Coordination Chemistry Reviews, 63 (1985) 127–160
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

TRANSITION METAL COMPLEXES OF SEMICARBAZONES AND THIOSEMICARBAZONES

SUBHASH PADHYÉ*

Department of Chemistry, University of Poona, Poona-411007 (India)

GEORGE B. KAUFFMAN

Department of Chemistry, California State University, Fresno, Fresno, CA 93740 (U.S.A.)

(Received 6 March 1984; in revised form 20 September 1984)

CONTENTS

A. INTRODUCTION

Of the sulfur donor ligands, thiosemicarbazones have perhaps not received as much attention as, e.g., dithiophosphates [1], dithiocarbamates [2,3],

---

* Address for the 1984–85 academic year: School of Chemical Sciences, University of Illinois, Urbana, IL 61801, U.S.A.

dithiolates [4], dithio-β-diketonates [5], dithiooxamides [6,7], or xanthates [3]. The real impetus toward developing the coordination chemistry of these potential ligands was probably provided by the remarkable antitumor [8], antiviral [9], and antimalarial [10,11] activity observed for some of these derivatives, which has since been shown to be related to their metal-complexing ability [12]. The recent literature shows that this general class of compounds exhibits a wide range of stereochemistries in complexation with transition metal ions; few of these coordination compounds have been adequately studied.

This review considers the important developments in the structural chemistry of transition metal complexes of thiosemicarbazones in the solid state which have taken place since Campbell's review of 1975 [13]. Developments prior to Campbell's review have been dealt with adequately by Livingstone [7] and Akbar Ali and Livingstone [14]. We shall not discuss equilibrium studies, analytical aspects [15], or biological activity of these ligands [16].

B. GENERAL SURVEY

(i) Occurrence

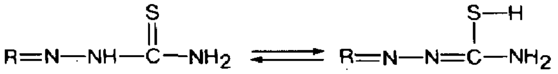
Thiosemicarbazone complexes reported so far involve predominantly the latter half of the transition metal ions, which reflects the central role played by sulfur coordination in these compounds and consequently their "soft acid–soft base" preference [17].

(ii) Preparative methods

A large number of thiosemicarbazone ligands have been derived by simply condensing aliphatic, aromatic, or heterocyclic aldehydes or ketones with thiosemicarbazide compounds [18]. Many of these compounds possess a wide spectrum of medicinal properties, including activity against tuberculosis [19]; leprosy [20]; bacterial [21] and viral infections [9]; psoriasis [22]; rheumatism [23]; trypanosomiasis [24]; coccidiosis [25]; and malaria [10]. Obviously, the molecular features essential for such activities must be ascertained by designing synthetic routes to modify, replace, or substitute the derived thiosemicarbazone ligand. However, very few studies have been devoted to such synthetic variations.

Klayman et al. [10,11] have outlined strategies for modifying the thiosemicarbazone ligand which are generally applicable to this generic class of compounds, namely, (1) exchange of the sulfur atom of the thiocarbonyl group by oxygen or selenium; (2) changing the point of attachment of the thiosemicarbazone moiety in the parent aldehyde or ketone (particularly those containing additional potential coordinating sites); (3) substitution on the terminal N^4 position; and (4) variation of the parent aldehyde or ketone.

In solution thiosemicarbazones or selenosemicarbazones probably consist of an equilibrium mixture of thione (I) and thiol (II) tautomers



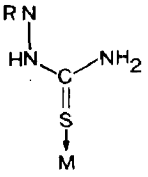
$$R{=}N{-}NH{-}\overset{\overset{\displaystyle S}{\|}}{C}{-}NH_2 \rightleftharpoons R{=}N{-}N{=}\overset{\overset{\displaystyle S{-}H}{|}}{C}{-}NH_2$$

(I) (II)

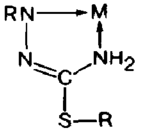
I acts as a neutral bidentate ligand, while the loss of the thiol proton from **II** yields a singly charged bidentate ligand. Therefore, depending upon preparative conditions (especially pH), the complex unit can be cationic, neutral, or anionic. However, most investigations of metal thiosemicarbazone complexes have involved ligands in the uncharged form (I), while definitive data on the complexes containing thiosemicarbazone in the thiol (II) form are generally lacking. Furthermore, it is possible to isolate complexes containing both tautomeric forms of the ligand. For example, Padhyé and Sonawane [26] have prepared a neutral cobalt chelate of 2-hydroxy-1,4-naphthoquinone-1-thiosemicarbazone (H_2NQTSC) with the molecular formula [Co(HNQTSC (NQTSC)]·H_2O (HNQTSC = the monoanionic thione form and NQTSC = the dianionic thiol form), which, according to magnetic and spectral data, appears to contain both ligand tautomers. Ablov and Gerbeleu [27] explained that formation of such mixed-ligand tautomeric complexes is promoted by the central metal ion and is generally accompanied by oxidation of the central metal ion, as in the case of cobalt complexes of salicylaldehyde thiosemicarbazone. The resulting complexes are thus found to be diamagnetic Co(III) complexes although the starting materials were Co(II) salts.

(iii) Bonding in thiosemicarbazone complexes

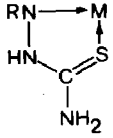
It has been shown [28] that the thiosemicarbazide molecule itself exists in the *trans* configuration (III), and while complexing in this configuration, it behaves as a monodentate ligand, bonding only through the sulfur atom. Gerbeleu et al. [29] have shown that bonding may also occur through the hydrazine nitrogen and the amide nitrogen (IV) if the sulfur center is substituted. On reinvestigating the crystal structure of thiosemicarbazide hydrochloride, Coghi et al. [30] explained these conformational changes on the basis of protonated ⇄ deprotonated isomeric forms and steric effects. In most of the complexes studied the thiosemicarbazone function coordinates to the metal ion in the *cis* configuration (V), as a bidentate ligand bonding both through the thione/thiol sulfur atom (or oxygen atom in the case of the semicarbazone moiety) and the hydrazine nitrogen atom in a bidentate manner.



(III)

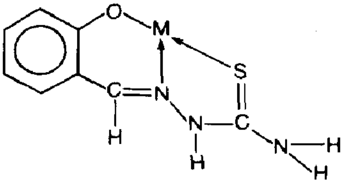


(IV)

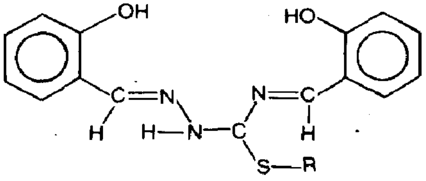


(V)

When an additional coordinating functionality is present in the proximity of the $\widehat{SN}$ donating centers, the ligands are found to act as tridentate species (**VI**), yielding a polymeric compound in some cases.

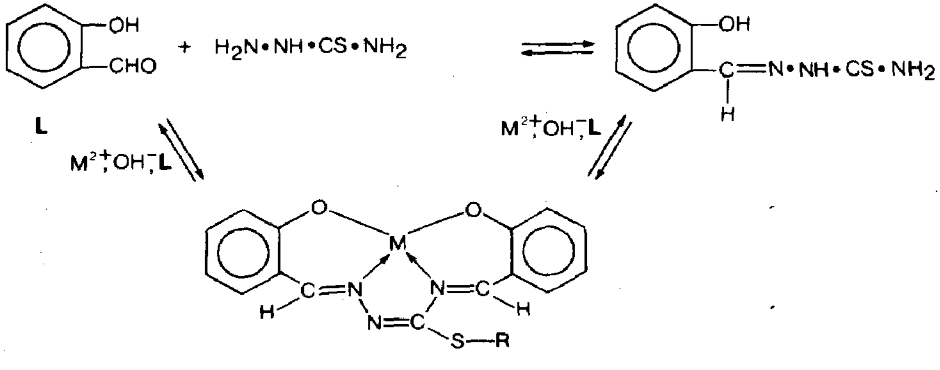


(VI)



(VII)

Recently Gerbeleu and co-workers [31(a)] showed that alkylation of the thiocarbonyl sulfur of thiosemicarbazone derivatives induces not only complexation through the terminal amino group but also enough acidic character for it to function as a monoacidic ligand. In the presence of various metal salts, e.g., Cu(II), Ni(II), VO(IV), these ligands are capable of condensing at the terminal amino nitrogen atom through another aldehyde or ketone to yield quadridentate ligands of type **VII**. Using such template reactions as shown in scheme 1, Gerbeleu and Zhovmir [31(b)] claimed to have isolated thiosemicarbazone complexes without sulfur coordination:



SCHEME 1

(M = VO^{2+}, Ni^{2+} or Cu^{2+}; R = H, NH$_4$, Na, or K)

Relevant to the bonding in thiosemicarbazone complexes is the ability to locate various group frequencies corresponding to typical linkages. Although there have been many attempts to assign empirically a few infrared bands of metal complexes of thiosemicarbazone ligands, no complete assignment of their IR spectra had been available. A fairly reliable assignment of infrared frequencies is now possible for semicarbazide and its hydrochloride [32(a)], selenosemicarbazide [32(b)], and thiosemicarbazide (along with its ionic and neutral complexes of the type MS_2N_2) through normal coordinate analysis using Wilson's GF matrix method and the Urey–Bradley force field functions [32(c)]. A computational method based on a normal coordinate analysis and quantum chemical dipole moment calculations has been suggested for predicting transition moment directions and dichroic ratios in molecular crystals of low symmetry such as thiosemicarbazide [33].

(iv) Stereochemistries and oxidation states

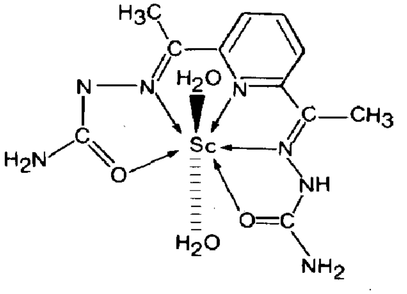
The stereochemistries adopted by thiosemicarbazone ligands while interacting with transition metal ions depend essentially upon the presence of an additional coordination center in the ligand moiety and the charge on the ligand, which, in turn, is influenced by the thione $\rightleftarrows$ thiol equilibrium. For example, benzaldehyde thiosemicarbazone is generally found to act as a neutral bidentate ligand, depending upon the pH of the synthetic medium, yielding complexes of the type $[ML_2X_2]$ (where M=Co(II), Ni(II), Cu(II), or Fe(II); L = the ligand in the thione form and X = the monoanionic ligand), whereas salicylaldehyde thiosemicarbazone is found to act as a tridentate uninegative ligand yielding compounds of type ML_2, which may be spin-free or spin-paired. As a result of the above considerations, the most common stereochemistries encountered in thiosemicarbazone complexes are octahedral and square planar. On rare occasions five-coordinate structures are also obtained, as in the cases of Co(II), Fe(II), and Ni(II) complexes of acetone thiosemicarbazone [34,35,48] and the Fe(III) complex of 2-acetylpyridine thiosemicarbazone [36]. Since some of these five-coordinate complexes possess biological activity, e.g., antimalarial and antitumor activity [12(h)], more studies of synthesis and structure, are required for this class of complexes.

