CHAPTER I

INTRODUCTION

OBJECT, SCOPE AND THEME OF THE WORK

The study of complexing behaviour of the transition metal ions with various ligands is at present undergoing a period of rapid development, and is engaging the attention of a large number of research workers in many diverse disciplines - both experimental and theoretical. Progress in this area of chemistry has received an added impetus because of many applications of complexes (and complexation processes) to physical and biological sciences, as well as to technology.

The ligands having sulphur as one of the donor atoms have been comparatively less extensively studied, and hence the nature of metal-sulphur bond is still more or less in a confused state.
Consequently, the available data on the metal-sulphur bond are not sufficient to provide a fairly coherent picture of the donor-acceptor relationship between sulphur and transition metal ions inspite of the fact that a considerable amount of work has been done in recent years in this field.

A few believe that the preferential bonding of sulphur (soft base) to some of the metal ions (soft acid) is due to the back-bonding from metal to sulphur utilizing the low-lying vacant 'd' orbitals on the sulphur atom. Jørgensen\textsuperscript{1} pointed out that the chemical softness of sulphur might have something to do with the empty orbitals is not a question of π back-bonding to the 3d orbitals of sulphur, but a question of continuum starting at a lower energy whereby the metal ion being polarized by sulphur. In 1968, Klopman\textsuperscript{2} using his theory of second order perturbation for the heteronuclear molecules derived a relationship wherein he has shown that when the difference in the energies of the frontier orbitals of the reactants is large, very little electron transfer occurs, and the interaction is ionic; but if the difference in the energies of the orbitals is small or they are degenerate, strong electron transfer occurs between them leading to the covalent type of bonding. The case of soft metals and soft ligand like sulphur belongs to the latter type while the hard acid-hard base like oxygen, etc. belong to the former type.

Some of the peculiar features of sulphur as a donor atom, as pointed out by Akbar Ali and Livingston\textsuperscript{3} are as follows:
(a) Sulphur ligands occupy a late position in the naphelauxetic series, which is, in effect, a measure of the degree of covalent bonding between metal and the ligand. The series of donor atoms (arranged according to decreasing values of $1 - \beta$) is roughly $F < O < N < Cl < Br < S \approx I < Se$.

(b) The low spin $d^9$ ions, viz., Pd(II), Pt(II) and Au(III), and the $d^{10}$ ions, viz., Cu(I), Ag(I), Au(I) and Hg(II) have high stability constants when complexed with sulphur ligands. Being typically 'b' class, they form strong $\sigma$-bonds with soft ligands and also $d\pi - d\pi$ bonds by donation of a pair of electrons to the ligands.

(c) Sulphur atoms in heterocyclic rings have very poor coordinating ability due to the pseudoaromatic nature of the ring, which has two-fold effect of causing the lone pair on sulphur atoms to be less available for donation and the $\pi$-orbitals to be less capable of accepting electrons from the metal. Towards 'b' class and "border" line metals the coordinating ability of the various types of sulphur donors is:

$$RS^- > R_2S > R.C=S \gg ring \ sulphur.$$  

(d) The spectrochemical series of ligands is arranged according to the spectroscopic splitting parameter $\Delta$ or 10 $Dq$. Although some sulphur donors including S-bonded $SCN^-$, $(RO)_2PS_2^-$, and $S^{2-}$ have low position in the series near $Cl^-$, $R_2S$ falls in the middle of the series, probably between $H_2O$ and N-bonded
SCN⁻, while S-bonded SO₃²⁻ has a later position near NO₂⁻. The position of RS⁻ has not been established.

(e) From a consideration of both electrostatic and covalent models, the strength of bonding to a metal ion is in the order: RO⁻ > RS⁻ and R₂O > R₂S. However, sulphur has vacant d-orbitals which can be used for dπ-dπ bonding such as can occur with later transition metals and with the early transition metals in unusually low oxidation states. Consequently, if π-bonding occurs, it can cause a reversal of the order to RS⁻ > RO⁻ > and R₂S > R₂O.

(f) Sulphur donors bind more strongly to 'b' class metals than do oxygen donors. Class 'b' metals form a triangular area in the centre of the Periodic Table. The oxidation state of the metal affects the degree of 'b' character, which is strongest for transition metal in low oxidation states, i.e., metals having non-bonding d-electrons and thus capable of forming dπ-dπ bonds by donating a pair of electrons to the ligand.

What has been stated about complexes of sulphur ligands applies also to complexes of sulphur-nitrogen chelating agents. However, the nitrogen atom tends to lower the solubility of the complexes in non-aqueous solvents so that the complexes of sulphur-nitrogen ligands are, in general, either sparingly soluble or insoluble in non-polar solvents.

From the sparse data available, sulphur-nitrogen ligands appear to give rise to a smaller reduction in the interelectronic
repulsion energy than sulphur-sulphur ligands. This presumably is due to nitrogen having a low position compared to sulphur in the nephelauxetic series. Consequently, sulphur-nitrogen donors would be expected to give rise to higher values of $\beta$ than sulphur donors alone.

The nature of ligand as well as that of the central metal atom play important role in deciding the metal-sulphur stretching frequencies in the complexes.\(^4\)-\(^8\) In the past few years, there has been a considerable interest in the electronic structure of square-planar complexes. This interest is partly due to the fact that relative energies of the d-orbitals in square-planar complexes are not known with certainty even in the highest symmetry cases, and partly because of the principal factors involved in the stabilization of the square-planar geometry in the transition metal chemistry have not yet been completely resolved.

