e]
		6.48		[7][b]
Mg^{2+}	6.80	6.40	6.09	[8][e]
		6.48		[7][b]
		7.30		[29][f]
Ca^{2+}	8.61	8.23	7.71	[6][a]
		8.27		[27][b]
		8.10		[29][f]
Sr^{2+}	6.59	6.22	5.53	[3,35][c]
		6.40		[29][f]
Ba^{2+}	5.11	4.85	4.21	[3,35][c]
		4.80		[29][f]
Mn^{2+}		11.37		[27][b]
Fe^{2+}		12.20		[27][b]
Co^{2+}		13.18	12.75	[27][b],[36][c]
Ni^{2+}		13.48	14.93	[27][b],[36][c]
Cu^{2+}	15.57	15.21	14.40	[6][a]
		15.21		[27][b]
Zn^{2+}		12.89	12.35	[27][b],[35][c]
Cd^{2+}		13.37	12.15	[31][e],[35][c]
Hg^{2+}		17.38		[31][e]
Pb^{2+}		13.89		[31][e]
Fe^{3+}	22.05	21.82	20.99	[6][a]
La^{3+}		11.39		[32][b]
Pr^{3+}		12.26		[32][b]
Nd^{3+}		12.63		[32][b]
Sm^{3+}		13.35		[32][b]
Eu^{3+}		13.65		[32][b]
Gd^{3+}		13.89		[32][b]
Tb^{3+}		14.46		[32][b]
Dy^{3+}		14.89		[32][b]
Ho^{3+}		15.18		[32][b]
Er^{3+}		15.55		[32][b]
Tm^{3+}		15.87		[32][b]
Yb^{3+}		16.06		[32][b]
Lu^{3+}		16.26		[32][b]

[a] $I=0.5$ M (KNO_3).
[b] $I=1$ M ($NaClO_4$).
[c] $I=0.1$ M (KCl).
[d] $I=0.1$ M (Et_4NClO_4).
[e] $I=0.5$ M ($NaClO_4$).
[f] $I=0.1$ M, $T=30$°C.

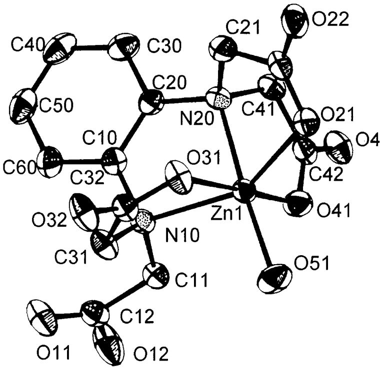


Fig. 2. ORTEP view of the $H_2[Zn(H_2O)L]$ complex, (L = *o*-PhDTA). Adapted from Ref. [21].

The complex formation in aqueous solution by the ligands 3,4-TDTA, *o*-PhDTA and 4-Cl-*o*-PhDTA has been intensively studied by Mederos et al. [6,8,9,23,24,33–37,42,43]. Complexes formed with alkaline [33] and alkaline earths [8,34,35], Zn(II) and Cd(II) [35], Co(II), Ni(II) and Cu(II) [36] have been studied by potentiometry. Mononuclear complexes are formed ($[MH_2L]$, $[MHL]$, $[ML]$ and $[M(OH)L]$), and the Irving–Williams order of complexation is fulfilled. The stability constants are presented in Table 1.

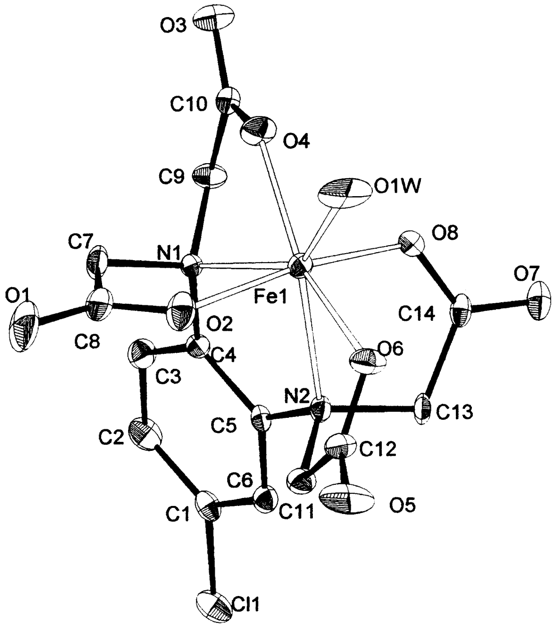


Fig. 3. ORTEP view of the $[Fe(OH_2)(4\text{-Cl-}o\text{-PhDTA})]^-$ anionic chelate complex. Adapted from Ref. [6].

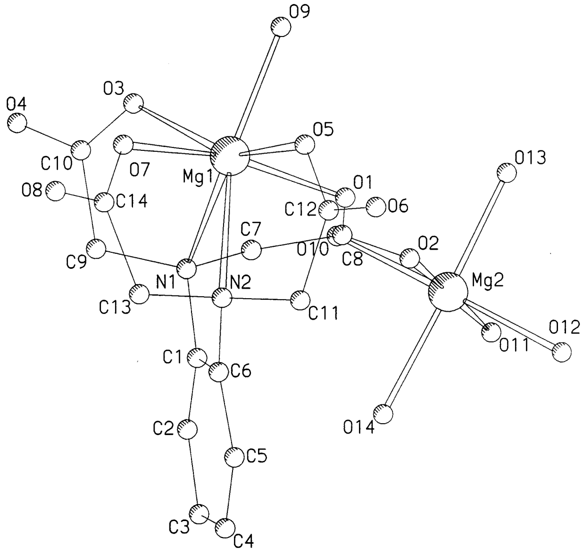


Fig. 4. View of the structure of the [$(H_2O)Mg$-μ-(*o*-PhDTA)-$Mg(H_2O)_5$] dinuclear complex. Drawn using data from Ref. [20].

The coordinating ability of the very toxic cation Be(II) has been widely studied in aqueous solution with the ligands 3,4-TDTA, *o*-PhDTA and 4-Cl- *o*-PhDTA [8,9,37]. This ligand forms the complexes $[BeHL]^-$ and $[BeL]^{2-}$. The stability constants are presented in Table 1. The selective uptake of Be(II) was analysed by means of the chemical speciation diagrams (Fig. 6 for 3,4-TDTA acid) as well as the so-called conditional of effective formation constants $K^{\text{eff}}_{\text{BeL}}$ [38,39]. With respect to H^+, the order 3,4-TDTA > *o*-PhDTA > 4-Cl-*o*-PhDTA ≫ EDTA is found [8,9]. This result indicates that, in competition with H^+, 3,4-TDTA, *o*-PhDTA and 4-Cl-*o*-PhDTA are good sequestering agents for Be(II) in the pH range 4.5–6, and analogously to *o*-PhDTA [7], these ligands can potentially be used for the analytical determination of Be(II). The lesser basicity of the nitrogen atoms of the aromatic diamines allows the complex $[BeL]^{2-}$ to compete favorably with the species H_2L^{2-} and HL^{3-} of the ligand, its formation beginning at $pH < 4$, hindering the formation of the hydrolytic species of the Be(II) (Fig. 6).

A Cu-ion selective electrode has been used for the determination of the stability constants of the complexes of Cu(II) [6], and metal to metal competition has been successfully used in order to establish the stability constants of the complexes formed by these ligands with Fe(III). Fig. 7 shows the effective binding constants ($\log K^{\text{eff}}_{\text{FeL}}$) [38,39], as a function of pH for Fe(III) with the ligands HBED, ENDA-HP and DTTA-HP, which as has been said by Martell et al. [5,40,41], are effective sequestering agents for Fe(III), compared with 3,4-TDTA, o-PhDTA, and 4-Cl-*o*-PhDTA. It is found that, in general, the ligands o-PhDTA and 3,4-TDTA are better sequestering agents in acid medium [6], which could be interesting from the industrial point of view. Calorimetric studies have been carried out for Cu(II) and Fe(III) complexes, the high stability of the complexes being found to be due to the large change in entropy [6]. Compared the stability constants of the complexes formed by EDTA, 3,4-TDTA, *o*-PhDTA and 4-Cl-*o*-PhDTA, the following order of complexation is mainly found:

EDTA > 3,4-TDTA > *o*-PhDTA > 4-Cl-*o*-PhDTA

3,4-TDTA, o-PhDTA and 4-Cl-*o*-PhDTA show a drastic decrease in the basicity of two nitrogen atoms compared with EDTA, as expected from the electron withdrawing effect of the benzene ring. The electron donor effect of the methyl group in 3,4-TDTA and the additional electron withdrawing effect of the Cl atom in 4-Cl-*o*-PhDTA produces the sequence. Although these ligands form lesser stable complexes than EDTA, it has been proved that due to the less affinity of the nitrogen atoms for the H^+ ion, these ligands are very good sequestering agents for most metal cations in acid medium [6,8].

The crystal structures of the complexes formed by 4-Cl-*o*-PhDTA with Co(II) [41] (Fig. 1) and Fe(III) [6] (Fig. 3) and by 3,4-TDTA with Zn(II) [23] and Fe(III) [24] have been solved. The molecular structures have been found to be analogous to those found for *o*-PhDTA. [17–21]. The Fe(III) is seven-coordinated $[FeL(OH_2)]^-$

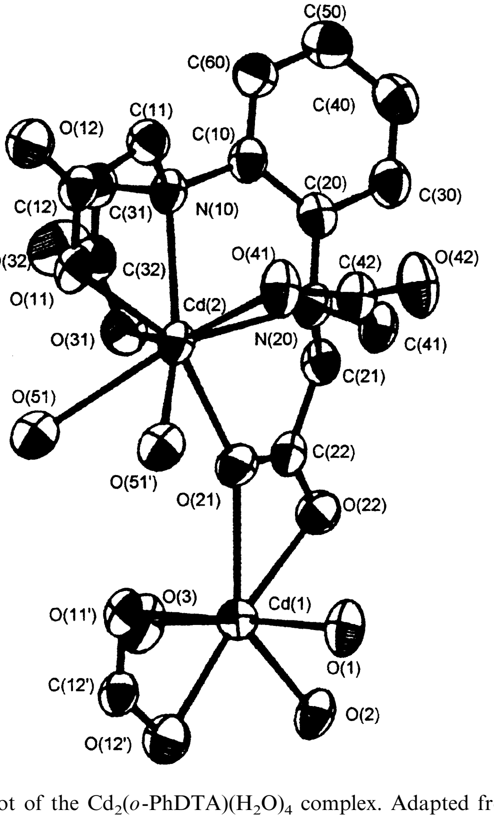


Fig. 5. ORTEP plot of the $Cd_2(o\text{-PhDTA})(H_2O)_4$ complex. Adapted from Ref. [19].

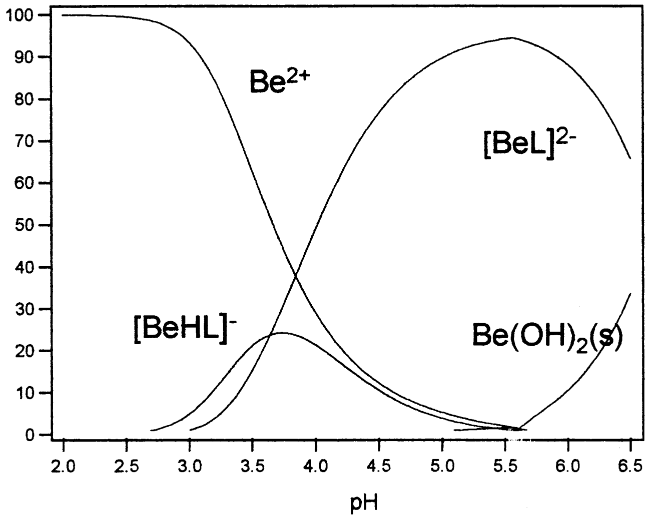


Fig. 6. Species distribution diagram as a function of pH for 3,4-TDTA–Be(II) at ligand:metal ratio 1:1 and $C_M = 3.0$ mM. Drawn using data from Ref. [8].

(Fig. 3) with one water molecule filling the seventh position. In diaminetetramethylenecarboxylic acid derivatives of *o*-phenylenediamines, the greater proximity of the nitrogen atoms permits the simultaneous coordination of both to the same metal cation, forming monomer complexes: Figs. 1–5 and Table 1. This table shows that *o*-PhDTA, 3,4-TDTA and 4-Cl-*o*-PhDTA are good chelating agents (Figs. 6 and 7 for Be(II) and Fe(III), respectively).

The complex formation of 3,4-TDTA and *o*-PhDTA with the very toxic metals Cd(II) and Pb(II) has been studied by potentiometry with very promising results [43]. The formation of $[ML_2]$ type complexes has been observed for Cd(II). This is the first time that complexes in ratio metal:ligand 1:2 have been observed for this type of ligands. 3,4-TDTA and *o*-PhDTA are very good sequestering agents for

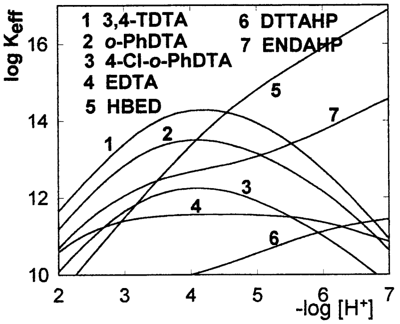
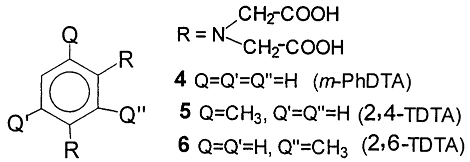


Fig. 7. Effective stability constants for Fe(III) with different ligands as a function of pH. Adapted from Ref. [6].

Cd(II) in acidic medium. Moreover, the crystal structures of the M[ML] compounds have been solved for the 3,4-TDTA complexes of Cd(II) and Pb(II). It has been found that the former forms discrete tetranuclear moieties whereas the latter has a chain structure. Cd(II) is seven-coordinated and Pb(II) hexacoordinated.

2.2. *m*-Phenylenediamine derivatives



The diaminetetramethylenecarboxylic acids, *m*-PhDTA (**4**) [44], 2,4-TDTA (**5**) [45], 2,6-TDTA (**6**) [46] and 2,6-PyDTA [47] were prepared according to the Blasius and Olbrich method [44], basically by the reaction of the aromatic diamine with sodium or potassium chloroacetate or bromoacetate in alkaline medium and subsequent addition of HCl (25%) to give a precipitate of *m*-PhDTA and monosodic or monopotassic salt of 2,4-TDTA [45] or 2,6-PyDTA, respectively [47]. When the acid is very soluble, addition at pH 7 of a concentrated solution of $Cd(NO_3)_2$ and subsequent addition of ethanol afforded a precipitate of the Cd_2L salt (ligands H_4L). The acids 2,4-TDTA [45], 2,6-TDTA [46] and 2,6-PyDTA [47] were isolated by passing a current of H_2S through a suspension of the salt in water and after separation of the precipitate of CdS by filtration. The acids were characterized by elemental analyses, ^{1}H-NMR, IR and mass spectra, potentiometric and conductimetric studies, and UV spectra in aqueous solution as a function of the pH [48]. The UV spectra confirm the protonation of the nitrogen atoms in aqueous solution [45–48]. Other ligands with two [45–47] or three [45] carboxylic groups were also prepared.

In the case of ligands derived from *o*-phenylenediamines (see Section 2.1), the greater proximity of the nitrogen atoms permits the simultaneous coordination of both to the same metal cation. Contrarily, the ligands derived from *m*-phenylenediamines can only coordinate one nitrogen atom to any one metal cation. The special conformation of the ligands with the nitrogen atoms in *meta* positions on the aromatic ring, facilitates the formation of the dimer complexes since the ligands act as a bridge. These ligands can therefore coordinate in two spheres, and bimetallic species M_2L are also possible. The formation of species with excess of ligand is also possible since each iminodiacetic group of the ligand is not sufficient coordinatively to saturate the central ion.

Previous potentiometric, spectrophotometric and conductimetric studies in aqueous solution of *m*-PhDTA acid by Uhlig and Hermann [49], González-García and Sánchez-Santos [50] and Mederos et al. [51,52] identified H_2ML, HML^- and ML^{2-} monomer complexes, and binuclear complexes M_2L (M(II) = Mg, Ca, Sr, Ba, Mn, Cd, Zn, Co, Ni, Cu) and the possibility of the formation of dimer complexes, in ligand:metal ratio 2:2 was considered. Similar studies of 2,4-TDTA acid were also carried out [53].

Potentiometric studies in aqueous solution (25°C, $I = 0.5$ M in $NaClO_4$) and analysing the experimental data by means of the NERNST/LETA version [54] of the LETAGROP program [55], for the Be(II)-*m*-PhDTA system [56], showed, for the first time, the formation of the complexes with excess of ligand $[Be(H_2L)_2]^{2-}$ and $[Be(HL)_2]^{4-}$, in addition to the 1:1 species $[BeH_2L]$, $[BeHL]^{-}$ and $[BeL]^{2-}$. The formation of complex species with excess of ligand, in a 2:1 ligand:metal ratio, was confirmed for Cu(II) with *m*-PhDTA in aqueous solution [57]. The formation of complexes with excess of metal (ratio ligand:metal 1:2), was also confirmed [57] in aqueous solution (complexes Cu_2HL^{+} and Cu_2L). These species with excess of Cu(II) were confirmed in aqueous solution for the 2,4-TDTA, 2,6-TDTA and 2,6-PyDTA acids [58]. The species M_2L (M = Cu, Ni) for *m*-PhDTA acid were identified in solid state by Uhlig and Hermann [59].

More recent potentiometric studies in aqueous solution (25°C, $I = 0.1$ M in KCl) for Co(II) with *m*-PhDTA [60] (ligand:metal ratios 2:1, 1:1 and 1:2, $C_M = 1$ or 2 mM; experimental data analyzed by LETAGROP [60,61]), Ni(II) with *m*-PhDTA [61] (ligand:metal ratios 2:1, 1:1 and 1:2, $C_M = 1$, 2 and 3 mM; experimental data analyzed by LETAGROP [60,61]); Cu(II) with *m*-PhDTA [62] (ligand:metal ratio 1:1, $C_M = 2$–10 mM; experimental data analyzed by LETAGROP [60,61] and MINIQUAD [65]); Ni(II) and 2,6-PyDATA [62] (ligand:metal ratio 3:1, 1:1 and 1:3, $C_M = 1$–12 mM; experimental data analyzed by LETAGROP [60,61] and MINIQUAD [65]); Cu(II), Ni(II), Co(II), Zn(II), Cd(II) and Mn(II) with 2,6-TDTA acid [63] (ligand:metal ratios 3:1, 2:1, 1:1, 1:2 and 1:3, $C_M = 0.5$–10 mM; experimental data analyzed by SUPERQUAD [66]); and Cu(II), Ni(II), Co(II), Zn(II) and Mn(II) with 2,4-TDTA acid [64] (ligand:metal ratio 3:1, 1:1 and 1:3, $C_M = 1$–10 mM; experimental data analyzed by SUPERQUAD [66]), confirm the presence of dimer species 2:2. The dimer species $[M_2L_2]^{4-}$ has been identified for the first time in potentiometric studies in aqueous solution. Moreover, species with excess of ligand (ratio ligand:metal 2:1) were confirmed for Cd(II) with 2,6-TDTA [63] and for Cu(II), Ni(II) and Zn(II) with 2,4-TDTA [64]. Species with excess of metal (ratio ligand:metal 1:2), were confirmed for Cu(II), Ni(II), Co(II) and Zn(II) for 2,4-TDTA [64]. The stability constants of the complex species formed are summarized in Table 2. In Figs. 8(a and b) are presented the species distribution diagrams as a function of $-\log[H^{+}]$ for the Cu(II)-2,4-TDTA system at $C_M = 2$ mM in the ratios ligand:metal 3:1 (a) and 1:3 (b). The formation of species with excess of ligand, dimer species and with excess of metal, respectively, was observed. In Figs. 9(a and b) is presented the species distribution diagram as a function of the $-\log[H^{+}]$ for the Ni(II)-2,4-TDTA system (ligand:metal ratio 1:1): (a) $C_M = 2$ mM; (b) $C_M = 10$ mM (similar diagrams can be drawn for Cu(II) and Co(II)). The diagram indicates that the percentage of the dimer species must increase with the concentration since the equilibria $2[ML]^{2-} \Leftrightarrow [M_2L_2]^{4-}$ are displaced to the right (Table 2).