HSAB considerations dictate that the oxidation state of a metal affects the degree of its "softness" character, and this is found to be stronger for transition metals in low oxidation states. Thus the low-spin d^8 ions Pd(II), Pt(II), and Au(III) and d^{10} ions Cu(I), Ag(I), Au(I), and Hg(II) exhibit higher stability constants with this class of sulfur ligands because of the formation of strong σ-bonds as well as d_π–d_π bonds by donation of a pair of electrons to ligands [14]. Thiols but not thioethers cause spin-pairing of

Co and Ni. Thiosemicarbazones are not capable of spin-pairing of Fe(III) ions, unlike other soft bases such as CN^-, diarsine, and certain charged sulfur ligands [37]. Consequently, intermediate spin states are found to be stabilized [36]. This potential of the class of thiosemicarbazone ligands has not been recognized to the extent as for diethyldithiocarbamate ligands.

C. TRANSITION METAL COMPLEXES

There were only about eight metal thiosemicarbazone complexes investigated at the time of Campbell's review [13]. The situation has changed substantially, and a number of metal thiosemicarbazone complexes have been reported during the past eight years. However, few of these investigations have been concerned with the synthetic aspects of these complexation reactions, even though the complexation is known to be influenced by the thione ⇄ thiol equilibrium. Many investigations are restricted to infrared spectral studies and tend to be tentative in nature. Similarly, the room-temperature magnetic moments of some thiosemicarbazone complexes, although much lower than those expected on the basis of the "spin-only" formula, have not been investigated in detail.



(VIII)

In the following discussion, we have classified the metal semicarbazone and thiosemicarbazone complexes according to the d^n configuration of the metal.

(i) d^1 *complexes*

Palenik and co-workers [38] have described a pentagonal bipyramidal structure (**VIII**) for the scandium(III) complex of the pentadentate ligand 2,6-diacetylpyridine semicarbazone on the basis of X-ray studies. In this compound two coordinated water molecules lie at distances of 2.084 Å and 2.123 Å, respectively, from the central metal atom. Crystal-structure data for another complex of the thio analog of this ligand have very recently become available [39] for the ferrous complex, i.e., bis(thiocyanato)(2,6-diacetylpyridine thiosemicarbazone)iron(II) dihydrate. Although this compound does not belong to the d^1 system, it is interesting to note that, despite the pentagonal bipyramidal geometry imposed by the ligands as seen in the earlier case, the thione sulfur atoms are considerably out (0.44 Å) of the least-squares plane defined by the remainder of the molecule as indicated by the lengthening of the iron–sulfur (2.639 Å) bonds. The observation is significant since it reflects the role played by other coordinating ligands in modifying or distorting the final stereochemistry of the molecule.

There are some interesting reports on oxovanadium(IV) complexes of semicarbazone and thiosemicarbazone ligands. For example, Jain et al. [40] have described dimeric vanadyl(IV) complexes of α-pyridyl thiosemicarbazone of the type $[\mathrm{LVO}(\mu\text{-X})_2\mathrm{VOL}]\mathrm{X}'_2$ (L = the ligand, X = OH, Cl, or CN, and X′ = H_2O, Cl, or CN, respectively). The vanadyl ions have square pyramidal geometry with oxygen at the apex, and with the bidentate ligand coordinating via the pyridine nitrogen (νM–N at 305–298 cm^{-1}) and the thione sulfur (νM–S at 442–430 cm^{-1}) atoms. The V=O frequency is observed between 996–980 cm^{-1}, while the bridging V–OH frequency is observed at 975 cm^{-1}. The nonparticipation of the hydrazino nitrogen atom, however, implies that sterically it is unavailable for coordination. On the other hand, Pino and co-workers [41] have shown that it is the pyridine nitrogen atom that either moves in or out of coordination making the ligand α-pyridyl thiosemicarbazone either tridentate or bidentate, respectively. Furthermore, it has been pointed out [42] that such dimeric oxovanadium(IV) complexes have room-temperature magnetic moments well below 1.68–1.78 B.M. Accordingly, the magnetic moments (1.73–1.82 B.M.) reported for the above complexes are open to reexamination.

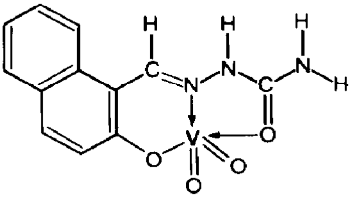
Monomeric oxovanadium(IV) complexes of cyclohexanone semicarbazone and thiosemicarbazone ligands of the type $[\mathrm{VOL}_2\mathrm{X}]\mathrm{X}$ (L = the ligand and X = Cl, Br, or 1/2 SO_4), which have tetragonal structures with anions interacting *trans* to the oxygen, have been reported by Chandra and Pandeya [43]. The complexes exhibit magnetic moments in the usual 1.67–1.73 B.M. range, corresponding to one unpaired electron, and they exhibit all three *d–d* transitions (Table 1). The *g* values of thiosemicarbazone complexes are found to be higher than those of the corresponding semicarbazone complexes, indicating a higher ligand field for the former.

Samus and co-workers [44] isolated the compound $\mathrm{NH}_4[\mathrm{VO}_2\mathrm{L}]$ (where L = the monoanion of 2-hydroxynaphthaldehyde semicarbazone) in which vanadium is in the pentavalent state. The formation of such a complex is attributed to the 'fixation of oxygen' from the air giving a diamagnetic complex. X-ray crystallographic studies revealed the vanadium atom to possess a distorted tetragonal pyramidal geometry in the complex anion (**IX**).

TABLE 1

Magnetic moments and electronic spectral bands for the oxovanadium(IV) complexes of cyclohexanone semicarbazone (CHSC) and thiosemicarbazone (CHTSC)

Complex	$\mu_{eff.}$ (B.M.)	$d_{xz}, d_{yz} \rightarrow d_{xy}$	$d_{xz}, d_{yz} \rightarrow d_{z^2}$	$d_{yz} \rightarrow d_{x^2-y^2}$	$10Dq$	Ds	Dt	g-values
$VO(CHSC)_2Cl_2$	1.73	14000	17400	24000	10000	2943	−1034	1.947
$VO(CHSC)_2Br_2$	1.67	13900	17200	23800	9900	2928	−1023	1.946
$VO(CHSC)_2SO_4$	1.68	14500	17200	24900	10400	3171	−997	1.948
$VO(CHTSC)_2Cl_2$	1.68	14800	17700	25200	10400	3186	−1049	1.990
$VO(CHTSC)_2Br_2$	1.71	14700	17400	25000	10300	3186	−1029	1.990
$VO(CHTSC)_2SO_4$	1.69	14800	17600	25700	10900	3271	−997	1.993



(IX)

(ii) d^2 *complexes*

Complexes of this type have not been reported.

(iii) d^3 *complexes*

Since complexes of trivalent chromium with sulfur–nitrogen ligands are uncommon, syntheses of some thiosemicarbazide complexes deserve mention. Matsumoto and co-workers [45] have described and characterized complexes of both types, ionic $[Cr(HTSC)_3]Cl_3 \cdot 3\ H_2O$ and neutral $[Cr(TSC)_3]$, mainly on the basis of spectral data. The lower energy band (15000–17000 cm^{-1}) in the electronic spectrum is assigned to the $^4A_{2g} \rightarrow {}^4T_{2g}$ transition. The spectra of ionic- and neutral-type chromium complexes are generally similar to those of the corresponding cobalt complexes except that the ionic chromium complexes have an intense band at ~ 31000 cm^{-1}, which is found to be much broadened in the corresponding cobalt complexes. The placement of the ligating sulfur atoms will be discussed later. Chebanu and Samus [46] similarly compared 5-chloro- and 5-bromosalicylaldehyde semicarbazone(5-XH_2SSC, where X = Cl or Br) complexes of the type $[M(5\text{-}XHSSC)_2]Cl \cdot H_2O$, which can be isolated by mixing ethanolic solutions of chromium(III) chloride and the ligands. On treatment with aqueous ammonia solution at pH 7–8, these complexes are initially converted into the neutral compounds $[Cr(5\text{-}XSSC)(5\text{-}XHSSC)] \cdot H_2O$, and on raising the pH to ca. 9–10, they can be obtained as ammonium salts, $NH_4[Cr(5\text{-}XSSC)_2] \cdot H_2O$. These authors have reported that similar conversions are also possible with other trivalent ions such as Fe(III) and Co(III).

In a recent paper Zelentsov and co-workers [47] described the formation of complexes of the type $[Cr(HL)(H_2O)_3]Cl_2$ (where HL = the monoanion of diacetyl monoxime semicarbazone) and [Cr(HL)L] (where L = the dianion of diacetyl monoxime semicarbazone/thiosemicarbazone) from the interaction of $[Cr(H_2O)_6]Cl_3$ with the corresponding ligand derivatives. The total replacement of aqua groups in the latter complex is explained on the basis of increased nucleophilic character upon going from the semicarbazone to the thiosemicarbazone ligand. It must, however, be pointed out that addition of base during the synthesis of the latter complex may also be a contributing factor towards the above observations.

Paramagnetic, octahedral complexes of the type [CrL_3] are also obtained with *p*-substituted benzaldehyde thiosemicarbazone where the ligand is found to be bidentate and monoanionic [48].

(iv) d^4 *complexes*

There is a solitary report [49] on the synthesis of Mn(III) complexes with some bidentate and tridentate Schiff base ligands, viz., 1-salicyl-4-benzylamidothiosemicarbazone and 1-phenyl-4-benzylamidothiosemicarbazone, respectively. The former yields an octahedral complex of the type $[ML_2]^+$, while the latter leads to pseudooctahedral compounds of the type $[ML_2(OH)_2]^+$. The complex structures are supported by IR data (1100 and 495 cm^{-1} bands due to coordinated OH^- groups), electronic spectral data (bands at 18870–19050 cm^{-1} and 22730–27400 cm^{-1}), and magnetic moments (4.54–4.87 B.M.). The characteristic low energy CT band observed for many manganese(III) complexes, is, however, absent in these compounds.

(v) d^5 *complexes*

Chebanu and Samus [46] have extended the reactions of 5-chloro- and 5-bromosalicylaldehyde semicarbazones to include reactions with iron(III) salts, which are found to yield complexes analogous to the chromium complexes, i.e., $[M(5\text{-XHSSa})_2]Y \cdot H_2O$ (where X = Cl or Br and Y = Cl or NO_3). Identical products can be obtained by oxidizing mixtures of iron(II) salts and the same ligands. Ionization constants for the acidic complexes of the three trivalent ions exhibit the order Co(III) > Cr(III) > Fe(III). The halo-substituted compounds are more acidic than the parent compounds, indicating that substituents influence the ionization constants for these complexes.

In a series of papers Zelentsov and co-workers [50] have described the structural features and magnetic properties of iron(III) complexes of substituted salicylaldehyde thiosemicarbazone ligands of the type $M[Fe(R\text{–}L)_2] \cdot nH_2O$ (where M = Cs, NH_4, or K; R = H, 5-Cl, 5-Br, 3,5-di-Cl, or 3,5-di-Br; $n = 0$ or 1.5; and L = salicylaldehyde thiosemicarbazone). It has been observed that the crystal field of these systems corresponds to the region of crossover of electronic terms $^6A_1$ and $^2T_2$ on Tanabe–Sugano energy diagrams. As a result, these compounds offer excellent opportunities for coordination chemists to examine correlations between structural and magnetic features.

The structural studies on the above complexes have shown that the ligands are tridentate and the iron atoms are octahedrally coordinated with S, O, and *trans*-N atoms. Although no substantial differences are observed between bond lengths and bond angles in the ligands of high-spin and low-spin compounds, the high-spin complexes have a highly distorted octahedral configuration. Of all the coordination parameters that could be correlated to the changes in $\mu_{\mathrm{eff.}}$ values of the spin-crossover compounds, the Fe–S bond length proved to be the most unambiguous criterion for characterizing the spin state, typical values being 2.44 Å for high-spin compounds and 2.24 Å for low-spin compounds. An entire spectrum of spin-crossover systems can be achieved with this series of compounds by varying M, R, and *n*.

