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Invited Review

Structural Features of ONS-Donor Salicylidene *Schiff* Base Complexes

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Summary. This review article summarizes the structural features of complexes of salicylidene *Schiff* bases containing, in addition to the phenolic-OH and the azomethine (–*R*C=N–) groups, a thiole group, and/or a sulfur atom participating in coordination. Structural aspects of metal complexes of salicylidene-2-aminothiophenol, salicylidene-3-aminothiophenol, salicylidenethiosemicarbazone, salicylidenedithiocarbazates, salicylidenedithiocarbazates, salicylideneaminopropyleneaminocyclopentenedithiocarboxylates, salicylideneimidazoles, and salicylidene-thiosalicylidene-1,3-propanediamine are reported.

Keywords. Salicylidene *Schiff* bases; ONS-Donors; Metal complexes.

Introduction

Schiff bases have played an important role in the development of coordination chemistry as they readily form stable complexes with most of the transition metals. They show interesting properties, *e.g.*, their ability to reversibly bind oxygen [1], catalytic activity in hydrogenation of olefins [2] and transfer of an amino group [3], photochromic properties [4], and complexing ability towards toxic metals [5]. The interest of studying *Schiff* bases containing ONS-donors arose from their significant antifungal, antibacterial, and anticancer activities [6]. In addition, the presence of both a hard and a soft donor group in one ligand increases the coordination ability towards hard as well as soft acidic metals.

Metal complexes of *Schiff* bases derived from salicylaldehyde and various amines have been widely investigated [7–13]. The salicyaldehyde-thio-*Schiff* bases have recently acquired a considerable importance due to their chemical and especially their promising biological properties [14, 15]. Antibacterial [16], antineoplastic [17], antimalarial [18], and antiviral [19] behaviour has been found. Relationships are evident between chelate formation in the complexes and the *in vivo* activity [20–23]. In the area of bioinorganic chemistry interest in *Schiff* base complexes has centred on the role such complexes may have in providing synthetic models for the metal containing sites in metalloproteins and metalloenzymes [24].

This review article focuses on the complexes of ONS-donor salicylidene *Schiff* bases, *i.e.* those containing, in addition to the phenolic OH and the azomethine (–*R*C=N–) groups, a thiole group, and/or a sulfur atom participating in coordination. The structural features of salicylidene-2-aminothiophenol, salicylidene-3-aminothiophenol, salicylidenethiosemicarbazone, salicylidene-dithiocarbazates, salicylidenedithiocarbazates, salicylideneaminopropyleneaminocyclopentenedithiocarboxylates, salicylideneimidazoles, and salicylidene-thiosalicylidene-1,3-propanediamine are reported.

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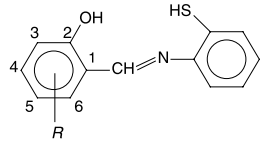
Salicylidene-2-aminothiophenol Complexes

Soliman et al. [25–28] described the preparation of substituted salicylidene-2-aminothiophenols *via* a condensation reaction between equimolar amounts of substituted salicylaldehydes and 2-aminothiophenol in ethanol (Fig. 1).

The *Schiff* bases obtained were filtered off and recrystallized from dilute Acetic acid to give sharp melting points ($L^1 = 128$, $L^2 = 168$, $L^3 = 170$, $L^4 = 160$, $L^5 = 155$°C). The structure of the prepared *Schiff* bases was confirmed by elemental analysis, UV-VIS, IR, ^{1}H NMR, mass spectral studies, and magnetic moments. The chelating behaviour of salicylidene *Schiff* bases towards metal ions was studied in detail [26–29]. Salicylidene-2-aminothiophenol complexes with cadmium [26], cerium [27], and vanadyl [29] ions, as well as 3-methoxysalicylidene-2-aminothiophenol complexes with cobalt, copper, and zinc [27] ions were also reported. As a general conclusion, the salicylidene-2-aminothiophenol *Schiff* bases behave as dibasic ligands in the 1:1 complexes, as monobasic ligands in the 1:2 complexes, and as tridentate ONS-donor ligands derived from the phenolic oxygen, the azomethine nitrogen, and the thiophenolic sulfur. On the basis of this conclusion, tetrahedral and octahedral structures are suggested for the 1:1 and 1:2 complexes of Co, Cu, Zn, and Cd, respectively (Fig. 2). For $V^{II}O$ trigonal bipyramidal geometry was proposed for the 1:1 and 1:2 complexes [29, 30].



R = H (L^1), 5-Br (L^2), 5-Cl (L^3), 3,5 di-Cl (L^4), 3-OCH_3 (L^5)

Fig. 1. Salicylidene-2-aminothiophenol *Schiff* base

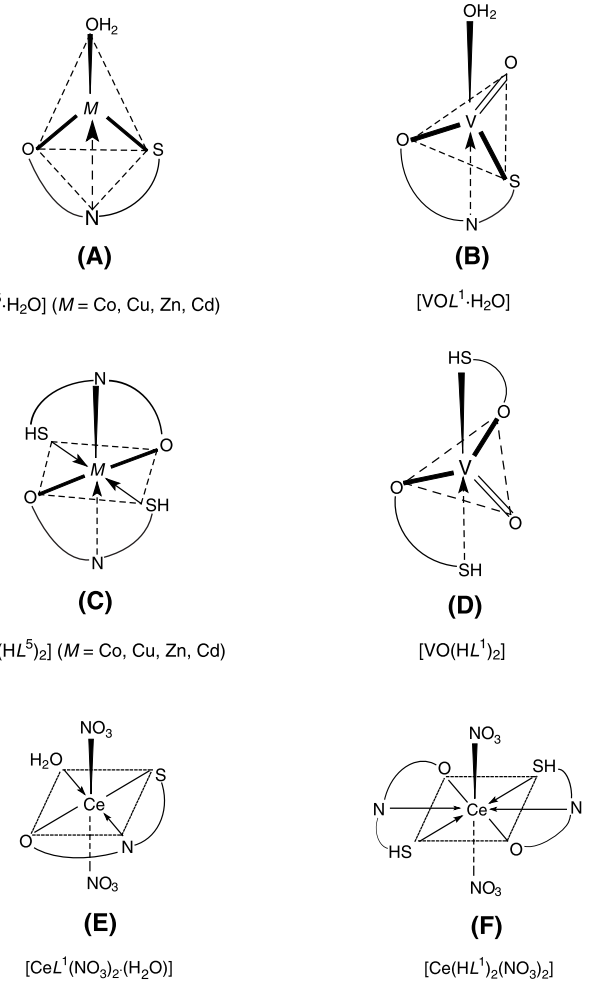


Fig. 2. Suggested structures of salicylidene-2-aminothiophenol complexes

Salicylidene-2-aminothiophenol–Catechol Mixed Complexes

The preparation, characterization, and electrochemical properties were reported for monooxo Mo(VI) complexes, MoO(*cat*)(*ssp*), containing bidentate cat-

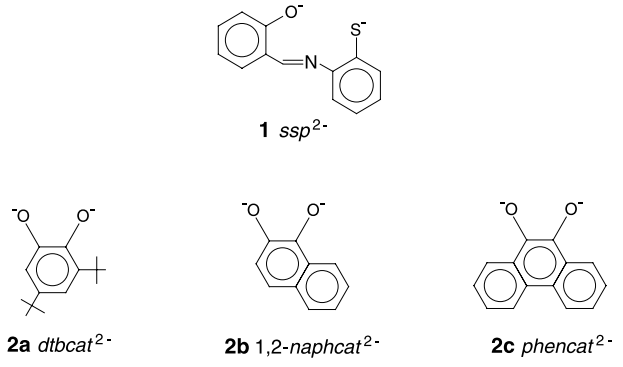


Fig. 3. Structure of salicylidene-2-aminothiophenol and catechol ligands

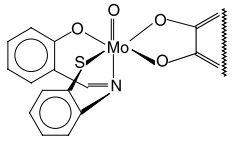
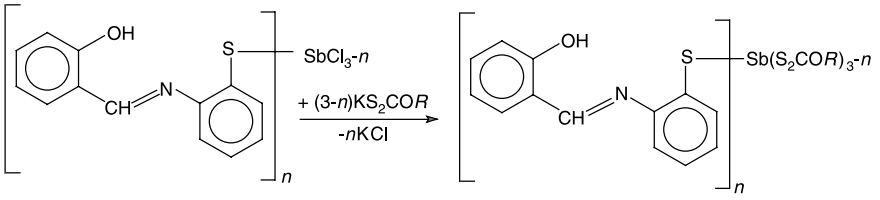
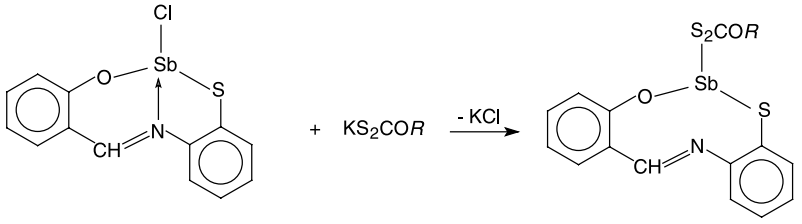