From a concentrated solution with a ligand:metal ratio of 1:1 at pH 6 (see Fig. 9), single crystals of the complexes $Na_4[Cu_2(m\text{-PhDTA})_2] \cdot 18H_2O$ (**a**) [62],

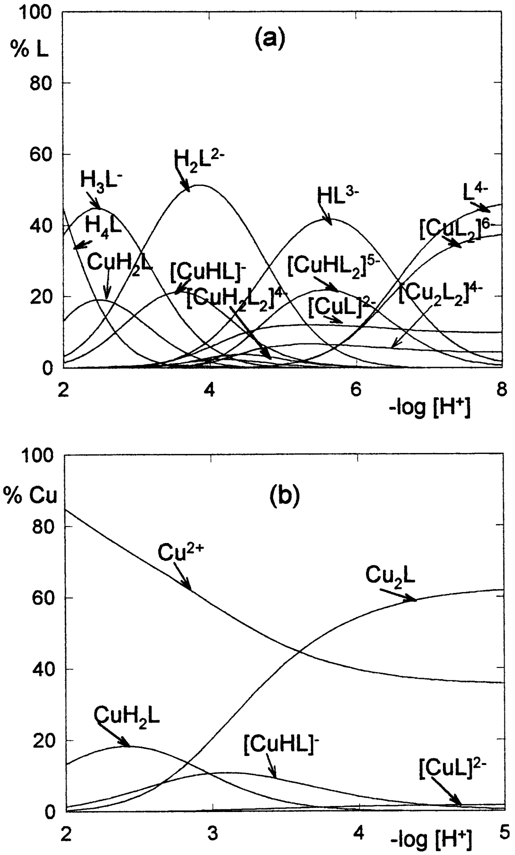


Fig. 8. Species distribution diagram as a function of pH for the Cu(II)-2,4-TDTA system at $C_M = 2.0$ mM, (a)% L, ligand:metal ratio 3:1; (b)% Cu, ligand:metal ratio 1:3. Adapted from Ref. [64].

$Na_4[Co_2(m\text{-}PhDTA)_2] \cdot 10H_2O$ (**b**) [62] (Fig. 10), $Na_4[Ni_2(2,6\text{-}PyDTA)_2] \cdot 8H_2O$ (**c**) [62], $Na_4[Ni_2(2,4\text{-}TDTA)_2] \cdot 15H_2O$ (**d**) [64] (Fig. 11), $Na_4[Zn_2(2,4\text{-}TDTA)_2] \cdot 15H_2O$ (**e**) [67] and $Na_4[Cu_2(2,4\text{-}TDTA)_2] \cdot 20H_2O$ (**f**) [64] (Fig. 12), were obtained and their crystal structures determined. X-ray diffraction structural analyses revealed that the structures (**a**) (**b**) (**c**) and (**f**) are centrosymmetrical (C_i), while (**d**) and (**e**) are C_1. For Co(II), Ni(II) and Zn(II) complexes, each metal atom is surrounded by four carboxylic oxygens and two amine nitrogens in a distorted octahedron, while for Cu(II) the octahedron is more distorted (elongated bipyramid, Jahn–Teller effect). The complexes $Na_4[Co_2(2,4\text{-}TDTA)_2] \cdot 12H_2O$ (**g**) [64] and $Na_4[Mn_2(2,4\text{-}TDTA)_2] \cdot 10H_2O$ (**h**) [64] were also characterized. The electronic properties of the complexes (**a**)–(**h**) have been characterized by spectroscopic techniques and variable-temperature magnetic susceptibility measurements. An orbital interpretation of the pathway of exchange interaction in this series of dimeric complexes is presented. Complexes (**d**) Ni(II), (**g**) Co(II) and (**h**) Mn(II) present a weak intramolecular antiferromagnetic interaction. Complexes (**c**) and (**f**), Cu(II) present magnetically isolated Cu(II) ions.

Table 2

(a) Ionization constants of the ligands (pK_i) (25°C and $I = 0.1$ M in KCl) [62,64,82]

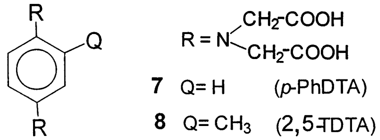
Equilibria	*m*-PhDTA	2,4-TDTA	2,6-TDTA	2,6-PyDTA	*p*-PhDTA	2,5-TDTA
$H_4L/H_3L^- + H^+$	2.11	2.08	2.31	2.12	2.10	1.85
$H_3L^-/H_2L^{2-} + H^+$	2.79	3.07	3.47	2.92	2.90	2.44
$H_2L^{2-}/HL^{3-} + H^+$	5.00	4.81	4.54	5.03	4.85	4.55
$HL^{3-}/L^{4-} + H^+$	5.75	6.57	6.14	6.07	6.05	7.21

(b) Formation constants (log K) of the complexes of *m*-PhDTA, 2,6-PyDTA, 2,4-TDTA and 2,6-TDTA ligands (25°C and $I = 0.1$ M in KCl) [62,64]

	m-PhDTA			2,6-PyDTA	2,4-TDTA			2,6-TDTA		
	Cu^{2+}	Co^{2+}	Ni^{2+}	Ni^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}
$M^{2+} + H_2L^{2-}/M(H_2L)$	4.47	2.06	1.70		3.57	1.10		3.37	1.57	
$M^{2+} + HL^{3-}/[MHL]^-$	6.65	3.33	3.98		5.41	3.21	2.65	4.92	2.19	2.10
$M^{2+} + L^{4-}/[ML]^{2-}$	8.22	5.02	5.26	4.59	7.49	5.20	4.71	6.30	2.73	2.27
$2M^{2+} + 2L^{4-}/[M_2L_2]^{4-}$	17.92	12.93	14.38	10.85	17.56	12.70	12.16	14.66	8.77	8.92
$M^{2+} + 2H_2L^{2-}/[M(H_2L)_2]^{2-}$	7.62									
$M^{2+} + H_2L^{2-} + HL^{3-}/[M(H_2L)(HL)]^{3-}$	9.65									
$M^{2+} + HL^{3-} + L^{4-}/[M(HL)L]^{3-}$	10.81									
$M^{2+} + 2L^{4-}/[ML_2]^{6-}$	10.65				10.33	7.27				
$2M^{2+} + HL^{3-}/[M_2(HL)]^+$						4.2	4.55		4.5	5.08
$2M^{2+}L^{4-}/[M_2L]$	12.07		7.86		11.42			9.69		
$M^{2+} + 2HL^{3-}/[M(HL)_2]^{4-}$	10.16				7.6	5.0				
$2[ML]^{2-}/[M_2L_2]^{4-}$	1.36	2.89	3.86	1.67	2.59	2.30	2.74	2.06	3.31	4.38
$[ML]^{2-} + M^{2+}/[M_2L]$	3.85		2.58		3.93			3.39		

m-Phenylenediamine-*N*,*N*′-disuccinic acid has been prepared and characterized [68] and its coordinating ability in aqueous solution (25°C, $I = 0.5$ M in NaCl) has been studied by potentiometric and conductimetric methods [69].

2.3. *p*-Phenylenediamine derivatives



7 Q=H (*p*-PhDTA)
8 Q=CH$_3$ (2,5-TDTA)

p-PhDTA acid (**7**) was prepared for the first time by Michaelis and Schubert [70], and later by Rodríguez Ríos et al. [71], Uhlig and Hermann [72] and Chopoorian et al. [73]. The *p*-PhDTA acid (**7**) is prepared according to the Blasius and Olbrich method [44], first precipitating and purifying the white disodium salt and then acidifying its concentrated aqueous solution with HCl to pH 1, to afford a white precipitate of the acid [57]. Precautions were taken to maintain an inert atmosphere (argon) and prevent the access of light during the preparation and preservation and the study of their solutions since they are photosensitive and oxidize readily [52]. In order to study the coordinating ability in solution it is better to prepare the very pure monosodic salt of *p*-PhDTA acid, [82]. *p*-Phenylenediamine-*N*,*N*-diacetic acid has also been prepared [74]. 2,5-TDTA acid (**8**), very soluble in aqueous solution, cited by Michaelis et al. [75], was prepared by Rodríguez Ríos and Mederos [76] by the Blasius and Olbrich method [44] and precipitated at pH 7 as the salt Cd$_2$L (ligand H$_4$L) and after separation of the Cd(II) as CdS with a current of H$_2$S [76]. The UV spectra as a function of the pH for *p*-PhDTA and 2,5-TDTA acids confirm the protonation of the nitrogen atoms in aqueous solution [48,52]. 2,5-PyDTA acid has also been prepared and characterized [47].

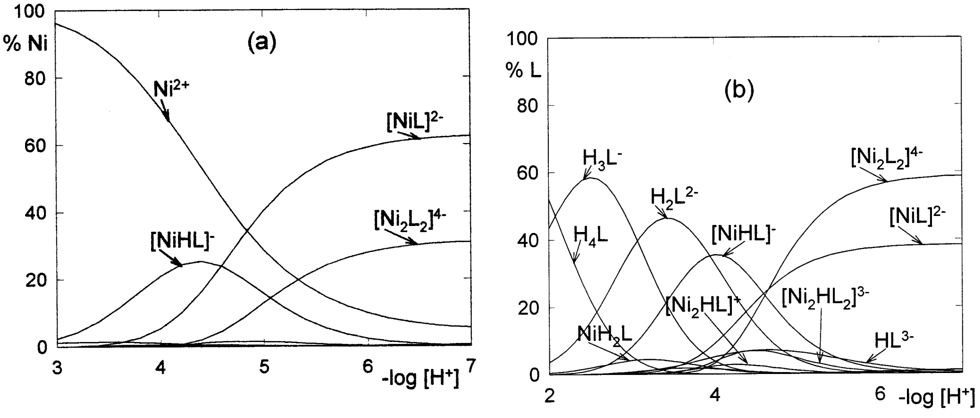


Fig. 9. Species distribution diagram as a function of pH for the Ni(II)-2,4-TDTA system (ligand:metal ratio 1:1). (a) %Ni, $C_M = 2.0$ mM; (b) %L, $C_M = 10.0$ mM. Adapted from Ref. [64].

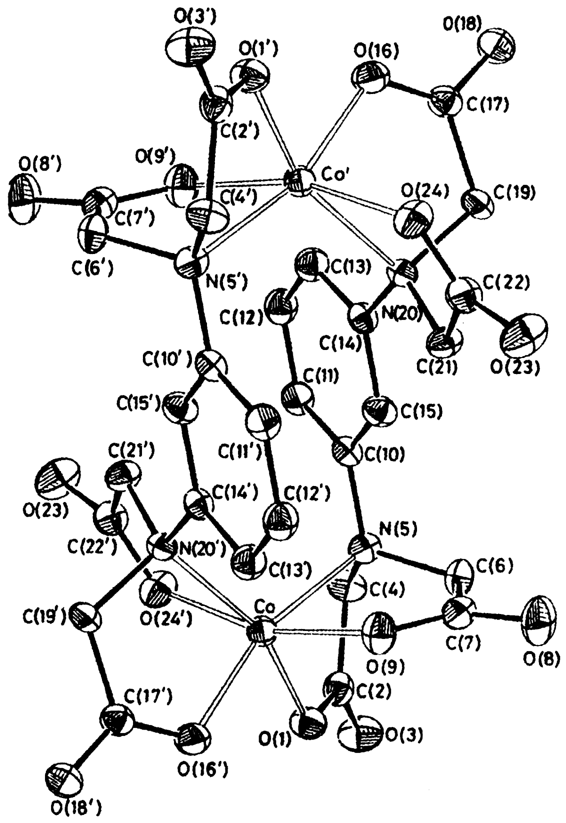


Fig. 10. View of the molecular structure of the anionic complex $[Co_2(m\text{-PhDTA})_2]^{4-}$. Adapted from Ref. [62].

Similar to *m*-PhDTA acid, the ligands derived from *p*-phenylenediamines, *p*-PhDTA and 2,5-TDTA can only coordinate one nitrogen atom to any one metal cation. Consequently, it is to be expected that the *para* positions of the nitrogen atoms on the aromatic ring facilitate the formation of polymer complexes since the ligand acts as a bridge. The formation of species with excess of metal such as the bimetallic species M_2L is possible, as well as the formation of the species with excess of ligand since each iminodiacetic group of the ligand is not sufficient coordinatively to saturate the central ion.

Previous potentiometric, spectrophotometric and conductimetric studies in aqueous solution (25°C, $I = 0.1$ M in KCl) of *p*-PhDTA acid [52,77] and 2,5-TDTA acid [78], identified MH_2L, MHL^- and ML^{2-} monomer complexes and binuclear complexes M_2L (M(II) = Mg, Ca, Mn, Cd, Zn, Co, Ni, Cu), and the possibility of the formation of dimer and polymer complexes was considered. The values for Cu(II) were the most questionable. Bimetallic complexes M_2L (M(II) = Mg, Ca, Ba, Mn, Cd, Zn, Co, Ni, Cu and Pb) for 2,5-TDTA acid [79] were prepared in solid state.

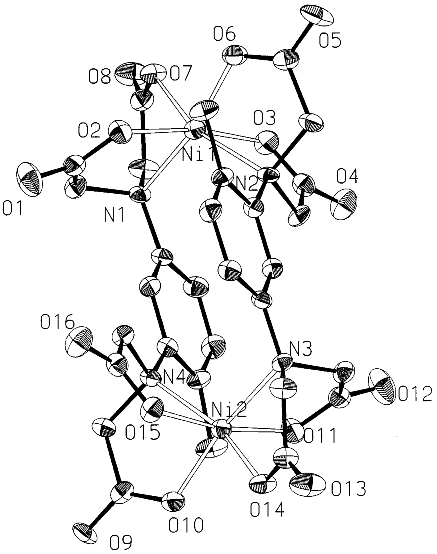


Fig. 11. ORTEP view of the anionic complex $[Ni_2(2,4\text{-}TDTA)_2]^{4-}$. Adapted from Ref. [64].

Potentiometric studies in aqueous solution (25°C, $I = 0.1$ M in KCl) and analysing the experimental data by means of the LETAGROP program [54,55] for both the Cu(II)-*p*-PhDTA system [57] and Cu(II)-2,5-TDTA system [80], showed, for the first time, the formation of complexes with excess of ligand ($[Cu(H_2L)_2]^{2-}$ to $[Cu(HL)L]^{5-}$) and with excess of metal Cu_2L. Single crystals of the bimetallic complex $[Cu_2(p\text{-}PhDTA)(H_2O)_4] \cdot 2H_2O$ were obtained and its structure determined by X-ray diffraction analysis (Fig. 13) [81].

Recently, the formation of the polymer complexes with *p*-PhDTA acid has been investigated [82]. Potentiometric investigations in aqueous solution at 25°C and

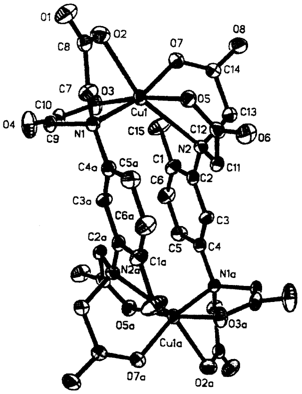


Fig. 12. ORTEP view of the anionic complex $[Cu_2(2,4\text{-}TDTA)_2]^{4-}$. Adapted from Ref. [64].

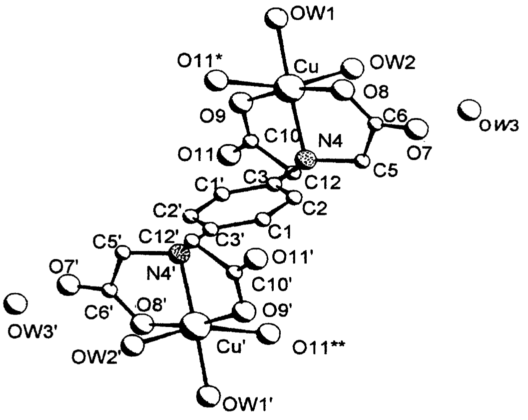


Fig. 13. View of the molecular structure of the complex $[Cu_2(p\text{-PhDTA})(H_2O)_4] \cdot 2H_2O$. Adapted from Ref. [81].

ionic strength 0.1 M (Cu(II), Ni(II), Co(II), Zn(II) and Cd(II)) and 0.5 M in KCl (Cu(II)), respectively, analysed by LETAGROP [54,55] and simulation calculus for a three component system [Z(pH) curves] show that *p*-PhDTA acid forms protonated and non protonated monomer and polymer complexes, and complexes with excess of metal and with excess of ligand. The formation constants β_{pqr} of the complexes have been determined and the Irving-Williams order of complexation is fulfilled (Tables 3 and 4). The species distribution diagrams as a function of $-\log[H^+]$ indicate that the more important non-protonated polymer complexes are: trimer and pentamer for Cu(II); pentamer for Ni(II) (Fig. 14); dimer and trimer for Co(II); trimer for Zn(II) and Cd(II). From a concentrated solution with a ligand: metal ratio 2:3 at pH 5, single crystals of the complex $Na_4[Co_2(p\text{-PhDTA})_2] \cdot 8H_2O$ were obtained. X-ray diffraction structural analysis revealed that in the dimer anion $[Co_2(p\text{-PhDTA})_2]^{4-}$ the cobalt atoms are hexa-coordinated with each metal surrounded by four carboxylic and two amine nitrogens in a distorted octahedron (Fig. 15).

p-Phenylenediamine-*N*,*N'*-disuccinic acid [83], *p*-phenylenediamine-*N*-succinic acid [84] and 2,5-toluenediamine-*N*,*N'*-disuccinic acid [85] have been prepared and characterized and their coordinating ability in aqueous solution (25°C, $I = 0.5$ M in NaCl) has been studied by potentiometric and conductimetric methods with the divalent cations Mg, Ca, Mn, Co, Ni, Zn and Cd. The stability constants of the complexes formed were determined. Polymer complexes were not considered.

3. Schiff bases derived from phenylenediamines

3.1. Introduction

Schiff bases (SB), so called since their synthesis was first reported by Schiff [86], result from the condensation of primary amines with aldehydes and ketones and

Table 3
Formation constants (log β_{pqr}) for *p*-PhDTA acid with Cu(II)[a]

pqr	Species	$I = 0.5$[b]	$I = 0.1$[c]
211	$[H_2ML]$	15.41 ± 0.02	15.42 ± 0.02
111	$[HML]^-$	12.78 ± 0.02	12.85 ± 0.02
011	$[ML]^{2-}$	Max 7.53	Max 7.44
222	$[H_2M_2L_2]^{2-}$	27.29 ± 0.10	27.41 ± 0.07
122	$[HM_2L_2]^{3-}$	23.65 ± 0.12	Max 23.27
022	$[M_2L_2]^{4-}$	Max 18.80	Max 18.68
133	$[HM_3L_3]^{5-}$	35.32 ± 0.07	35.36 ± 0.05
033	$[M_3L_3]^{6-}$	30.89 ± 0.06	Max 30.34
044	$[M_4L_4]^{8-}$	–	–
055	$[M_5L_5]^{10-}$	53.01 ± 0.19	53.02 ± 0.09
066	$[M_6L_6]^{12-}$	Max 64.34	Max 63.58
121	$[HM_2L]^+$	14.93 ± 0.15	Max 14.88
021	$[M_2L]$	12.42 ± 0.02	12.84 ± 0.08
032	$[M_3L_2]^{2-}$	–	–
412	$[H_4ML_2]^{2-}$	29.62 ± 0.10	
312	$[H_3ML_2]^{3-}$	26.33 ± 0.08	
212	$[H_2ML_2]^{4-}$	22.22 ± 0.07	
112	$[HML_2]^{5-}$	16.82 ± 0.12	
012	$[ML_2]^{6-}$	–	
223	$[H_2M_2L_3]^{6-}$	Max 33.67	

[a] At 25°C; $I = 0.5$ and 0.1 M; ligand, H_4L.

[b] Number of titrations, 5 (ratio 1:1, $C_M = 1$, 2 and 16 mM; L:M 4:1 and 1:4, $C_M = 4$ mM). Number of points 152; $[\sigma(Z)] = 0.015$; $-\log[H^+]$ range, 2.56–5.77.

[c] Number of titrations, 6 (ratio 1/1, $C_M = 2$, 6, 15, 20 and 30 mM; L:M 1:3; $C_M = 2$ mM). Number of points 345; $[\sigma(Z)] = 0.032$; $-\log[H^+]$ range 2.12–5.42.

contain a C=N double bond. This direct reaction is the most common method of obtaining a SB. Other synthetic methods have been widely reviewed by Dayagi and Degani [87]. However, few SBs commonly used as ligands have been prepared and characterized in their uncomplexed state [88] since the corresponding metal complexes have been directly obtained by other procedures [88]. Thus, many metal complexes containing H_2salen may be obtained directly by reaction between metal ions, salicylaldehydes and ethylenediamine [89]. Metal–chelate SB complexes have continued to play the role of one of the most important stereochemical models in main group and transition metal coordination chemistry due to their preparative accessibility, diversity and structural variability [90]. The chemistry of SBs has been widely reviewed [91–99].