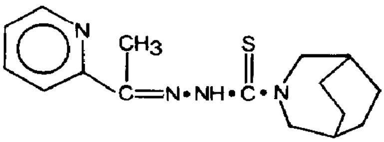
Cryomagnetic studies have indicated that for $Cs[Fe(STSC)_2]$ and $NH_4[Fe(5\text{-}Cl\text{-}STSC)_2]$ the spin state as well as the coordination geometry of the iron atom remains unchanged between 103 and 298 K, while for $NH_4[Fe(5\text{-}Br\text{-}STSC)_2]$ there are two morphologically different types of ‘micro’ crystals, each exhibiting a peculiar magnetic behavior. Thus the tablet-shaped species, which is low spin at room temperature ($\mu_{\mathrm{eff.}} = 2.16$ B.M.), undergoes a sharp transition in magnetic moment at 400 K ($\mu_{\mathrm{eff.}} = 5.10$ B.M.), while black mica-like crystals, which are high-spin compounds at room temperature ($\mu_{\mathrm{eff.}} = 5.06$ B.M.), exhibit a similar transition at 220 K ($\mu_{\mathrm{eff.}} = 2.29$ B.M.). These two modifications are isostructural and probably represent rather rare examples of spin isomers that are established in crystals.

The complexes $NH_4[Fe(3,5\text{-}di\text{-}Cl\text{-}STSC)_2]\cdot 1.5\ H_2O$ and $K[Fe(3,5\text{-}di\text{-}Cl\text{-}STSC)_2]$ are crossover complexes of the spin-equilibrium type with values of $\mu_{\mathrm{eff.}}$ that are intermediate between high-spin and low-spin values. The characteristic features of these isostructural compounds are two crystallographically independent positions for the iron atoms and magnetic properties which are determined by the site distributions of Fe(III) atoms within the crystals. Whether this distribution is static or dynamic needs to be investigated.

Recalling our earlier discussion, it may be pointed out that in iron(III) complexes of these ligands the placement of coordinating nitrogen atoms is *trans*, whereas in the corresponding chromium(III) complexes it is *cis*. With cobalt, both *cis* and *trans* isomers are obtained. Further investigations are obviously needed to determine whether any preferential role is played by the metal ions in yielding these isomers.

Another group of iron(III) complexes that has been receiving considerable attention in recent years are those derived from α-(N)-heterocyclic carboxyaldehyde thiosemicarbazone, perhaps because of their importance in chelation therapy. Thus, Spingarn and Sartorelli [51] have synthesized several tridentate ligands of the 2-pyrazinecarboxyaldehyde thiosemicarbazone class and have evaluated their potential for removing excess iron from iron-loaded mice. These ligands seem to be very potent for removing excess iron accumulated in patients suffering from Cooley's anemia. Similarly, 2-acetylpyridine thiosemicarbazone derivatives have been found to possess inhibitory activity for the RNA-polymerases of the influenza virus, which is thought to be mediated through chelation [52]. Support for this hypothesis has come through recent observations on the enhanced antileukemic properties of 1 : 1 complexes of Fe(III), Cu(II), and Ni(II) with 2-acetylpyridine thiosemicarbazone ligands [12(h)]. In view of this, Raina and Srivastava [53] have described the characterization of low-spin iron(III) complexes of 2-acetylpyridine thiosemicarbazone of the type $Fe(APTSC)_2X$ (where APTSC = the monoanion of 2-acetylpyridine thiosemicarbazone, and $X = NO_3^-$, OH, Cl, N_3, NCS, or NO_2). These are believed to have a pentagonal bipyramidal configuration around the Fe atom with a rhombic distortion as indicated by solid state EPR spectra at liquid-nitrogen temperatures showing three *g*-values. The broad isotropic signal ($g = 2.120$) observed for the azide complex is possibly due to spin–spin relaxation via dipolar interactions, which seems to suggest that the anions in these complexes are capable of influencing the environment of the iron(III) ion in the solid state.

Bhoon et al. [36] reported an iron(III) complex of N^4,N^4-disubstituted 2-acetylpyridine thiosemicarbazone (X), a potential antimalarial drug. The temperature-independent magnetic moment (4.19 ± 0.03 B.M.) and the Mössbauer data ($\delta = 0.13 \pm 0.02$ mm s^{-1}; $\Delta Eq = 4.09 \pm 0.04$ mm s^{-1}) have led these workers to assign a square pyramidal geometry to the complex $[FeLCl_2]$ (where L = the thiolate anion of X). The complex has the same antimalarial activity as that of the free ligand, but it is found to possess enhanced antitumor activity [12(h)]. Further studies [54] on this series of compounds have revealed the important role played by the gegenion (counterion) in stabilizing a particular spin state of iron(III) ions, which could pave the way to some 'tailor-made' biologically active compounds.



(X)

Another pentacoordinated iron(III) complex with a square pyramidal configuration and $s = 3/2$, derived from the 2-hydroxy-1-naphthaldehyde thiosemicarbazone ligand, has been described recently by Bhoon [55]. The detailed magnetic susceptibility measurements (Table 2), carried out on the powdered sample at different temperatures, yield magnetic moments for this complex that rise continuously from near 3.00 B.M. at 4.2 K to 4.46 B.M. at 143.4 K. The slightly higher magnetic moment of 4.47 B.M. at room

TABLE 2

Temperature dependence of the magnetic susceptibility of $Fe(HNATSC)Cl_2$ [55]

T (K)	143.4	106.9	89.5	50.5	31.3	21.1	15.7	12.0	10.4	7.5	5.2	4.4
$\chi_M^{corr.}$	0.01733	0.02100	0.02370	0.04019	0.05818	0.08400	0.10850	0.13330	0.15088	0.19390	0.15675	0.29167
$\mu_{eff.}$	4.46	4.24	4.16	4.03	3.82	3.76	3.69	3.54	3.55	3.42	3.29	3.21

temperature has been thought to be due to contributions from the closely-lying excited states. This is supported by EPR spectra recorded for polycrystalline samples at room temperature exhibiting signals at $g \simeq 4.0$ and $g \simeq 2.0$, although a $g \simeq 6.0$ signal has not been observed.

The results of the resonance Raman spectra of Fe(III) complexes of 2-formylpyridine thiosemicarbazone measured in acid (pH 3.9–4.2) and alkaline (pH 7.4) solutions indicate strong enhancement of skeletal modes (primarily CN and CS stretches) and ring deformations [56]. The strong visible absorption of these complexes is therefore attributed to a $p\pi(\mathrm{S}) \rightarrow \sigma^*(\mathrm{Fe})$ ligand to metal charge transfer transition.

Pradhan and Rao [57] have described octahedral complexes in the case of manganese(II) ions with thiosemicarbazide and acetone thiosemicarbazone ligands. Reactions of $MnCl_2$ with another class of N^4,N^4-disubstituted thiosemicarbazones of 2-acetylpyridine (**X**) also gives a bisligand complex possessing an octahedral structure [12(h)].

(vi) d^6 *complexes*

Gerbeleu et al. [34(b)] described iron(II) complexes of various alkyl thiosemicarbazones of the type $[FeL_2X_2] \cdot nH_2O$ (where L = the uncharged thiosemicarbazone derivative of acetone, ethyl methyl ketone, cyclopentanone, or cyclohexanone; X = Cl or Br; and $n = 0$, 1, 2). The cryomagnetic measurements ($\mu_{\mathrm{eff.}} \simeq 4.59$–$5.22$ B.M.) and Mössbauer parameters ($\delta = 1.25$–1.37 mm s^{-1} and $\Delta\mathrm{Eq} = 2.96$–3.19 mm s^{-1}) led these workers to suggest a pentacoordinated high-spin iron(II) configuration for these compounds. The lower $\mu_{\mathrm{eff.}}$ value observed for $[Fe(CPTSC)_2Cl_2] \cdot 1.5\ H_2O$ (where CPTSC = cyclopentanone thiosemicarbazone), however, could not be explained at that time. In a further study Campbell et al. [58] suggested that room-temperature magnetic moments and features of diffuse reflectance spectra of this and other related alkyl thiosemicarbazones are indeed compatible with either a five-coordinate or a distorted octahedral geometry. Based on characteristic isomer shift values ($\delta \simeq 0.82$ mm s^{-1}) and the absence of halogen-dependent bands above 200 cm^{-1} in the far-IR region, these authors have concluded that the iron(II) high-spin species in these compounds is in a tetragonally distorted octahedral environment with very weakly-coordinated halides. However, Mössbauer quadrupole splittings found for these complexes are sufficiently large (ca. 3.0 mm s^{-1}) to rule out a predominantly d_{xz}, d_{yz} ground state and thereby a hexacoordination. The ground state must therefore be predominantly $d_{x^2-y^2}$, d_{xy}, or d_{z^2}. It has been further argued that the increase in quadrupole splittings on going from 300 K to 70 K may be the result of thermal equilibrium between an electronic orbital singlet ground state and a doublet excited state which perhaps is more compatible with a pentacoordinated species. Unfortunately, a slow electronic relaxation at liquid helium temperature prevents determination of the sign of the quadrupole coupling constant by means of magnetic perturbation techniques and thereby making a clear distinction between d_{xy} and d_{z^2} ground states.

The crystal structure of the chloro complex of iron(II) with acetone thiosemicarbazone, $[Fe(ACTSC)_2Cl]Cl \cdot H_2O$, was determined by Malinovskii and co-workers [59], who confirmed a pentacoordinate configuration for this compound. The light, green compound is unstable in air and crystallizes in the space group $P2_1/b$. The coordination polyhedron around the iron atom is intermediate between a square pyramid and a trigonal bipyramid. Although the covalent radii of nickel(II) and iron(II) are almost identical, the Fe–S distances (2.375 Å) are much greater than the analogous five-coordinate nickel(II) complex [60] but slightly smaller than the six-coordinate complex of iron(II) with thiosemicarbazide [61]. The water molecules and the uncoordinated chloride ions lie in the cavities between the complex cations and are linked by hydrogen bonds. Comparison of the structures of the coordination compounds of some first-row transition metal ions with alkyl thiosemicarbazones show that whereas the nature of the metal ion affects the coordination number of the resulting complex, the donor ability and size of the ligand derivatives influence the final stereochemistries obtained for these complexes.

Chandra et al. [62] have carried out Mössbauer and magnetic studies on the oxygen analog of the above complex, i.e., the acetone semicarbazone complex of iron(II) chloride. According to Ingalls [63], the maximum values for quadrupole splittings turn out to be 4.0 and 2.0 mm s^{-1} for singlet and doublet ground states, respectively. The chloro and nitrato complexes of the semicarbazone series exhibit ΔEq values between 1.60 and 1.79 mm s^{-1}, which are suggestive of a doublet ground state for six-coordinate tetragonal structures, while higher quadrupole splitting values in the case of the sulfato complexes (2.82–2.96 mm s^{-1}) are indicative of a singlet ground state in a trigonal bipyramidal geometry. This indication is supported by IR spectral data for these complexes, showing S–O stretching bands at 943 (ν_1), 1048 (ν_3) and 1120 (ν_2) cm^{-1} characteristic of a monodentate sulfato group.

The single-crystal X-ray structural determination of the parent thiosemicarbazide complex of iron(II) [64] shows that $[Fe^{II}(H_2TSC)_2SO_4]$ is a sulfato-bridged polymer consisting of alternating $FeS_2N_2O_2$ octahedra with different spatial orientations in a monoclinic unit cell.