Fig. 4. [MoO(*cat*)(*ssp*)] complexes



n = 1, *R* = *Me* (**1**), *Et* (**2**), *i-Pr* (**3**), *n-Bu* (**4**), *i-Bu* (**5**);
n = 2, *R* = *Me* (**6**), *Et* (**7**), *i-Pr* (**8**), *n-Bu* (**9**), *i-Bu* (**10**)

Scheme 1



R = *Me* (**11**), *Et* (**12**), *i-Pr* (**13**), *n-Bu* (**14**), *i-Bu* (**15**)

Scheme 2

echolate ($cat^{2-} = 3,5$-di-*tert*-butylcatecholate, naphthalene-1,2-diolate, phenanthrene-9,10-diolate) and tridentate NOS-donor *Schiff* base ($ssp^{2-} = N$-salicylidene-2-aminobenzenethiolate (**1**)) ligands [31]. [MoO(*cat*)(*ssp*)] complexes with catecholate ligands **2a**–**2c** (Fig. 3), were prepared by oxo abstraction from MoO_2(*ssp*) with $EtPh_2P$ in *THF* followed by oxidative addition of the appropriate quinone (see Eqs. (1)–(3)).

$$Mo^{VI}O_2(ssp) + EtPh_2P \rightarrow Mo^{IV}O(ssp) + EtPh_2PO \quad (1)$$

$$Mo^{IV}O(ssp) + Mo^{VI}O_2(ssp) \rightarrow {Mo_2}^{IV}O_3(ssp)_2 \quad (2)$$

$$Mo^{IV}O(ssp) + Q \rightarrow Mo^{VI}O(cat)(ssp) \quad (3)$$

The product of the oxo-abstraction reaction appears as a reddish brown solid which did not give a satisfactory elemental analysis for MoO(*ssp*) or $Mo_2O_3(ssp)_2$ and was assumed to be a mixture of these two species. When quinone was added to this material in refluxing CH_2Cl_2, a light brown solid formed. The solid was separated by filtration and identified by elemental analysis to be $Mo_2O_3(ssp)_2$. The filtrate yielded purple MoO(*dtbcat*)(*ssp*), blue MoO(1,2-*naphcat*)(*ssp*) and burgundy MoO(*phencat*)(*ssp*) when layered with hexane. The general structure of the complexes is given in Fig. 4.

Salicylidene-2-aminothiophenolalkyldithiocarbonate Complexes

Dichloro- and monochloroantimonyl complexes of *N*-(salicylidene)-*o*-mercaptoaniline (salicylidene-2-aminothiophenol) as well as chlorobis[*N*-(salicylidene)-*o*-mercaptoaniline] have been synthesized and characterized [32]. The mixed derivatives have been synthesized either by the reaction of chlorobis[*N*-(salicylidene)-*o*-mercaptoaniline] or by the dichloroantimony(III) derivative of *N*-(salicylidene)-*o*-mercaptoaniline with potassium alkyldithiocarbonate in 1:1 and 1:2 molar ratios, respectively [33] (Scheme 1).

Similarly, mixed derivatives of monochloro[*N*-(salicylidene)-*o*-mercaptoaniline]antimony(III) were synthesized with potassium alkyl dithiocarbonates in 1:1 molar ratio (Scheme 2).

The complexes were characterized by elemental analyses, melting points, molecular weight determi-

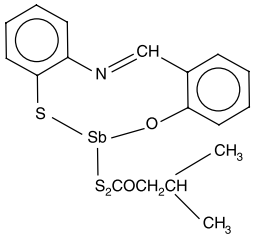


Fig. 5. Isobutyl xanthate complex

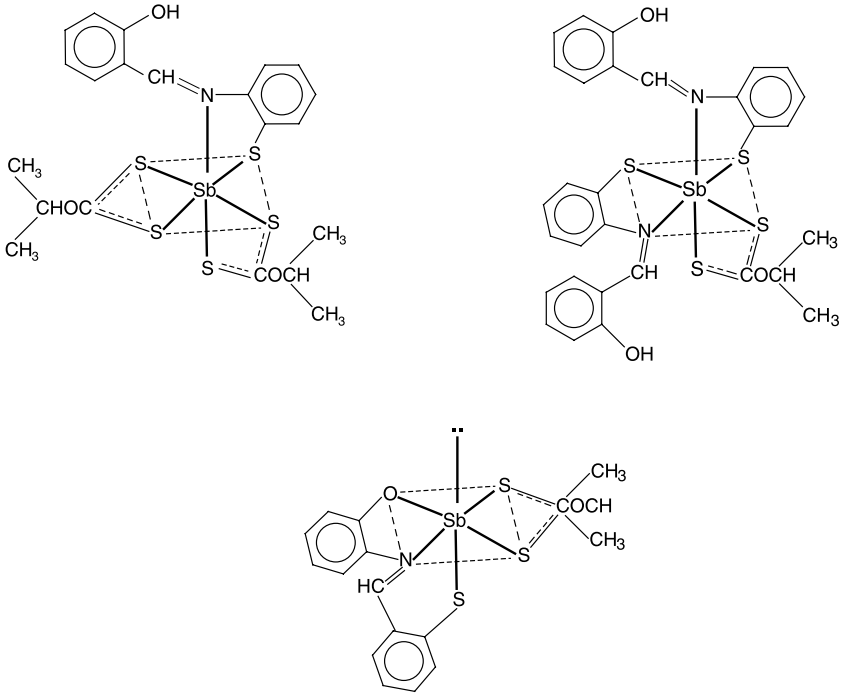


Fig. 6. Suggested structures for the three types of complexes

nation as well as IR and NMR (^{1}H and ^{13}C) spectroscopy. The data obtained indicated a bidentate mode of attachment of both types of ligands to the metal atom. The central antimony atom appears to acquire a coordination number of four. The most plausible geometry for these complexes appeared to be a distorted octahedral if the presence of the stereochemically active lone pair is also considered to be part of the coordination sphere (Figs. 5 and 6).

Salicylidene-2-aminothiophenol-o-diphenylphosphinophenolate Complexes

The reaction of [*TBA*][$ReOBr_4(OPPh_3)$] with [$HOC_6H_4C(H)=NC_6H_4SH$)] and [HOC_6H_4-2-$P(C_6H_5)_2$] in methanol yielded [$ReO\{\eta^3$-$(OC_6H_4C(H)=NC_6H_4S)\}\{\eta^2$-$OC_6H_4P(C_6H_5)_2\}$] (**1**). The coordination environment around the rhenium coordination centre shows a distorted octahedral with the ONS-donors of the *Schiff* base and the phosphorus of the phosphinophenolate ligand occupying the equatorial plane, while the axial sites are occupied by the oxo-group and the oxygen atom of the PO ligand, as shown by single-crystal X-ray analysis of **3** (Fig. 7). The reaction is an example of the 3 + 2 $\{Re(V)O\}^{3+}$ core complex carrying the ONS/PO donor atom set, a tridentate ligand of charge −2 and a bidentate ligand of charge −1 [34].