For most simple ligands\(^9\) the metal donor stretching frequencies are expected in the range of 250-600 cm\(^{-1}\). The framework bending vibrations cover a wider frequency range, being as high as 800 cm\(^{-1}\) and as low as 100 cm\(^{-1}\) with some modes being a little lower in energy depending on the vibration masses. It is clear then that in order to derive detailed information about the potential forces within the framework of a complex, spectra must be measured to low energy. The replacement of the ligand or metal ion in a complex is generally accompanied by: (a) an
increase in point mass, and equilibrium separation may be expected to decrease the corresponding frequencies, and in case the ligand replacement involves a change in bond-type, it will have a more pronounced effect leading to an increase in frequency as the bond increases; (b) a variation in bonding capacity of the central metal ion in complexes MiL, where Mi are the various metal ions, and L is a particular ligand.

It will, therefore, be interesting to seek these types of correlations using various types of sulphur-containing ligands and different metal ions. For the present study, the following common and less-common metal ions were taken for complexation.

Cu(I) Cu(II) Fe(II) Fe(III) Pt(IV)
Ag(I) Ag(II) Ru(II) Ru(III) Ce(IV)
Hg(II) Pd(II) Rh(II) Rh(III)
Pb(II) Cd(II) Au(III) Bi(III)
Co(II) Ni(II) Ti(III) Sb(III)
VO(II) UO$_2$(II) Sm(III) Pr(III)

The present work is an attempt to seek a correlation between the different physico-chemical properties including metal-sulphur frequencies of the complexes of these metal ions with a ligand having isothiocyanato sulphur and nitrogen as potential donors.

The ligand whose complexing properties have been studied is ALLYL-ISOTHIOCYANATE (CH$_2$=CH-CH$_2$NCS). Hereafter the ligand shall be abbreviated as AITc. AITc contains for coordination,
one active sulphur and one nitrogen within a same isothiocyanato functional group (-N=C=S). Practically no work has so far been done on this particular compound (AITc). The only known metal complexes of AITc are those of Co(II), Pd(I), and Cr(III), reported by A.D. AHMED\textsuperscript{10} in 1968.

Allyl-isothiocyanate (AITc) is the allyl ester of isothiocyanic acid (HNCS), and is one of the commonest and readily accessible organic ligands. Though mostly the available AITc is synthetic, but it widely occurs in nature also. It occurs naturally in mustard and cabbage seeds, radish and horseradish. It is also found in the seeds of wasabi and a Cruciferous plant Descurainia sophia.

Besides having two active donor sites, viz., N and S, in the -NCS group, the ligand also has one olefinic double bond in the terminal vinyl group. Like other donor atoms the olefinic double bond is also capable of forming coordinate linkages with transition metal ions.\textsuperscript{11} It will be interesting to study whether the ligand molecule will act as a unidentate ligand (structure 1A and 1B) or bidentate (structure 2) or two or more molecule will link up with the central metal ion to form giant complexes (structure 3 and 4) with coordination through nitrogen or sulphur. The possibility of the formation of olefinic metal complexes of the type shown in structures 5-7 shall also be looked into. In these structures M stands for metal; X for an anion; $L = \text{CH}_{2}C\equiv C\text{NH}_{2}\text{NCS.}$
Analogous to thiocyanate ion, the donor site in AITc can be either sulphur or nitrogen, or both depending upon whether it acts as monodentate or bidentate. In general AITc is likely to act as a monodentate and bonding in complexes may take place through nitrogen or sulphur atom as in thiocyanates and in isoperthiocyanic acid not only with 'b' class of metal ions but with 'a' class of metal ions as well. However, infrared spectral measurements indicate that the ligand is coordinated through nitrogen in the Co(II) and Cr(III) complexes but on the other hand metal-sulphur and metal-olefin linkages are present in the Pd(I) complex.

The nature of bonding in AITc complexes can be either ionic or covalent as in thiourea depending on the nature of metal ion used for complexation. It has been observed that the ionic complexes can be either 1:2, 1:4 or 1:6 types.

The stereochemistry of the complexes as determined by the structure of some of the AITc complexes is either tetrahedral or octahedral. The complex CoL₄Cl₂ is tetrahedral but CrL₆Cl₃ complex is octahedral.

Our study with the metal complexes of AITc is aimed at having a better understanding of: (a) the donor property of sulphur in general; (b) nature of metal-sulphur linkage; (c) position of the ligands, having isothiocyanato sulphur and nitrogen as donor sites, in the spectrochemical and nephelauxetic series; (d) stereochemistry and coordination number of the
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<th>Br</th>
<th>I</th>
<th>O</th>
<th>S</th>
<th>Se</th>
<th>Te</th>
<th>M</th>
<th>P</th>
<th>As</th>
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<td>2.8</td>
<td>2.5</td>
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<td>6.2</td>
<td>1.3-2.0</td>
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*Pauling's scale.

transition metal ions; (e) nature of the metal-olefinic complexes; and finally (f) the stability of the square-planar complexes with ligands having delocalized system. Also, it will be interesting to seek a correlation between the infrared, metal-sulfur stretching frequencies, i.e., $\nu(M-S)$, and various ions in the complexes of the type $M_iL$ or $ML_i$ [$M =$ metal; $L =$ ligand; $M_i =$ metal ion; $L_i =$ ligand ion].