It exhibits one of the largest quadrupole splittings (ca. 4.33 mm s^{-1}) [65], a fact which was explained on the basis of a positive sign for the splitting with a ^5B ground term based on the d_{xy} orbital. Recently Eisman and Reiff [66] have made a detailed low-temperature magnetic susceptibility and

Mössbauer study of this compound. It showed (Fig. 1) both that there is nothing unusual about the susceptibility in the higher temperature region ($T > 20$ K), an observation also noted earlier, and that the compound behaves as expected for a quintet ground state. However, the magnetic moment drops significantly, from 4.48 to 2.63 B.M., as the temperature approaches 15 K, indicating significant ($D = 5.00$ cm^{-1}) zero field splitting. The magnetic data for this sulfato-bridged system, however, do not indicate any significant exchange interactions although observed in similar sulfato-bridged chains [67]. The Mössbauer data ($\delta = 1.03$ mm s^{-1} and ΔEq $= 4.37$ mm s^{-1} at 77 K) implying $D > 0$ have been interpreted to suggest the presence of single sulfato bridges between metal atoms, as opposed to two found in the ferrous hydrazinium sulfate ($[Fe(N_2H_5)_2(SO_4)_2]$) systems.

Padhyé and Sonawane [68] have described yet another interesting interaction of ferrous sulfate with 2-hydroxy-1,4-naphthoquinone thiosemicarbazone and its oxygen analog (the semicarbazone derivative), both of which are known antibacterial and antifungal compounds of the naphthoquinone series. The thiosemicarbazone complex is found to be a low-spin iron(III) compound ($\mu_{\mathrm{eff.}} = 2.8$ B.M.) containing a normal *cis* coordination mode, while the semicarbazone exhibits a rather unusual *trans* mode of coordination for the low-spin iron(II) compound. The former shows a small quadrupole splitting (0.43 mm s^{-1}), while the latter exhibits a large quadrupole splitting of ca. 3.1 mm s^{-1}. Low-temperature magnetic susceptibility data and Mössbauer data may perhaps provide more information on the type of crystal field splittings in these compounds.

Diamagnetic Ru(II) complexes of thiosemicarbazide derivatives of 4-nicotinamide as well as of substituted 4-benzamide ligands of the type RuL_2X_2 have been prepared by Sahni et al. [69]. In these complexes Ru–N and Ru–S frequencies have been assigned at 490–500 and 350–390 cm^{-1}, respectively. Far-infrared spectra of these complexes show bands at 290–375 cm^{-1}

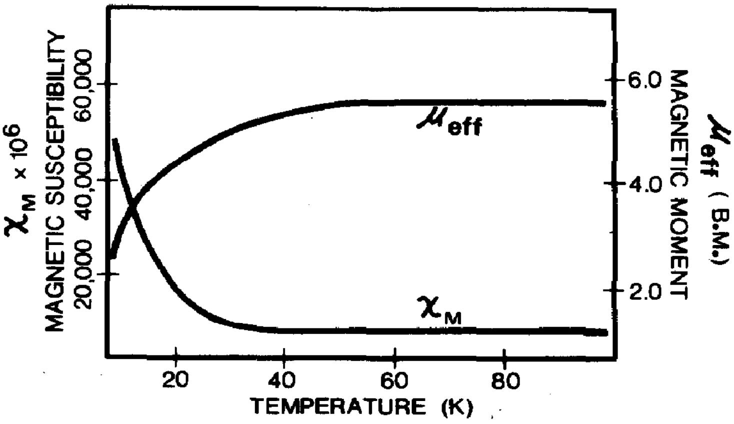


Fig. 1. Magnetism of $[Fe^{II}(H_2TSC)_2SO_4]$ [66].

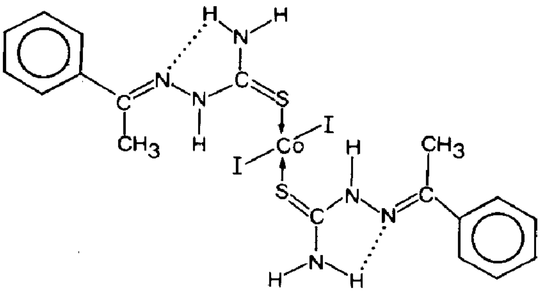
(assigned to the M–Cl stretching mode) and at 260 cm^{-1} (assigned to the M–Br stretching mode). The appearance of only a single νM–X mode in the low-frequency region suggests the *trans* placement of the anions in these complexes in an octahedral symmetry. Sahni et al. [70] further studied the octahedral Ru(III) complexes (obviously belonging to the d^5 class) of long-chain thiosemicarbazides and thiosemicarbazones exhibiting 1 : 2 stoichiometries. However, their suggestion that the lowered magnetic moments (1.95–1.95 B.M.) of these complexes are due to low-symmetry fields needs further proof regarding the absence of bridged structures.

By reacting the unsubstituted salicylaldehyde thiosemicarbazone ligand with $RhCl_3 \cdot 3\ H_2O$ Ablov and Bologa [83] isolated a compound containing the cation $[Rh(HSTSC)_2]^+$, in which the ligand is found to be tridentate. If an alcoholic solution of this complex is heated with sodium acetate, a dark brown compound, $[Rh(HSTSC)(STSC)] \cdot 3\ H_2O$, sparingly soluble in water, precipitates. It can be reconverted to the original compound, $[Rh(HSTSC)_2]Cl \cdot 4\ H_2O$, by treatment with HCl. Heating this complex with concentrated ammonia yields a pale brown substance, $NH_4[Rh(STSC)_2] \cdot 3\ H_2O$, while treatment with KOH first yields an intensely dark red solution from which the salt $K[Rh(STSC)_2] \cdot 3\ H_2O$ gradually precipitates.

(vii) d^7 *complexes*

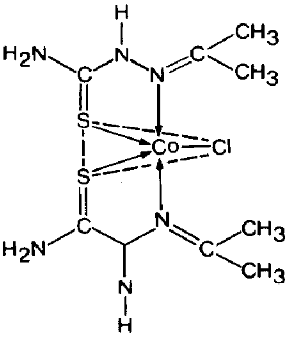
The influence of the parent ligand moiety on the final geometry of the coordination complex derived from it is evident from interaction of cobalt(II) halides with potentially bidentate/tridentate thiosemicarbazone (or semicarbazone) ligands of the type $R_1R_2C{=}NHNCSNH_2$. The aryl-substituted derivatives, i.e., acetophenone thiosemicarbazone (APTSC) and benzaldehyde thiosemicarbazone (BZTSC), have magnetic moments between 4.24 and 4.90 at 295 K and possess two systems of bands lying in the ranges 4500–9000 cm^{-1} and 13000–17000 cm^{-1} without any intermediate absorptions, which is indicative of tetrahedral stereochemistry [71,72]. The X-ray crystal structure for the former complex shows that the ligands are monodentate, bonding through sulfur, while the N^4 atoms are projected outward (i.e., the *trans* mode of coordination) from the metal ion (XI). It is likely that the bulky methyl substituent adjacent to the imine nitrogen atom may be imposing steric constraints on its participation in coordination.

On the other hand, salicylaldehyde semicarbazone, a potentially tridentate ligand, is found to act as a bidentate monoanion because of nonparticipation of the carbonyl oxygen of the semicarbazone moiety [73]. This seems to be a typical ligating behavior of aryl derivatives and has been termed the 'flip-tail bidenticity' of semicarbazone ligands [74]. The resulting complex in the above case is found to be pseudooctahedral of the type $[Co(HSSC)'_2(H_2O)_2]$.



(XI)

The other class includes complexes of thiosemicarbazone ligands bearing aliphatic substituents. Of these, benzylmethyl ketone and methyl-n-hexyl ketone have been found to react [75] with cobalt halides in alkaline media in their enolic forms to yield neutral bischelates of the type ML_2, which seem to be six-coordinate polymeric species, as suggested by their insolubility in common organic solvents and magnetic behavior. On the other hand, complexes of acetone thiosemicarbazone (ACTSC) and cyclohexanone thiosemicarbazone (CHTSC) ligands have magnetic moments between 4.13 and 4.40 B.M. at 295 K and show relatively intense but broad bands between 11 500 and 13 500 cm^{-1}, indicative of five-coordination [76]. This is borne out by X-ray crystal structure studies of Scarmuzza and co-workers [77] on



(XII)

$[Co(ACTSC)_2Cl]Cl \cdot H_2O$ (XII). The complex was found to possess a trigonal bipyramidal configuration with two sulfur atoms and one of the chlorine atoms lying approximately in a plane, while the azomethine nitrogen atoms are situated *trans* to each other.

Pandeya and co-workers [78] reported that the cobalt complex of cyclohexanone thiosemicarbazone can be obtained in two forms. For example, a reddish-brown complex ($\mu_{eff.} = 4.57$ B.M.) can be obtained from interaction of an ammoniacal solution of a cobalt(II) salt with a hot, ethanolic solution of cyclohexanone thiosemicarbazone. The chloroform solution of this complex is green in color and, upon removing the solvent under reduced pressure, yields a green-colored complex, which shows a magnetic moment of 4.33 B.M. The reddish-brown complex can be converted to the green complex by heating at ca. 60°C for about one hour. The conversion is reversible, and upon cooling, the green complex changes back to the reddish-brown complex. The authors suggested a tetrahedral geometry for the green complex and a pseudooctahedral structure achieved through sulfur bridges by a stacking arrangement for the reddish-brown complex.

Dessy and Fares [72] have suggested that a distinction between low-symmetry tetrahedral and five-coordinate Co(II) complexes of these ligands can be made on the basis of differences in their electronic spectral characteristics. For example, the aryl-substituted thiosemicarbazone complexes show charge transfer bands in the region 21000–24500 cm^{-1}, while those bearing aliphatic substituents exhibit bands between 11000–14000 cm^{-1}.

The oxygen analogs of aliphatic thiosemicarbazones, viz. acetone and ethyl methyl semicarbazones, interact with cobalt(II) salts to give compounds of the type CoL_2X_2 (where L = the neutral semicarbazone ligand; X = Cl, Br, I, CNS, or 1/2 SO_4). These compounds are paramagnetic, exhibiting magnetic moments in the range 4.5–5.3 B.M. at room temperature and the electronic as well as IR spectral features are suggestive of six-coordinate cobalt(II) compounds [79].

Crystal structure data are now available on yet another complex, $[CoL_2(CH_3COO)]I$ (where L = the neutral, bidentate acetone-S-methylthiosemicarbazone ligand) (Fig. 2). The coordination around cobalt is found to be close to that of a trigonal bipyramid formed by four nitrogen atoms and one oxygen atom of the acetyl group [80]. The compound thus constitutes a rare example of a series of thiosemicarbazone complexes wherein the sulfur

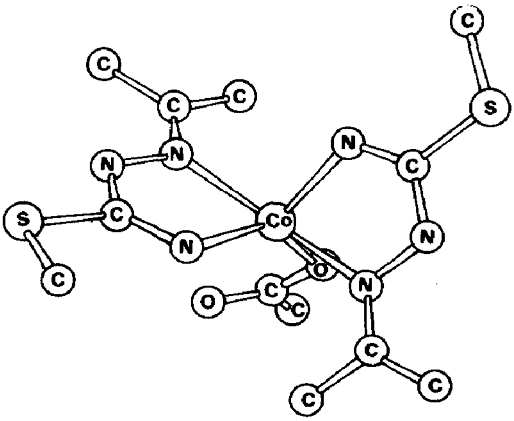


Fig. 2. Molecular structure of acetatobis(acetone-S-methyl-thiosemicarbazone)cobalt(II) iodide.

atom does not take part in coordination. It may be recalled here that when sulfur is not alkylated (as in the present case), the parent ligand coordinates through sulfur [35,77].