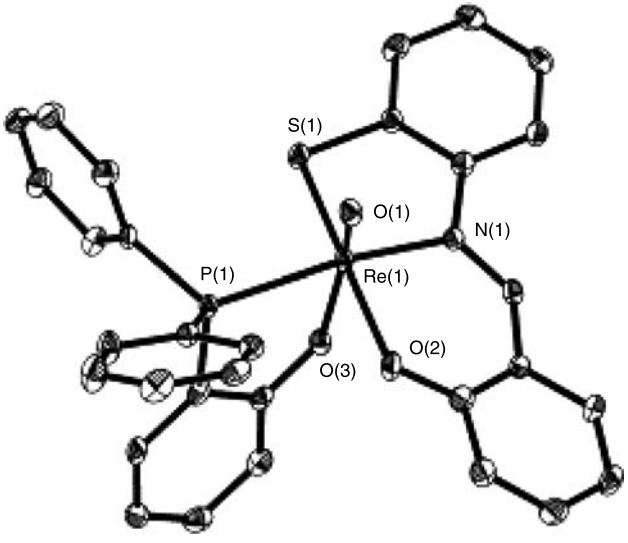


Fig. 7. A view of the structure of [$ReO\{\eta^3$-$(OC_6H_4C(H)=NC_6H_4S)\}\{\eta^2$-$OC_6H_4P(C_6H_5)_2\}$] (**3**) showing the atom labelling scheme with 50% thermal ellipsoids

Salicylidene-2-aminothiophenolcarbonyl Complexes

The reactions between [$M_3(CO)_{12}$], $M = Ru$ and Os, and salicylideneimine-2-thiophenol *Schiff* base

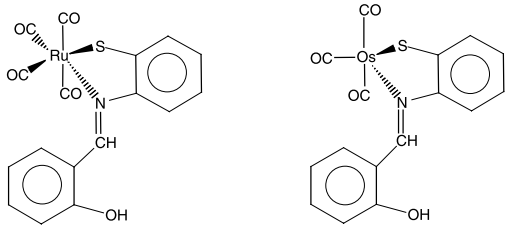


Fig. 8. Ruthenium and osmium complexes

dissolved in *THF* under reflux conditions gave $[Ru(CO)_4$-(*satp*H)] and $[Os(CO)_3(satpH_2)]$ complexes (Fig. 8). Structures of the two complexes were proposed on the basis of spectroscopic studies. Magnetic study of $[Ru(CO)_4(satpH)]$ suggested that a change in oxidation state of the ruthenium atom from zero to +I was achieved *via* oxidative addition of the SH group with a proton displacement to give a low-spin d^7 electronic configuration. UV-Vis spectra of the two complexes in different solvents exhibited visible bands due to metal-to-ligand charge transfer. Electrochemical investigation of the free ligand and complexes showed that both cathotic and anodic peaks are irreversible due to interconversion through electron transfer [35].

Salicylidene-3-aminothiophenol Complexes

Some Zr(IV) complexes of the type $[Zr(OH)_2L \cdot CH_3OH]_2$ (where LH_2 is a tridentate dibasic *Schiff* base derived from 3-aminothiophenol and salicylaldehyde, 5-chlorosalicylaldehyde, 5-bromosalicylaldehyde, and 5-nitrosalicylaldehyde) (Fig. 9) have been synthesized and characterized by elemental analyses, electrical conductance, molecular weight, IR and mass spectra, and magnetic susceptibility measurements [36].

The IR data indicate that the *Schiff* bases are tridentate ONS-donor ligands. The absence of the ν(Zr=O) (850–960 cm^{-1}) [37] and the appearance of a new band at 1135–1145 cm^{-1} due to the δ(Zr–OH) favours the formation of the complexes as $[Zr(OH)_2L \cdot CH_3OH]_2$. The two Zr atoms are bridged

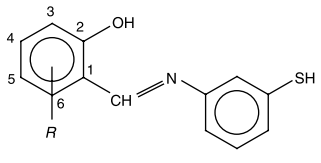


Fig. 9. Salicylidene-3-aminothiophenol

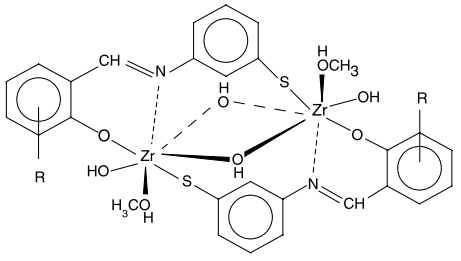
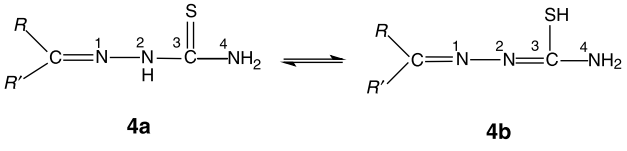


Fig. 10. The bimetallic Zr-salicylidene-3-aminothiophenol complexes, $[Zr(OH)_2L \cdot CH_3OH]_2$

by two OH groups in a di-μ-hydroxo type structure (Fig. 10). The Zr(IV) were found to be seven coordinated and a pentagonal bipyramidal geometry was proposed for the complexes. A bimetallic structure was suggested where the oxygen and nitrogen atoms of the *Schiff* base are chelated to one of the Zr atoms and its sulfur atom is coordinated to the other Zr atom. It is interesting to note that the corresponding U(VI) complexes $[UO_2L \cdot CH_3OH]_2$ which were prepared under similar reaction conditions as Zr(IV) complexes are also bimetallic and seven-coordinated [38].

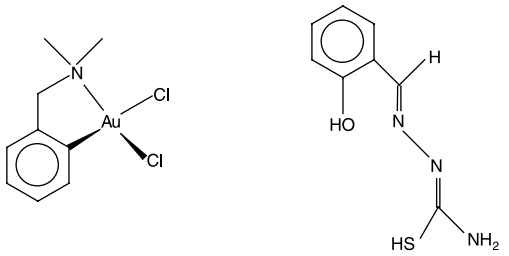
Salicylidenethiosemicarbazone Complexes

Thiosemicarbazones (there tautomeric forms are shown in Scheme 3, **4a** and **4b**) and their metal complexes are of considerable interest because of their chemical and promising biological properties [14, 15]. They can easily be modified by variation of the parent aldehyde or ketone used for the synthesis, particularly with compounds having additional potential coordinating sites (position *R*) or by substitutions on the terminal N-position (Scheme 3). Although capable of deprotonation at both the phenol and thioamide function to give a dianionic ligand, they can also act as monoanionic chelating ligands, coordinating to a metal centre through the deprotonated phenolic oxygen, the thione sulfur, and the azomethine nitrogen. The dianionic form of the ligand is promoted at high *pH* whereas the monoanionic form is favoured at lower *pH* [39, 40]. There



4a **4b**

Scheme 3



[Au(*damp*-C^1,*N*)Cl_2] [H_2*saltsc*]

Fig. 11. [H_2*saltsc*] and [Au(*damp*-C^1,*N*)Cl_2]

are many studies dealing with the complex formation and structural properties of the salicylidenethiosemicarbazone (*saltsc*) *Schiff* base complexes with gold [41], vanadium [39], cobalt [42], nickel [43], copper [44, 45], and other transition metals [46–50].

Dichloro[2-(*N,N*-dimethylaminomethyl)phenyl-C^1,*N*]gold(III), [Au(*damp*-C^1,*N*)Cl_2], reacts with salicylaldehydethiosemicarbazone (H_2*saltsc*) through cleavage of the Au-N bond and protonation of the dimethylamino group [41]. Pale yellow crystals of the compound of the general formula [Au(H*damp*-C^1)Cl(H*saltsc*)](PF_6) have been isolated and characterized. The presence of the σ-bonded 2-(dimethylaminomethyl)phenyl ligand is mandatory to prevent reduction of the gold(III) centre. The observed C–S bond length (1.76 Å) proved the predominant contribution of the tautomeric thiolate form **1b** to the bonding situation (Fig. 11).

The crystal structure of [Au(H*damp*-C^1)Cl(H*saltsc*)](PF_6) has been elucidated, showing the gold atom in distorted square-planar coordination environments (Fig. 12).