Tetradentate SBs, especially those with a N_2O_2 donor set, resulting from the condensation of aliphatic diamines such as ethylenediamine or derivatives with acetylacetone or salicylaldehyde, have been extensively studied [88]. SBs derived from aromatic diamines have received much less attention and are considered in this review.

Table 4
Formation Constants (log β_{pqr}) for p-PhDTA acid with Ni(II), Co(II), Zn(II) and Cd(II) (25°C; $I = 0.1$ M), ligand H_4L [82]

pqr	Species	Ni(II)[a]	Co(II)[b]	Zn(II)[c]	Cd(II)[d]
211	$[H_2ML]$	13.72 ± 0.05	13.30 ± 0.08	13.85 ± 0.09	13.19 ± 0.22
111	$[HML]^-$	10.87 ± 0.03	Max.9.29	Max. 9.33	9.24 ± 0.10
011	$[ML]^{2-}$	Max. 5.75	Max. 5.66	Max. 5.31	3.98 ± 0.20
222	$[H_2M_2L_2]^{2-}$	–	Max. 22.99	Max. 23.83	Max. 22.01
122	$[HM_2L_2]^{3-}$	20.11 ± 0.17	19.58 ± 0.22	19.84 ± 0.23	Max. 17.17
022	$[M_2L_2]^{4-}$	Max. 15.64	15.72 ± 0.19	Max. 15.46	Max. 11.86
133	$[HM_3L_3]^{5-}$	–	–	Max. 29.73	–
033	$[M_3L_3]^{6-}$	–	26.09 ± 0.07	Max. 25.77	Max. 20.03
044	$[M_4L_4]^{8-}$	–	–	–	–
055	$[M_5L_5]^{10-}$	44.64 ± 0.15	–	–	–
066	$[M_6L_6]^{12-}$	Max. 54.03	Max. 54.68	–	–
021	$[M_2L]$	9.35 ± 0.25	Max. 9.06	Max. 9.14	Max. 7.38
032	$[M_3L_2]^{2-}$	–	Max. 18.83	–	–
043	$[M_4L_3]^{4-}$	29.30 ± 0.12	Max. 28.99	–	–
412	$[H_4ML_2]^{2-}$	–	Max. 26.27	27.22 ± 0.24	–
312	$[H_3ML_2]^{3-}$	23.86 ± 0.16	23.78 ± 0.10	24.02 ± 0.09	23.14 ± 0.23
212	$[H_2ML_2]^{4-}$	20.85 ± 0.03	20.66 ± 0.04	20.74 ± 0.06	Max. 18.88
112	$[HML_2]^{5-}$	15.98 ± 0.06	16.31 ± 0.07	Max. 16.30	13.99 ± 0.19
012	$[ML_2]^{6-}$	10.59 ± 0.03	10.97 ± 0.07	–	8.56 ± 0.15
123	$[HM_2L_3]^{7-}$	Max. 25.40	–	–	–
134	$[HM_3L_4]^{9-}$	Max. 35.34	Max. 35.78	–	–

Polymerization equilibria, log K values (25°C; $I = 0.1$ M)

Equilibria	Cu(II)	Ni(II)	Co(II)	Zn(II)	Cd(II)
(9) $2[MHL]^- \rightleftarrows [H_2M_2L_2]^{2-}$	1.71	–	4.41	5.17	3.53
(10) $2[ML]^{2-} \rightleftarrows [M_2L_2]^{4-}$	3.80	4.14	4.40	4.84	3.90
(11) $3[ML]^{2-} \rightleftarrows [M_3L_3]^{6-}$	8.02	–	9.11	9.84	8.09
(12) $5[ML]^{2-} \rightleftarrows [M_5L_5]^{10-}$	15.82	15.89	–	–	
(13) $2[M_3L_3]^{6-} \rightleftarrows [M_6L_6]^{12-}$	2.90	–	2.50	–	–

[a] Fourteen titrations (ratio 1:1, $C_M = 1$, 2, 4, 6, 10, 15, 20, 30 and 50 mM; L:M, 1:3, $C_M = 3$ and 4.5 mM; L:M, 3:1, $C_M = 1$, 1.5 and 2 mM); 384 points; $[\sigma(Z)] = 0.039$; $-\log[H^+]$ range 2.70–6.15.

[b] Sixteen titrations (ratio 1:1, $C_M = 0.3$, 0.5, 0.7, 1, 4, 6, 10, 15, 20 and 30 mM; L:M, 1:3, $C_M = 3$, 4.6 and 6 mM; L:M, 3:1, $C_M = 1$, 1.6 and 2 mM); 534 points; $\sigma(Z) = 0.050$; $-\log[H^+]$ range 2.71–5.86.

[c] Five titrations (ratio 1:1, $C_M = 0.4$, 0.5 and 0.8 mM; L:M, 3:1, $C_M = 0.5$ and 0.8 mM); 103 points; $\sigma(Z) = 0.033$; $-\log[H^+]$ range 2.87–4.05.

[d] Four titrations (ratio 1:1, $C_M = 0.4$, 0.5, 0.8 and 1.0 mM); 81 points; $\sigma(Z) = 0.025$; $-\log[H^+]$ range 3.21–5.84.

Of special interest in the last years is the discovery of the ability of tetradentate SB to stabilise the M–C bond [14,15].

Thermodynamic data available in the literature for SB complexes derived from phenylenediamines are limited [10,12,13,100,101]. This can be attributed mainly to

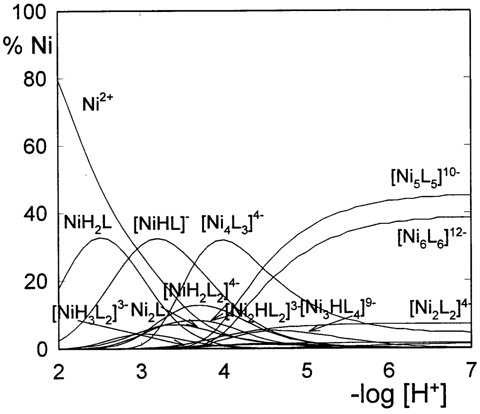


Fig. 14. Species distribution diagram as a function of pH for the Ni(II)-*p*-PhDTA system at ligand:metal ratio 1:1 and $C_M = 10.0$ mM. Adapted from Ref. [82].

the insolubility of such compounds in water which is the most common solvent for potentiometric determination of stability constants and also to the possible hydrolysis of some compounds to give the starting organic fragments. Thus, the study of these SBs requires the use of an organic or aquo-organic solvent which can dissolve these compounds and which furthermore presents compatibility with the standard glass electrode, such that the e.m.f. measurements can be carried out in a manner similar to when using water. In this context, dmso–water 80:20 wt./wt.

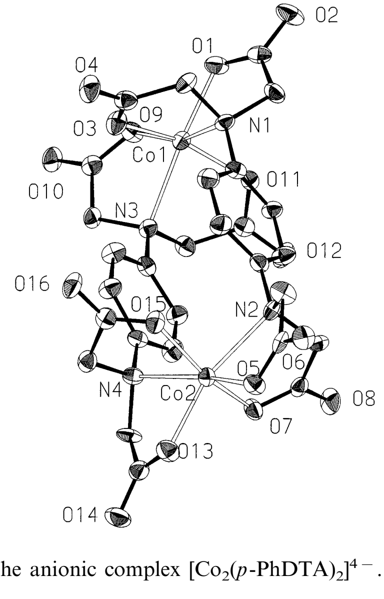


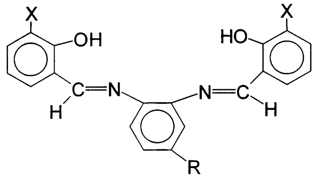
Fig. 15. ORTEP view of the anionic complex $[Co_2(p\text{-PhDTA})_2]^{4-}$. Adapted from Ref. [82].

[10,12,13,101–103] as well as dioxane–water [100,104] mixtures have been reported to be suitable solvents for the potentiometric study of SB complexes. Other aquo-organic solvents such as ethanol–water [105–107], acetone–water [107] etc. have also been used although less extensively.

The majority of the thermodymanic data reported on stability constants and/or protonation constants of SBs are related to bidentate bases [105–111] with a NO donor set mainly derived from salicylaldehydes or benzaldehydes (or derivatives) and anilines or substituted anilines. Tetradentate SBs have been less studied. In this context, stability constants for the Fe(III), Cu(II) and Ni(II) complexes of the tetradentate H_2salen have been reported [11] in dmso–water 80 wt./wt. Martell et al. [100] also carried out studies of H_2salen in dioxane–water 70:30 v/v in order to determine the oxygenation constants of the complex Co(salen) which it is well known can reversibly bind molecular oxygen. Thermodynamic data for tetradentate SBs derived from phenylenediamines are considered below.

3.2. Thermodynamic studies in solution

3.2.1. Protonation constants



9 X = H, R = H (H_2sal-o-phen)
10 X = H, R = CH_3 (H_2sal-3,4-toluen)
11 X = H, R = Cl (H_2sal-4-Cl-o-phen)
12 X = F, R = H (3-F-H_2sal-o-phen)
18 X = OC_2H_5, R = CH_3 (3-EtO-H_2sal-3,4-toluen)
19 X = OCH_3, R = Cl (3-MeO-H_2sal-4-Cl-o-phen)

The protonation constants for the SBs (H_2L) derived from *o*-phenylenediamines H_2sal-*o*-phen (**9**) [12], H_2sal-3,4-toluen (**10**) [13] and H_2sal-4-Cl-*o*-phen (**11**) [112] have been determined in dmso–water 80:20 wt./wt. (25°C; $I = 0.5$ M $NaClO_4$). Protonation constants have also been reported by Martell et al. for 3-F-H_2sal-*o*-phen (**12**) [100] in dioxane–water 70:30 v/v (25°C; $I = 0.1$ M KCl). The pK_i values for these ligands are listed in Table 5. The protonation constants for H_2sal-*o*-phen has also been reported in ethanol-water mixtures of different composition [105]. These SBs are tetradentate with two adjacent weak imine donors and two strongly basic phenolate groups. Thus, they behave like weak diprotic acids. Only one protonation constant was reported above pH 2.5, indicating the low basicity of the imine nitrogen. A second protonation step was not evident. The basicity sequence found was: H_2sal-3,4-toluen > H_2sal-*o*-phen > H_2sal-4-Cl-*o*-phen. The higher values of pK_i for H_2sal-3,4-toluen was attributable to the electron-donor effect of the methyl substituent on the diamine and the lower pK_i values for H_2sal-4-Cl-*o*-phen are due to the electron-withdrawing effect of chloride on the diamine. The pK_i values for 3-F-H_2sal-*o*-phen [100] are similar to those described above despite the differences in the solvent, ionic strength and structural features of the ligands.

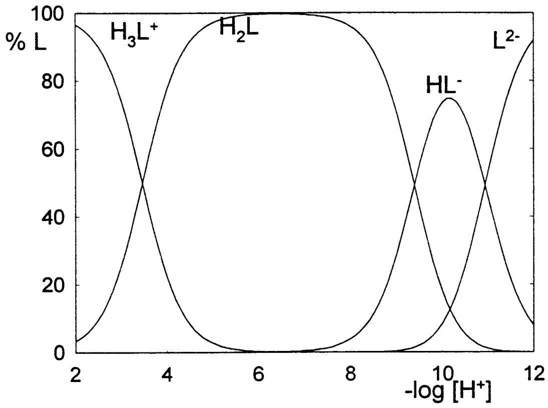
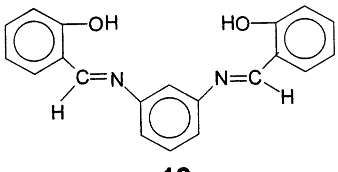


Fig. 16. Species distribution diagram as a function of pH for H_2sal-*o*-phen. Adapted from Ref. [12].



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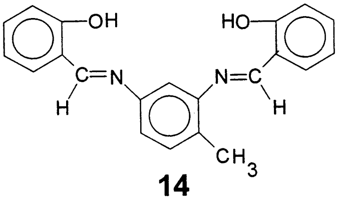

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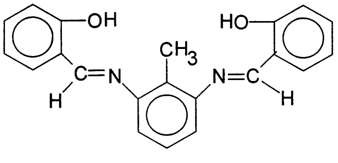
Protonation constants have also been reported for the SBs derived from *m*-phenylenediamines H_2sal-*m*-phen (**13**) [101], H_2sal-2,4-toluen (**14**) and H_2sal-2,6-toluen (**15**) in dmso–water 80:20 wt./wt. (25°C; $I = 0.1$ M $NaClO_4$). These *meta* SBs behave similarly to the *ortho* SBs previously described. The sequence of basicity is H_2sal-2,6-toluen ~ H_2sal-2,4-toluen > H_2sal-*m*-phen, as a consequence of the inductive effect of the methyl group.



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The species distribution diagrams as a function of pH for H_2sal-*o*-phen (Fig. 16) indicate that in the pH range 5–8, the only existing species is the neutral SB H_2L, whereas in the pH range 9–11 the species H_2L, HL^- and L^{2-} coexist. The deprotonation of both OH^- is completed at pH > 12, the only existing species being L^{2-}. Similar diagrams are obtained for the other SBs.

Table 5
Ionization constants (pK_i) for Schiff base ligands (H_2L) derived from phenylenediamines (25°C)

Equilibrium	H_2sal-*o*-phen[a]	H_2sal-3,4-toluen[a]	H_2sal-4-Cl-*o*-phen[a]	3-F-H_2sal-*o*-phen[b]	H_2sal-*m*-phen[c]	H_2sal-2,4-toluen[c]	H_2sal-2,6-toluen[c]
L^{2-}/HL^-	10.94(1)	11.49(1)	10.26(1)	11.23(2)	10.49(1)	10.61(1)	10.72(1)
HL^-/H_2L	9.39(1)	9.41(1)	9.20(1)	8.41(5)	9.30(1)	9.43(1)	9.42(1)
H_2L/H_3L^+	3.46(1)	3.63(1)	2.70(1)	3.17(4)	3.70(1)	3.96(1)	3.80(1)
Reference	[12]	[13]	[112]	[100]	[101]	[101]	[101]

[a] dmso–water 80:20 wt./wt., $I = 0.5$ M $NaClO_4$.
[b] Dioxane–water 70:30 v/v, $I = 0.1$ M KCl.
[c] dmso–water 80:20 wt./wt., $I = 0.1$ M $NaClO_4$.

The SBs derived from ethylenediamine (H_2salen) and its complexes [11,102,103] undergo hydrolytic decomposition in strongly acidic dmso–water 80:20 wt./wt. solution induced by the highly basic character of the nitrogen atoms of the aliphatic diamine. Contrarily, no hydrolysis was observed for SBs derived from *ortho*- or *meta*-phenylenediamines in dmso-water 80:20 wt./wt. above pH 2.5 [12,13,101]. The low basic character of the nitrogen atoms on the aromatic diamine which remain unprotonated in the media where the ethylenediamine is fully protonated is believed to be responsible for the stability of the SBs and their complexes in acidic dmso–water solution.

3.2.2. Stability constants of the complexes derived from o-phenylenediamines

Stability constants have been reported for the systems H_2sal-3,4-toluen-M (M = Ca(II), Mg(II), Ni(II), Co(II), Zn(II) and Cd(II)) [13], H_2sal-*o*-phen-M (M = Ca(II), Mg(II), Fe(III), Ni(II), Co(II), Zn(II) and Cd(II)) [12] and H_2sal-4-Cl-*o*-phen-M (M = Ca(II), Mg(II), Co(II) and Zn(II)) [112] in dmso-water 80:20 wt./wt. (25°C; $I = 0.5$ M $NaClO_4$) (Table 6). Only the monomer species $[MHL]^+$ and [ML] were found to be formed (the hydroxocomplex [FeOHL] was also observed for the system sal-*o*-phen-Fe(III)). The species ML results from the coordination of the metal with the ligand fully deprotonated. The monoprotonated complex $[MHL]^+$ may be assumed to be protonated at the phenol oxygen on one salicylaldehyde moiety as in the case of protonation of the free SB. The systems H_2sal-3,4-toluen-M(II) (M(II) = Ni, Co, Zn, Cd, Ca and Mg) give complexes that are more stable than those for H_2sal-*o*-phen-M(II) due to the electron-donor effect of the methyl group of H_2sal-3,4-toluen which is favourable to coordination. For H_2sal-4-Cl-*o*-phen-M(II) the opposite effect applies, and the stability of their complexes is less than those for H_2sal-*o*-phen as a consequence of the electron-withdrawing effect of the chloride susbtituent. Thus, for any metal the sequence of stability was:

Table 6
Stability constants (log *K*) for Schiff base complexes derived from *o*-phenylenediamines (25°C)

Ligand	Species	Fe(III)	Ni(II)	Co(II)	Zn(II)	Cd(II)	Mg(II)	Ca(II)	Reference
H_2sal-*o*-phen[a]	$[MHL]^+$	10.58(2)	9.08(2)	9.81(6)	7.07(1)	4.83(1)	3.62(1)	2.55(1)	[12]
	[ML]	17.80(2)	14.82(1)	14.64(2)	13.31(1)	7.23(1)	6.28(1)	4.27(1)	[12]
	[FeOHL]	31.24(4)							
H_2sal-3,4-toluen[a]	$[MHL]^+$		9.29(2)	9.74(2)	7.13(2)	4.92(2)	3.70(2)	2.83(2)	[13]
	[ML]		15.76(2)	15.77(3)	13.90(1)	7.90(1)	6.90(1)	4.31(1)	[13]
H_2sal-4-Cl-*o*-phen[a]	$[MHL]^+$			9.13(2)	6.36(2)		3.42(1)	2.05(2)	[112]
	[ML]			14.41(2)	11.93(1)		4.41(1)	3.45(1)	[112]
3-F-H_2sal-*o*-phen[b]	$[MHL]^+$			10.62(2)					[100]
	[ML]			14.91(2)					

[a] Dmso–water 80:20 wt./wt., $I = 0.5$ M $NaClO_4$.

[b] Dioxane–water 70:30 v/v, $I = 0.1$ M KCl.

H_2sal-3,4-toluen > H_2sal-*o*-phen > H_2sal-4-Cl-*o*-phen, in concordance with the basicity order.

The complexes ML (M = Fe(III), Ni(II), Co(II) and Zn(II)) are very stable, thus indicating coordination of both imino groups and the phenolate oxygens to metal. The stability constants for the Ni^{II} and Co^{II} complexes are similar and slightly higher than those for Zn^{II}. This result is in agreement with the structural data indicating that M–O and M–N bond distances in the solid complexes Co(sal-*o*-phen) [113] (average 1.84 and 1.87 Å, respectively) and [Ni(sal-3,4-toluen)] · 1.5$CHCl_3$ [13] (average, 1.84 and 1.87 Å, respectively) are almost the same.

For the system H_2sal-*o*-phen-Fe(III), the hydroxocomplex FeOHL was also formed in dmso–water 80:20 wt./wt. solution. Solutions of Fe(sal-*o*-phen)Cl in dmso–water 80:20 wt./wt. are stable and do not undergo any decomposition by addition of strong acids [10]. However, $Fe(salen)^+$ hydrolyses in acidic solutions to give salicylaldehyde and ethylenediammonium [11]. The stability of $Fe(sal\text{-}o\text{-}phen)^+$ in acidic media is attributed to the only slightly basic character of *o*-phenylenediamine. The complex $Fe(sal\text{-}o\text{-}phen)^+$ hydrolyses in basic solution to give the μ-oxo dimer $[Fe(sal\text{-}o\text{-}phen)]_2O$ [10], this process being accompanied by a colour change from reddish-brown to yellow. The relevant equation is as follows:

$$2Fe(sal\text{-}o\text{-}phen)^+ + H_2O \Leftrightarrow [Fe(sal\text{-}o\text{-}phen)]_2O + 2\ H^+ \qquad K_D = 1.5 \times 10^{-12}$$

The dimerization constant ($K_D = 1.5 \times 10^{-12}$) has been determined in dmso-water 80:20 wt./wt. by potentiometric and spectrophotometric titration of $Fe(sal\text{-}o\text{-}phen)^+$ with KOH [10]. The stability constant for the complex resulting from the interaction of $Fe(sal\text{-}o\text{-}phen)^+$ with cathecol, $[Fe(sal\text{-}o\text{-}phen)(cat)]^-$ has been reported [10]:

$$Fe(sal\text{-}o\text{-}phen)^+ + H_2cat \Leftrightarrow [Fe(sal\text{-}o\text{-}phen)(cat)]^- + 2H^+$$

$$K = 1.09(2) \times 10^{14}$$

The catecholate complex competes efficiently with the dimerization reaction.