It is also well established that some of the transition metal ions have a greater affinity for sulfur as compared to other atoms (cf. class 'a' and class 'b' type metals). This could also be examined in the light of the possibility of $\pi$-bond formation*, the symmetry of the ligand field, and the hybridization involved. The stoichiometry, the bond-types and oxidation states of the central metal ion in these complexes have been studied by infrared and visible spectra, magnetic susceptibility measurements and conductance data.

The ligand has also been used as a spot-test reagent for the detection of Bi(III) and iodide ions.

NATURE OF METAL-SULPHUR BOND

In the following paragraphs, the nature of metal-sulfur bond along with the recent work on the complexing properties of

*Though there has been some doubt regarding this explanation.
the ligands containing sulphur and nitrogen as donor sites has been reviewed.

The strength and stability of the metal-donor bond depends on the size, electronegativity, polarizability, nature and energies of the orbitals involved in the bond formation, their overlapping capacity and more specifically on the electronic structures of the donor and metal atoms. The ligand donor site may be monoatomic or attached to other atoms in the ligand molecule. The number and nature of the attached atoms also influence the stability of the M-L bond. It is very difficult to isolate the influence of the nature of the donor atoms on the stability, since the donor atom must be considered in relation to the acceptor atom. However, the difference in the stabilities of bonds between M-L₁ and M-L₂, where L₁ and L₂ are different donor atoms and M, the same or similar metal atom, may be correlated with the electronic properties of L₁ and L₂. Thus, the nature of metal-sulphur bond should be studied under two headings:

(1) Study of sulphur as donor, in relation to the other donor atoms when attached to similar metal atoms.

(2) Study of the relative affinities of different metal atoms for sulphur.

In the extreme ionic bonds, a metal ion M^{+n} is attached to a certain number of donors, either charged or uncharged in which the bonding energy between metal and ligand is purely electro-
static (ion-ion or ion-dipole type). While in the extreme covalent type, the bonding is essentially of the type as encountered in the covalent molecules like hydrogen molecule. However, in metal-donor bonds the extreme covalent or extreme ionic type of bond can not exist as: (a) the bonded atoms are of different size; (b) they have different electronegativities; (c) they have different polarizabilities, etc. Thus, in most of the cases, the bonds will have both partial ionic and covalent characters.

Besides $\sigma$-type of covalent bonds, in which the electron density is greatest along the internuclear axis, $\pi$-type of bonds may also be formed in certain metal complexes. The latter type of bond is formed either by the donation of a lone pair of electrons from metal to donor atoms of the ligand or those of the ligand donor atoms to the metal. The formation of $\pi$-bond also affects the bonding energy to a great extent.

In transition metal complexes, $\pi$-bonds may be either $d\pi$-$p\pi$ (e.g., in Ni(CO)$_4$) or $d\pi$-$d\pi$ (e.g., in Ni(PF$_3$)$_4$). In the complexes of phosphine or arsine, the situation is not clear cut, and the general consensus seems to be against extensive $\pi$-back bonding.$^{1,18,19}$

SULPHUR AS DONOR ATOM IN RELATION TO OTHER DONOR ATOMS

The electronegativity, polarizability, ionization potential and the electron affinity of sulphur alongwith those of other donor atoms are given in Table I.1.
Table 1.2

Periodic Table

Class 'a'

Class 'b'

Border region
Assuming the ionic bond between metal-oxygen and metal-sulphur, sulphur will have lower co-ordinating ability than oxygen due to the lower charge to radius ratio of the former. On PAULING's or MULLIKAN's scale, the electronegativity of sulphur is very nearly the same as that of iodine. The polarizability of certain donor atom is related to its electronegativity in conjunction with the properties of the neighbouring atoms within the ligands. If the donor atom exists as an elementary ion, e.g., Cl\(^-\), its own electronegativity is, therefore, the only factor of importance and a decrease of electronegativity will imply an increase in polarizability.

The polarizabilities of the donor atoms fall in the series: 
\( F^- < O^{2-} < Cl^- < Br^- < I^- < S^{2-} < Se^{2-} < Te^{2-} \) which is just the electronegativity series in the reverse order. Since the increase in the polarizability of an anion means an increased tendency to form a covalent bond, the metal-sulphur bond should have more of partial covalent character than that in M-O, M-Cl, M-Br and M-F bond. This is true only when these ions act as ligands in the form of the elementary ion because, as mentioned above, the electronegativity of an atom and the polarizability is changed by the presence of other groups or atoms attached to the donor atom.

Another factor which affects coordinating ability in the unidentate ligands is the total dipole moment (\( \mu \)) of the ligands, 
\( \mu = P + \alpha E \); where \( P \) is the permanent dipole moment, \( \alpha \), the
polarizability, and $E$, the inducing electrostatic field. Thus, the coordinating power of the neutral molecules increases in the order: $H_2S < RSH < R_2S$ which corresponds to the order of increasing dipole moment. Although the polarizability of the coordinating atom decreases by alkyl group substitution, but the decrease is so small (5-10%) that the increase in dipole moment along the series outweighs the small decrease of polarizability. Similar effect is observed in the reverse order in the series: $H_2O > ROH > R_2O$. In this series, the decrease of polarizability (24%) surpasses the increase in dipole moment. The effect of the dipole moment is also obvious if one compares the coordinating power of $H_2O$ and $H_2S$ or similar ligands; $H_2S$ has a lower dipole moment than $H_2O$ ($\mu_{H_2S} \approx 1.1 \text{ D}; \mu_{H_2O} \approx 1.9 \text{ D}$), but the polarizability of sulphur in $H_2S$ is much larger than that of oxygen in $H_2O$. Thus, $H_2S$, as compared with $H_2O$, will be bonded with cations having high field strength more strongly due to its large value of $(P + \alpha E)$ as compared to that of $H_2O$. With cations of low field, however, the reverse holds true.