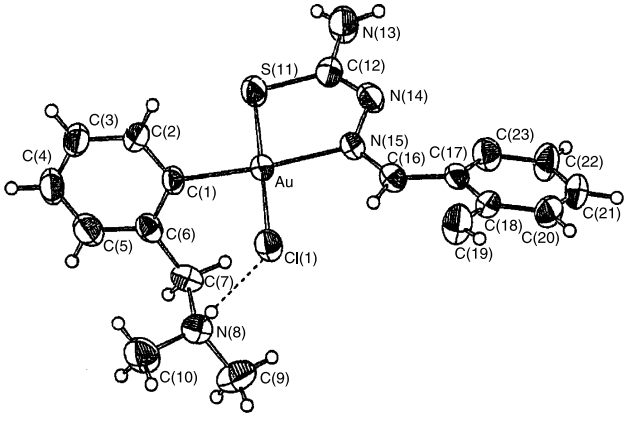
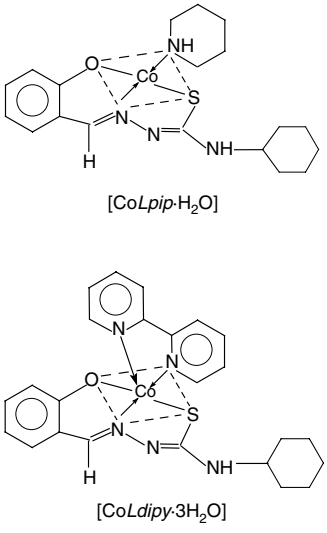


Fig. 12. Molecular structure and crystallographic numbering scheme for [Au(H*damp*-C^1)Cl(H*saltsc*)](PF_6)

The IR spectrum showed an O–H valency vibration at $\bar{\nu} = 3410\,\mathrm{cm}^{-1}$ and suggested that the OH group of the salicylaldehyde thiosemicarbazone does not contribute to the coordination. The complex molecule was involved in intramolecular hydrogen bonding [N(8)–H(8)----Cl(11)] and extended intermolecular hydrogen bonding network with the counter ions and solvent molecules [O(19)–H(19)---F], and was frequently incorporated into the solid-state structure of the compound. Preliminary results from the antiproliferation tests on tumor cells proved the cytotoxicity of the new gold complexes.

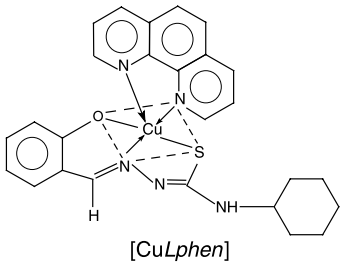
Co(II) complexes containing salicylaldehyde *N*(4)-cyclohexylthio-semicarbazone and heterocyclic bases have been synthesized and characterized by elemental analyses and electronic, IR, and EPR spectral measurements [42]. The analytical data obtained showed that the formation of mixed ligand complexes of Co(II) with H_2L and heterocyclic bases was according to Eq. (4) where, *B* is a heterocyclic base, *viz* pyridine (*py*), piperidine (*pip*), imidazole (*imz*), 1,10-phenanthroline (*phen*), or 2,2′-dipyridyl (*dipy*). Elemental analysis data were consistent with 1:1:1 ratio of *metal ion:thiosemicarbazone:heterocyclic base* for all complexes prepared. The EPR studies of low-spin Co(II) complexes indicated the presence of unpaired electron in the dz^2 orbital. The salicylidenethiosemicarbazone was coordinated to Co(II) ions as an ONS-tridentate ligand and the fourth (and fifth) coordination site(s) was (were) occupied by N-atom(s) of the heterocyclic base. The magnetic and spectroscopic data indicated a square-planar structure for the

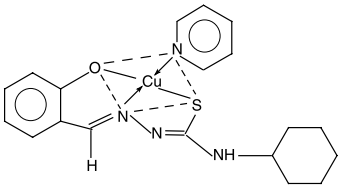


[Co*Lpip*·H_2O]

[Co*Ldipy*·$3H_2O$]

Fig. 13. Cobalt complexes





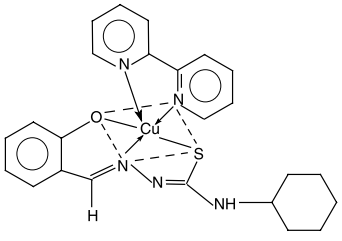


Fig. 14. Copper complexes

four-coordinate and a square-pyramidal structure for the five-coordinate complexes (Fig. 13).

$$\mathrm{Co(O}Ac)_2 \cdot \mathrm{H_2O} + \mathrm{H_2}L + B \xrightarrow{E\mathrm{tOH\ reflux\ 8-10\,h}} \mathrm{Co}LB \cdot n\mathrm{H_2O} + \mathrm{CH_3COOH} \quad (4)$$

Similar structures were proposed for salicylaldehyde *N*(4)-cyclohexylthiosemicarbazone (H_2L) – heterocyclic base ternary copper(II) complexes (Fig. 14), where the heterocyclic base was either pyridine (*py*) or phenanthroline (*phen*) [44] and for salicylaldehyde *N*(4)-phenylthiosemi-carbazone – heterocyclic base ternary copper(II) complexes, where the heterocyclic base was pyridine, piperidine, 1,10-phenanthroline, or 2,2′-bipyridine [45].

Binuclear μ-squarate complex of the formula $[Cu_2(sq)(ST)_2]$ has been synthesized and characterized by elemental analyses, IR, conductivity measurements, and electronic spectra (Fig. 15) [51].

Ruthenium(III) complexes of the $[RuY(LL')(E_2)$ type (Y = Cl or Br; LL' = tridentate *Schiff* base; $E = PPh_3$ or $AsPh_3$) [52] have been synthesized by reacting $[RuX_3(EPh_3)_3]$ (X = Cl, or Br; E = P or As)

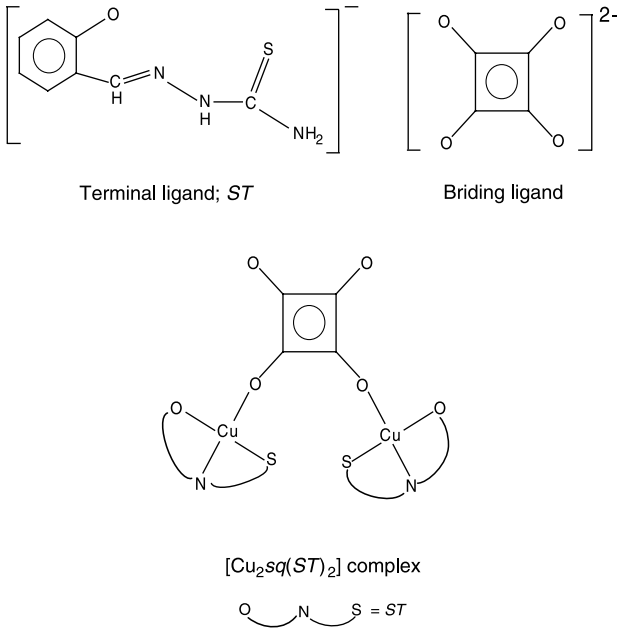
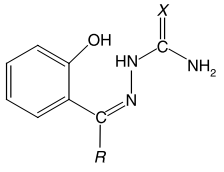


Fig. 15. *ST* and *sq* ligands as well as their mixed complex with copper



R	*X*	abbreviation
H	S	*sal-tsc*
H	O	*sal-sc*
Me	S	*o-hyac-tsc*
Me	O	*o-hyac-sc*

Fig. 16. The salicylidenesemicarbazones and salicylidenethiosemicarbazones

or $[RuBr_3(EPh_3)_2(MeOH)]$ with *Schiff* base having the donor group ONX *viz.*, salicylidenethiosemicarbazone (X=S), salicylidenesemicarbazone (X=O), *o*-hydroxyacetophenonethiosemicarbazone (X=S) and *o*-hydroxyacetophenone-semicarbazone (X=O) (Fig. 16).