The cobalt(II) complexes of SBs such as H_2salen and its analogues have been the first and most extensively investigated oxygen carriers [114]. Four coordinate Co(II) chelates do not by themselves bind oxygen strongly, but their adducts with suitable monodentate Lewis bases such as pyridine readily bind oxygen under suitable conditions of temperature and oxygen pressures as a result of the stabilization of the Co(II)–dioxygen bond through an increase in electron density at the metal center provided by the axial base. The dioxygen ligand binds in a position *trans* to the axial base [115,116]. The synthesis and oxygen affinities of several four-coordinate SB Co(II) complex derivatives of H_2sal-*o*-phen have been reported [115]. In this context, Motekaitis and Martell also studied by potentiometric means the multicomponent system 3-fluorosalicylaldehyde-*ortho*-phenylenediamine-cobalt(II)-4-methylpyridine-oxygen [100] in dioxane–water 70:30 v/v (25°C; $I = 0.1$ M KCl) in order to obtain the oxygenation constants of the Co(II) complex. From this study, one protonation reaction for *o*-phenylenediamine ($\log K = 4.41$) was reported [1]. The mono(SB) and bis(SB) were found to be formed and their protonation constants reported. The anaerobic coordination chemistry of this SB shows that

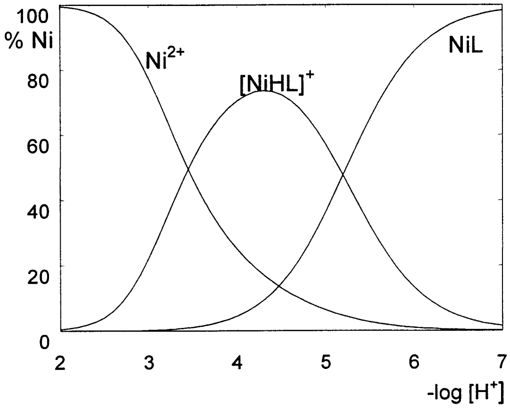


Fig. 17. Species distribution diagram as a function of pH for H_2sal-*o*-phen–Ni(II) at ligand:metal ratio 1:1 and $C_M = 3.0$ mM. Adapted from Ref. [12].

two species are formed: a normal complex CoL and a singly protonated complex of the fully formed SB which stability constants are collected in Table 6.

The stability constants for the Ca(II) and Mg(II) species with H_2sal-3,4-toluen [13] and H_2sal-*o*-phen [12] are considerably smaller than those for the above 3d cations, the Mg(II) species being more stable than the Ca(II). The Mg^{2+} (smaller in size than Ca^{2+}) can be better accommodated by the N_2O_2 compartment of the ligand than Ca^{2+}, thus giving more stable species. Studies in the solid state [117] have shown the dimeric nature of $[\{Mg(sal\text{-}o\text{-}phen)\}_2]$, $[\{Mg(salen)\}_2]$ and $[\{Mg(acen\}_2]$. For the latter, the cystal structure has been reported. The acen molecules are bridging the two metal atoms. The high tendency of Mg to achieve five coordination favors dimerization. However, this structure may differ from that in solution of oxygen-donor solvents because of the equilibrium:

$$[\{Mg(L\text{–}L)\}_2] + 2\ \text{solv} \Leftrightarrow 2(MgL)\text{solv}$$

where L = salen, sal-*o*-phen, acen; solv = thf, acetone.

It has been suggested that only one of two forms is detectable in solution. In dmso-water 80:20 wt./wt. only the monomer form was observed in which magnesium probably binds a dmso molecule to achieve five coordination.

The stability sequence observed for the species ML ($H_2L = H_2$sal-3,4-toluen, H_2sal-*o*-phen) [12,13] is: Fe(III) > Ni(II) ~ Co(II) > Zn(II) > Cd(II) > Mg(II) > Ca(II). Thus, the Irving–Williams order of complexation which is related to the ligand-field stabilization energy is fulfilled.

For *ortho*-SB-M (M = Ni(II), Co(II) and Zn(II)) the species distribution diagrams (Fig. 17) indicates that the neutral ML is the only existing species at pH > 7, so a concentrated solution of ligand:metal ratio 1:1 at pH > 7 is the most suitable for the preparation of a complex ML [Ni(II), Co(II) and Zn(II)] in the solid state. Thus, these complexes are normally prepared in the solid state from the corresponding metal acetate which provides the necessary basic medium.

3.2.3. *Stability constants of the complexes derived from m-phenylenediamines*

SB ligands (H_2L) derived from *m*-phenylenediamines (**13**–**15**) are very versatile and may form monomers, dimers, as well as species in the ratio ligand:metal 2:1 and 1:2 [101]. All these species may show different protonation extents (Table 7). In the monomer species $[MHL]^+$ and ML, the metal is coordinated to only one NO group of the ligand. For dimers M_2L_2 both metals are coordinated to a N_2O_2 donor set, in which each NO corresponds to different ligands. The positive values obtained for the dimerization equilibrium $2ML \rightleftarrows M_2L_2$, indicate a thermodynamically favourable process.

In the species with excess of ligand the metal may be four-coordinated by two NO groups from different ligands. For M_2L species each metal is coordinated to each NO group of the SB.

The $\log K$ order was: H_2sal-2,4-toluen > H_2sal-*m*-phen > H_2sal-2,6-toluen. For complexes derived from H_2sal-2,4-toluen the inductive electron-donor effect of the methyl group predominates over the repulsive steric effect, in contrast to H_2sal-2,6-toluen.

The stability sequence found for most species was Cu(II) ≫ Ni(II) ∼ Co(II) > Zn(II). The Irving–Williams order of complexation is thus fulfilled.

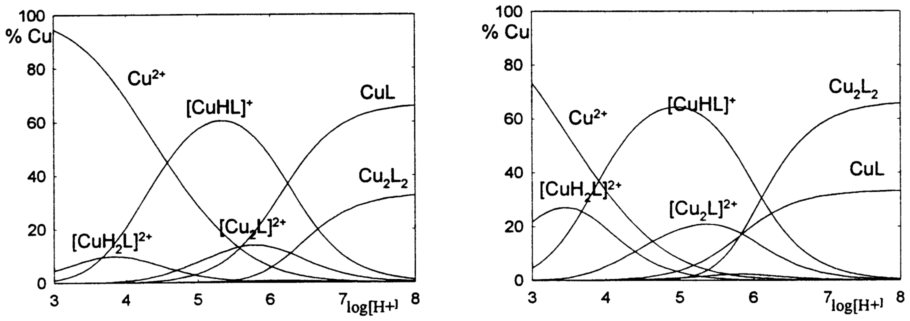
Comparing the $\log K$ for ML species for H_2sal-*m*-phen [101] with those corresponding to ML species for H_2sal-*o*-phen [12], it is deduced that the $\log K_{ML}$ for the *meta* SBs are practically half those corresponding to *ortho* SBs, thus indicating a donor set NO for the former, as expected, due to the conformation of the ligand.

Table 7

Stability constants ($\log K$) for the main species of H_2sal-*m*-phen, H_2sal-2,4-toluen and H_2sal-2,6-toluen with Cu(II), Ni(II), Co(II) and Zn(II) in dmso–water 80:20 wt./wt. (25°C, $I = 0.1$ M $NaClO_4$)[a]

Species	Cu(II)	Ni(II)	Co(II)	Zn(II)
H_2sal-m-phen				
$[MHL]^+$	8.13(3)	5.51(1)	5.11(3)	4.69(5)
[ML]	13.0(1)	7.45(1)	7.13(6)	6.56(1)
$[M_2L_2]$	30.20(3)	18.04(2)	17.75(6)	16.80(1)
$[ML_2]^{2-}$		11.16(1)	11.06(3)	
$[M_2L]^{2+}$	16.47(2)	11.69(1)	10.82(3)	10.35(2)
H_2sal-2,4-toluen				
$[MHL]^+$	8.32(1)	5.71(1)	5.57(3)	5.27(1)
[ML]	13.42(1)	7.84(2)	7.85(5)	7.29(2)
$[M_2L_2]$	31.36(2)	18.67(3)	19.19(7)	18.25(4)
$[ML_2]^{2-}$		11.60(3)	12.12(3)	
$[M_2L]^{2+}$	17.20(2)	11.75(1)	11.73(3)	10.07(6)
H_2sal-2,6-toluen				
$[MHL]^+$	8.17(1)	5.47(1)	5.01(1)	4.46(1)
[ML]	12.66(1)	7.62(1)	6.90(4)	7.01(1)
$[M_2L_2]$	28.14(4)	17.47(6)	16.80(5)	16.8(2)
$[ML_2]^{2-}$		11.10(4)	11.1(1)	
$[M_2L]^{2+}$	16.58(1)	11.67(1)	10.74(1)	9.8(1)

[a] Values taken from Ref. [101].



(a) **(b)**

Fig. 18. Species distribution diagram as a function of pH for the system H_2sal-2,6-toluen–Cu(II) at ligand:metal ratio 1:1 (a) $C_M = 0.5$ mM; (b) $C_M = 4.0$ mM.

The species distribution diagrams as a function of pH for the system H_2sal-2,6-toluen-Cu(II) at ligand:metal ratio 1:1 and $C_M = 0.5$ and 4 mM are shown in Figs. 18(a and b), respectively. It can be seen that at pH 8 the only existing species are CuL and Cu_2L_2, the percentage of dimer species increase with the concentration.

No stability constants have been reported to date for SB complexes derived from *p*-phenylenediamines.

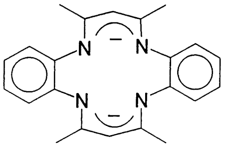
3.3. Chemical and structural properties

3.3.1. Complexes derived from o-phenylenediamines

The crystal structure of H_2sal-*o*-phen has been reported [113]. The molecule shows intramolecular hydrogen bonds between the phenolic oxygen and the imine nitrogen. The hydrogen bonds formation in the same salicylideneimine residue prevents planarity of the whole molecule, its geometry being determined by a rotation around the N–C bond.

The tendency of these SB to form complexes with alkaline metals has not been reported, however in some cases Li(I) or Na(I) may be encapsulated in ligands or macrocycles containing the SB moiety, but not complexed by it (Fig. 19) [118,119]. Ba(II) may behave similarly and has been found to be very useful as template for synthetic purposes in the complex formation or synthesis of macrocycles containing different complexation sites with electrophilic metal cations [120].

The stability constants for the alkaline earths Ca(II) and Mg(II) with H_2sal-3,4-toluen [13] and H_2sal-*o*-phen [12] are considerably smaller than those for the 3 d cations, and structural data have only been reported for the complex of Mg(II) with H_2sal-*o*-phen [117]. The high tendency of Mg to achieve five coordination explains the formation of the dimer [{Mg(sal-*o*-phen)}$_2$], obtained by the reaction of dibenzylmagnesium in thf with H_2sal-*o*-phen in which the sal-*o*-phen molecules are bridging the two metals through the oxygen atoms [117]. The same synthetic procedure using the N_4 macrocycle ligand (**16**) afforded the five-coordinate complex [Mg(mac)thf] which structure was characterised by X-ray analyses [117].



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Ni(sal-*o*-phen) was found to react with $TiCl_4$ thf to give [Ti(sal-*o*-phen)Cl_2]. A ligand migration from the lower to the higher oxidation state took place as a consequence of the higher stability for the same ligand associated with the metal ion having the higher oxidation state [121]. The complex [Zr(sal-*o*-phen)Cl_2(thf)] (Fig. 20) [14] has been prepared by the reaction of [$ZrCl_4(thf)_2$] with Na_2(sal-*o*-phen) in thf. The Zr(IV) has a $N_2O_3Cl_2$ coordination. In the presence of the very rigid tetradentate ligand, the two chlorine atoms are forced to be in *trans*- position. With less rigid tetradentate ligands, i.e. acen, *cis*- and *trans*- isomers have been found [14]. The reduction of the complex [Zr(sal-*o*-phen)Cl_2(thf)] with sodium metal, led to the reductive coupling of two imino groups belonging to two different SB molecules. The reduction does not affect the degree of oxidation of the metal and the resulting compound is still a Zr(IV) derivative. The dimeric resulting compounds may behave as reducing agent by four electrons. This dimerization was firstly observed for Ni(II) [119] complexes with H_2sal-*o*-phen, and it seems to be more dependent of the nature of the ligand than of the nature of the metal, since significant examples can be found for different metals and oxidation states (Co(II) [15], Mn(II) [122], Mo(IV) [123] and V(III) [14,124]), but strictly limited to the rigid planar sal-*o*-phen.

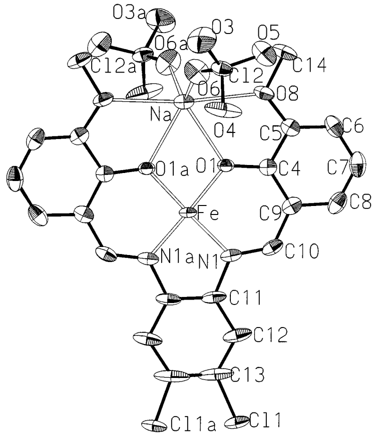


Fig. 19. ORTEP view of the binuclear complex [NaFe(3MeO-sal-4-Cl-*o*-phen)imd_2]$(ClO_4)_2$. Adapted from Ref [118].

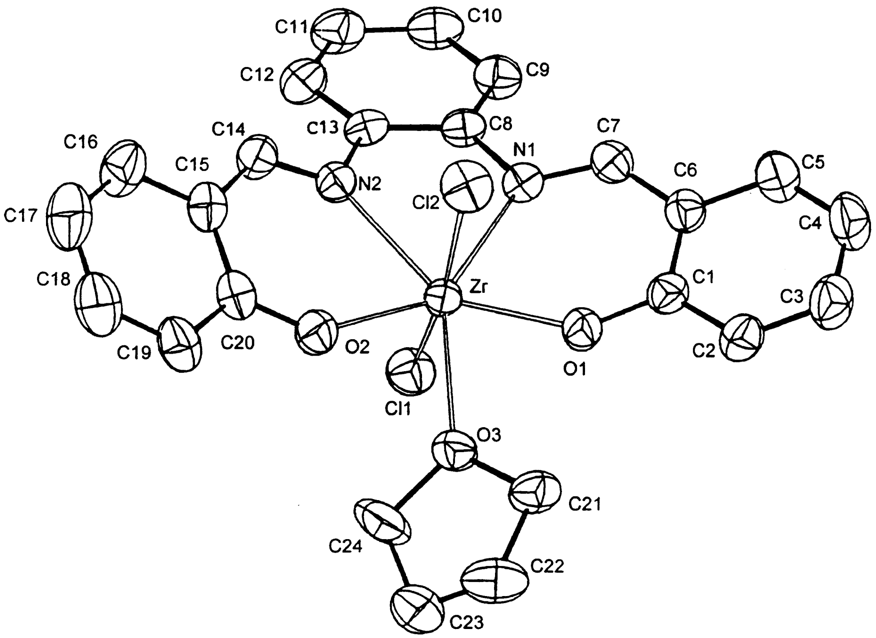
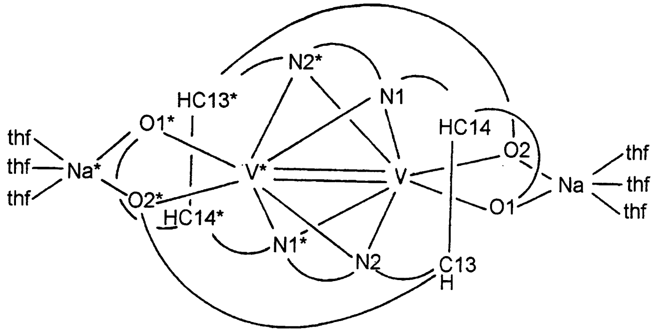


Fig. 20. ORTEP view of [Zr(sal-*o*-phen)Cl_2(thf)]. Adapted from Ref. [14].

The preparation of VO(sal-*o*-phen) [125] and the crystal structure of [VO(sal-*o*-phen)CH_3CN] [126] have been reported. The complex is five-coordinated, the geometry being a distorted square based pyramid. The V(III)-tetradentate SB complex, [V(sal-*o*-phen)(thf)Cl] [127], was prepared by reductive deoxygenation of [VO(sal-*o*-phen)] by a thf solution of [$TiCl_3(thf)_3$] or by the reaction of [$VCl_3(thf)_3$] with the sodium salt of the SB Na_2sal-*o*-phen. Moreover, the synthesis of the related compounds [V(sal-*o*-phen)(X)$(py)_n$] (X = Cl, Br; py = pyridine; $n = 1,2$) has been reported [128]. All these V(III) SB complexes are hexa-coordinated. V(III) achieves hexa-coordination by coordination of a solvent molecule or by sharing an oxygen of the SB ligand. In the structure of [V(sal-*o*-phen)(thf)Cl], the chlorine and thf ligands are *trans*- to each other in the axial positions, while the equatorial plane is defined by the sal-*o*-phen ligand. Coordination of sal-*o*-phen to vanadium is not strictly planar, the four coordinating atoms being tetrahedrally displaced from the mean coordination plane. The sal-*o*-phen shows an umbrella conformation. The coordination geometry is a distorted octahedron elongated along the O(thf)-V-Cl direction. The reaction of [V(sal-*o*-phen)Cl(thf)] with sodium metal caused the dimerization of two metallic moieties through two C-C bonds leading to a tetranucleating ligand, binding two sodium cations and two V(III) joined by a double bond [14,124]. The compound formed, [V_2(sal-*o*-phen)$_2Na_2(thf)_6$] (**17**), is diamagnetic, sodium atoms are five-coordinated and vanadium(III) are seven-coordinated. The complex is very reactive with many substrates and it is characterized by its polyfunctionality provided by the presence of very different reactive sites. An acid site is occupied by sodium whereas the vanadium in low oxidation state is an electron rich nucleophilic site. The compound has an electron rich nature since it can be considered as a potential six electron reservoir. [V(sal-*o*-phen)$(Cl)_2$] was also prepared by Floriani et al. [14,129]. Deoxygenation of [VO(sal-*o*-phen)] with $SOCl_2$ gives [V(sal-*o*-phen)$(Cl)_2$] which after reduction by Zn dust in thf gave {[V(sal-*o*-phen)$(py)_2$][$ZnCl_3py$]} [126].



17 [V_2(sal-o-phen)$_2$$Na_2$$(thf)_6$]

The compounds [Mo(sal-*o*-phen)Cl_2] and [Mo(tbsal-*o*-phen)Cl_2] have been recently prepared by Solary et al. [123] by the reaction of the respective SB with [$MoCl_4(MeCN)_2$] in the presence of a base in thf. The coordination around Mo(IV) in [Mo(tbsal-*o*-phen)Cl_2] is pseudo-octahedral, two chlorine atoms being bonded to a Mo(tbsal-*o*-phen) moiety in a *trans*- arrangement. The Mo–O and Mo–N distances fall in the range of values found for molybdenum SB complexes. The Mo atom lies in the N_2O_2 core and shows considerable tetrahedral distortion. In this study it is also described how the Mo(IV) bonded to the tetradentate sal-*o*-phen ligand behaves in the alkylation reaction and the formation of Mo–C functionalities. The reaction with $(PhCH_2)_2Mg$ led to the formation of *trans*-[Mo(sal-*o*-phen)$(PhCH_2)_2$] containing two alkyl groups at the metal in *trans*- position. The reaction of [Mo(sal-*o*-phen)Cl_2] with Mg(mes)Br (mes = mesityl; 2,4,6-$Me_3C_6H_2$) led to the arylation of both imino carbons and the metal, along the oxidation of Mo(IV) to Mo(V) (Fig. 21). Two mesityl groups are bonded to the two imino carbon atoms of the sal-*o*-phen ligand and the third mesityl group is σ bonded to molybdenum(V) which achieves five coordination. The reduction of [Mo(sal-*o*-phen)Cl_2] with sodium metal in the presence of PhCCPh in thf produces the formation of a dimeric compound via a complex path way. This dimeric compound contains two tetraanionic ligands derived from the alkylation of one of the imino carbons of the SB by diphenylacetylene. This leads to the loss of the square planar rigid arrangement of the SB and allows the dimerization of the monomeric unit, a Mo–Mo quadruple bond is formed containing two bridging vinyl functionalities.