Besides the importance of difference in polarizabilities of the different donor atoms in the coordinating power, sulphur along with Se, Te, P, As, Sb have low lying d-orbitals capable of forming $d\pi-d\sigma$ type bonds. The effect of $\pi$-bonding could not explain the position of sulphur atom among the various donor atoms.

The polarizabilities of the sulphur in the following ligands decrease in the order: $S^- > RS^- > R_2S$. Therefore, if the bonding
properties of the sulphur are considered, the distinction between sulphide, mercaptide and thioether should also be born in mind. Besides the polarizabilities, the number of lone pairs on the sulphur atom also decrease along the series, which have a definite effect on the bonding properties of sulphur. This was considered by WILLIAMS who also suggested that the principal difference between thiols and thioethers as ligands is that the former are more highly polarizable but not as effective dπ-electron acceptors as the latter.

From the above discussion, it appears that the sulphur due to high polarizability and continuum starting at a lower energy in order to accept some electron density in the continuum orbitals from the metal ions behaves differently from those of the first atoms of the V, VI and VII groups (N, O, F). In complexes of the latter elements (N, O, F) the bonding should mainly be ionic due to high charge in contrast to the heavy members of the group, e.g., S, where the covalent character should predominate.

TAUBE has shown unambiguously that it is the back bondings between metal and the ligand atoms which are responsible for the difference in the stability of complexes with ligands having F, O, N, on the one hand and S, P, Se etc. on the other.

If the complexes are formed by the charged sulphur ligands such as RS⁻, (EtO)₂PS⁻, ROCS₂⁻, the sulphur atom is bicovalent and has a V-shaped configuration and in complexes with R₂S, it
is tricovalent and trigonal-pyramidal; when the thio group acts as a bridge, the sulphur atom is tricovalent and pyramidal.

**RELATIVE AFFINITIES OF METAL IONS FOR SULPHUR**

The effect of the metal ions on the metal-sulphur $\sigma$-bond will depend on the ionization potential, electron affinity, and the ionic or the covalent radius of the metal ion. If the metal-sulphur bond is formed in solvent, by replacement of one ligand with another, solvation energy also plays an important part in the formation of the compound due to different $\Delta G$ (free energy charge) values in the gas and the solid phases. Besides, the strength of the metal-sulphur bond will also be affected by the presence of the non-bonding electrons in the low-lying orbitals on the metal ions.

The strength of coordination of the $\text{XMe}_2$ ($X = O, S, Se, Te$) to $\text{AlMe}_3$ was first studied by COATES$^{24}$ who arranged the ligands in the order: $O > S > Se > Te$. He also found that Pd(II), Pt(II) and Hg(II) coordinate strongly with dialkyl sulphides, dialkyl selenides, and dialkyl tellurides, but with ethers the same metals do not coordinate. WILLIAMS$^{25}$ and CARLESON & IRVING$^{26}$ also arranged the metals into two groups according to their affinities for halides. However, no rigid classification scheme was proposed until 1958 when AHRLAND et al.$^{17}$ made an extensive review of the relative affinities of ligand atoms for acceptor molecules or ions. They divided the metal ions into two
classes: (a) those which form the most stable complexes with the first ligand atoms of each group (O, N, F), (b) those which form the most stable complexes with the second or subsequent ligand atom in aqueous solution.

For class 'a' metals the sequence $\text{O} \gg S \gg Se \gg \text{Te}$ occurs; for class 'b' metals, the sequence $S \gg O$ occurs, but any sequence can occur between $S$, $Se$ and $Te$. In all complexes the stability was measured by free energy change of a reaction, usually quoted just as an equilibrium constants, without any regard to solvent.

It was stated that class 'b' cationic acceptors (in water) in their normal valency states form a more or less triangle with a somewhat diffused border in the particular part of Periodic Table. The base of the triangle stretches in the 6th Period (from about tungsten to polonium) and it has its apex in the first period at copper as given in Table I.2. Coordination of $C_2H_4$, CO, CNR occurs only with metals of the pronounced 'b' character. AHRLAND, et al.\textsuperscript{17} proposed that this order of affinity of class 'b' metal ions depends on the availability of electrons from $(n-1)d$ orbitals of the metal for dative $\pi$-bonding.

The general idea that $\pi$-bonding to halides is important has been criticized by many workers.\textsuperscript{27-29} Other workers\textsuperscript{30,31} have given different explanations for 'a' and 'b' type of behaviour towards halides which could be extended to sulphur.