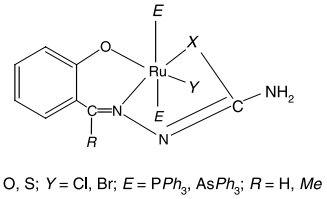


Fig. 17. Ru(III) complexes

The complexes were characterized by elemental analysis, spectral (IR, UV-Vis, EPR), magnetic moment and cyclic voltametry data. In all reactions, the *Schiff* base ligand behaves as a binegative tridentate (O,N,S^- or O,N,O^-) ligand and the complexes have a pseudo-octahedral geometry (Fig. 17).

Salicylidenedithiocarbazates Complexes

Several *Schiff* base complexes derived from dithiocarbazate and its derivatives with *o*-hydroxy aromatic aldehydes have been reported in detail [53–55].

Copper(II), nickel(II), cadmium(II), and mercury(II) complexes with *S*-benzyl-*β*-*N*-[[2-hydroxy-5-[(4-nitrophenyl)azo]phenyl]methylene]dithiocarbazate have been reported [56] The ligand (Fig. 18) has the following structure.

The complexes prepared were characterized by elemental analysis and magnetic, IR, ^{1}H NMR, and UV-Vis spectral measurements. The results suggested the following general structure for the complexes in which the *S*-benzyl-*β*-*N*-[[2-hydroxy-5-[(4-nitrophenyl)azo]phenyl]methylene]dithiocarbazate acted as tridentate ligand *via* the azomethine nitrogen, the CS, and the deprotonated OH group (Fig. 19).

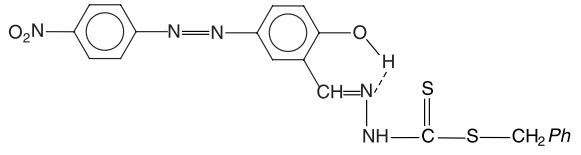
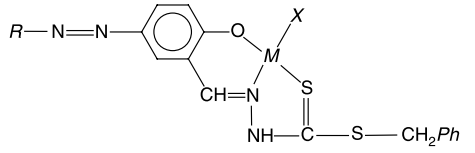


Fig. 18. Salicylidene dithiocarbazate



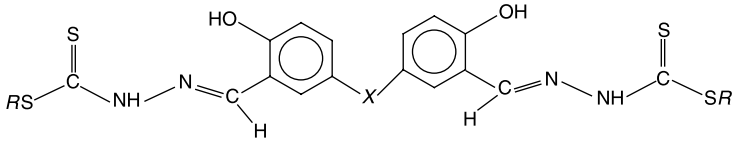
M = Cu(II), Ni(II), Cd(II), HG(II); *X* = Cl$^-$, Ac$^-$; *R* = $C_6H_4NO_2$

Fig. 19. Complex with tridentate salicylidene dithiocarbazate

Hexadentate tetraanionic *Schiff* bases were obtained by the condensation of methylene- or dithiobis(salicylaldehyde) with *S*-methyldithiocarbazate and *S*-benzyldithiocabazate [57] (Fig. 20).

This *Schiff* base reacts with $[MoO_2(acac)_2]$ in a 1:2 molar ratio under reflux in methanol and yields complexes of the type $[(MoO_2)_2L]$. These complexes show an intense ν(Mo=O) band at 924–948 cm^{-1} and a broad but strong band at *ca.* 850 cm^{-1} due to weakened ν(Mo=O) as a result of Mo – O → Mo interactions. An oligomeric structure, in which each Mo(IV) ion achieves a pseudo-octahedral structure *via* Mo – O → Mo bridging, has been suggested for these complexes (Fig. 21). $[(MoO_2)_2L]$ reacted with monodentate ligands (*D*) like pyridine, 4-methylpyridine, and dimethylsulfoxide forming six-coordinated complexes of the type $[(MoO_2)_2L(D)_2]$ which are monomers.

Three new dioxovanadium(V) compounds, $[K(H_2O)][VO_2(sal\text{-}sbdt)]$ (**5**), $[K(H_2O)_2][VO_2(Clsal\text{-}sbdt)]$ (**6**), and $[K(H_2O)_2][VO_2(Brsal\text{-}sbdt)]$ (**7**) (where H_2sal-sbdt are the *Schiff* bases formed between salicylaldehyde and dithiocarbazates) have been synthesized, and the structures of **5** and **6** have been revealed by X-ray diffraction analyses [58]. The ligands coordinate in the tridentate ONS fashion out of the enethiolate tautomeric form (see Scheme 4). The potassium counterions, coordinated to water molecules, the phenolate-O, the oxo groups on vanadium and, in the case of **5** (Fig. 22), to the thiolate, provide interlinkages between the anions and thus a complex supramolecular network, further reinforced by intermolecular hydrogen bonds between oxogroups and water molecules. *In vitro* tests of the antiamoebic activity against the protozoan parasite *Entamoeba histolytica* showed comparable



	X	*R*	abbreviation
5	CH_2	CH_3	$CH_2(H_2sal\text{-}SMDTC)_2$
6	CH_2	$CH_2C_6H_5$	$CH_2(H_2sal\text{-}SBDTC)_2$
7	S-S	CH_3	$S_2(H_2sal\text{-}SMDTC)_2$
8	S-S	$CH_2C_6H_5$	$S_2(H_2sal\text{-}SBDTC)_2$

Fig. 20. Hexadentate tetraionic ligand

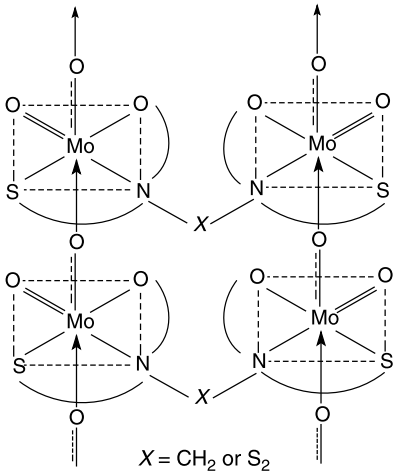
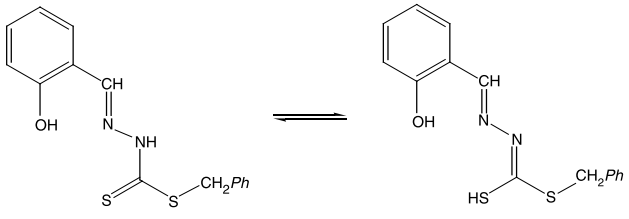


Fig. 21. Proposed oligomeric structure of $[(MoO_2)_2L]$



Scheme 4

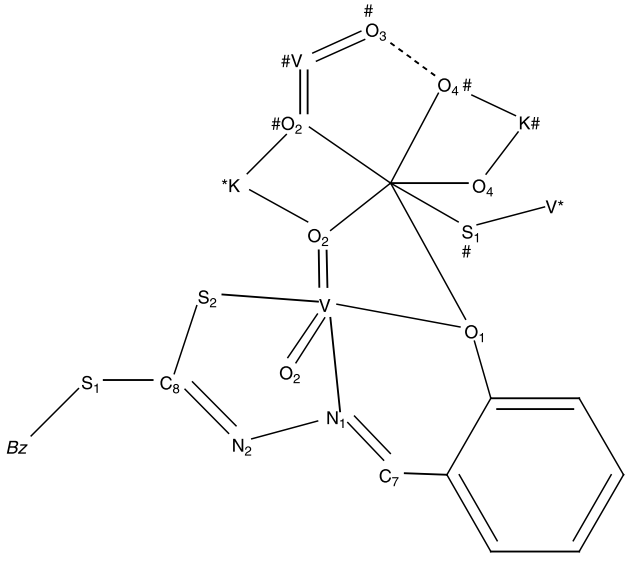


Fig. 22. Schematic representations of the coordination environments of vanadium (bold) and potassium, and numbering schemes of **5**; O_3 is the apical oxo group, O_4 and O_5 are water molecules; *Bz* = benzyl; # and * refer to atoms not belonging to the formula unit

(**5** and **6**) or substantially better (**7**) amoebocidal action than metronidazole, a commonly used drug against amoebobiasis.