The synthesis of pure salt free, anhydrous [{Mn(sal-*o*-phen)(thf)}$_2$] (Fig. 22(a)) and [Mn(salen)] has been reported [122]. It consists of the reaction of Mn_3Mes_6 (Mes = 2,4,6-$Me_3C_6H_2$) with the protic form of the respective SB in thf [122,130]. The analogous [{Mn(sal-*o*-phen)(py)}$_2$], prepared in pyridine has been structurally characterized [131]. The reduction of the [{Mn(sal-*o*-phen)(thf)}$_2$] by sodium metal in thf, and the recristalization in DME led to [Mn$_2$(sal-*o*-phen$_2$)Na$_4$(DME)$_6$], a Mn(II) dimer from a two fold reductive coupling of imino groups on adjacent [Mn(sal-*o*-phen)] units (DME = dimethoxyethane). In the dimeric compound the two Mn(II) atoms are anchored to the four nitrogen atoms at distances ranging from 2.166(6) to 2.287(7) Å. The hexa-coordination of each Mn is completed by two *cys*- oxygen atoms. The Mn–Mn distance is exceptionally short for such a complex. The compound shows a strong antiferromagnetic coupling between the two Mn atoms. The reaction of [Mn$_2$(sal-*o*-phen)$_2$Na$_4$(DME)$_6$] with an appropriate oxidising agent may lead to the cleavage of the two C–C bonds across the dimer to restore the original imino functionalities and the oxidation of Mn(II) to Mn(III).

The reaction of the complexes of general formula [{Mn^{II}(SB)(L)}$_2$] (SB = sal-*o*-phen or tbsalophen, L = thf or py) with dioxigen under very controlled conditions has been investigated [131]. The reaction products vary (Fig. 22), depending on the solvent. The reaction of [{Mn(SB)(py)}$_2$] in pyridine led to the selective oxidation of an imino to an amido group within the sal-*o*-phen ligand. In the monomeric compound formed (Fig. 22(b)), Mn(III) is hexa-coordinated, being two pyridine ligands in *trans*- position. If the reaction is performed in thf a polymeric compound is formed (Fig. 22(c)), that gave the same monomeric compound (Fig. 22(b)) when pyridine is added. The starting dimer material, the polymer and the final

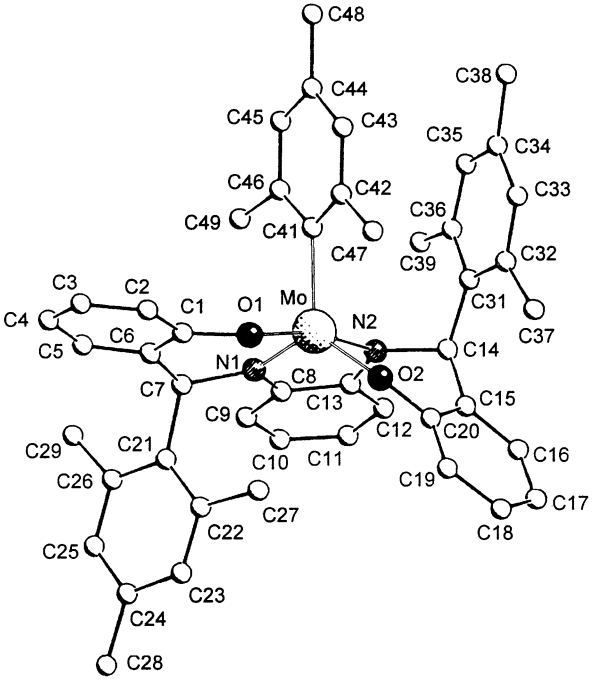


Fig. 21. SCHAKAL drawing of an alkylated compound derived from [Mo(sal-*o*-phen)Cl$_2$]. Adapted from Ref. [123].

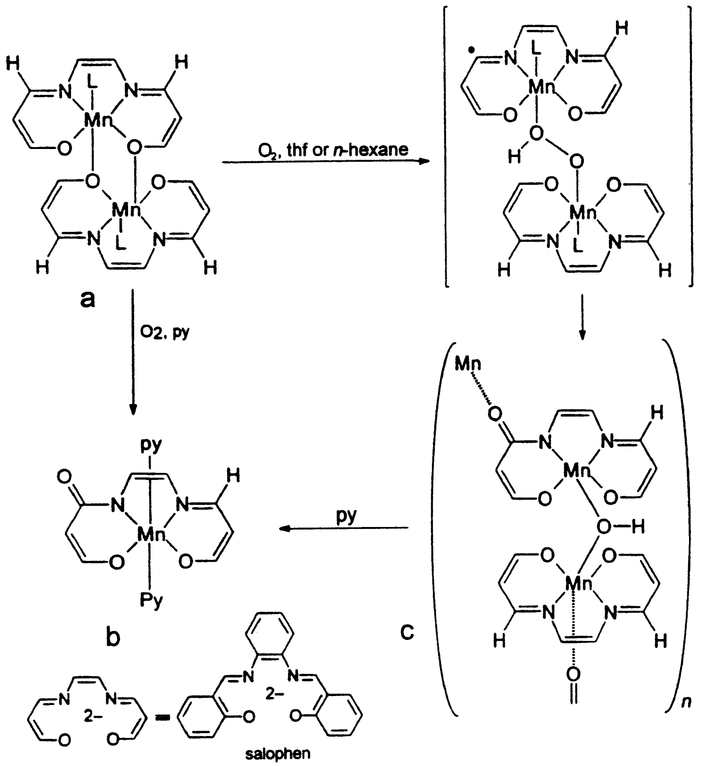


Fig. 22. Selective oxidation of an imino to an amido group in [Mn(sal-*o*-phen)L]. L = thf or py. Adapted from Ref. [131].

monomeric compound have been structurally characterized by single crystal X-ray diffraction [131].

Mn(III) complexes employing a variety of monovalent anions and the anionic SB tetradentate ligand sal-*o*-phen and various substituted salicylaldehyde derivatives were prepared [132] and characterized. In these compounds Mn(III) is five-coordinated. Cyclic voltammetry experiments on these high-spin Mn materials reveal a quasireversible Mn(III)/Mn(II) redox effect on the catodic peak potential. Comparing with salen complexes it was observed that the electron withdrawing effect of the aromatic ring in the [Mn(sal-*o*-phen)X] complexes (and derivatives), make the Mn(III) reduction more favourable while electron-donating groups require a more negative potential before the reduction is possible. The SB derived from aromatic diamines decreases the electronic density on the Mn(III) favouring the reduction [133].

A series of Mn(III) complexes of the type $[\{MnL(H_2O)\}_2]^{2+}$ (L = dianion of N_2O_2 tetradentate SB such as sal-*o*-phen) in aqueous solution liberate dioxygen and reduce *p*-benzoquinone to hydroquinone when irradiated with visible light. The photoactivity is critically dependent on the structure of the ligand. The water photolized is that bound to the manganese, the manganese complex being converted to [{MnL}$_2$O] in the photolysis with no oxidation state change of the manganese. These complexes represent a model for the manganese site of photosystem II of green plants [134].

The di-μ-oxodimanganese (IV) complex [Mn^{IV}(μ-sal-*o*-phen)(μ-O)]$_2$ (Fig. 23) was obtained by the reaction of H$_2$sal-*o*-phen with KMnO$_4$ in MeCN [135]. Its structure consists of two Mn^{IV} centres bridged by two oxygens to give a planar Mn$_2$O$_2$ core. Two tetradentate SB ligands bridge two manganese atoms via one phenolic oxygen atom and one imine nitrogen atom to each manganese atom to give a distorted octahedral environment [135].

The preparation of the Fe(III) chloro complex Fe(sal-*o*-phen)Cl was first described by Pfeifer and Tsumaki [136] in 1933, although this complex was later studied by Gerloch et al. [137] more extensively. The crystal structure of Fe(sal-*o*-phen)Cl has also been reported [138]. The geometry around Fe^{III} is a square-based pyramid, with the N$_2$O$_2$ donor set from the SB in the basal plane and the chlorine at the apical position, the iron atom raise above the basal mean plane ca. 0.5 Å. Fe(sal-*o*-phen)Cl hydrolyses in basic media to give the μ-oxo-dimer [Fe(sal-*o*-phen)]$_2$ O which was first prepared by Lewis et al. [139]. An improved method of preparation and its crystal structure have also been reported [140]. The structure consists of μ-oxo-bridged ferric sal-*o*-phen dimers and dimethylsulfoxide of crystallization. Each iron environment is a square-based pyramid. The complex Fe(sal-*o*-phen)Cl can react with other ligands to give complexes such as [Fe(sal-*o*-phen)(Hcat)] (cat = cathecol-1,2-dioxygenase) [141] which crystal structure exhibits properties typical of square-pyramidal geometry.

Complexation of metal halides by square-planar SB complexes led to bimetallic complexes such as [ClFe(sal-*o*-phen)FeCl(thf)$_2$]. In this complex the [Fe(sal-*o*-phen)Cl]$^-$ anion acts as a bidentate oxygen-donor ligand towards the [FeCl(thf)$_2$]$^+$ cation [121]. The coordination around one of the irons is square pyramidal

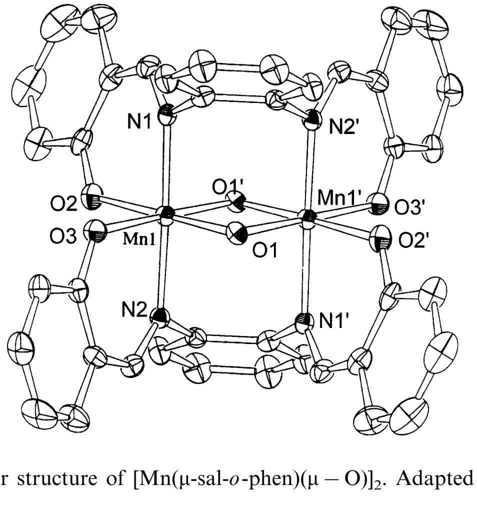


Fig. 23. Molecular structure of [Mn(μ-sal-*o*-phen)(μ – O)]$_2$. Adapted from Ref. [135].

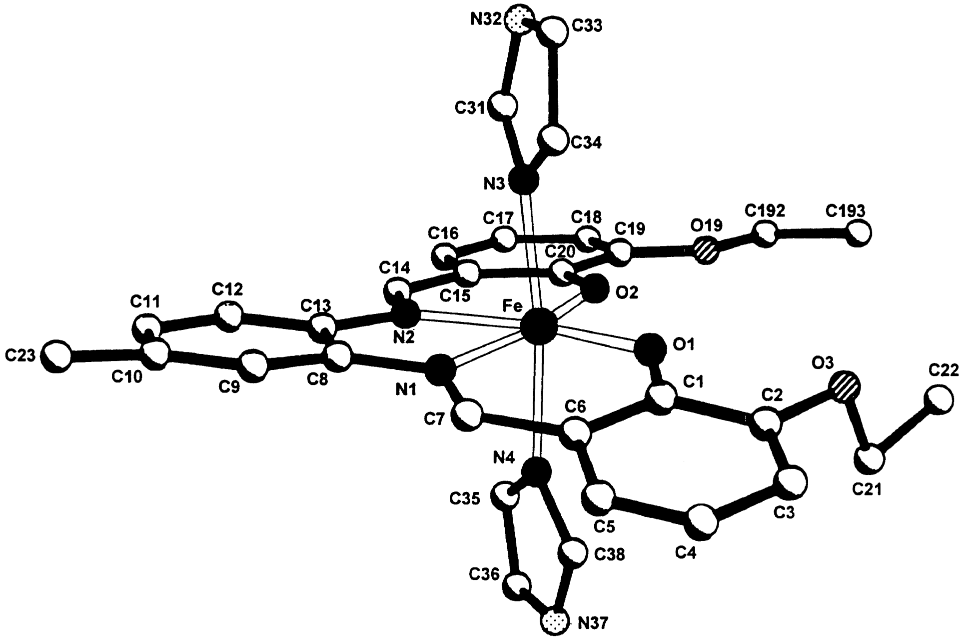


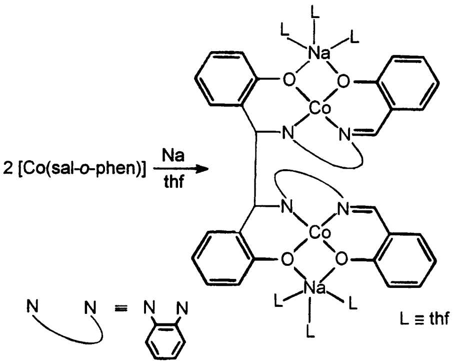
Fig. 24. View of the cationic complex $[Fe(3\text{-}EtO\text{-}sal\text{-}3,4\text{-}toluen)imd_2]^+$. Adapted from Ref. [143].

involving the donor atoms of the sal-*o*-phen ligand in the basal plane and a chlorine atom in the axial position. The sal-*o*-phen ligand exhibits an umbrella conformation. The other iron has a square-pyramidal geometry.

The complex Fe(sal-*o*-phen)Cl or its derivatives are also the starting material for the preparation of adducts with Lewis bases such as imidazole of general formula $[Fe(SB)imd_2]Y$ (SB = tetradentate SB with N_2O_2 donor set; imd = imidazole; Y = ClO_4^-, PF_6^- or BPh_4^-). These N_4O_2 complexes have interesting magnetic properties since they may exhibit thermally induced spin-crossover behaviour between the high spin (HS) and the low spin state (LS) ($S = 5/2 \Leftrightarrow S = 1/2$). Minor variations in all components of the complexes (counterion, substituents on the SB, structural features of the axial ligand, solvent molecules and intermolecular effects in solid state) can lead either to HS, LS or spin-crossover behaviour. In this context, the complexes derived from (**9**), (**18**) and (**19**), $[Fe(sal\text{-}o\text{-}phen)imd_2]BPh_4$ (HS) [142], $[Fe(3\text{-}EtO\text{-}sal\text{-}3,4\text{-}toluen)imd_2]ClO_4$ (HS) [143] (Fig. 24) and $[NaFe(3\text{-}MeO\text{-}sal\text{-}4\text{-}Cl\text{-}o\text{-}phen)imd_2](ClO_4)_2$ (LS) [118] (Fig. 19), respectively, have been prepared and structurally characterised. The latter constitutes one of the few examples of a pure low spin Fe(III) SB complex. For the three complexes, the coordination geometry around iron is a distorted octahedron with the *cis* SB in the equatorial plane and the two imidazole molecules occupying the axial positions. The $[NaFe(3\text{-}MeO\text{-}sal\text{-}4\text{-}Cl\text{-}o\text{-}phen)imd_2](ClO_4)_2$ (Fig. 19) complex is binuclear with the iron environment similar to that described before and with the sodium atom surrounded in a very distorted geometry by six oxygens: two phenoxo oxygens, two oxygens from the methoxy group and two from the perchlorate anion [143]. Fe–N bond distances which are very sensitive to the spin state of iron (III) were found to be ca. 0.15 Å longer for the HS complexes than those for the LS complex. The monohydrated complex [Fe(3-MeO-sal-4-Cl-*o*-phen)imd$_2$]ClO$_4$ · H$_2$O undergoes spin-crossover (HS⇔LS) behaviour when varying the temperature while the anhydrous complex is a pure HS [143]. The mononytrosyl Fe^{II} complex Fe(sal-*o*-phen)NO was found to exhibit spin crossover between $S = 1/2$ and $S = 3/2$ [144]. Electrochemical studies of [Fe(sal-*o*-phen)]$_2$O [145] and Ni(sal-*o*-phen) [146,147] have been reported.

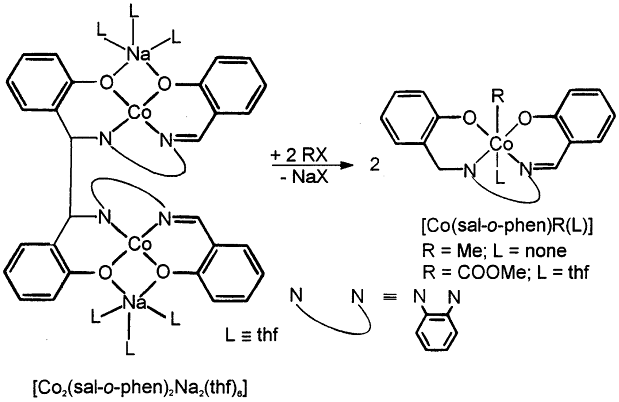
The complex Co(sal-*o*-phen) [113] crystallizes in two modifications, which differ only in their planarity: one exhibits molecules slightly distorted towards an umbrella conformation while the other is more planar. Despite having a rigid *o*-phenylene group, the flexibility of the molecular framework of sal-*o*-phen (planar⇔umbrella-shaped) analogous to that of salen having an ethylene group is noteworthy. The cobalt atom in both modifications has an approximately square planar geometry. The behaviour of this complex and derivatives as oxygen carriers has been commented in the previous section (see Section 3.2.2).

The formation of carbon–carbon bonded dimers in the reduction of [Co(sal-*o*-phen)] and their reactivity with electrophiles to form Co–C bonds has been studied by Floriani et al. [15]. The reduction of [Co(sal-*o*-phen)] and [Co(MeOsal-*o*-phen)] with sodium metal in thf led to the dimeric Co(II) derivatives containing a bridging C–C bond across two units in [Co$_2$(sal-*o*-phen)$_2$Na$_2$(thf)$_6$] and [Co$_2$(MeOsal-*o*-phen)$_2$Na$_2$(thf)$_4$]. In this process the reductive coupling of imino groups was observed (**20**). On the other hand, the reduction of [Co(MeOsalen)] under the same conditions led to the monomeric [Co^I(MeOsalen)Na(thf)$_2$] and a dimeric [{Co^I(MeOsalen)Na(thf)}$_2$] compound.



20 [Co$_2$(sal-*o*-phen)$_2$Na$_2$(thf)$_6$]

The structures of [Co$_2$(sal-*o*-phen)$_2$Na$_2$(thf)$_6$] and [Co$_2$(MeOsal-*o*-phen)$_2$Na$_2$(thf)$_4$] consist of the respective [Co(sal-*o*-phen)] and [Co(MeOsal-*o*-phen)] units linked in centrosymmetric dimers through a C–C bond provided by a reduced imino carbon of the SB. [Co$_2$(sal-*o*-phen)$_2$Na$_2$(thf)$_6$] is isostructural with the analogous nickel derivative [119]. The reaction of [Co^I(MeOsalen)Na(thf)$_2$] and dimeric [{Co^I(MeOsalen)Na(thf)}$_2$] compounds with alkylating agents such as MeI and ClCOOMe gave rise, as expected, to the corresponding Co–C containing derivatives. Usually this process has been explained as an attack on the RX electrophilic carbon by the Co(I) nucleophile. The reaction of [Co_2(sal-*o*-phen)$_2Na_2$(thf)$_6$] and [Co_2(MeOsal-*o*-phen)$_2Na_2$(thf)$_4$] with the alkylating agents led to a similar result, but by a different mechanism since these compounds contain Co(II) (**21**).



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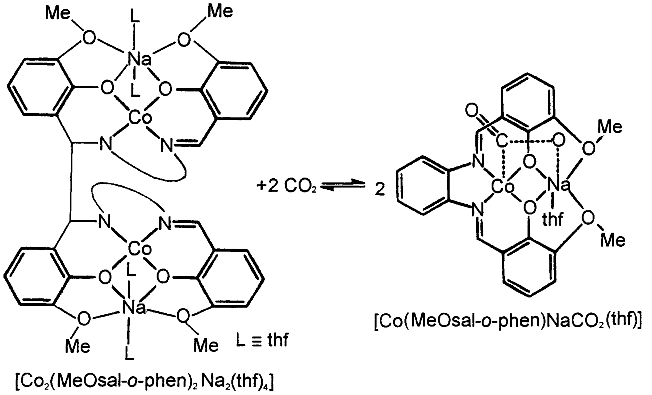
[Co(sal-*o*-phen)] and [Co(MeOsal-*o*-phen)] are inert respect to any alkylation under the same conditions, even in the presence of $NaBPh_4$. The cleavage and formation of the C–C bond linking the two sal-*o*-phen units has been observed in the reversible reactions of [Co_2(sal-*o*-phen)$_2Na_2$(thf)$_6$] and [Co_2(MeOsal-*o*-phen)$_2Na_2$(thf)$_4$] with carbon dioxide, leading to the CO_2 adducts [Co(sal-*o*-phen)$NaCO_2$(thf)] and [Co(MeOsal-*o*-phen)$NaCO_2$(thf)] (**22**). The cleavage and formation of the C–C bond can be used for storing and releasing a pair of electrons. A transition metal in combination with the C–C bonds can be used as a molecular battery in chemical transformations.