PEARSON\textsuperscript{32-34} has classified metal ions and ligands into hard and soft Lewis acids and bases. Soft acids are qualitatively
THE LIGAND

\[ \text{CH}_2=\text{CH}-\text{CH}_2-\text{NCS} \]

UNIDENTATE COMPLEXATION

\[ \text{CH}_2=\text{CH}-\text{CH}_2-\text{NCS} \]

\[ \downarrow \quad \text{M-X} \]

\((1A)\)

\[ \text{CH}_2=\text{CH}-\text{CH}_2-\text{NCS} \]

\[ \downarrow \quad \text{M-X} \]

\((1B)\)

BIDENTATE COMPLEXATION

\[ \text{CH}_2=\text{CH}-\text{CH}_2-\text{N}==\text{C}==\text{S} \]

\[ \downarrow \quad \text{M} \]

\[ \quad \text{X} \]

\((2)\)

TETRA-COORDINATED COMPLEX

\[ \begin{bmatrix}
L \\
\downarrow
\end{bmatrix} \quad \begin{bmatrix}
L \\
\downarrow
\end{bmatrix} \quad \begin{bmatrix}
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\end{bmatrix} \quad \begin{bmatrix}
L \\
\downarrow
\end{bmatrix} \]

\[ \text{M} \quad \text{L} \quad \text{L} \quad \text{L} \]

\[ \quad \text{X}^- \quad \text{X}^- \]

\((3)\)

HEXA-COORDINATED COMPLEX

\[ \begin{bmatrix}
L \\
\downarrow
\end{bmatrix} \quad \begin{bmatrix}
L \\
\downarrow
\end{bmatrix} \quad \begin{bmatrix}
L \\
\downarrow
\end{bmatrix} \quad \begin{bmatrix}
L \\
\downarrow
\end{bmatrix} \]

\[ \text{M} \quad \text{L} \quad \text{L} \quad \text{L} \]

\[ \quad \text{X}^- \quad \text{X}^- \]

\((4)\)

OLEFINIC COMPLEXES

\[ \text{CH}_2=\text{CH}-\text{CH}_2-\text{NCS} \]

\[ \downarrow \quad \text{M} \quad \text{X} \]

\((5)\)

\[ \text{CH}_2=\text{CH}-\text{CH}_2-\text{NCS} \]

\[ \downarrow \quad \text{M} \quad \text{X} \]

\((6)\)

\[ \text{CH}_2=\text{CH}-\text{CH}_2-\text{SCN} \]

\[ \downarrow \quad \text{M} \quad \text{X} \]

\((7)\)
defined as those in which the acceptor atom is of high polarizability, low electronegativity, and with filled outer orbitals. These properties are the result of low positive charge and the large size of the coordinating atoms. Such acids may be classified as 'b' type. Hard acids have the opposite properties and may be grouped as 'a'. These acids combine with bases which bind strongly to protons. Similarly, soft bases are defined as those in which valence electrons of the donor atoms are easily polarizable. They are of low electronegativity and easily oxidizable. PEARSON\textsuperscript{32,33} thus, formulated a general principle based on experimental observations according to which hard acids prefer to combine with hard bases and soft acids prefer to combine with soft bases. The explanation which he gave for such a behaviour of hard and soft acids and bases includes: (1) various degrees of ionic and covalent bonding; (2) \(\pi\)-bonding; (3) electron correlation phenomenon; (4) solvent effect; and (5) Van der Walls forces.

However, WILLIAMS and HALE\textsuperscript{35} deplored the qualitative notion of hard and soft acids and bases. They believe that the 'a'/'b' classification is little more than reflection of \(\sigma\)-bonding and the gross controlling factor of the classification is clearly the relative importance of ionic and covalent bonding which has been measured by the value of \(\frac{1}{I.P. \times r_e}\), where I.P. is the ionization potential of the acceptor and \(r_e\) is the metal ligand bond distance. Higher the value of this function, higher the ionic character of the bond.
Various physical definitions have subsequently been proposed, and the analogies found between the idea one has of hardness or softness and several properties such as polarizability of low-lying 'd' orbitals and the oxidizing property. None of these, however, correlates very well with the experimental facts and none accounts for all the properties attributed to hardness or softness.¹

JØRGENSEN²⁶ classified the 'b' class metal ions into three types: (i) metals with usually low oxidation number; (ii) metals with certain high oxidation number; (iii) $S^2$ family Sn(II), Sb(III), Tl(I), Pb(II), Bi(III), showing 'b' character to chalcogenides. There are some metal ions which show 'b' character in high and low oxidation states and 'a' character in intermediate oxidation state, e.g., Mn.

In general, there seems to be an increase in 'b' class character for ions of the A-groups in the Periodic Table (IA < IIA < IIIA) and this is also true in the B-groups (Ag⁺ < Cd²⁺ < In³⁺). However, for any one element, the series are quite unpredictable, e.g., Cu(I) < Cu(II), Tl(I) > Tl(III). Sn(II) < Sn(IV), Pt(II) > Pt(IV) exhibit 'a' class character. The 'a' or 'b' class character seems to depend on the relative magnitude of electron affinity of cations, exposure of the relevant orbitals (overlap), interatomic distance, charge, and cation polarizability.

AHRLAND²⁷ pointed out an interesting difference between the formation of hard and soft complexes. According to him the
hard-hard interaction is mostly ionic, while the soft-soft interaction is of covalent type which is variable from one case to another. But, how important is the \( \gamma_f \)-back bonding in the soft-soft interaction is still an undecided question.