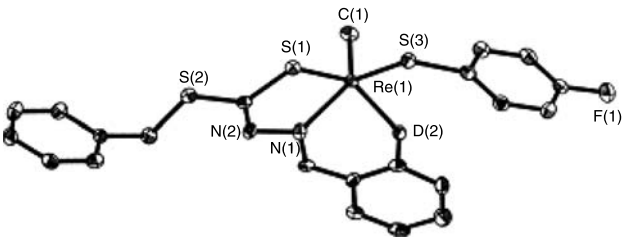
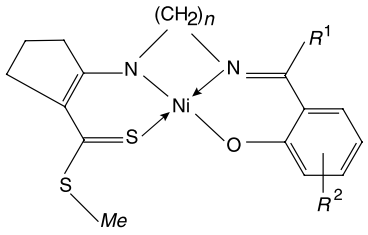


Fig. 23. ORTEP drawing of $[ReO\{\eta^3\text{-}OC_6H_4\text{-}2\text{-}CH{=}N{-}N{=}C(SCH_2Ph)\text{-}S\}(\eta^1\text{-}C_6H_4F\text{-}4\text{-}S)]$ (**8**); ellipsoids correspond to 50% probability

The reaction of $ReOCl_3(PPh_3)_2$ with the potentially tridentate ligand *S*-benzyl-β-*N*-[(2-hydroxyphenyl)methylene]dithiocarbazate (ONS donor set) and *para*-substituted benzenethiols $[C_6H_4X\text{-}4\text{-}SH]$ (where X = H, F, Cl, Br, OCH_3) in the presence of Et_3N afforded a series of integrated 3 + 1 oxorhenium(V) complexes with general formula $[ReO\{\eta^3\text{-}OC_6H_4\text{-}2\text{-}CH{=}N{-}N{=}C(SCH_2Ph)S\}(\eta^1\text{-}C_6H_4X\text{-}4\text{-}S)]$. The molecular structure of $[ReO\{\eta^3\text{-}OC_6H_4\text{-}2\text{-}CH{=}N{-}N{=}C(SCH_2Ph)\text{-}S\}(\eta^1\text{-}C_6H_4F\text{-}4\text{-}S)]$ (**4**) was determined by single-crystal X-ray analysis. Complex **4** (Fig. 23) consists of a central oxorhenium(V) core with phenolic oxygen, azomethine nitrogen, and thiol sulfur donor from the thiosemicarbazone *Schiff* base ligand and one sulfur donor from monothiol ligand completing a distorted square pyramidal environment [59].

Salicylideneaminopropyleneamino-cyclopentenedithiocarboxylate Complexes

A set of seven tetradentate ligands derived from salicylaldehyde and aminopropyleneaminocyclopentenedithiocarboxylates was prepared and the corresponding nickel(II) complexes with coordination spheres NNOS were synthesized and studied by spectroscopic and electrochemical techniques. The structure of (methyl 2-{3-[(2-hydroxyphenyl)methyleneamino]propylamino}cyclopent-1-ene-1-dithiocarboxylato) nickel(II) has been examined by X-ray crystallography (Fig. 24). The complex has a tetrahedrally distorted square-planar geometry, and spectroscopic results indicated that this structure is retained even in strong coordinating solvents. Electrochemical and EPR data showed that the complexes listed below are typically reduced to four-coordinate nickel(I) species (in solution) although, with some of the ligands, formation of six-coordinate nickel(I) complexes was observed and an explanation is given to account for these different properties [60].



R^1	R^2	$n = 2$	$n = 3$
H	H	[Ni(*cdsalen*)]	[Ni(*cdsalpd*)
Me	H	[Ni(*cdMesalen*)]	[Ni(*cdMesalpd*)]
H	3-*Me*O	[Ni(*cdMeOsalen*)]	[Ni(*cdMeOsalpd*)]
Me	5-*Me*O	[Ni(*cdMeOsalen*)]	[Ni(*cdMeOsalpd*)]
H	4,6-(*Me*O)	[Ni(*cd*(*MeO*)$_2$*salen*)]	[Ni(*cd*(*MeO*)$_2$*salpd*)]
H	3,5-Cl_2	[Ni(*cd*Cl_2*salen*)]	[Ni(*cd*Cl_2*salpd*)]

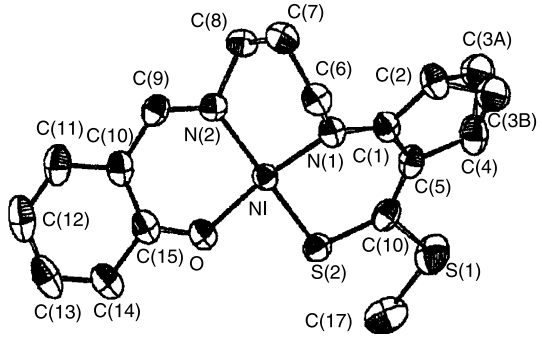


Fig. 24. Molecular structure and crystallographic numbering scheme for [Ni(*cdsalpd*)]

The ligand skelton of the [Ni(*cdsalpd*)] molecule showed an umbrella configuration, with the trimethylene bridge in a twisted conformation, for which C(6) and C(8) are above and below the coordination plane and C(7) is very close to it. Bond lengths and angles within the ligand are indicative of a strong π-delocalization through the six-membered metallocycles. The delocalization of the π-system in the cyclopentene fragment indicates that it coordinates in a *Schiff*-base mode and this is in accordance with similarity of the two Ni–N bond lengths and the Ni–S bond length that is typical of anionic sulfur donors in low-spin nickel(II) complexes [61–63].

Salicylideneimidazole Complexes

Salicylidene-2-aminoethylthiomethylimidazoles

Histidine imidazole nitrogen and cysteine sulfur atoms are typical donors in metalloproteins. These mostly

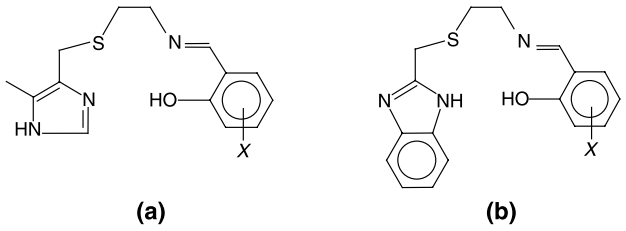


Fig. 25. *Schiff* bases (a) 4-[2-aminoethyl)thiomethyl]-5-methylimidazole (H_2*MIS*-*X*) and (b) 2-[2-aminoethyl)thiomethyl]benzimidazole (H_2*BIS*-*X*)

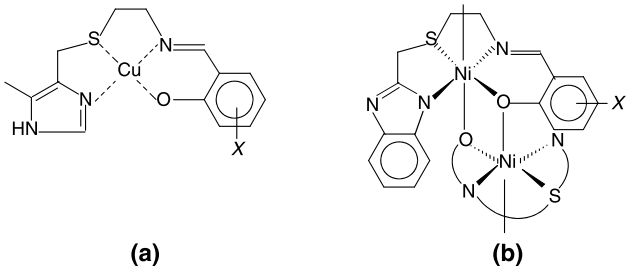


Fig. 26. Schematic representations for (a) [Cu(H*MIS*-*X*)]ClO_4 and (b) [Ni(*BIS*-*X*)] $\cdot n H_2O$

contain tyrosine phenolic groups as well. Therefore ligands containing sulfur, (benz)imidazole nitrogen, and/or phenolic oxygen donor atoms, could be interesting for a better understanding of the metal-protein binding. Thus *Schiff* base complexes containing these groups could act as versatile models of metallic biosites [64]. Accordingly, complexes of *Schiff* bases derived from substituted salicylaldehyde and aminothioetherimidazoles were studied (Fig. 25) [65].

Copper(II) complexes [66] containing monoanionic ligands, derived from aminothioetherimidazoles and substituted salicylaldehyde have been prepared by refluxing (10 min) of an equimolar mixture of copper perchlorate, ligand, and NaOH. A schematic planar structure of [Cu(H*MIS*-*X*)]ClO_4 is shown in Fig. 26(a). Complexes with their dianionic related ligands were obtained from the first series of the complexes with slight molar excess of methanolic NaOH, or by refluxing (30 min) of the ligand with copper acetate.