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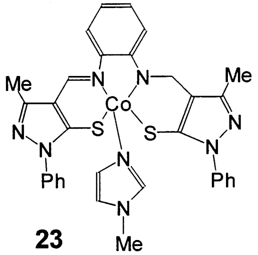
A trinuclear Co(II) complex derived from H_2sal-*o*-phen with both imino groups hydrogenated has been characterised by X-ray [148]. In its structure, two terminal Co(II) are five-coordinated while the central Co(II) is hexa-coordinated. Each phenolic oxygen of the central (hydrogenated) cobalt salicylaldimine molecule forms an intermolecular contact with the cobalt atom of a terminal Co(sal-*o*-phen) [148]. [Co(sal-*o*-phen)] can bind an axial ligand to give complexes of the type [Co(sal-*o*-phen)B], (where B = imidazole, 1-MeIm, 2-MeIm, pyridine, 3,4-lutidine). The preparation of [Co(sal-*o*-phen)(imidazole)] was first reported by Marzilli et al. [149]. The magnetic properties of this compound in solution and in solid state suggest that in both instances the complex exhibits equilibrium between high- (HS) and low-spin (LS) forms [150]. The crystal structure of the high-spin complex [Co(sal-*o*-phen)(2-MeIm)] was reported [151]. A report [152] has appeared on the preparation, magnetic properties and crystal structure of the Co^{II} SB complex [CoL(mim)] (**23**) (H_2L = *N*,*N*′-bis(5-mercapto-3-methyl-1-phenylpyrazol-4-ylmethylene)-*o*-phenylenediamine; mim = *N*-methylimidazole). Complex **23** has a S_2N_3 donor set and exhibits a thermally induced spin-crossover behaviour ($S = 1/2 \Leftrightarrow S = 3/2$).



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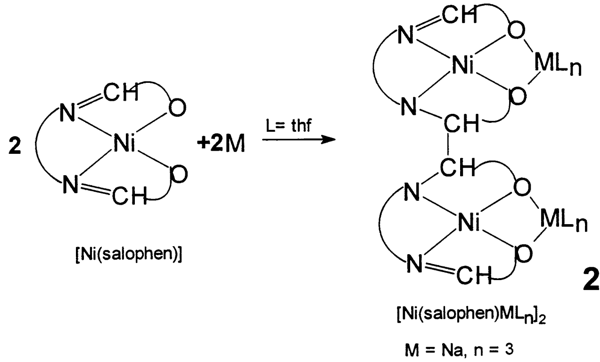
The structure was solved at 293 K ($\mu_{eff} = 3.6$ M. B.) and 103 K ($\mu_{eff} = 2.3$ M. B.), at which the complex is in the HS and LS state, respectively. The metal-ligand bonds distances decrease by 0.02–0.05 Å when passing from the HS to the LS form. The coordination geometry around the cobalt centre is a distorted trigonal bipyramid with one N and one S atom as axial ligands and the other N, S atoms and the *N*-imidazole nitrogen situated in the equatorial plane.

Alkali metals (M = Li, Na) promote the reductive coupling of two Ni(sal-*o*-phen) units generating polynuclear nickel(II)-alkali ion complexes [119]. The [Ni(sal-*o*-phen)] complex acts as a bidentate ligand toward alkali metal. Two Ni(sal-*o*-phen) units are joined through a C–C bond to form a dimeric structure of formula $[Ni(sal\text{-}o\text{-}phen)ML_n]_2$ (L = thf, M = Li, $n = 2$; M = Na, $n = 3$) (**24**).



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No change in the oxidation state of the metal and in its coordination geometry was observed as a consequence of the reaction with alkali metals. Mild oxidising agents remove two electrons from the dimeric compounds promoting the two C–C cleavage and restoring the original imino group. The crystal structures of $[Ni(sal\text{-}o\text{-}phen)Na(thf)_3]_2 \cdot C_4H_8O_2$ and $[Ni(sal\text{-}o\text{-}phen)Li(thf)_2]_2 \cdot 2thf$ have been reported. The formation of dimers does not modify the coordination of nickel, but markedly influences the conformation of the organic ligand. Thus, in both complexes coordination around nickel is nearly planar with small tetrahedral displacements that are significant only for the sodium derivative. In both complexes the two oxygens atoms of each Ni(sal-*o*-phen) unit are chelating the alkali metal. The tetrahedral coordination around lithium is achieved by the oxygens from two thf molecules [119].

A novel method for the complexation of neutral guest molecules by macrocyclic hosts, using an electrophilic metal cation (Ni^{2+}, Cu^{2+}, Zn^{2+} and UO_2^{2+}), immobilized within a SB moiety derived from *o*-phenylenediamine of a macrocyclic ligand has been reported [120]. The crystal structure of a 1:1 complex of urea and Ni(II) was solved. The first step involves the immobilizing of the metal cation in the SB cavity and in a second step the complexation of urea was carried out by recrystallizing the Ni(II) complex from a 0.1 M solution of urea in MeOH. Urea is not complexed within the macrocyclic cavity in an encapsulated fashion, nor coordinated to the nickel ion. The Ni(II) is in square planar coordination which prevents the cooperative interaction with a urea bound in the polyether cavity. The planar pentagonal coordination required for the co-complexation of urea with assistance by the polyether is not energetically favourable enough for the Ni(II) cation. On the other hand, the uranyl complexes with salen [153] and sal-*o*-phen [154] ligands show preferentially pentagonal bipyramidal coordination with the oxygen atoms in axial positions. The synthesis and structural properties of a complex $[UO_2(urea)mac]$ has been reported [120]. The encapsulation of the guest results in both coordination of the neutral guest to the metal ion and in hydrogen bonding with the polyether moiety of the macrocycle, when the cation prefers pentagonal planar coordination.

A series of substituted *o*-phenylenebis(salicylideneiminato) complexes of Cu(II), Cu(5-X-sal-*o*-phen) ($X = H, OCH_3, Cl$) have been prepared. For X = H (**9**) the crystal structure was reported [155]. The geometry around the copper is almost square planar, similarly to that of Co(sal-*o*-phen) [113]. These copper complexes show changes in colour when varying the solvents, which was attributed to coordination of the solvent to metal or interaction of solvent molecule with the sal-*o*-phen moiety changing its molecular conformation [155]. Waters and Hall [156] have attributed the violet and brown colour in Cu^{II} SB complexes to tetra-coordination and the green colour to strong five-coordination for copper.

The complexes of H_2sal-*o*-phen with Co(II) [113], Pd(II) [157], Ni(II) [158] and Cu(II) [159] are isomorphous. However, a new crystal modification for [Cu(sal-*o*-phen)] was reported [155]. [Cu(sal-*o*-phen)] with TCNQ gives a molecular 2:1 adduct of formula $[Cu(sal\text{-}o\text{-}phen)]_2 \cdot TCNQ$ [160] under critical conditions of crystallization. A mixture of [Cu(sal-*o*-phen)] solution and TCNQ in acetonitrile gave no appreciable complex formation over 24 h, but after a much longer period some formation occurred. The adduct is largely dissociated in solution and the following equilibrium was proposed:

$$2\mathrm{Cu(sal}\text{-}o\text{-}\mathrm{phen)} + \mathrm{TCNQ} \rightleftarrows [\mathrm{Cu(sal}\text{-}o\text{-}\mathrm{phen)}]_2 \cdot \mathrm{TCNQ}$$

where the rate of formation of the adduct may be slow. The crystal structure of $[\mathrm{Cu(sal}\text{-}o\text{-}\mathrm{phen)}]_2 \cdot \mathrm{TCNQ}$ has been reported. The unit cell contains a pair of centrosymmetrically related Cu(sal-*o*-phen) molecules and a centrosymmetrical TCNQ molecule. Cu(sal-*o*-phen) is nearly planar. This adduct shows at low temperature an intramolecular coupling within the dimer units which arise from-interactions either directly between two neighbouring stacked molecules of Cu(sal-*o*-phen) or through the molecules of TCNQ [160].

A crystallographic characterization of the $[\mathrm{Zn(H_2O)(salen)}]$ complex shows that the complex is monomeric and that Zn is five-coordinated [161]. The solubility of this neutral complex was found to be low. It seems that because of this not so many studies have been carried out with this neutral complex. On the other hand, the complexes of Zn(II) with the terbutylated version of sal-*o*-phen has been synthesised and its structure determined by X-ray diffraction [162]. [Zn(thf)(tbsal-*o*-phen)] (Fig. 25) was prepared by the neutralisation of the SB with $\mathrm{NEt_3}$ and subsequent addition of anhydrous $\mathrm{ZnCl_2}$ in thf. [Zn(py)(tbsal-*o*-phen)] is prepared by dissolving [Zn(thf)(tbsal-*o*-phen)] in pyridine. In both compounds Zn atom is five-coordinated in a square pyramidal geometry. In this geometry the ligand occupies the basal plane while the solvent molecule occupies the apical position. The Zn atoms are 0.29 and 0.40 Å, respectively, above the plane formed by the $\mathrm{N_2O_2}$ core. Attempts to prepare four-coordinate, desolvated derivatives by heating the compounds under vacuum proved unsuccessful. This terbutylated version of salen do enforce a monomeric geometry for zinc.

Lanthanoid (III) complexes of $\mathrm{H_2}$sal-*o*-phen with the composition $\mathrm{Ln_2}$(sal-*o*-phen)$_3$ were first reported in 1968 although no structural characterisation was provided [163]. A family of lanthanide (III) (La, Gd, Yb and Y) complexes with sal-*o*-phen of formula $[\mathrm{M(Ln(sal}\text{-}o\text{-}\mathrm{phen)_2}]$ ($\mathrm{M^+} = \mathrm{Li^+}$, $\mathrm{Na^+}$, $\mathrm{K^+}$or $\mathrm{Cs^+}$) have been prepared [164].

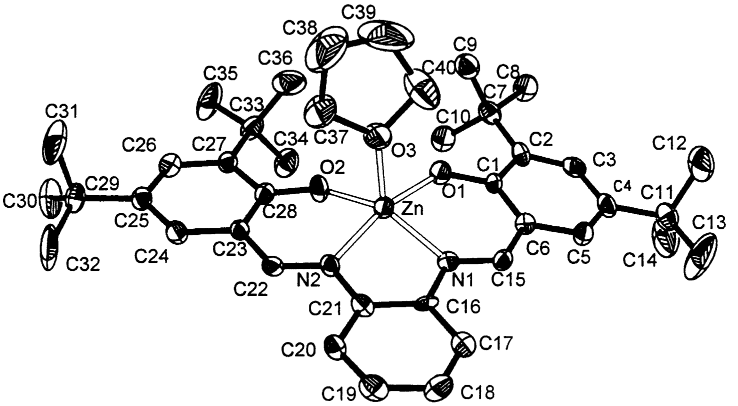


Fig. 25. ORTEP view of [Zn(tbsal-*o*-phen)(thf)]. Adapted from Ref. [162].

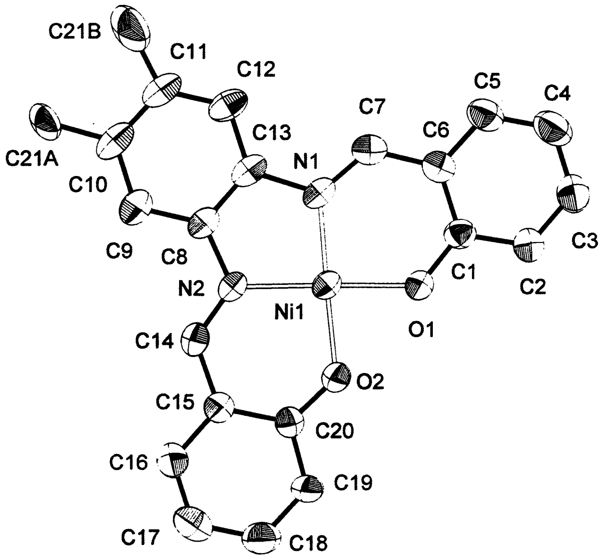


Fig. 26. Molecular structure of Ni(sal-3,4-toluen) · 1.5$CHCl_3$. Adapted from Ref. [13].

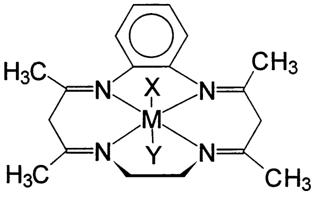
The syntheses of complexes of general formula [UO_2(L)(sal-*o*-phen)] (L = H_2O or EtOH) has been reported [154]. The coordination around the uranium is pentagonal bypiramidal with the oxygen atoms in the apical positions. The H_2O or EtOH occupe the fifth equatorial position. The structure is analogous to [UO_2(H_2O)-(salen)] [153]. Then UO_2(sal-*o*-phen) can be viewed as an immobilized neutral Lewis acid, which can be easily incorporated into more elaborate structures for use in complexation studies. Thus the role of the UO_2(sal-*o*-phen) complex as electrophilic catalyst in nucleophilic additions to the carbonyl group of acid derivatives has been studied [165]. Kinetic investigation showed that the uranyl centre does play a role as a built-in Lewis acid catalyst of ester cleavage.

Reports on the free SBs H_2sal-3,4-toluen [166,167] and H_2sal-4-Cl-*o*-phen [166] and their complexes with Cu(II) [166,167] and Ni(II) [166] have been published. The crystal structure of [Ni(sal-3,4-toluen)] · 1.5$CHCl_3$ (Fig. 26) has been recently determined [13]. The red complex is diamagnetic and presents a square-planar geometry, analogously to Ni(sal-*o*-phen) [168,169].

The macrocyclic ligand obtained by nickel (II) template condensation of *o*-phenylenediamine with 2,4-pentadione (**16**) was first described by Jäger [170]. Transition metal complexes derived from this type of ligands have been prepared and characterized by a number of researchers with most of the studies confined to Ni(II) [170–173], although a few studies of complexes with Co(II) [174], Fe(III), Fe(II) [175] and Mo [176] have been reported. Both the ligand and its four-coordinate Fe(II) complex have been structurally characterized [177] and have a markedly nonplanar saddle shape because of steric interactions of the methyl group with the benzene rings. Also the crystal structures of three five-coordinate complexes of (**16**) of formula [M(mac)X] (mac = macrocyclic ligand; M = Co(III), Fe(III), Mn(III), X = I, Cl, $N(C_2H_5)_3$, respectively) have been determined [178]. Raman studies [179,180] have been carried out for the Mn(II), Fe(II), Ni(II), Cu(II) and Zn(II) complexes of (**16**).

A series of macrocyclic Ni(II) and Cu(II) complexes derived from acetylacetone and *o*-, *m*-phenylendiamines or 3,4-toluenediamine have been prepared by template method and characterised by electronic, IR, ESR, NMR spectra and CV. The free ligands could not be isolated [181].

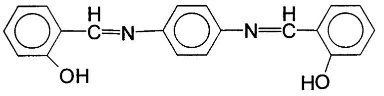
The template reaction between a divalent transition metal, *o*-phenylenediamine and bisacetylacetone-ethylenediamine yields 14-membered tetraaza macrocyclic six-coordinate complexes of the type $[M(mac)Cl_2]$ and $[M(mac)(SO_4)(H_2O)]$ (**25**) (where M = Fe(II), Co(II) and Cu(II); mac = macrocyclic ligand) [182]. The metal ions are coordinated by four azomethine nitrogen atoms bridged by acetylacetone moieties. These complexes are characterized by IR, electronic spectra and magnetic measurements [182].



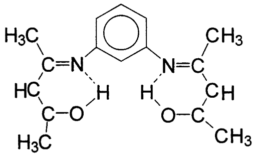
25 where M = Fe^{2+}, Co^{2+}, Cu^{2+}
X= Y =Cl^- or X= H_2O , Y= SO_4^{2-}

3.3.2. *Complexes derived from m- and p-phenylenediamines*

The SBs H_2sal-*m*-phen (**13**) and H_2sal-*p*-phen (**26**) were first prepared by Pfeifer and Pfitzner [183] in 1936 by reaction of salicylaldehyde with *m*-phenylenediamine or *p*-phenylenediamine, respectively. These authors [183] also obtained the complexes formulated as dimers Cu_2(sal-*m*-phen)$_2$ and Ni_2(sal-*m*-phen)$_2$ and the complex formulated as a polymer Cu_n(sal-*p*-phen)$_n$. The latter was formulated as a polymer based on its insolubility. Other reports on the preparation and characterisation of the SBs H_2sal-*m*-phen [184], H_2sal-2,4-toluen (**14**) [184] and H_2ac-*m*-phen (**27**) [185] have also been published.



26 H_2sal-*p*-phen



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SBs derived from *m*-phenylenediamines can only coordinate one nitrogen atom to any metal cation, giving dimeric complexes. The Co(II) and Cu(II) complexes with H_2ac-*m*-phen have been prepared and their dimeric structure has been established by mass spectrometry [185]. The magnetic susceptibility measurements as a function of temperature have shown the existence of weak antiferromagnetic interactions for SB complexes derived from *m*-phenylenediamine or 2,6 diaminopyridine and acetylacetone with Mn(II), Fe(II), Ni(II), Co(II) and Cu(II), and consequently these complexes have been formulated as dimers [186]. Several zirconium (IV) complexes of (**13**) or derivatives have been reported and their dimeric structure was suggested [187]. Magnetic studies for Cu_2(sal-*m*-phen)$_2$ [188,189], [Ni_2(sal-*m*-phen)$_2$] · $3H_2O$ [189] and Cu_2(sal-*p*-phen)$_2$ [189] have revealed the presence of weak intradimer antiferromagnetic interactions. Such interactions have also been reported [101] recently for a series of Cu(II), Co(II) and Ni(II) complexes with H_2sal-*m*-phen, H_2sal-2,4-toluen and H_2sal-2,6-toluen (**13**–**15**).

The complexes [Cu_2(sal-*m*-phen)$_2$] · $2CHCl_3$ [190] and [Co_2(sal-*m*-phen)$_2$] · $CHCl_3$ [101] (Fig. 27) have been characterised by X-ray crystallography. Both complexes

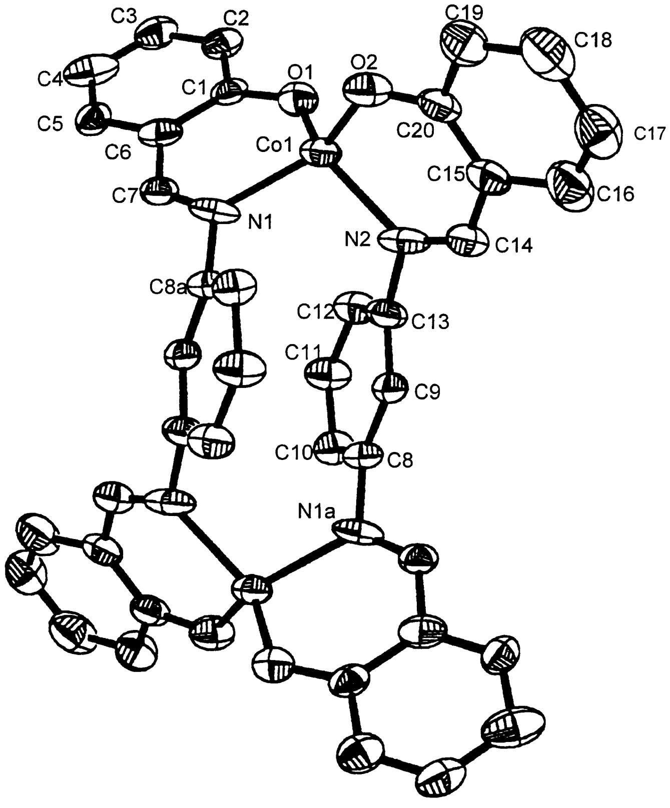


Fig. 27. ORTEP view of the binuclear complex [Co_2(sal-*m*-phen)$_2$]. Adapted from Ref [101].

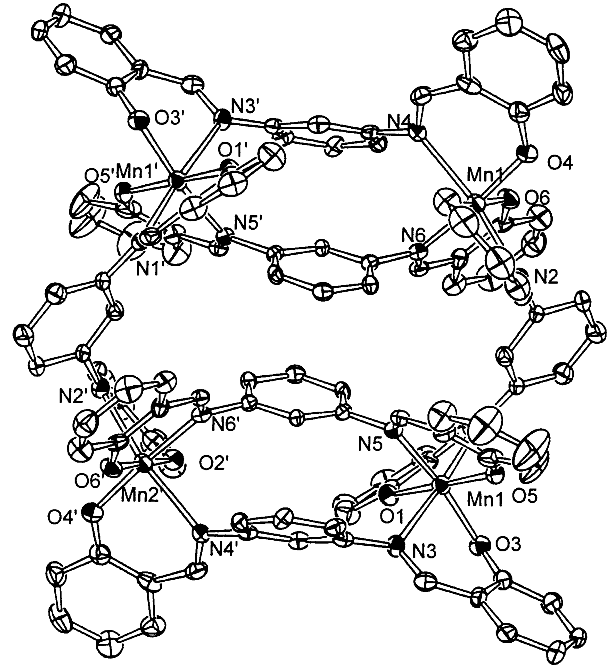


Fig. 28. The molecular structure of $[\mathrm{Mn}_4^{\mathrm{III}}(\mathrm{sal}\text{-}m\text{-}\mathrm{phen})_6]$. Adapted from Ref. [192].

are dimeric and centrosymmetrical with each coordination centre bridged by two *m*-phenylene groups. The coordination geometry is more distorted for the Cu(II) complex, being almost midway between *cis*-planar and tetrahedral while for the Co(II) complex (Fig. 27), the geometry is distorted tetrahedral.