The Spectrochemical and Nephelauxetic Series

The spectrochemical series can be written empirically to a good approximation as a product of two functions (ligands and metal ion): \( \Delta = f(\text{ligand}) \times g(\text{metal ion}) \). Jørgensen\(^3\) has given the values of \( f \) and \( g \) in some cases. Most of the commonly used ligands can be arranged in accordance with the increasing values of \( \Delta \) as follows:

\[
\begin{align*}
&I^- < Br^- < SCN^- < Cl^- < (\text{EtO})_2 \text{PSe}_2 < S^2^- < (\text{EtO})_2 \text{PS}_2 < F^- < \\
&\text{Et}_2 \text{NCS}^- < \text{urea}^- < \text{OH}^- < C_2\text{O}_4^{2-} < \text{H}_2\text{O}^- < \text{NCS}^- < \text{glycine} < \text{py}^- < \\
&\text{NH}_3^- < \text{en} < \text{SO}_3^{2-} < \text{NO}_2^- < \text{phen} < \text{bipy} < \text{H}^- < \text{CH}_3^- < \text{CN}^- < \text{CO}.
\end{align*}
\]

\( \text{py} = \text{pyridine; } \text{en} = \text{ethylenediamine; } \text{bipy} = 2,2'\text{-bipyridyl; } \text{phen} = 1,10\text{-phenanthroline.} \)

In the above series the position of sulphur varies with ligand to ligand and \( R_2S \) probably occurs between \( \text{H}_2\text{O}^- \) and \( \text{NCS}^- \). The position of \( RS^- \) is not yet decided. As \( \Delta \) is the difference between the \( \sigma \)-antibonding effect on the higher sub-shell (e.g. in octahedral chromophore, \( MX_6 \); \( t_{2g} \) in tetrahedral chromophore, \( MX_4 \)) and the \( \pi \)-antibonding effects on the lower sub-shell (\( t_{2g} \) or \( e_g \) respectively), one can rationalize that the ligands containing one lone pair such as \( \text{NH}_3 \), \( \text{SO}_3^- \) form only \( \sigma \)-bonds
and have large values of $\Delta$. On the other hand, ligands with several lone pairs have also $\pi$-bonding effects on the partially filled shell of the metal ion and decreasing $\Delta$: $(C_2H_3)_2PS_2^{-} < (C_2H_5)_2NCS_2 < C_2H_5OCS$. This effect has also been observed in sulphur-containing ligands alone by Jørgensen: $^{21}$ dtp$^- < exan < dtc^- < dmp < thioglycollate < dithiomalonate < amines.$

As discussed above, one should expect that the metal-sulphur bond should have a high percentage of covalency and more so if sulphur is attached to the 'b' type of metal ion. The nephelauxetic series is a measure of covalent tendency of the ligands.$^{38-40}$ The repulsion between the 'd' electrons which is measured by the reduction in the value of $B$ (Racah parameter); is decreased by complex formation by 5-40% for 3d electrons.$^{41}\left[\beta = \frac{B'}{B}\right]$ is the ratio of electronic repulsion parameters for the complex (B') and for gaseous ion (B). Thus, the sulphur ligand should have high nephelauxetic effect. However, sufficient data are not available to ascertain this. The positions of some of the sulphur ligands in the above series in which the ligands are arranged in the decreasing order of $\beta$, are shown below:

$$F^- > H_2O > RCO_2^- > (NH_2)_2CO > NH_3 > (COO)_2 ^\sim \sim NH_2-CH_2-CH_2-NH_2$$
$$NCS^- > CH^- > Cl^- > CN^- > SCN^- > Br^- > (C_2H_5O)_2PS_2 ^\sim \sim S ^\sim \sim I^-$$
$$(EtO)_2PSe_2^-$$

It appears that this series follows roughly the order of decreasing electronegativity $F > O > N > Cl > Br > S ^\sim \sim I > Se.$
Optical electronegativity \( (X_{\text{opt}}) \) values of different elements are derived from visible and ultraviolet spectral data. The electron transfer bands of a chromophore \( MX_6 \) shift as the \( X_{\text{opt}} \) values,\(^{42}\) and this shift is closely related to the concept of electronegativity of the donor atom \( M \). The values of \( X_{\text{opt}} \) for sulphur in sulphur ligands are those expected on the basis of electronegativity of the sulphur atom\(^{43}\) whereas the situation with oxygen ligands is much more complicated.\(^{44}\) It also varies with the oxidation number of a given atom.\(^{42,43}\)

The trans-effect depends upon the permanent dipole moment, the induced dipole moment, the polarizability, the charge, the size of the ligand and the degree of the bonding in a particular bond. The dependence of trans-effect on the degree of \( \pi \)-bonding has been criticized by WILLIAM\(^{25,27}\) and VENANZI\(^{18}\) (non \( \pi \)-bonding ligands activate the trans position by polarization and through \( \sigma \)-covalent bonding). So this effect should be very strong in sulphur ligands\(^{45-47}\) due to large polarizability of sulphur. Although CHATT, et al.\(^{48,49}\) have suggested a relative order of the strength of trans-effect among a number of various ligands; many of the data are based on the relative yields obtained under different sets of conditions. But in a complex the presence of strong trans-directing ligands may influence the trans-directing ability of the other ligand and so, the positions of sulphur ligands compared with other ligands having a strong trans directing influence may vary considerably according to the particular system being studied. Thus, its position is still uncertain.
METAL COMPLEXES INVOLVING INORGANIC THIOCYANATE (NCS\(^-\)) ION