Finally, there is also a report on a cobalt(II) complex of a heterocyclic thiosemicarbazone, 2-furaldehyde thiosemicarbazone, which was found to be planar ($\mu_{\text{eff.}} \simeq 2.09$ B.M.), with a silent EPR both at room temperature and at 77 K, and which exhibited characteristic spectral shifts indicative of complexation through imine nitrogen and thiocarbonyl sulfur atoms (shifts in the bands at 1570 and 850 cm^{-1}, respectively) in IR spectra [81]. No evidence was, however, presented to indicate exclusion of coordination through heterocyclic oxygen, of which examples are known [10(h), 36].

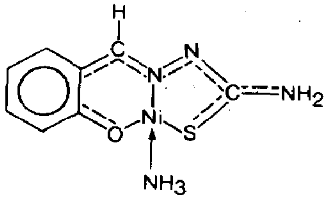
We noted earlier that, depending upon the pH and the presence or absence of oxidizing agents, the interaction of potentially tridentate dibasic semicarbazone ligands such as salicylaldehyde semicarbazone (H_2SSC) with cobalt(II) salts, yields complexes of the type $[Co(HSSC)(SSC)] \cdot H_2O$ and $K[Co(SSC)_2] \cdot 2\ H_2O$, respectively, which are both diamagnetic [46]. Clearly, such compounds are examples of low-spin cobalt(III) species, a d^6 rather than d^7 system. We have included them here since the starting materials have been cobaltous (d^7 system) salts. What is perhaps more important to note in these compounds is the presence of both thione and thiol forms of the ligand since it is known that it is the thiol form and not the thione form that causes spin-pairing of cobalt(III) ions. Complexes containing such mixed tautomeric forms of the thiosemicarbazone ligands have also been described by Padhyé and Sonawane [26] in the case of the 2-hydroxy-1,4-naphthoquinone thiosemicarbazone cobalt(III) complex.

The action of an alcoholic HCl solution on the former complexes that contain both tautomeric forms of this semicarbazone ligand gives compounds of the type $[Co(HSSC)_2]Cl \cdot H_2O$. The formation of similar complexes has been reported by Patil and Shah [82] with the tridentate ligand *p*-substituted *o*-hydroxyacetophenone thiosemicarbazone. Chebanu and Samus [46] have reported the formation of a paramagnetic complex at pH 5–6 from the interaction of a Co(II) salt and H_2SSC although the details of its characterization are not available. It will probably be a low-spin complex.

Additional ligands which also yield anionic, neutral, or cationic complexes include pyruvic acid thiosemicarbazone [84], 4-nicotinamide thiosemicarbazide [69], 4-phenylthiosemicarbazide [65] and its substituted derivatives [85,86].

(viii) d^8 *complexes*

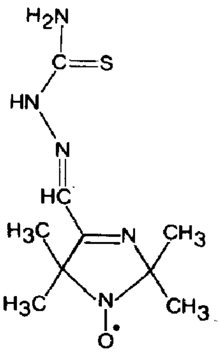
Paramagnetic, octahedral nickel(II) complexes have been reported in the case of thiosemicarbazones of acetone and cyclohexanone [87], while planar, diamagnetic complexes are known with 3-hydroxy-2-naphthaldehyde thiosemicarbazone [88], 2-hydroxyacetophenone [89], and its substituted derivatives [90]. The crystal structure of one such planar nickel(II) complex (**XIII**)



(XIII)

shows that attachment of an aryl moiety to the conjugated thiosemicarbazone ligand leads to partial dearomatization of the internal C–C bonds [91]. The other relevant interatomic distances are Ni–S = 2.146 Å, Ni–O = 1.851 Å, $Ni–N_{(TSC)}$ = 1.853 Å and $Ni–N_{(NH_3)}$ = 1.941 Å, respectively.

The synthesis and properties of Ni(II), Pd(II), and Pt(II) complexes with a paramagnetic thiosemicarbazone derivative obtained from (4-formyl-2,2,5,5-tetramethyl-3-imidazoline-1-oxyl thiosemicarbazone (**XIV**) (a stable nitroxyl

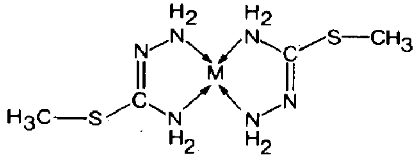


(XIV)

radical of piperdine) have been investigated by Ovcharenko and Larionov [92]. The thiosemicarbazone ligand is found to behave as a tridentate ligand in nickel(II) complexes, coordinating through imine nitrogen in addition to the usual sulfur and nitrogen centers, yielding distorted octahedral compounds in which there is a weak exchange interaction between the unpaired electrons of the paramagnetic centers. On the other hand, in Pd(II) and Pt(II) complexes the ligand is found to be bidentate, giving essentially planar compounds which exhibit ESR spectra characteristic of radical ion complexes with nitrogen hyperfines ($a_N \simeq 7.0G$).

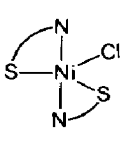
Nickel complexes of thiosemicarbazone ligands also provide rare examples of complexes in which the sulfur atom is not involved in the coordination

[29]. The complexation thus takes place through the hydrazinic nitrogen atom and the amide nitrogen atom, resulting in the square planar geometry shown in **XV**. The analogous cobalt complex, $[Co(CH_3{-}S{-}TSC)_3]I_3$, is obviously octahedral. Similar results are also observed in the case of acetone thiosemicarbazone methylated at the sulfur atom. On the other hand, the salicylaldehyde thiosemicarbazone ligand when methylated at the sulfur atom does not undergo complexation with metals [93]. Obviously, this behavior reflects the presence of a *trans* configuration for the ligands in these complexes. The ligands in such a configuration are known to be monodentate, bonding only through sulfur atoms, which may not be possible because of substitution. It is likely that aryl substituents might also be exercising steric restraints on the conversion to the *cis* configuration.

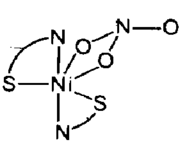


(**XV**)

Another interesting report illustrating the role of other coordinating anions on the final stereochemistries attained by nickel thiosemicarbazone complexes was produced by Gerbeleu and co-workers [87]. The interaction of Ni(II) salts with thiosemicarbazone derivatives of acetone and cyclohexanone give complexes of the type $[NiL_2X_2]\cdot(H_2O)_n$, (where L = the neutral thiosemicarbazone ligand and X = Cl, Br, NO_3, or ClO_4), which were initially thought to be high-spin octahedral complexes. Comparison of the number and energy of electronic spectral bands indicates that bromo and perchlorato complexes are analogous to the chloro compound. Subsequent X-ray diffraction studies, however, revealed the attachment of only one chlorine atom to the central nickel ion, indicating an essentially five-coordinate complex (**XVI**). On the other hand, when X = NO_3, the resulting complex is found to be octahedral with the resulting polyhedron greatly distorted to a geometry close to trigonal bipyramidal (**XVII**). The electronic spectrum of this compound did not show a band at 22370 cm^{-1} [$^3E'(F) \rightarrow {}^3E''(P)$], whereas this band is observed fairly clearly for the chloro complex. For other compounds the same transition appears as a shoulder on the band



(**XVI**)



(**XVII**)

at ca. 25 000 cm^{-1}, which indicates that the ligand fields around the central metal ion in these compounds are such that components of the term $^3P(^3A'_2$ and $^3E'')$ are almost equivalent in energies.

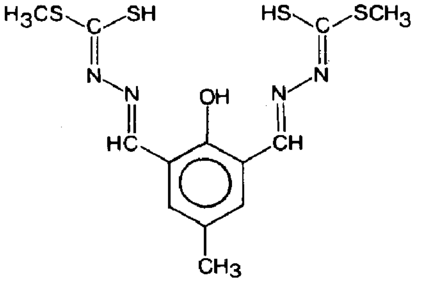
The effective magnetic moments calculated over the temperature range 100–300 K clearly indicate that the above compounds are of the high-spin type. However, the observed values of $\mu_{eff.}$ are slightly lower than those calculated for a high-spin five-coordinated trigonal bipyramidal configuration [94], which is thought to arise from quenching of the orbital contribution to the magnetic moment due to distortion of D_3h symmetry. It would have been interesting to include SO_4^{2-} ions in such a comparison, but unfortunately such data are not available. Involvement of sulfate ions in the coordination of transition metal thiosemicarbazone complexes has been noted by other workers [58,68]. Preparation of such mixed ligands should be useful in examining contributory factors to the final stereochemistries of this genre of complexes.

The cationic complexes of Pt(II) and Pd(II) with thiosemicarbazide of general formula $[ML_2]X_2$ (where L = the neutral semicarbazone ligand and X = Cl, Br, I, CN, CNS, NO_3, or 1/2 SO_4) have been prepared from $H_2PtCl_6 \cdot xH_2O$ and $PdCl_2$, respectively, using the method of substitution of the anion in ML_2Cl_2. The preparation of two neutral complexes of the type $[M(HL)_2]$ is also described by Murthy and co-workers [95]. These complexes are planar and diamagnetic, and they exhibit absorptions at about 28500 and 23500 cm^{-1}, characteristic of planar geometry with charge transfer (L → M) and intraligand transitions at 38000 and 42000–48000 cm^{-1}, respectively. Infrared spectra of these compounds show that NH modes of the ligands at 3389, 3285, and 3194 cm^{-1} move to lower wavenumbers on complexation in the ionic complexes, while they show a shift toward higher wavenumbers in the neutral complexes. A peculiar feature observed in the infrared spectra of the neutral complexes is the appearance of a band at 958 cm^{-1}, which is thought to be due to a νN–H stretch as a result of the elongation of the N^2–N^3 bond.

These studies have also provided evidence for the influence of some anions (e.g., Br^- or I^-) in yielding *trans* isomers even though the starting materials are *cis* compounds, which is thought to be due to their interaction at the axial positions of the molecule. The evidence for *cis–trans* isomerism among these complexes is advocated on the basis of IR spectral data. The *trans* isomer exhibits two sharp bands in the region 3400–3000 cm^{-1}, a doublet at ca. 1600 cm^{-1} and a distinct peak around 435 cm^{-1}, while the *cis* isomer shows only broad bands in both the former regions and a number of peaks in the latter M–L frequency region. X-ray powder patterns obtained for these compounds also support a symmetrical *trans* arrangement in the former and an absence of a center of symmetry in the *cis* isomers.

The diamagnetic complexes of Pt(II) with the ligands 4-nicotinamide thiosemicarbazone and 4-benzamidothiosemicarbazone of the type [$PtLX_2$] (where L = the neutral ligand and X = Cl or Br) have been described by Sahni et al. [69]. In addition to the absorptions due to the Pt–N (460–465 cm^{-1}) and Pt–S (350–390 cm^{-1}) stretches, two additional bands are observed at 270–280 and 200–220 cm^{-1} which are assigned to Pt–Cl and Pt–Br stretching modes. In view of the tendency of these ions to form polymeric structures, some additional support for the monomeric structures suggested for these compounds would be desirable.