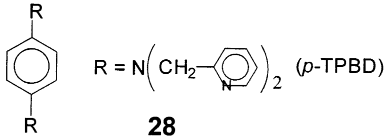
An electrochemistry study has shown that $\mathrm{Cu}_2(\mathrm{X}\text{-}\mathrm{sal}\text{-}m\text{-}\mathrm{phen})_2$ gives a single bielectronic reduction [191].

Matsushita et al. [192] have reported the preparation and characterisation of two cyclic tetranuclear manganese (III) complexes of formula $\mathrm{Mn}_4^{\mathrm{III}}(\mathrm{X}\text{-}\mathrm{sal}\text{-}m\text{-}\mathrm{phen})_6$ (X = H, 5-Br). The complexes were prepared by the reaction of KMnO_4 or manganese (III) acetate dihydrate with X-sal-*m*-phen. In contrast, using the same synthetic method the SB $\mathrm{H}_2\mathrm{sal}\text{-}o\text{-}\mathrm{phen}$ gave the di-μ-oxo-di-manganese (IV) $[\mathrm{Mn}^{\mathrm{IV}}\ (\mathrm{sal}\text{-}o\text{-}\mathrm{phen})(\mu\text{-}\mathrm{O})]_2$ [133]. These structural differences may be attributed to the different conformation of the SBs $\mathrm{H}_2\mathrm{sal}\text{-}o\text{-}\mathrm{phen}$ and $\mathrm{H}_2\mathrm{sal}\text{-}m\text{-}\mathrm{phen}$, the latter having a much longer distance between the two imine nitrogens than the former. In $\mathrm{Mn}_4^{\mathrm{III}}(\mathrm{sal}\text{-}m\text{-}\mathrm{phen})_6$ [192], two manganese ions are bridged by two sal-*m*-phen ligands giving a dimeric unit $[\mathrm{Mn}_2(\mathrm{sal}\text{-}m\text{-}\mathrm{phen})_2]^{2+}$. Two dimeric units are bridged by two residual sal-*m*-phen ligands (Fig. 28). Each manganese is surrounded by an octahedral $\mathrm{N}_3\mathrm{O}_3$ donor set. Electronic spectra, magnetic properties and cyclic voltammetry for these tetranuclear complexes have been reported [192].

No crystal structures have been reported to date for complexes derived from $\mathrm{H}_2\mathrm{sal}\text{-}p\text{-}\mathrm{phen}$ which is attributed to the insolubility of such compounds in the most common solvents, making the crystallization difficult.

4. Other ligands

4.1. *Tetrakis-N,N,N′,N′-(2-pyridylmethyl)benzene-p-diamine, p-TPBD*



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A new bis(tridentate) compound, tetrakis-*N*,*N*,*N*′,*N*′-(2-pyridylmethyl)benzene-*p*-diamine, *p*-TPBD (**28**), its diprotonated derivative, $[H_2(p\text{-TPBD})]^{2+}$, and a dicopper complex $[Cu_2(p\text{-TPBD})(H_2O)_4][S_2O_6]_2$ (Fig. 29) have been prepared and structurally characterized [193]. The pyridyl nitrogen atoms are strongly hydrogen bonded in the crystal structure of the yellow diprotonated salt $p\text{-TPBD}\cdot 2HClO_4\cdot 2Me_2CO$. Magnetic susceptibility measurements on $[Cu_2(p\text{-TPBD})(H_2O)_4][S_2O_6]_2$ indicate that the *p*-PDA bridge commutes a weak antiferromagnetic coupling. Two related dicopper complexes, $Cu_2(p\text{-TPBD})Cl_4$ and $Cu_2(p\text{-TPBD})(NO_3)_4$, were also isolated. Reaction of *p*-TPBD with one-electron oxidants generated a purple radical cation which was characterized.

The construction of positively charged one-dimensional coordination polymers is conceivable if metal ions with a preference for octahedral geometry are bound by the tridentate ends of two *p*-TPBD ligands and the *p*-TPBD acts as a bridging ligand. The mono- and di-nuclear transition metal complexes $[ZnCl_2(p\text{-TPBD})]$, $[ClPd(p\text{-TPBD})PdCl]^{2+}$ as well as the bis-coordinated complex $[Ru(p\text{-TPBD})_2]^{2+}$ are prepared [194]. Thus, the structural elements required for the construction of one-dimensional coordination polymers of *p*-TPBD were established. Such structures are likely for products formulated as $[M(p\text{-TPBD})]_n^{2n+}$ (M = Fe or Ni).

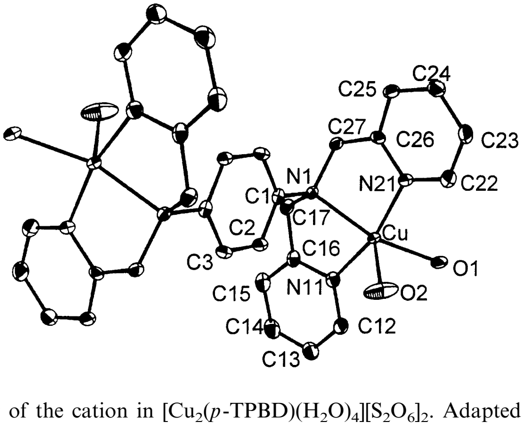
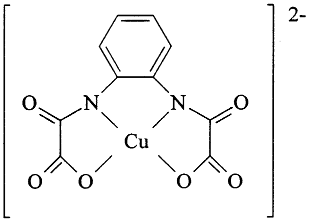


Fig. 29. ORTEP drawing of the cation in $[Cu_2(p\text{-TPBD})(H_2O)_4][S_2O_6]_2$. Adapted from Ref. [193].

4.2. Compounds derived from o-phenylenebis(oxamato), o-PBA

The ligand is synthesised as the diethylester Et_2H_2(*o*-PBA) of the *o*-phenylenebis(oxamic acid) by the reaction of ethyloxalyl chloride with *o*-phenylenediamine in thf [195]. Complexes based on this ligand have particular structural, magnetic and catalytic properties. With this ligand molecular bricks can be prepared that can be used as precursors of heterobimetallic compounds. One of these precursors is the $[Cu(o\text{-PBA})]^{2-}$ unit (**29**). This anionic precursor can give compounds with almost all kinds of countercations, including radical cations. Depending on the solvent, the charge and the ratio cation: $[Cu(o\text{-PBA})]^{2-}$, chain, bidimensional or fully interlocked three-dimensional structures have been obtained [195–197].



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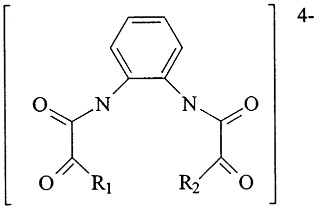
The strategy of the group of Kahn et al. [195,196] has consisted in designing molecular based magnets by assembling Mn(II)–Cu(II) molecular units in such a way that the Cu(II) ion interacts with the Mn(II) through the oxamate groups, which efficiently transmit an antiferromagnetic interaction between the carriers. In this way several compounds have been prepared. $MnCu(o\text{-PBA})(dmso)_3$ has a zig-zag chain structure, and chains are almost perfectly isolated within the crystal lattice [195]. The Cu(II) atom has an approximately square pyramidal surrounding with two nitrogen and two oxygen atoms from the *o*-PBA group in the basal plane, and a dmso oxygen atom in the apical position. The Mn(II) atom has a somewhat distorted octahedral surrounding. Two dmso molecules coordinate in *cis* positions and the other positions are occupied by oxygen atoms from two *o*-PBA ligands. It is remarkable that there is no indication of three-dimensional magnetic ordering for this compound down to 1.7 K. This is due to the fact that the bulky dmso molecules isolate the chains from each other. From this family of compounds is outstanding the compound of formula $(rad)_2Mn_2[Cu(o\text{-PBA})]_3(dmso)_2 \cdot 2H_2O$ [196], the radical cation 2-(4-*N*-methylpyridinium)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide being rad. Its structure consists of two nearly perpendicular graphite-like networks with edge-sharing $Mn(II)_6$ $Cu(II)_6$ hexagons. The two networks are fully interlocked with the same topological relationship as that between adjacent rings of a necklace. The compound has three kinds of spin carriers: Mn(II) and Cu(II) are antiferromagnetically coupled through oxamate bridges, with the radical cations bridging the Cu(II) ions through the nitronyl nitroxide groups and forming Cu-rad chains. This compound is a magnet below 22.5 K. All the Mn(II)–Cu(II) molecular based magnets mentioned present a magnetic hysteresis loop with a weak coercive field, when manganese is replaced by cobalt, and when compounds with this general formula $(rad)_2Co_2[Cu(o\text{-}PBA)]_3$ S (S = solvent) are prepared, a large coercive field is obtained. One of this kind of compounds $(rad)_2Co_2[Cu(o\text{-}PBA)]_3 \cdot 0.5dmso \cdot 3H_2O$ has a Tc of 34 K, and a coercive field as large as 3.0 kOe [197]. New metal oxamates as precursors of low dimensional heterobimetallic compounds have been prepared with ring substituted derivatives such as 4,5-dichloro-*o*-phenylenebisoxamato [198].

Journaux et al. [199] have studied the electrochemical behavior of a family of monomeric copper(II) complexes of the tetraanionic ligand *N*,*N*′-*o*-phenylenebis(oxamate) (**30**), and its methylamide (**31**) and bis(methylamide) derivatives (**32**).



	R_1	R_2
30	O	O
31	O	NMe
32	NMe	NMe

The copper(III)-copper(II) reduction potentials have been found to span a potential range from + 0.41 to − 0.02 V versus SCE. Thus, they explore the capacity of one specific family of tetraanionic chelating ligands in the stabilisation of Cu(III) complexes. Also, the crystal structure of copper(III) complex $[PPh_4][CuL] \cdot MeCN$ is reported (L = (**32**)), which constitutes one of the few examples of structurally characterised copper compounds in the rare + III oxidation state. In this compound, the Cu atom is coordinated to the four deprotonated amido nitrogen atoms of the chelating ligand in a nearly square-planar geometry. The Cu atom has a low spin d^8 configuration and it can be concluded that the selective stabilisation of this rather high oxidation state of copper in this complex is rendered possible by the strong electron-donating ability of the deprotonated-amide nitrogen atoms and the nearly square planar coordination afforded by the disubstituted oxamide ligands. Also with this ligand a Ni(III) complex has been prepared [199]. The synthesis and physical characterization, and the crystal and molecular structure of the compound $[NMe_4]_3[Fe(o\text{-}PBA)(CO_3)] \cdot 5H_2O$ have been reported [200]. This new iron(III)-carbonate monomeric complex of *ortho*-phenylenebis(oxamato) shows a moderately efficient non-heme catalyst for the aerobic epoxidation of alkenes with co-oxidation of pivalaldehyde. The iron(III) atom has a rhombically distorted octahedral coordination geometry. The coordination of the metallic atom to the carbonate imposes a nonplanar conformation for the tetradentate *o*-PBA ligand. A dimer compound of Mn(IV) with the ligand *o*-PBA has been prepared, and the activity in the oxidation of secondary alcohols to ketones by dioxygen and pivalaldehyde has been recently investigated [201].

4.3. Miscellany

Synthesis of novel polycyclic nucleoside analogues: 4-O-[(triisopropylphenyl)-sulphonyl]pyrimidine nucleosides were reacted with aromatic diamines leading to fused, polycyclic ring systems [202].

3-Aminophenazin-2-ol has been isolated from the chemical oxidation of *o*-PDA and characterized [203]. This ligand combines both phenazine and *o*-aminohydroxy moieties, that can be exploited to create metal complexes with novel chemical properties.

Tetraisopropyl-*p*-phenylenediamine has been prepared and its crystal structure determined [204].

Acknowledgements

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References

[1] A. Mederos, S. Domínguez, R. Hernández-Molina, J. Sanchiz, F. Brito, Coord. Chem. Rev. (1999) in press, Table 1.
[2] C.F.J. Barnard, S.P. Fricker, O.J. Vaugham, in: D. Thompson (Ed.), Insights into Speciality Inorganic Chemicals, Chapter 3, The Royal Society of Chemistry, Cambridge, UK, 1995.
[3] A.E. Martell, R.D. Handcock, Metal Complexes in Aqueous Solutions, Modern Inorganic Chemistry Series, Chapter 5, Plenum Press, New York, 1996.
[4] A.E. Martell, in: A.E. Martell, W.F. Anderson, D.G. Badman (Eds.), Development of Chelators for Clinical Use, Elsevier/North-Holland, New-York, 1981, pp. 67–104.
[5] R.J. Motekaitis, Y. Sun, A.E. Martell, Inorg. Chim. Acta 198–200 (1992) 421.
[6] J. Sanchiz, S. Domínguez, A. Mederos, F. Brito, J.M. Arrieta, Inorg. Chem. 36 (1997) 4108.
[7] N. Nakasuka, K. Takahashi, M. Tanaka, Anal. Chim. Acta 207 (1988) 361.
[8] E. Chinea, S. Domínguez, A. Mederos, F. Brito, J.M. Arrieta, A. Sanchez, G. Germain, Inorg Chem. 34 (1995) 1579.
[9] A. Mederos, S. Domínguez, E. Chinea, F. Brito, S. Midollini, A. Vacca, Bol. Soc. Chil. Quím. 42 (1997) 281.
[10] F. Lloret, M. Mollar, J. Moratal, J. Faus, Inorg. Chim. Acta 124 (1986) 67.
[11] F. Lloret, M. Mollar, J. Faus, M. Julve, W. Díaz, Inorg. Chim. Acta 189 (1991) 195.
[12] R. Hernández-Molina, A. Mederos, P. Gili, S. Domínguez, P. Núñez, Polyhedron 16 (1997) 4191.

[13] R. Hernández-Molina, A. Mederos, P. Gili, S. Domínguez, P. Núñez, G. Germain, T. Debaerdemaeker, Inorg. Chim. Acta 256 (1997) 319.
[14] C. Floriani, Polyhedron 8 (1989) 1717.
[15] S. De Angelis, E. Solari, E. Gallo, C. Floriani, A. Chiesi-Villa, C. Rizzoli, Inorg. Chem. 35 (1996) 5995.
[16] E.F. McCandlish, T.K. Michael, J.A. Neal, E.C. Lingafelter, N.J. Rose, Inorg Chem. 17 (1978) 1383.
[17] N. Nakasuka, Sh. Azuma, Ch. Katayama, M. Honda, J. Tanaka, M. Tanaka, Acta Cristallogr. C41 (1985) 1176.
[18] N. Nakasuka, Sh. Azuma, M. Tanaka, Acta Cristallogr. C41 (1986) 1482.
[19] N. Nakasuka, Sh. Azuma, M. Tanaka, Acta Cristallogr. C42 (1986) 1736.
[20] N. Nakasuka, M. Shiro, Acta Cristallogr. C45 (1989) 1487.
[21] N. Nakasuka, Sh. Azuma, M. Tanaka, Acta Cristallogr. C42 (1986) 673.
[22] M. Mizuno, S. Funahashi, N. Nakasuka, M. Tanaka, Inorg. Chem. 30 (1991) 1550.
[23] M. Hernández-Padilla, S. Domínguez, A. Mederos, J.M. Arrieta, Acta Cristallogr. C51 (1995) 1549.
[24] M. Hernández-Padilla, J. Sanchiz, S. Domínguez, A. Mederos, J.M. Arrieta, F.J. Zuñiga, Acta Cristallogr. C52 (1996) 1618.
[25] K. Otazai, I. Kato, Jpn. Anal. 8 (1959) 259.
[26] (a) A. Mederos, J.V. Herrera, J.M. Felipe, M.L. Quesada, An. Quim. 80B (1984) 281. (b) A. Mederos, J.V. Herrera, J.M. Felipe, M. Hernández-Padilla, An. Quim. 82B (1986) 150.
[27] (a) N. Nakasuka, M. Kunimatsu, K. Matsumura, M. Tanaka, Inorg. Chem. 24 (1985) 10. (b) K. Matsumura, N. Nakasuka, M. Tanaka. Inorg. Chem. 26 (1987) 1419.
[28] A. Mederos, J.V. Herrera, J.M. Felipe, An. Quím. 79B (1983) 328.
[29] J.H. Grimes, A.J. Huggard, S.P. Wilford, J. lnorg. Nucl. Chem. 25 (1963) 1225.
[30] N. Nakasuka, Y. Natsume, Inorg. Chem. 29 (1990) 147.
[31] S. Azuma, N. Nakasuka, M. Tanaka, Bull. Chem. Soc. Jpn. 65 (1992) 2333.
[32] M. Yamamoto, N. Nakasuka, M. Tanaka, Bull. Chem. Soc. Jpn. 65 (1992) 1566.
[33] A. Mederos, J.V. Herrera, J.M. Felipe, An. Quim. 81B (1985) 152.
[34] A. Mederos, J.V. Herrera, J.M. Felipe, An. Quim. 83B (1987) 22.
[35] A. Mederos, S. Domínguez, M. Hernández-Padilla, F. Brito, J. Coord. Chem. 2 (1990) 283.
[36] F. Brito, A. Mederos, J.V. Herrera, S. Domínguez, M. Hernández-Padilla, Polyhedron 7 (1990) 1187.
[37] A. Mederos, J.M. Felipe, M. Hernández-Padilla, F. Brito, E. Chinea, K. Bazdikian, J. Coord. Chem. 14 (1986) 277.
[38] J.J.R. Frausto Da Silva, R.J.P. Williams, The Biological Chemistry of Elements: The Inorganic Chemistry of Life, Clarendon Press, Oxford, UK, 1991.
[39] A. Ringbom, Complexation in Analytical Chemistry, Interscience, New York, 1963.
[40] R. Ma, I. Murase, A.E. Martell, Inorg. Chim. Acta 223 (1994) 109.
[41] E.T. Clarke, A.E. Martell, Inorg. Chim. Acta 86 (1991) 103.
[42] M. Hernández-Padilla, S. Domínguez, P. Gili, A. Mederos, C. Ruíz-Pérez, Polyhedron 11 (1992) 1965.
[43] A. Mederos, S. Domínguez, P. Esparza, J. Sanchiz, D. Saysell, R. Ruano, A. Sanchez, J.M. Arrieta, in preparation.
[44] E. Blasius, G. Olbrich, Z. Analyt. Chem. 151 (1956) 81.
[45] A. Mederos, J.V. Herrera, M. Modolell, A. Rancel, J.M. Felipe, An. Quím. 80B (1984) 213.
[46] A. Mederos, A. Rancel, S. Domínguez, J.V. Herrera, A. Benítez, An. Quím. 87 (1991) 795.
[47] A. Mederos, J.V. Herrera, A. Benítez, A. Rancel, An. Quím. 84B (1988) 5.
[48] (a) A. Mederos, F.G. Manrique, J.V. Herrera, M. Alvarez-Romero, J.M. Felipe, An. Quím. 82B (1986) 133. (b) F.G. Manrique, A. Mederos, A. Rodriguez-González, A. Hardisson, Y.G. Smeyers, An. Quím. 69 (1973) 305.
[49] (a) E. Uhlig, D. Hermann, Z. Chem. 4 (1964) 436. (b) Z. Anorg. Allg. Chem. 359 (1968) 135; 365 (1969) 79.