The most simple ligand containing nitrogen and sulphur as donor atoms is the thiocyanate ion. Except for ionic compounds, the thiocyanate can coordinate in at least four ways as shown below:

\[ \text{M-S-CN} \quad \text{M-N=C=S} \quad \text{M-S-C=N} \rightarrow \text{M} \quad \text{M-S} \rightarrow \text{M} \]

(I) (II) (III) (IV)

It forms complexes with most of the transition metals although some of the non-transition metals also form complexes, Cr(III), Fe(III), Mo(III), Ru(III), Rh(III), Os(III), Ir(III) form octahedral complexes with M:NCS as 1:6. Cr(III), Mo(III) and Fe(III) form nitrogen bonded complexes while the other metal ions form the sulphur bonded ones. Quite a large number of workers have reported Re(IV) and Re(V) complexes, but only adequately well characterized rhenium thiocyanate complex ions are \([\text{Re(SCN)}_6]^{-}\) and \([\text{Re(SCN)}_6]^{2-}\). In these complexes the bonding is shown through sulphur. Other isothiocyanate complexes of rhenium(V) have also been identified. Stannous, technetium, yttrium, lanthanum and uranyl thiocyanate complexes have also been prepared which are all nitrogen bonded. The non-transition elements generally form bonds with thiocyanate through nitrogen. Nb(V) and Ta(V) form well characterized 1:6 complexes. They have been shown to be nitrogen bonded. Mo and Sc (1:6) nitrogen bonded complexes
have been reported. Brown and Knox have indicated that the mode of bonding in thiocyanate complexes is dependent on the oxidation state of the metal ion.

In general, the thiocyanate ion coordinates to 'a' class of metal ions through nitrogen atom and 'b' class metals through sulphur atom, but it is known from X-ray analysis that with thiocyanate ion, the first row transition metals, Cr, Mn, Co, Ni, Cu and Zn form M-N bonds.

The infrared spectra for a large number of thiocyanate complexes especially γ(C-N) have been recorded by various workers. An analysis of these spectra in three regions, viz. γ(C=N) (2160-2050 cm⁻¹), γ(C=S) (690-880 cm⁻¹) and δ(N=C=S) clearly indicate the infrared criteria for characterization of the metal-sulphur bonds. Various canonical structures for the thiocyanate group and its compounds are given below:

<table>
<thead>
<tr>
<th>Free ion</th>
<th>M-N bonding</th>
<th>M-S bonding</th>
</tr>
</thead>
<tbody>
<tr>
<td>N≡C=S⁻</td>
<td>M-N⁺≡C=S⁻</td>
<td>S-C≡N</td>
</tr>
<tr>
<td>(a)</td>
<td>(d)</td>
<td>M</td>
</tr>
<tr>
<td>=N=C=S</td>
<td>M=N⁺≡C=S</td>
<td>²⁺S≡C=N⁻</td>
</tr>
<tr>
<td>(b)</td>
<td>(e)</td>
<td>M</td>
</tr>
<tr>
<td>=N=C≡S⁺</td>
<td>N=C=S</td>
<td>=M=S≡C=N⁻</td>
</tr>
<tr>
<td>(c)</td>
<td>(f)</td>
<td></td>
</tr>
</tbody>
</table>

It has been suggested that structure (a) predominates in KSCN and structures (d) and (f) predominate in N-bonded complexes.
While for S-bonded complexes structure (g) is important,\textsuperscript{85} Thus, a change in the triple bond to one having more double bond character [cf. (f) in -(C≡N) group] will result in the corresponding increase in the double bond character of the -(C-S) bond.\textsuperscript{85} Thus, in N-bonded complexes having predominantly (d) and (f) structures an increase in covalent character of the coordinate bond results in the decrease of the stretching frequency of C≡N and an increase in $\nu$(C=S) and $\delta$(N≡C-S), and deformation frequency of N≡C-S. In the M-S bonded complexes, due to predominancy of the structure (g) there will be practically no change in the C≡N stretching frequency, but $\nu$(C=S) will decrease. It has been found that in sulphur bonded complexes $\nu$(C=S) band occurs between 690-720 cm$^{-1}$ while in N-bonded ones the range\textsuperscript{75} is 780-860 cm$^{-1}$.

Furthermore, this type of bonding in N-bonded ligands allows for M-N-C bond [structure (f)] to be angular rather than linear and this would explain sometimes the presence of more than one absorption band in $\nu$(C≡N) region. (The M-SCN linkage is always angular but M-NCS linkage can be collinear or angular with the M-N-C angle of 140°.\textsuperscript{83,85}) On the assumptions that (a) the lone pairs on the sulphur atom are more easily polarized and (b) that the permanent lone pair dipole on the nitrogen atom is larger than that on the sulphur. Lewis, et al.\textsuperscript{85} suggested that, when thiocyanate ion is the only monodentate ligand and no other ligand is present in the complex, the way in which NCS group is bound, is decided by the relative bond energy of a
covalent M-S bond and the more ionic M-N bond.