McFadyen et al. [96] have derived complexes of formula [$LM_2(Z)$] (where the bridging species Z coordinates strongly enough to stabilize a binuclear structure) for nickel group ions and copper(II) ions and the trianionic, multidentate ligand 2-hydroxy-4-methyl-isophthaldehyde-di-2′-mercaptoanil dithiosemicarbazone (**XVIII**). In the absence of a good bridging group and in the presence of pyridine as a solvent, 3 : 2 complexes of formula [$L_2M_3(py)_2$] are produced in which the binucleating ligands fail to bond the two metal atoms in close proximity.



(XVIII)

(ix) d^9 *complexes*

Tetragonally distorted octahedral complexes of formula [$Cu(HTSC)_2X_2$] (X = Cl, Br, NO_3, or ClO_4) were reported in the case of 4-benzylamidothiosemicarbazone and 1-(α)-furyl-4-benzylamidothiosemicarbazone by Jain et al. [97]. ESR powder spectra support the tetragonal symmetry for copper(II) ions in these complexes, involving the $d_{x^2-y^2}$ (or d_{xy}) ground state except for the chloride complexes for which isotropic spectra are observed, suggestive of grossly misaligned tetragonal axes. The metal–nitrogen frequency in these complexes is found to be at 430 cm^{-1}, while M–Cl and M–Br stretches are observed at 270 and 212 cm^{-1}, respectively.

Zelentsov et al. [98] have described some novel binuclear and trinuclear copper complexes, designated as 'super-complexes', by the interaction of copper(II) salts with quadridentate ligands derived from *o*-hydroxyben-

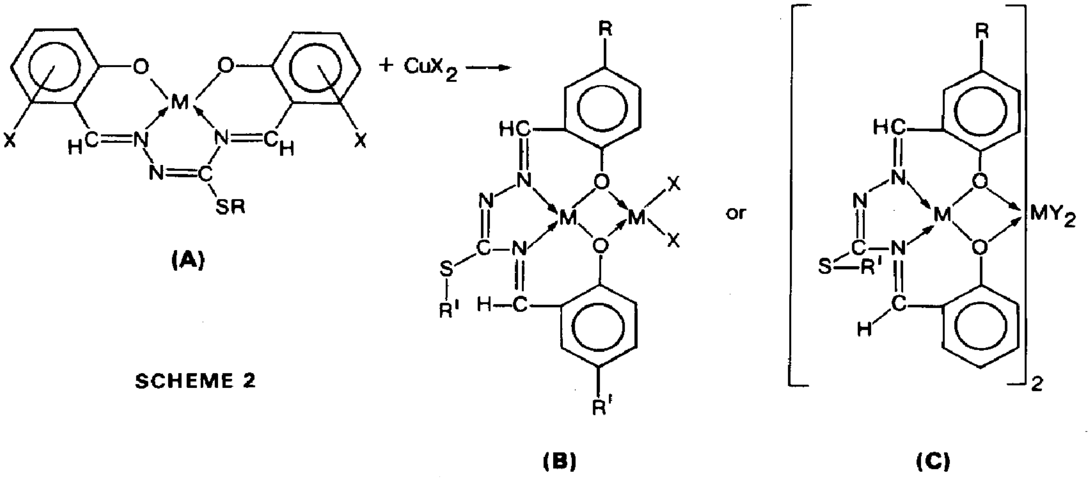
TABLE 3

Temperature dependence of the magnetic susceptibility of the copper adducts [98]

(a) $[(CuL)_2Cu]\cdot(NO_3)_2$; $N\alpha = 60\times10^{-6}$ e.s.u.										
T (K)	290.3	258.0	231.7	205.0	186.0	164.6	145.7	129.5	107.8	77.4
$\mu_{eff.}$	1.85	1.80	1.78	1.76	1.72	1.68	1.63	1.58	1.49	1.34
(b) $[(CuL)_2Zn]\cdot(NO_3)_2$; $N\alpha = 60\times10^{-6}$ e.s.u.										
T (K)	289.5	243.0	204.5	175.5	158.0	139.5	124.0	107.0	77.4	
$\mu_{eff.}$	1.82	1.81	1.80	1.78	1.77	1.76	1.74	1.71	1.64	

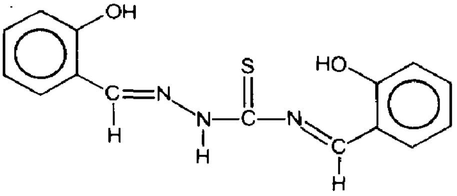
zaldehyde and its thiosemicarbazones (**A**), as shown in Scheme 2. The formation of such 'super-complexes' has been shown to depend upon the nature of the reactants and the anions. Thus in ethanol–chloroform medium only copper(II) and nickel(II) complexes gave adducts, while the corresponding oxovanadium(IV) compounds could not be obtained. Similarly, chlorides and bromides gave binuclear adducts (**B**) of the type $[ML\cdot M'X_2]$, while perchlorate and nitrate salts gave trinuclear compounds (**C**) of the type $[(ML)_2M]Y_2$ (where Y = ClO_4 or NO_3), in which the perchlorate and nitrate ions are not coordinated to the metal atom but are present as free ions in the crystal lattice. Exchange interaction of the antiferromagnetic type takes place between the paramagnetic atoms of the trimeric molecule. The trimeric structure was further confirmed by preparation of an essentially heterobinuclear complex, $[(CuL)_2\cdot Zn(NO_3)_2]$, which shows no such exchanges and consequently very little temperature dependence for its magnetic moment (see Table 3).

When methanolic solutions of copper(II) salts are allowed to interact with 2-hydroxynaphthalenecarbaldehyde semicarbazone at pH ≃ 3–4, complexes

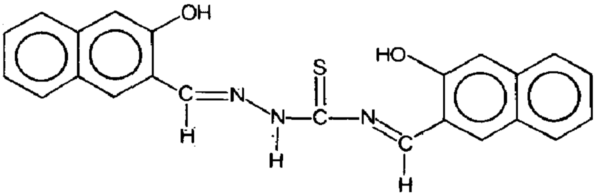


SCHEME 2

of the type $[Cu(HL)X(H_2O)_2]$ (where HL = ligand monoanion, and X = Cl, Br or NO_3) are formed [99]. In ammoniacal or near neutral pH medium, replacement of the acid residue X by neutral NH_3 or H_2O ligands takes place with concomitant deprotonation of the ligand yielding a dianionic species. The resulting complexes have the formula $[Cu(L)Y(H_2O)_2]$ (where L = the ligand dianion and Y = NH_3 or H_2O) and exhibit distorted octahedral geometries. A comparison of pK' values for the salicylal and naphthalene series of copper complexes shows that the acid properties of the latter series of compounds are stronger, in agreement with their pronounced electron-withdrawing properties. In alkaline media both series of compounds can undergo condensations at the amido nitrogens with another mole of the same ligand to yield the potentially quadridentate dianionic ligands **XIX** and **XX**.



(**XIX**)



(**XX**)

The octahedral complexes of type $[CuLX(solv.)_n]$, where L = the ligand monoanion; X = Cl; solv. = H_2O or DMF; and $n = 0$, 1, or 2), have also been derived from ligands such as ethylacetoacetate thiosemicarbazone [100], benzoin thiosemicarbazone [101], and 9,10-phenanthraquinone [102].

Caric et al. [103] reported X-ray powder diffraction data for copper complexes of type $[Cu(HL)X] \cdot nH_2O$ (where HL = the ligand monoanion and X = Cl, Br, NO_3, or ClO_4), obtained by reaction of copper(II) chloride and salicylaldehyde-*S*-methyl thiosemicarbazones. The compounds are examples of thiosemicarbazone complexes in which the sulfur atoms are not involved in coordination. They possess square planar structures in which three of the coordinating sites are occupied by the phenolic oxygen atom, the hydrazinic nitrogen atom, and the terminal amide nitrogen atom, while the fourth site is occupied by the gegenion [104]. The complex $[Cu(HL)ClO_4]$ is, however, found to possess a lower magnetic moment than the spin-only value, which is explained by considering a dimeric structure in which phenolic oxygen atoms serve as the bridging elements. This is advocated on the ground that the conversion of $Cu(HL)ClO_4$ into $Cu(L)NH_3 \cdot H_2O$ is possible without apparent reduction of the copper(II) ion.

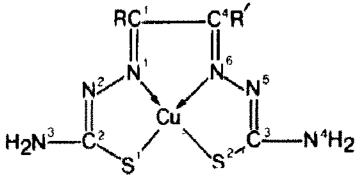
Square planar geometries are also suggested by Jain et al. [105] for copper(II) complexes of α-pyridylthiosemicarbazone derivatives on the basis of magnetic moments (1.40–1.55 B.M.) and electronic spectral bands at 15680–16000 ($^2B_{1g} \rightarrow {}^2E_g$) and 24900–25700 ($^2B_{1g} \rightarrow {}^2A_{1g}$) cm^{-1}, respectively. The bidentate nature of the ligand and the coordinating sites (pyridyl nitrogen and thione sulfur atoms) have been established on the basis of frequency shifts of corresponding absorptions in the infrared spectra and the occurrence of Cu–S and Cu–N stretching vibrations at 454–425 and 315–250 cm^{-1}, respectively, in the far-infrared region.

Campbell et al. [106] studied the ESR spectrum and covalency parameters of the antitumor agent 3-ethoxy-2-oxo-butyraldehyde thiosemicarbazone-copper(II), commonly referred to as the "Cu(KTS)-complex" and found the bonding parameters to be similar to those of bis(thiosemicarbazido)copper(II) sulfate. This confirms the idea that Cu–N and Cu–S bonds may be regarded as essentially independent. It has now been established that inhibition of RNA-directed DNA-polymerase in the viron by thiosemicarbazone copper(II) complexes prevents malignant transformation by *Rous sarcoma* virus [107]. Crystal structures of 3-ethoxy-2-oxo-butyraldehyde thiosemicarbazone, its copper complex (the Cu(KTS)-complex), and the benzil-bis(thiosemicarbazone)copper(II) complex were investigated by Bushnell and Tasang [108] in order to investigate the antitumor mechanism at the molecular level. Comparison of their structures (Table 4) led these authors to suggest that bonding of sulfur to the axial copper site is probably not totally dominant over the forces of double hydrogen bonding and that hydrogen bonding may be an important factor in their antitumor mechanism. Adenine, guanine, and cytosine all have amine groups adjacent to unprotonated ring nitrogen atoms and are thus well suited to form double hydrogen bonds with the bis(thiosemicarbazone)copper(II) complex. These authors have pointed out the striking structural similarity between the copper complex of 3-ethoxy-2-oxo-butyraldehyde thiosemicarbazone (**XXI**) and the nucleoside (**XXII**) formed from guanine and ribose (or deoxyribose), which is in some way related to their antitumor activity.