[50] S. González García, F.J. Sánchez-Santos, An. Quím. 71 (1975) 775; 72 (1976) 148, 153; 77B (1981) 175, 178.
[51] A. Mederos, A. Rodríguez-González, B. Rodríguez-Ríos, An. Quím. 66 (1970) 531.
[52] A. Mederos, A. Rodríguez-González, B. Rodríguez-Ríos, An. Quím. 69 (1973) 731.
[53] A. Mederos, J.V. Herrera, J.M. Felipe, An. Quím. 81B (1985) 26.
[54] F. Brito, J.M. Gonçalvez, Project No. 51.78.-31-51-1228, CONICIT, Caracas, Venezuela, 1981.
[55] R. Arnek, L.G. Sillén, O. Wahlberg, Ark. Kemi 61 (1969) 353.
[56] A. Mederos, S. Domínguez, M. Hernández-Padilla, F. Brito, E. Chinea, Bol. Soc. Quím. Per 50 (1984) 277.
[57] A Mederos, J.M. Felipe, F. Brito, K. Bazdikian, J. Coord. Chem. 14 (1986) 285.
[58] A. Mederos, A. Benítez, A. Rancel, R. Guerra, F. Brito, K. Bazdikian, J. Bruzal, J. Coord. Chem. 15 (1986) 85.
[59] E. Uhlig, D. Hermann, Z. Anorg. Allg. Chem. 360 (1968) 158.
[60] F. Brito, A. Mederos, P. Gili, S. Domínguez, P. Martín-Zarza, J. Coord. Chem. 17 (1988) 311.
[61] F. Brito, A. Mederos, P. Gili, R. Guerra, S. Domínguez, M. Hernández-Padilla, J. Coord. Chem. 20 (1989) 1969.
[62] A. Mederos, P. Gili, S. Domínguez, A. Benítez, M.S. Palacios, M. Hernández-Padilla, P. Martín-Zarza, M.L. Rodríguez, C. Ruiz-Pérez, F.J. Lahoz, L.A. Oro, F. Brito, J.M. Arrieta, M. Vlassi, G. Germain, J. Chem. Soc. Dalton Trans. (1990) 1477.
[63] S. Domínguez, A. Rancel, J.V. Herrera, A. Mederos, F. Brito, J. Coord. Chem. 25 (1992) 271.
[64] S. Domínguez, A. Mederos, P. Gili, A. Rancel, A.E. Rivero, F. Brito, F. Lloret, X. Solans, C. Ruiz-Pérez, M.L. Rodríguez, I. Brito, Inorg. Chim. Acta 255 (1997) 367.
[65] A. Sabatini, A. Vacca, P. Gans, Talanta 21 (1974) 53.
[66] P. Gans, A. Sabatini, A. Vacca, J. Chem. Soc. Dalton Trans. (1985) 1195.
[67] M.L. Rodríguez, I. Brito, S. Domínguez, A. Mederos, in: Preparación de Materiales, Coord. Xavier Solans, Universitat of Barcelona, Spain, 1991, p. 175.
[68] B. Rodríguez-Rios, J. Fuentes, R. Reboso, An. Quím. 80B (1984) 424.
[69] J. Fuentes, R. Reboso, A. Rodríguez, Polyhedron 8 (1989) 2693.
[70] L. Michaelis, M.P. Schubert, J. Biol. Chem. 106 (1934) 331.
[71] B. Rodríguez-Ríos, A. Peralonso, A. Mederos An. Quím. 59B (1963) 493, 501; 61B (1965) 717, 723.
[72] E. Uhlig, D. Hermann, Z. Chem. 4 (1964) 151, 436, 463.
[73] (a) J.A. Chopoorian, K.O. Loeffler, W.F. Marzluff, G.H. Dorion, Nature, 204 (1964) 180. (b) J.A. Chopoorian, K.O. Loeffler, US 3 (1966) 272, 646.
[74] J. Fuentes, M.R. Rodríguez-Bravo, R. Reboso, A. Rodríguez, An. Quím. 83 (1987) 48.
[75] L. Michaelis, M.P. Schubert, S. Granick, J. Am. Chem. Soc. 61 (1939) 1981.
[76] B. Rodríguez-Ríos, A. Mederos, An. Quím. 64B (1968) 983.
[77] B. Rodríguez-Ríos, A. Mederos, An. Quím. 65B (1969) 649.
[78] B. Rodríguez-Ríos, A. Mederos, An. Quím. 65B (1969) 557, 743, 751.
[79] B. Rodríguez-Ríos, A. Mederos, An. Quím. 64B (1968) 47.
[80] F. Brito, P. Gili, A. Mederos, S. Domínguez, A.E. Rivero, J. Coord. Chem. 21 (1990) 29.
[81] C. Ruíz-Pérez, M.L. Rodríguez, F.V. Rodríguez-Romero, A. Mederos, P. Gili, P. Martín-Zarza, Acta Crystallog. C46 (1990) 1405.
[82] C.A. González, M. Hernández-Padilla, S. Domínguez, A. Mederos, F. Brito, J.M. Arrieta, Polyhedron 16 (1997) 2925.
[83] B. Rodríguez Ríos, J. Fuentes, R. Reboso, An. Quím. 80B (1984) 32, 37.
[84] B. Rodríguez Ríos, J. Fuentes, R. Reboso, An. Quím. 80B (1984) 60.
[85] J. Fuentes, R. Reboso, A. Rodríguez, Polyhedron 8 (1989) 1365.
[86] H. Schiff, Ann. Chim (Paris) 131 (1864) 118.
[87] S. Dayagi, Y. Degani, in: S. Patai (Ed.), The Chemistry of the Carbon–Nitrogen Double Bonds, Wiley-Interscience, New York, 1970, p. 71.
[88] M. Calligaris, L. Randaccio, in: G. Wilkinson (Ed.), Comprehensive Coordination Chemistry, vol. 2, Pergamon Press, Oxford, 1987, p. 715.
[89] F.P. Dwyer, D.P. Mellor, Chelating Agents and Metal Chelates, Academic Press, London, 1964.

[90] A.D. Garnovskii, A.L. Nivorozhkin, V.I. Minkin, Coord. Chem. Rev. 126 (1993) 1.
[91] L.F. Lindoy, Chem. Soc. Rev. 25 (1971) 379.
[92] M. Calligaris, G. Nardin, L. Randaccio, Coord. Chem. Rev. 7 (1972) 385.
[93] M.D. Hobday, T.D. Smith, Coord. Chem. Rev. 9 (1972) 311.
[94] H.S. Masleu, T.N. Waters, Coord. Chem. Rev. 17 (1975) 137.
[95] H. Connors, C.A. McAuliffe, J. Tames, Rev. Inorg. Chem. 3 (1981) 199.
[96] S. Yamada, A. Takeuchi, Coord. Chem. Rev. 43 (1982) 187.
[97] A. Syamal, M.R. Maurya, Coord. Chem. Rev. 95 (1989) 183.
[98] J. Costamagna, J. Vargas, R. Latorre, A. Alvarado, G. Mena, Coord. Chem. Rev. 119 (1992) 67.
[99] A.D. Garnovskii, A.L. Nivorozhkin, V.J. Minkin, Coord. Chem. Rev. 126 (1993) 1.
[100] R.J. Motekaitis, A.E. Martell, Inorg. Chem. 27 (1988) 2718.
[101] R. Hernández-Molina, A. Mederos, P. Gili, S. Domínguez, F. Lloret, J. Cano, M. Julve, C. Ruiz-Pérez, X. Solans, J. Chem. Soc. Dalton Trans. (1997) 4327.
[102] F. Lloret, J. Moratal, J. Faus, J. Chem. Soc. Dalton Trans. (1983), 1743.
[103] F. Lloret, J. Moratal, J. Faus, J. Chem. Soc. Dalton Trans. (1983) 1749.
[104] R.J. Motekaitis, A.E. Martell, D.A. Nelson, Inorg. Chem. 23 (1984) 275.
[105] M.S. Masoud, F.M. Eizawawy, Ind. J. Chem. 23A (1984) 149.
[106] E.S. Jayadevappa, S.C. Galgali, J. Chem. Soc. LX (1987) 366.
[107] G.P. Sengupta, C.R. Bera, N.N. Gosh, J. Ind. Chem. Soc. LXIV (1987) 366.
[108] H.N. Pandey, Acta Ciencia Indica XVI (1990) 273.
[109] N. Shori, Y. Dutt, R.P. Singh, J. Inorg. Nucl. Chem. 34 (1972) 2007.
[110] M.S. Mayadeo, R.K. Banavali, Ind. J. Chem. 25A (1986) 396.
[111] T. Gündüz, E. Kili, E. Canel, F. Köseoglu, Anal. Chim. Acta 282 (1984) 149.
[112] R. Hernández-Molina, A. Mederos, P. Gili, S. Domínguez, unpublished results.
[113] N.B. Pahor, M. Calligaris, P. Delise, G. Dodic, G. Nardin, L. Randaccio, J. Chem. Soc. (1976) 2478.
[114] A.E. Martell, M. Calvin, Chemistry of the Metal Chelate Compounds; Prentice Hall: Englewood Cliffs, NJ, 1952, Chapter 6 and references therein.
[115] D. Chen, A.E. Martell, Y. Sun, Inorg. Chem. 28 (1989) 2647.
[116] (a) D. Chen, A.E. Martell, Inorg. Chem. 26 (1987) 1026. (b) R.J. Motekaitis, A.E. Martell, Inorg. Chem. 27 (1988) 2718.
[117] F. Corazza, C. Floriani, A. Chiesi-Villa, C. Guastini, S. Ciurli, J. Chem. Soc. Dalton Trans. (1988) 2341.
[118] R. Hernández-Molina, A. Mederos, S. Domínguez, P. Gili, C. Ruiz-Pérez, A. Castiñeiras, X. Solans, F. Lloret, J.A. Real, Inorg. Chem. 37 (1998) 5102.
[119] S. Gambarotta, F. Urso, C. Floriani, A. Chiesi-Villa, C. Guastini, Inorg. Chem. 22 (1983) 3966.
[120] C.J. van Staveren, J. van Eerden, F.C.J.M. van Veggel, S. Harkema, D.N. Reinhoudt, J. Am. Chem. Soc. 110 (1988) 4994.
[121] E. Solari, F. Corazza, C. Floriani, A. Chiesi-Villa, C. Guastini, J. Chem. Soc. Dalton Trans. (1990) 1345.
[122] E. Gallo, S. De Angelis, E. Solari, C. Floriani, N. Re, A. Chiesi-Villa, C. Rizzoli, J. Am. Chem. Soc. 115 (1993) 9850.
[123] E. Solari, C. Maltese, M. Latronico, C. Floriani, A. Chiesi-Villa, C. Rizzoli, J. Chem. Soc. Dalton Trans. (1998) 2395
[124] S. Gambarota, M. Mazzanti, C. Floriani, M. Zehnder, J. Chem. Soc. Chem. Comm. (1984) 1116.
[125] M. Mazzanti, S. Gambarotta, C. Floriani, A. Chiesi-Villa, C. Guastini, Inorg. Chem. 25 (1986) 2308.
[126] X. Wang, X.M. Zhang, H.X. Liu, Polyhedron 14 (1995) 293.
[127] M. Mazzanti, S. Gambarotta, C. Floriani, A. Chiesi-Villa, C. Guastini, Inorg. Chem. 25 (1986) 2308.
[128] K.S. Murray, G.R. Simm, B.O. West, Aust. J. Chem. 26 (1973) 991.
[129] M. Pasquali, F. Marchetti, C. Floriani, Inorg. Chem. 18 (1979) 2401.
[130] E. Gallo, E. Solari, C. Floriani, N. Re, A. Chiesi-Villa, C. Rizzoli, Inorg. Chem. 36 (1997) 2178.

[131] E. Gallo, E. Solari, C. Floriani, N. Re, A. Chiesi-Villa, C. Rizzoli, Angew. Chem. Int. Ed. Engl. 35 (1996) 1981.
[132] R.K. Boggess, J.W. Hughes, W.M. Coleman, L.T. Taylor, Inorg. Chim. Acta 38 (1980) 183.
[133] W.M. Coleman, R.K. Boggess, J.W. Hughes, L.T. Taylor, Inorg. Chem. 20 (1981) 1253.
[134] F.M. Ashmawy, C.A. McAuliffe, R.V. Parish, J. Tames, J. Chem. Soc. Dalton Trans. (1985) 1391.
[135] H. Torayama, T. Nishida, H. Asada, M. Fujiwara, T. Matsushita, Polyhedron 17 (1998) 105.
[136] P. Pfieffer, T. Tsumaki, Annalen 504 (1933) 84.
[137] M. Gerloch, J. Lewis, F.E. Mabbs, A. Richards, J. Chem. Soc. A (1968) 112.
[138] A. Elmani, Y. Elerman, I. Svoboda, H. Fuess, Acta Cryst. C49 (1993) 1365.
[139] J. Lewis, F.E. Mabbs, A. Richards, J. Chem. Soc. A (1967) 1014.
[140] F.M. Ashmawy, A.R. Ujaimi, Ch.A. McAuliffe, R.V. Parish, R.G. Pritchard, Inorg. Chim. Acta 187 (1991) 155.
[141] E. Solari, F. Corazza, C. Floriani, A. Chiesi-Villa, C. Guastini, J. Chem. Soc. Dalton Trans. (1990) 1345.
[142] Y. Nishida, K. Kino, S. Kida, J. Chem. Soc. Dalton Trans. (1987) 1157.
[143] R. Hernández-Molina, A. Mederos, S. Domínguez, P. Gili, C. Ruiz-Pérez, A. Castiñeiras, X. Solans, F. Lloret, J.A. Real, Inorg. Chem. 37 (1998) 5102.
[144] O.R. Leeuwenkamp, C.M. Plug, A. Bult, Polyhedron 6 (1987) 295.
[145] J.P. Costes, J.B. Tommasino, B. Carré, F. Soulet, P.L. Fabre, Polyhedron 14 (1995) 771.
[146] A.A. Isee, A. Gennaro, E. Vianello, Electrochim. Acta 37 (1992) 113.
[147] S. Gambarotto, F. Urso, C. Floriani, A. Chiese-Villa, C. Guastini, Inorg. Chem. 22 (1983) 3966.
[148] E. Solari, C. Floriani, D. Cunningham, T. Higgins, P. McArdle, J. Chem. Soc. Dalton Trans. (1991) 3139.
[149] L.G. Marzilli, P.A. Marzilli, J. Halpern, J. Am. Chem. Soc. 93 (1971) 1374.
[150] L.G. Marzilli, P.A. Marzilli, Inorg. Chem. 11 (1972) 457.
[151] B.J. Kennedy, G.D. Fallon, B.M.K.C. Gatehouse, K.S. Murray, Inorg. Chem. 23 (1984) 580.
[152] A.L. Nivorozhkin, H. Toftlund, M. Nielsen, J. Chem. Soc. Dalton Trans. (1994) 361.
[153] G. Bandoli, D.A. Clemente, J. Chem. Soc. Dalton Trans. (1975) 612
[154] G. Bandoli, D.A. Clemente,U. Croatto, M. Vidali, P.A. Vigato, J. Chem. Soc. Chem. Com. (1971) 1330
[155] E. Suresh, M.M. Bhadbhade, D. Srinivas, Polyhedron 15 (1996) 4133.
[156] T.N. Waters, D.J. Hall, J. Chem. Soc. (1959) 1200.
[157] G.D. Fallon, B.M. Gatehouse, Acta Cryst. B32 (1976) 2591.
[158] A. Radha, M. Seshasayee, K. Ramalingam, G. Aravamudan, Acta Cryst. C41 (1985) 1169.
[159] H. Montgomery, B. Morosin, Acta Cryst. B32 (1961) 551.
[160] P. Cassoux, A. Gleizes, Inorg. Chem. 19 (1980) 665.
[161] M.J. O'Conner, B.O. West, Aust. J. Chem. 20 (1967) 2077.
[162] V. Van Axel Castelly, R. Cacciapaglia, G. Chiosis, F.C.J.M. van Veggel, L. Mandolini, D.N. Reinhoudt, Inorg. Chim. Acta 246 (1996) 181.
[163] N.K. Dutt, K. Nag, J. Inorg. Nucl. Chem. 30 (1968) 2493.
[164] H. Chen, R.D. Archer, Inorg. Chem. 33 (1994) 5195.
[165] A.L. Singer, D.A. Atwood, Inorg. Chim. Acta 277 (1998) 157.
[166] (a) A. Mederos, F.G. Manrique, A. Medina, P. Núñez, An. Quim. 81B (1985) 285. (b) A. Mederos, A. Medina, P. Gili, F.G. Manrique, P. Núñez, An. Quim. 82B (1986) 338.
[167] S.J. Gruber, C.M. Harris, E. Sinn, Inorg. Chem. 7 (1968) 268.
[168] H.C. Clark, A.L. Odell, J. Chem. Soc. (1955) 3431.
[169] J.B. Willis, D.P. Mellor, J. Am. Chem. Soc. 69 (1947) 1237.
[170] E.G. Jäger, Z. Chem. 4 (1964) 437.
[171] H. Hiller, P. Dimroth, H. Pfitzner, Justus Liebigs Ann. Chem. 717 (1968) 137.
[172] P. Chave, C.L. Honeybourne, Chem. Comm. (1969) 279.
[173] E.G. Jäger, Z. Anorg. Allg. Chem. 364 (1969) 177.
[174] V.L. Goedken, S.M. Peng, Y.A. Park, J. Am. Chem. Soc. 96 (1974) 284.
[175] (a) V.L. Goedken, Y.A. Park, S.M. Peng, J. Molin-Norris, J. Am. Chem. Soc. 96 (1974) 7893. (b) V.L. Goedken, Y.A. Park, J. Chem. Soc. Chem. Commun. (1975) 214.

[176] L.G. Bell, J.C. Dabrowiak, J. Chem. Soc. Chem. Comm. (1975) 512.
[177] V.L. Goedken, J.J. Pluth, S.M. Peng, B. Bursten, J. Am. Chem. Soc. 98 (1976) 8014.
[178] M.C. Weiss, B. Bursten, S.M. Peng, V.L. Goedken, J. Am. Chem. Soc. (1976) 8021.
[179] W.H. Woodruff, R.W. Pastor, J.C. Dabrowiak, J. Am. Chem. Soc. (1976) 7999.
[180] L.A. Nafie, R.W. Pastor, J.C. Dabrowiak, W.H. Woodruff, J. Am. Chem. Soc. (1976) 8007.
[181] K.H. Reddy, M.R. Reddy, K.M. Raju, Polyhedron 16 (1997) 2673.
[182] K.H. Reddy, G. Krishnaiah, Y. Sreenivasulu, Polyhedron 10 (1991) 2785.
[183] P. Pfeiffer, H. Pfitzner, J. Prakt. Chem. 145 (1936) 243.
[184] A. Mederos, F.G. Manrique, A. Medina, An. Quim. 76B (1980) 33.
[185] A. Mederos, F.G. Manrique, A. Medina, G. de la Fuente, An. Quim. 79B (1983) 377.
[186] D.P. Singh, V.K. Chavhan, V.B. Rana, M.P. Teotia, J. Coord. Chem. 13 (1984) 159.
[187] N.S. Biradar, A.L. Locker, J. Inorg. Nucl. Chem. 37 (1975) 1308.
[188] D.Y. Jeter, W.E. Hatfield, Inorg. Chim. Acta 6 (1972) 440.
[189] E.F. Hasty, L.J. Wilson, D.N. Hendrickson, Inorg. Chem. 17 (1978) 1834.
[190] C.A. Bear, J.M. Waters, T.N. Waters, J. Chem. Soc. A (1970) 2494.
[191] G.S. Patterson, R. Holm, Bioinorg. Chem. 4 (1975) 257.
[192] H. Torayama, T. Nishida, H. Asada, M. Fujiwara, T. Matsushita, Polyhedron 16 (1997) 3787.
[193] T. Buchen, A. Hazel, C.J. Mc Kenzie, L.P. Nielsen, J.Z. Pedersen, D. Schollmeyer, J. Chem. Soc. Dalton Trans. (1997) 2697.
[194] A. Hazel, C.J. Mc Kenzie, L.P. Nielsen, J. Chem. Soc. Dalton Trans. (1998) 1751.
[195] H.O. Stumpf, Y. Pei, O. Kahn, J. Sletten, J.P. Renard, J. Am. Chem. Soc. 115 (1993) 6738.
[196] H.O. Stumpf, L. Ouahab, Y. Pei, D. Grandjean, O. Kahn, Science 261 (1993) 447.
[197] H.O. Stumpf, Y. Pei, C. Michaut, O. Kahn, J.P. Renard, Chem. Mater. 6 (1994) 257.
[198] M. Fettouhi, L. Ouahab, A. Boukhari, O. Cador, C. Matonier, O. Kahn, Inorg. Chem. 35 (1996) 4932.
[199] R. Ruiz, C. Surville-Barland, A. Aukauloo, E. Anxolabehere-Mallart, Y. Journaux, J. Cano, M. Muñoz, J. Chem. Soc. Dalton Trans. (1997) 745.
[200] R. Ruiz, M. Triannidis, A. Aukauloo, Y. Journaux, I. Fernández, J. Pedro, B. Cervera, I. Castro, M. Muñoz, Chem. Commun. 23 (1997) 2283.
[201] R. Ruiz, A. Aukauloo, Y. Journaux, I. Fernández, J.R. Pedro, A. Roselló, B. Cervera, I. Castro, M. Muñoz, Chem. Comm. 9 (1998) 989.
[202] N. Bischofberger, M.D. Matteucci, J. Am. Chem. Soc. 111 (1989) 3041.
[203] P.W. Iseminger, M.G. Timothy, T.J.R. Weakley, G. Caple, A.G. Sykes, J. Org. Chem. 62 (1997) 2643.
[204] A. Bock, I. Göbel, C. Näther, Z. Haulas, A. Gavezotti, G. Filippini, Angew. Chem. Int. Ed. Engl. 32 (1993) 1755.