Owing to the difficulties found to obtain neutral copper(II) complexes with related ligands, an electrochemical procedure was investigated [65]. Thus, these and other neutral complexes as *M*(*MIS*-*X*) $\cdot$ nH_2O (M = Zn, Cd, Ni, Cu; X = H, 5-*Me*O, 5-Br, 4,6-*Me*O, 3,5-Br; $n = 0$–3) and *M*(*BIS*-*X*) $\cdot$ nH_2O (M = Zn, Cd, Ni; X = 5-*Me*O, 4,6-*Me*O; $n = 0$–3)

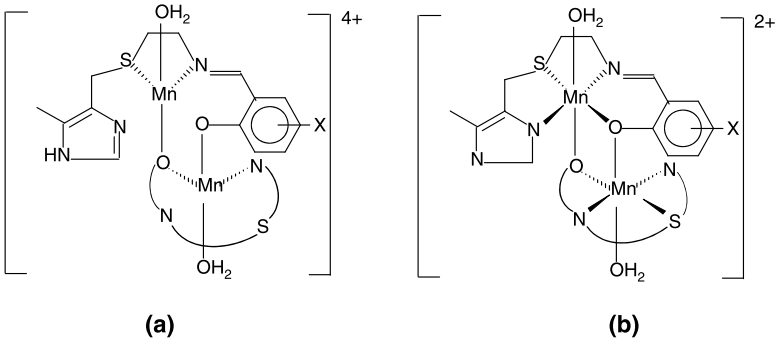


Fig. 27. Schematic representation for (a) $[Mn(HMIS\text{-}X)H_2O)]_2(ClO_4)_4$ and (b) $[Mn(HMIS\text{-}X)H_2O)]_2(ClO_4)_2$

have been prepared. A dimeric structure postulated for $Ni(BIS\text{-}X) \cdot nH_2O$ is shown in Fig. 26(b).

Octahedral geometry could be achieved based on a dimeric structure either through the phenolic oxygen or the imidazole nitrogen.

The great diversity of structural features observed in manganese(III) complexes, especially with tetradentate *Schiff* base ligands is another interesting point. Thus, different coordinating modes for the same type of ligands, as well as redox rearrangement processes have been observed for these compounds, with symmetrical or asymmetrical ligands [67–69].

The preparation of both types of manganese(III) complexes is illustrated below by two example syntheses with the same ligand H_2MIS (Eqs. (5) and (6)). The complex $[Mn(MIS)(H_2O)]ClO_4 \cdot 4H_2O$ has been synthesized following a method proposed by *Boucher* [70], whereas $[Mn(HMIS)(H_2O)](ClO_4)_2 \cdot 4H_2O$ has been prepared by a variation of it. The complexes had been characterized by elemental analyses, Λ_M, IR, UV-Vis, and mass spectrometry, magnetic measurements at room temperature, and cyclic voltammetry.

$$\begin{aligned} H_2MIS \quad & 1.\ \xrightarrow[EtOH,\,10\,min]{Mn(ClO_4)_2\cdot 6H_2O} \\ & 2.\ \xrightarrow[MeOH,\,rt,\,5\,d]{2\,N\,NaOH} \quad [Mn(MIS\text{-}X)(H_2O)]ClO_4 \end{aligned} \tag{5}$$

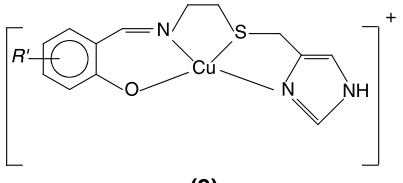
$$\begin{aligned} H_2MIS \quad & 1.\ \xrightarrow[reflux,\,30\,min]{2N\,NaOH,\,EtOH} \\ & 2.\ \xrightarrow[MeOH,\,rt,\,1\,d]{Mn(ClO_4)_2\cdot 6H_2O} \quad [Mn(MIS\text{-}X)(H_2O)](ClO_4)_2 \end{aligned} \tag{6}$$

The visible and magnetic data pointed to an octahedral geometry for both mono- and dicationic complexes, which are shown in Fig. 27.

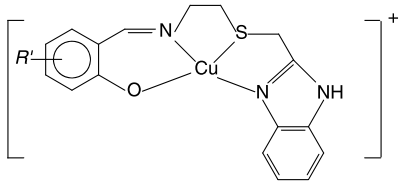
As result of this study, it was observed that Mn(III) exhibits coordination versatility with the same ligand, forming two different types of complexes. The presence of a soft S donor atom seems to be remarkable, because it is not common for hard manganese(III) centres. Furthermore, no ligand reorganization has been detected with complexes containing these unusual ONSN donor-set ligands. This fact indicates their high stability compared with the complexes previously described as well as those formed with asymmetrical ligands containing salicylaldehyde derivatives. This can be ascribed to reorganization reactions, which occur in solution. Their stability is probably favoured by their low solubility in most solvents. However, their low solubility makes wider studies somehow difficult.

Salicylideneaminothioimidazoles Complexes

Cationic copper(II) complexes of tetradentate *Schiff* bases derived from aminoetherimidazoles and sali-



(9)



(10)

(R' = H, 3-Br, 3-NO_2, 5-NO_2, 3-Cl, 3,5-Cl_2)

Fig. 28. Cationic copper(II) complexes of tetradentate *Schiff* bases

cylaldehydes, Fig. 28, have been synthesized by reaction of the appropriate ligand with $Cu(ClO_4)_2 \cdot 6H_2O$ and NaOH in methanol [71]. The corresponding neutral copper(II) complexes may be generated either by the reaction of the cationic complex with a molar amount of NaOH or by reaction of copper(II) acetate with the ligand in acetonitrile.

The neutral nickel(II), zinc(II), and cadmium(II) complexes with salicylidene-2-[(2′-aminoethyl)thiomethyl]imidazole (Fig. 28 (9)) and salicylidene-2-[(2′-aminoethyl)thiomethyl]benzimidazole (Fig. 28 (10)) were then prepared by the electrochemical route using the appropriate metal as sacrificial anode in acetonitrile as solvent [72].

The reaction with benzimidazole-*Schiff* bases involved in the preparation of the complexes can be represented by Eq. (7).

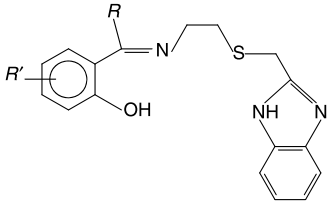
$$M + H_2L \rightarrow ML + H_2 \tag{7}$$

The electrochemical efficiency, defined as the quantity of metal dissolved per *Faraday* of charge, is close to 0.5 mol F^{-1}, indicating that the synthesis of the complexes involves the processes shown by Eqs. (8) and (9).

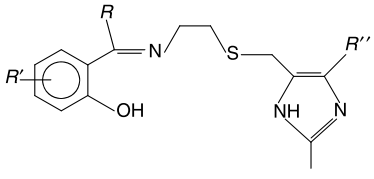
$$\text{Cathode: } H_2L + 2e^- \rightarrow L^{2-} + H_2 \tag{8}$$

$$\text{Anode: } L^{2-} + M \rightarrow ML + 2e^- \tag{9}$$

On the other hand, the electrochemical efficiency of the imidazole complexes was close to 1 mol F^{-1}, indicating that the synthesis involves the processes

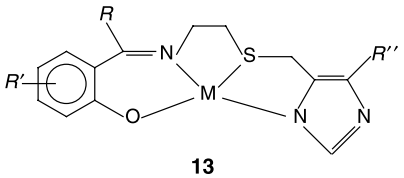


(11)



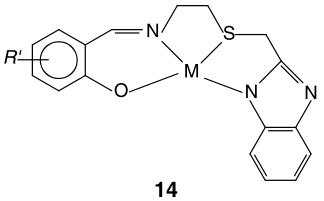
(12)

Fig. 29. Neutral nickel(II), zinc(II), and cadmium(II) complexes with salicylidene-2-[(2-aminoethyl)thiomethyl]imidazole (**9**)) and salicylidene-2-[(2-aminoethyl)-thiomethyl]benzimidazole (**10**)