Binding of the anticancer agent 2-formylpyridine thiosemicarbazonato-copper(II) with Ehrlich ascites tumor cells has been recently described by

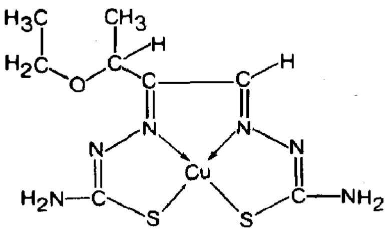
TABLE 4

Comparison of the structural data on copper(II) complexes of 3-ethoxy-2-oxo-butyraldehyde thiosemicarbazone (**A**) and benzilthiosemicarbazone (**B**)

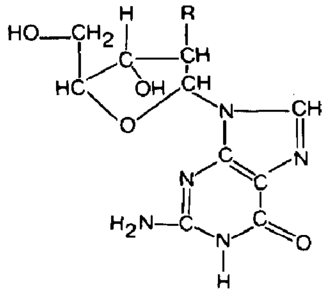


$R' = H$; $R = CH(OC_2H_5)CH_3$, **A**; $R = R' = C_6H_5$, **B**

Compound	Bond length (Å)									Bond angle (°)	
	C^1C^4	C^1N^1	C^4N^6	N^2C^2	N^5C^3	CuN^1	CuN^6	CuS^1	CuS^2	N^1CuN^6	S^1CuS^2
A	1.45	1.30	1.30	1.29	1.34	1.97	1.97	2.23	2.23	79.9	112.3
B	1.49	–	–	–	–	1.98	1.95	2.26	2.26	81.1	108.6



(XXI)



R = H or OH

(XXII)

Petering and co-workers [109]. The compound is found to inhibit cellular DNA formation at low concentrations, but the RNA formation is seen to be less sensitive. The binding sites are indicated to be glutathione thiol groups, confirming the earlier observations of Bushnell and Tasang [108].

(x) d^{10} *complexes*

Tetrahedral as well as octahedral zinc(II) complexes of parent thiosemicarbazide and thiosemicarbazone, in which ligands are known to be bidentate, have been reported [57]. On the other hand, ligands such as ethylacetoacetate semicarbazone and thiosemicarbazone are found to be tridentate in their zinc complexes [110], in which the third coordinating center is provided by the acyl carbonyl group (shift in infrared frequency from 1720 to 1700 cm^{-1}), and the presence of the M–O frequency is shown in its far-infrared spectra at 450 cm^{-1}, in addition to M–S and M–N frequencies at 260 and 370 cm^{-1}, respectively.

D. CONCLUSIONS

Of the metal thiosemicarbazone complexes reported since the approximately eight compounds mentioned in Campbell's review article of 1975 [13], a variety of interesting cationic, neutral, and anionic species are represented. Although the ligand is usually involved in its neutral form, complexes are sometimes formed from the anionic ligand. The ligand may be monodentate, bidentate, or tridentate. Bonding to the metal ion may be through the sulfur atom, one or more of the nitrogen atoms, or both sulfur and nitrogen atoms. Coordination numbers of seven (pentagonal bipyramidal), six (octahedral), five (trigonal bipyramidal or square pyramidal), or four (square planar or tetrahedral) are found, and both mononuclear and polynuclear complexes have been prepared. Complexes of the following d^n configurations have been reported: d^1 Sc(III), VO(IV); d^3 Cr(III); d^4 Mn(III); d^5 Fe(III), Mn(II), Ru(III); d^6 Fe(II), Co(III), Ru(II), Rh(III); d^7 Co(II); d^8 Ni(II), Pd(II), Pt(II); d^9 Cu(II); and d^{10} Zn(II).

Despite their potential medical applications, most of the new complexes have not been investigated in detail, and further studies, particularly of their syntheses and magnetic properties, are needed.

ACKNOWLEDGMENTS

S.P. thanks Dr. Nivrutti Sonawane, Prafulla Garge, Mahesh Mulay, Michelle Cohn, and Mark Timken for their help extended during completion of the review. He is also greatly indebted to Prof. David Hendrickson of the University of Illinois, Urbana for the hospitality extended during his visiting fellowship. G.B.K. is indebted to Sharon Turner and George McCann for technical assistance.

REFERENCES

1 J.R. Wasson, G.M. Woltermann and H.J. Stoklosa, Transition Metal Dithio- and Diselenophosphate Complexes in Inorganic Chemistry, Topics in Current Chemistry, Vol. 35, Springer-Verlag, Berlin, 1973, p. 65.

2 G.D. Thorn and R.A. Ludwig, The Dithiocarbamates and Related Compounds, Elsevier, Amsterdam, 1962.

3 D. Coucovanis, Prog. Inorg. Chem., 11 (1970) 233.

4 H.B. Gray, Transition Met. Chem., 1 (1965) 240; C.K. Jørgensen, Inorg. Chim. Acta Rev., 2 (1968) 65; J.A. McCleverty, Prog. Inorg. Chem., 10 (1968) 49.

5 S.E. Livingstone, Coord. Chem. Rev., 7 (1971) 59; M. Cox and J. Darken, Coord. Chem. Rev., 7 (1971) 29.

6 G.C. Pellaconi and T. Feltri, Inorg. Nucl. Chem. Lett., 8 (1972) 325 and references therein.

7 S.E. Livingstone, Q. Rev. Chem. Soc., 19 (1965) 386.

8 R.W. Brockman, J.R. Thomson, M.J. Bell and H.E. Skipper, Cancer Res., 16 (1956) 167; H.G. Petering, H.H. Buskirk and G.E. Underwood, Cancer Res., 64 (1964) 367; A. Giner-Sorolla, M. McCravey, J. Longley-Cook and J.H. Burchenal, J. Med. Chem., 16 (1973) 984; K.C. Agrawal, A.J. Lin, B.A. Booth, J.R. Wheaton and A.C. Sartorelli, J. Med. Chem., 17 (1974) 631; D.A. Winkelmann, Y. Bermke and D.H. Petering, Bioinorg. Chem., 3 (1974) 261; D.J. Leggett and W.A.E. McBryde, Talanta, 21 (1974) 1005; K.C. Agrawal, B.A. Booth, S.M. DeNuzzo and A.C. Sartorelli, J. Med. Chem., 18 (1975) 368; D.C. Dunn and E.M. Hodnett, Eur. J. Med. Chem. Ther., 12 (1977) 113; L.F. Lim, S.J. Lee and C.T. Chen, Heterocycles, 7 (1977) 347; W.E. Antholine, J. Knight, H. Whelan and D.H. Petering, Mol. Pharmacol., 13 (1977) 89; W.E. Antholine, J. Knight and D.H. Petering, Inorg. Chem., 16 (1977) 569.

9 (a) R.L. Thompson, S.A. Minton, Jr., E. Officer and G.H. Hitchings, J. Immunol., 70 (1953) 229.
(b) D.H. Jones, R. Slack, S. Squires and K.R.H. Wooldridge, J. Med. Chem., 8 (1965) 676.

(c) N.N. Orlova, V.A. Aksenova, D.A. Sclidovkin, N.S. Bogdanova and G.N. Perskhin, Russ. Pharm. Toxicol., (1968) 348.
(d) K. Butler, U.S. Patent No. 3,382,266 (1968).
(e) D.J. Bauer, L. St. Vincent, C.H. Kempe and A.W. Downe, Lancet, 2 (1963) 494.
(f) J.C. Logan, M.P. Fox, J.H. Morgan, A.M. Makohon and C.J. Pfau, J. Gen. Virol., 28 (1975) 271.
(g) E. Winkelmann and H. Rolly, Arzneim.-Forsch., 22 (1972) 1704; C. Shipman, Jr., S.H. Smith, J.C. Drach and D.L. Klayman, Antimicrob. Agents Chemother., 19 (1981) 682.

10 (a) D.L. Klayman, J.E. Bartosevich, T.S. Griffin, C.J. Mason and J.P. Scovill, J. Med. Chem., 22 (1979) 855.
(b) D.L. Klayman, J.P. Scovill, J.F. Bartosevich and C.J. Mason, J. Med. Chem., 22 (1979) 1367.
(c) D.L. Klayman, J.P. Scovill, J.F. Bartosevich and C.J. Mason, Eur. J. Med. Chem. Ther., 16 (1981) 317.

11 D.L. Klayman, J.P. Scovill, J.F. Bartosevich and J. Bruce, J. Med. Chem., 26 (1983) 35.

12 For example, (a) H.G. Petering, H.H. Buskirk and J.A. Crim, Cancer Res., 27 (1967) 1115.
(b) J.A. Crim and H.G. Petering, Cancer Res., 27 (1967) 1278.
(c) G.J. Van Giessen, J.A. Crim, D.H. Petering and H.G. Petering, J. Nat. Cancer Inst., 51 (1973) 139.
(d) F.A. French, E.J. Blanz, Jr., J.R. DoAmaral and D.A.J. French, J. Med. Chem., 13 (1970) 1117.
(e) K.C. Agrawal and A.C. Sartorelli, Prog. Med. Chem., 15 (1978) 349.
(f) L.A. Saryan, E. Ankel, C. Krishnamurti, D.H. Petering and H.J. Elford, J. Med. Chem., 22 (1979) 1218.
(g) M. Das and S.E. Livingstone, Br. J. Cancer, 37 (1978) 463.
(h) D.L. Klayman, J.P. Scovill and C.F. Franchino, J. Med. Chem., 25 (1982) 1261.

13 M.J.M. Campbell, Coord. Chem. Rev., 15 (1975) 279.

14 M. Akbar Ali and S.E. Livingstone, Coord. Chem. Rev., 13 (1974) 101.

15 R.B. Singh, B.S. Garg and R.P. Singh, Talanta, 25 (1978) 619.

16 E. Krueger-Thiemer, H. Kroger and H.J. Nestler, Infektioskr. Ihre Erreger, 4 (3) (1975) 289.

17 N.V. Gerbeleu, Doctoral Thesis, Moscow State University, Moscow, 1973.

18 For example, A.I. Vogel, Practical Organic Chemistry, Longmans, London, 1973, p. 344; P.T. Sah and T.C. Daniels, Rec. Trav. Chim., 69 (1950) 1545; F.E. Anderson, J.C. Duca and J.W. Scudi, J. Chem. Soc., (1951) 4967 and references therein.

19 G. Domagk, R. Behnisch, F. Mietzsch and H. Schmidt, Naturwissenschaften, 33 (1946) 315; D.J. Drain, C.L. Goodacre and D.E. Seymour, J. Pharm. Pharmacol., 1 (1949) 784; R. Protivinsky, Antibiot. Chemother. (Basel), 17 (1981) 101; W.H. Wagner and E. Winkelmann, Arzneim.-Forsch., 22 (1972) 1713.

20 A. Lewis and R.G. Shepherd in A. Burger (Ed.), Medicinal Chemistry, Wiley, New York, 1970, p. 431.

21 P. Malatesta, G.P. Accinelli and G. Quaglia, Ann. Chim. (Rome), 49 (1959) 397; Chem. Abstr., 53 (1959) 19942; J. Jolačny, N. Štimac, B. Sajko, B. Balenovič and B. Urbas, Ark. Kemi., 26 (1954) 71.