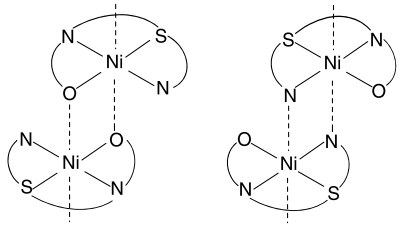
13

13a *R* = H, *R′′* = H
13b *R* = H, *R′′* = *Me*
13c *R* = *Me*, *R′′* = H



14

R′ = H, 3-O*Et*, 5-O*Me*, 5-Br, 4,6-(O*Me*)2, 3,5-Br_2, 5-*Me*



15a **15b**

Fig. 30. Dimeric structure of nickel-salicylideneaminothioimidazole complexes

given by Eqs. (10) and (11), followed by the oxidation reaction shown by Eq. (12).

$$\text{Cathode: } H_2L + e^- \rightarrow HL^- + 1/2H_2 \tag{10}$$

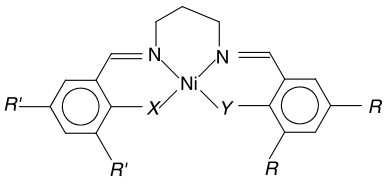
$$\text{Anode: } HL^- + M \rightarrow M(HL) + e^- \tag{11}$$

$$M(HL) \rightarrow ML + 1/2H_2 \tag{12}$$

The complexes obtained were recovered as powders, and characterized by elemental analysis, IR, mass, and visible spectroscopy. The results suggested the monomeric distorted tetrahedral structures (Fig. 30; **13** and **14**) for the zinc and cadmium complexes and a dimeric structure for nickel complexes (Fig. 30; **15**), either through the phenolic oxygen (a) or the imidazole nitrogen (b), with an octahedral geometry around the metal.

Salicylidene-thiosalicylidene-1,3-propanediamine Complexes

Nickel complexes with *Schiff* bases obtained by condensation of 1,3-propanediamine with salicylalde-



Complex		X	Y	R	R′
16	[Ni(*salpd*)]	O	O	H	H
17	[Ni(*t-salsalpd*)]	S	O	H	H
18	[Ni(*t-salpd*)]	S	S	H	H
19	[Ni(Cl_2*salpd*)]	O	O	Cl	Cl
20	[Ni(*t-sal*-Cl_2*salpd*)]	S	O	Cl	H

Fig. 31. Nickel complexes

hyde and thiosalicylaldehyde, which present a N_2OS or N_2S_2 coordination sphere, were synthesized and studied [73].

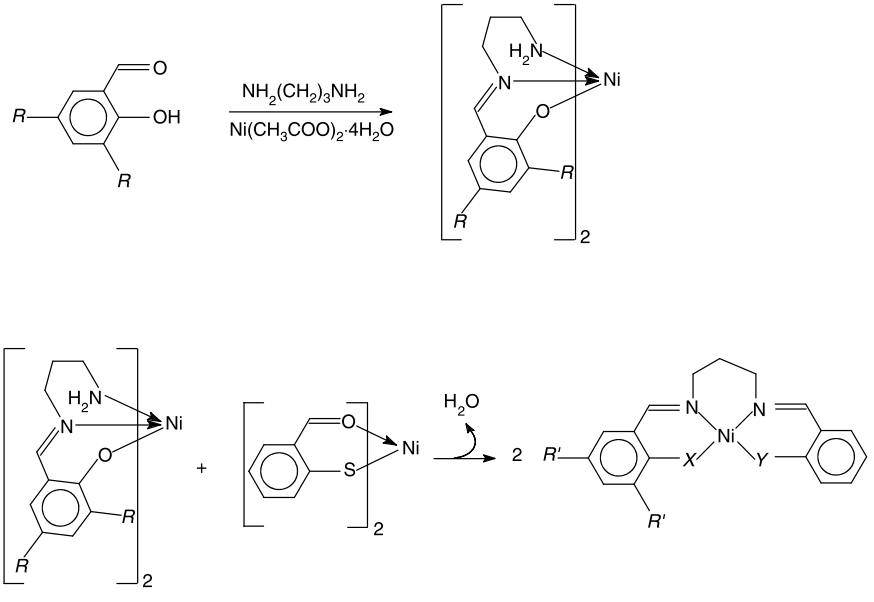
The complexes were prepared by stepwise condensation of 1,3-propanediamine with salicylaldehyde in presence of nickel acetate followed by condensation of the product obtained with bis(thiosalicylaldehydate) nickel(II) (Scheme 5).

The complexes were characterized by elemental analysis, electronic spectra, EPR, and electrochemical techniques. The molecular and crystal structure of the asymmetric complex [2-({3-[(3,5-dichloro-2-hydroxyphenyl) methyleneamino]propyl}iminomethylene)benzenethiolate-O,N,N′,S] nickel(II), [Ni(*t-sal*Cl_2*salpd*)], has been determined by X-ray crystallography and showed a tetrahedrally distorted square-planar coordination geometry for the nickel centre (Fig. 32).

Elemental analysis and ^{1}H NMR spectroscopy agree with the formulae proposed, and the observation of a ^{1}H NMR signal within the expected diamagnetic region, even in a strong coordinating solvent such as $(CD_3)_2SO$, suggested that the complexes retain their square-planar structure in solution.

The study allowed some advanced conclusions about the consequences of O/S replacement in the coordination sphere of Ni complexes. It was found that one of the most important factors for the reduction potentials for donors are expected to contribute to the stabilization of metal ions in low oxidation states, no evidence was found for this effect in the complexes under study, and the differences in $E_{1/2}$ values for the complexes with N_2O_2, N_2OS, and N_2S_2 coordination spheres have been shown to be mainly related to differences in the tetrahedral distortion of the Ni(II) complexes. Moreover, the dependence of reduction potentials with the substituents of the salicylate moiety is probably due to significant structural changes induced by the substituents and is not of an electronic nature.

On the other hand, spectroscopic data for Ni(II) complexes are almost independent of ligand substituents, thus implying that Ni(I) is not so sensitive as Ni(II) to structural changes induced by ligand substituents. EPR data showed that observed g values



Scheme 5

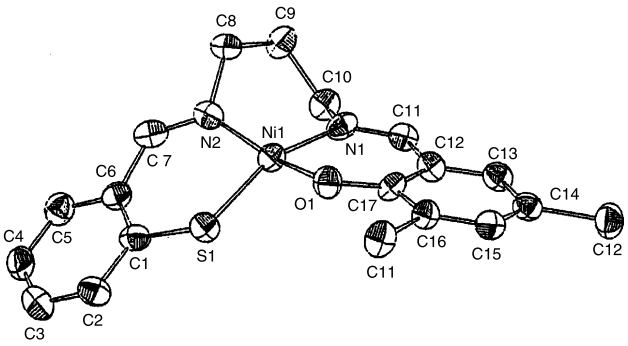


Fig. 32. Molecular structure and crystallographic numbering scheme for [Ni(*t-sal*Cl_2*salpd*)]

are very sensitive both to the coordination sphere and to the extent of tetrahedral distortion, but showed little dependence on the substituents of the ligand skeleton.

All results pointed to a weak interaction between Ni(I) and thiolate donors, implying that the presence of sulfur donors in the coordination sphere of nickel is not very important to the accessibility of Ni(I) complexes. The only relevant factor that contributes to higher reduction potentials for nickel complexes with sulfur donors is an indirect effect, since sulfur donors show a higher tendency than oxygen donors towards tetrahedral distortion, probably due to the lower ligand-field strength of sulfur donors. The results suggest that the thiolate rich coordination sphere of nickel in hydrogenase is not a determinant factor in the stabilization of low oxidation states for this metal ion, at least in what concerns electronic effects.

Conclusions

The structural features of complexes of salicylidene-2-aminothiophenol, salicylidene-3-aminothiophenol, salicylidenethiosemicarbazone, salicylidene-dithiocarbazates, salicylidenedithiocarbazates, salicylideneaminopropyleneaminocyclopentenedithiocarboxylates, salicylideneimidazoles, and salicylidene-thiosalicylidene-1,3-propanediamine reflect the versatility of the salicylidene *Schiff* bases and act as model ligands for the interaction with different metal ions. These ligands can supply many interesting structures, monomeric, dimeric, with a variety of metal ions which help to understand the coordination chemistry of these metal ions and simulate the interactions which might take place in biological systems.

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