22 A. Kaminski, Prensa Méd. Argent., 40 (1953) 1263.

23 L. Heilmeyer, Klin. Wochenschr., 28 (1950) 254; French Patent No. 5536 (1967); Chem. Abstr., 71 (1969) 42301v.

24 H.R. Wilson, G.R. Ravankar and R.L. Tolman, J. Med. Chem., 17 (1974) 760.
25 E. Winkelmann, W.H. Wagner and H. Wirth, Arzneim.-Forsch., 27 (1977) 950.
26 S.B. Padhyé and N.J. Sonawane, unpublished results.
27 A.V. Ablov and N.V. Gerbeleu, Russ. J. Inorg. Chem., 9 (1964) 1260.
28 P. Domiano, G. Gasparri Fava, M. Nardelli and P. Sgarabotto, Acta Crystallogr., 25B (1969) 343; G.D. Andreetti, P. Domiano, G. Fava, M. Nardelli and P. Sgarabotto, Acta Crystallogr., Sect. B, 26 (1970) 1005.
29 N.V. Gerbeleu, M.D. Revenko and V.M. Leovats, Russ. J. Inorg. Chem., 22 (1977) 1009.
30 L. Coghi, A.M.M. Lanfredi and A. Tiripicchio, J. Chem. Soc., Perkin Trans. 2, (1976) 1808.
31 (a) V.M. Leovac, N.V. Gerbeleu and V.D. Canic, Russ. J. Inorg. Chem., 27 (1982) 514. (b) N.V. Gerbeleu and F.K. Zhovmir, Russ. J. Inorg. Chem., 27 (1982) 309 and references therein.
32 (a) S.V. Kasmir Raja, G.A. Savariraj and D.N. Sathyanarayana, Ind. J. Chem., 18A (1979) 297.
(b) D.N. Sathyanarayana, K. Volka and K. Geetharani, Spectrochim. Acta, 33A (1977) 517.
(c) K. Geetharani and D.N. Sathyanarayana, Aust. J. Chem., 30 (1977) 1617.
33 G. Keresztury, J. Mol. Struct., 46 (1978) 127.
34 N.V. Gerbeleu, K.I. Turta, J.T. Kashkaval and F. Tui, Russ. J. Inorg. Chem., 26 (1981) 1154; N.V. Gerbeleu, K.I. Turta, F. Tui and A.M. Vedyanu, Russ. J. Inorg. Chem., 22 (1977) 865.
35 M. Mathew, G.J. Palenik and G.R. Clark, Inorg. Chem., 12 (1973) 446.
36 Y.K. Bhoon, S. Mitra, J.P. Scovill and D.L. Klayman, Transition Met. Chem., 7 (1982) 264.
37 R.K.Y. Ho, S.E. Livingstone and T.N. Lockyer, Aust. J. Chem., 19 (1966) 1179.
38 D.M. McRitchie, R.C. Palenik and G.J. Palenik, Inorg. Chim. Acta, 20 (1976) L27.
39 G. Dessy and V. Fares, Cryst. Struct. Commun., 10 (1981) 1025.
40 C.L. Jain, R.C. Saxena and R.K. Gupta, Curr. Sci., 47 (1978) 766.
41 M.P. Martinez, M. Valcarcel and F. Pino, Anal. Chim. Acta, 81 (1976) 157.
42 A. Syamal, Coord. Chem. Rev., 16 (1975) 309 and references therein.
43 S. Chandra and K.B. Pandeya, Transition Met. Chem., 6 (1981) 110.
44 V.Kh. Kravtsov, K.F. Belyaeva, V.N. Biyushkin, Yu.T. Struchkov, V.G. Bodyu and N.M. Samus, Sov. J. Coord. Chem., 7 (1981) 776.
45 Y. Shibutani, K. Shinra and C. Matsumoto, J. Inorg. Nucl. Chem., 43 (1981) 395.
46 V.G. Chebanu and N.M. Samus, Russ. J. Inorg. Chem., 21 (1976) 3280.
47 V.Yu. Plotkin, M.G. Felin, N.A. Subbotina and V.V. Zelentsov, Russ. J. Inorg. Chem., 28 (1983) 1463.
48 U.N. Pandey, J. Ind. Chem. Soc., 55 (1978) 645.
49 M.C. Jain, R.K. Sharma and P.C. Jain, J. Inorg. Nucl. Chem., 42 (1980) 1229.
50 For example, N.A. Ryabova, V.I. Ponomarev, L.O. Atomyan, V.V. Zelentsov and V.I. Shipilov, Sov. J. Coord. Chem., 4 (1976) 95; N.A. Ryabova, V.I. Ponomarev, V.V. Zelentsov, V.I. Shipilov and L.O. Atomyan, J. Struct. Chem. U.S.S.R., 2 (1981) 234; N.A. Ryabova, V.I. Ponomarev, V.V. Zelentsov and L.O. Atomyan, Dokl. Akad. Nauk, Physical (Engl. trans.), 4 (1981) 715 and references therein.
51 N.E. Spingarn and A.C. Sartorelli, J. Med. Chem., 22 (1979) 1314.
52 J.S. Oxford and D.D. Perrin, Gen. Virol., 23 (1974) 59.
53 R. Raina and T.S. Srivastava, Ind. J. Chem., 22A (1983) 701.
54 Y.K. Bhoon, S.B. Padhyé, S.K. Date, M.P. Gupta and D.L. Klayman, unpublished results.

55 Y.K. Bhoon, Polyhedron, 5 (1983) 365.
56 H. Beraldo and L. Tosi, Inorg. Chim. Acta, 75 (1983) 249.
57 B. Pradhan and D.V. Ramana Rao, J. Ind. Chem. Soc., 54 (1977) 136.
58 M.J.M. Campbell, R. Grzeskowiak, R. Thomas, B.W. Fitzsimmons and C.A. Yong, Inorg. Chim. Acta, 50 (1981) 179.
59 L.I. Petukhov, A.V. Ablov, G.F. Volodina and T.I. Malinovskiĭ, Dokl. Chem. (Engl.), 241 (1978) 330.
60 M. Mathew and G.J. Palenik, J. Am. Chem. Soc., 91 (1969) 4923.
61 G.F. Volodina, L.I. Petukhov, A.V. Ablov and N.V. Gerbeleu, Dokl. Chem. (Engl.), 218 (1974) 722.
62 S. Chandra, K.B. Pandeya, G.L. Sawhney and J.S. Baijal, Gazz. Chim. Ital., 111 (1981) 53.
63 R. Ingalls, Phys. Rev. A, 133 (1964) 787.
64 D.V. Naik and G.J. Palenik, Chem. Phys. Lett., 24 (1974) 260.
65 A.V. Ablov, N.V. Gerbeleu, V.I. Goldanskiĭ, R.A. Stukan and K.I. Turta, Russ. J. Inorg. Chem., 16 (1971) 90.
66 G.A. Eisman and W.M. Reiff, Inorg. Chim. Acta, 50 (1981) 239.
67 For example, H.T. Witteveen and J. Reedijk, J. Solid State Chem., 10 (1974) 151; B.W. Dockum and W.M. Reiff, Inorg. Chem., 21 (1982) 391 and references therein.
68 S.B. Padhyé and N.J. Sonawane, Proc. XXII ICCC, Budapest, Abstr. No. TuP33 (1982) p. 393.
69 S.K. Sahni, P.C. Jain and V.B. Rana, Ind. J. Chem., 18A (1979) 161.
70 S.K. Sahni, P.C. Jain and V.B. Rana, Ind. J. Chem., 16A (1978) 699.
71 C. Bellitto, A.A.C. Tomlinson, C. Furlani and G. de Munno, Inorg. Chim. Acta, 27 (1978) 269.
72 G. Dessy and V. Fares, J. Chem. Soc. Dalton Trans., 11 (1978) 1549.
73 P.L. Maurya, B.V. Agarwala and A.K. Dey, Ind. J. Chem., 19A (1980) 807.
74 S.B. Padhye, S.K. Date and M.P. Gupta, Proc. All India Conf. on Mössbauer Effect, Amritsar, 1983.
75 S. Chandra and K.K. Sharma, Synth. React. Inorg. Met. Org. Chem., 13 (1983) 559.
76 I. Bertini, D. Gatteschi and A. Scozzafava, Inorg. Chem., 14 (1975) 812 and references therein.
77 G. Dessy, V. Fares and L. Scarmuzza, Cryst. Struct. Commun., 5 (1976) 605.
78 S. Chandra, K.B. Pandeya and R.P. Singh, Ind. J. Chem., 18A (1979) 476.
79 S. Chandra, K.B. Pandeya, S.P. Dubey and R.P. Singh, Synth. React. Inorg. Met.-Org. Chem., 13 (1983) 585.
80 V. Divjaković and V. Leovac, Cryst. Struct. Commun., 7 (1978) 689.
81 K.K. Arvindakshan and C.G.R. Nair, Ind. J. Chem., 20A (1981) 684.
82 M.S. Patil and J.R. Shah, Proc. Ind. Acad. Sci., 90 (1981) 147.
83 A.V. Ablov and O.A. Bologa, Russ. J. Inorg. Chem., 22 (1977) 127.
84 O.A. Bologa, N.I. Belichuk and A.V. Ablov, Russ. J. Inorg. Chem., 23 (1978) 1036.
85 M.M. Mostafa, A.M. Shallaby and A.A. El-Asmy, J. Ind. Chem. Soc., 60 (1983) 109.
86 S. Ghosh, P.K. Ray, M.S. Mitra and T.K. Banik, J. Ind. Chem. Soc., 58 (1981) 533.
87 F. Tui, K.I. Turta and N.V. Gerbeleu, Russ. J. Inorg. Chem., 22 (1977) 1497.
88 C.B. Mahto, J. Ind. Chem. Soc., 58 (1981) 935.
89 M.S. Patil and J.R. Shah, Proc. Indian Acad. Sci., 89 (1980) 387.
90 L.D. Dave and S.K. Thampy, J. Ind. Chem. Soc., 58 (1981) 538.
91 E. Geypes, F. Pavelcik and A. Beňo, Collect. Czech. Chem. Commun., 46 (1981) 975.
92 V.I. Ovcharenko and S.V. Larionov, Russ. J. Inorg. Chem., 26 (1981) 1477.

93 V.I. Gerasimov, M.D. Revenko, V.N. Biyushkin, V.M. Golyshev, N.V. Gerbeleu and N.V. Belov, Kristallografiya, 21 (1976) 399.
94 J.S. Wood and P.T. Greene, Inorg. Chem., 8 (1969) 491.
95 D.S. Mahadevappa, B.T. Gowda and A.S.A. Murthy, Ind. J. Chem., 14A (1976) 985.
96 W.D. McFadyen, R. Robson and H.A. Schaap, J. Coord. Chem., 8 (1978) 59.
97 M.C. Jain, A.K. Srivastava and P.C. Jain, Inorg. Chim. Acta, 23 (1977) 199.
98 V.V. Zelentsov, Y.V. Rakitin, Y. Do, A.K. Stroesku, M.D. Revenko, K.I. Turta and N.V. Gerbeleu, Russ. J. Inorg. Chem., 22 (1977) 233.
99 N.M. Samus and R.G. El-Magd, Russ. J. Inorg. Chem., 24 (1979) 544.
100 N.C. Mishra and B. Mohapatra, J. Inorg. Nucl. Chem., 41 (1979) 408.
101 B.P. Mohapatra and S.K. Pujari, Ind. J. Chem., 22A (1983) 525.
102 Y.K. Bhoon, Ind. J. Chem., 22A (1983) 433.
103 S. Caric, D. Petrovic, D. Lazar and V.M. Leovac, Z. Kristallogr., 148 (1978) 153.
104 V.M. Leovats and N.V. Gerbeleu, Zh. Neorg. Khim., 23 (1978) 1272.
105 G.L. Jain, R.C. Saxena, B.S. Saxena and L.R. Gupta, Curr. Sci., 47 (1978) 328.
106 M.J.M. Campbell, A.J. Collis and R. Grzeskowiak, Bioinorg. Chem., 6 (1976) 305.
107 W.C. Kaska, C. Carrano, J. Michalowski, J. Jackson and W. Levinson, Bioinorg. Chem., 8 (1978) 225.
108 G.W. Bushnell and A.Y.M. Tasang, Can. J. Chem., 57 (1979) 603.
109 L.A. Saryan, K. Mailer, C. Krishnamurti, W. Antholine and D.H. Petering, Biochem. Pharmacol., 30 (1981) 1595 and references therein.
110 N.C. Mishra, B.B. Mohapatra and S. Guru, J. Inorg. Nucl. Chem., 41 (1979) 408.