In preceding paragraphs only those complexes were considered where NCS is the sole ligand attached with the metal ion. However, in complexes where NCS is not the sole ligand, the type of bonding of the thiocyanate group may also depend on the nature of the other ligand partner. There must be a central point, where with a particular ligand, change (M-SCN to M-NCS) in coordination of NCS group can occur. Complexes with general formula, M(CNS) X, have been prepared and found that these complexes may occur in two structural isomers of the same compound depending on the correct choice of the X-ligand or alternatively, by changing the ratio of m:n. Such a case has been reported in Pd-complexes. They used triphenylphosphine, pyridine and triphenylarsine as X. In these cases they found two isomers (one sulphur bonded and the other nitrogen bonded). This change from M-S to M-N bonding has been explained on the basis of π-electron accepting capacity of X-ligand. There are two sets of antibonding π-orbitals in the thiocyanate ion and both are localized on S-atom; use of the empty 'd' orbitals of sulphur can confer further acceptor properties on sulphur end of the group. Interaction of dπ-electrons on the metal atom with these empty orbitals will result in additional stability of the M-S bond. Thus, strong π-electron acceptors like trisubstituted phosphines can make 'd' electrons on the metal ion less available for binding with the π-orbital of SCN, that is, for a bond on the sulphur end. The compounds cis-Mn(CO)₃(am)₂NCS (am = Py,
p-toludine or 2,2'-bipyridyl) and trans-Mn(\text{CO})_3(\text{PPh}_3)_2\text{NCS} are N-bonded but cis-Mn(\text{CO})_3(\text{SbPh}_3)_2\text{SCN} is sulphur bonded. It also appears that in the presence of \pi-bonding ligands the effective charge on the metal also plays an important role. Most of the first row transition metals are N-bonded, where all the coordinating ligands are NCS groups. However, Co(\text{SCN})_2(\text{PPh}_3)_2 and Cu(\text{SCN})_2(\text{PPh}_3)_2 are sulphur bonded.\text{102, 103} The Mn(\text{Co})_5\text{SCN} is sulphur bonded, whereas [Cr(\text{Co})_5\text{NCS}] and [Fe(\text{Co})_4\text{NCS}]\text{104} are N-bonded. The decrease in the charge on the metal causes a change from S to N-bonding.\text{105, 106} Recent work on thiocyanate derivatives of the transition metals has demonstrated that in a few cases the exchange from a S-bonded thiocyanate group is sufficiently slow so that both isomers may be identified.\text{106-110}

There are some complexes in which thiocyanate acts as a bridge and both nitrogen and sulphur of NCS group are donor atoms. Such type of bonding is found in HgM(\text{NCS})_4 (M = Mn, Fe),\text{111} Ni(\text{NH}_3)_2(\text{NCS})_2,\text{112} Cu(\text{Py})_2(\text{NCS})_2,\text{113} Cd(\text{etu})_2(\text{SCN})_2,\text{114} Ag(\text{SCN}),\text{115} Ag(\text{SCN})(\text{PEt}_3)_2,\text{116} Pt_2\text{Cl}_2(\text{SCN})_2(\text{PF}_3)_2,\text{117} Ni\text{en}_2(\text{NCS})\text{ClO}_4;\text{118} Ni(\text{NCS})_2L_2 (L = \text{thiourea, N-methylurea, N,N-dimethylurea, N,N'-ethylenedithiourea, N-ethylthiourea, N-phenylthiourea, N,N'-dicyclohexylthiourea and [Cd(Tu)_4][Co(\text{SCN})_4].}\text{120} Probably no compound containing two or more coordinate thiocyanate ions shows mixed M-NCS and M-SCN bonding in the same molecule with the exception of bridge compounds or except perhaps [Cu(Tren)(\text{NCS})(\text{SCN})].\text{121}
Steric factors and electronic effects also influence the manner of attachment of the thiocyanato group in the complexes $ML_2(\text{SCN})_2$ ($M = \text{Pd, Pt}; L = \text{amine, } \frac{1}{2}\text{ diamine, } \text{PR}_3, \text{SbR}_3$). Thiocyanate complexes of various transition metal complexes in pyridine solution have been investigated by Larsson using infrared spectroscopy and potentiometry. Nilsson studied silver thiocyanate system in aqueous medium.

The intermediate derivatives of the thermal decomposition of $M(\text{Py})_4(\text{SCN})_2$, having the composition $M(\text{Py})_2(\text{SCN})_2$ have been prepared where $M = \text{Mn(II), Co(II), Ni(II)}$ and shown to be distorted octahedral polynuclear structures.

Metal complexes of various esters of isothiocyanic acid have been prepared by Ahmed, Barbucci, et al. studied the i.r. and electronic spectra of certain isothiocyanato and thiocyanato-polyamine copper(II) complexes. Freni, et al. have prepared and studied oxodiisothiocyanato complexes of rhenium. A cobalt(III) sulphito complex, trans-sulfitoisothiocyanato-bis(ethylenediamine)cobalt(III) dihydrate, $\text{Co(en)}_2\text{SO}_3\text{NCS}.2\text{H}_2\text{O}$, has been reported by Boggia and Becka. The coordination around the metal ion in this complex is octahedral, the sulphito group being bonded through sulphur to the metal, and in the trans configuration. The Co-N(NCS) distance is not significantly different from the Co-N(en) distance.

The position of the thiocyanate ion in the spectrochemical series depends upon whether it is sulphur-bonded or nitrogen-
bonded. When S-bonded, it occupies a position approximately equal to Cl\(^-\), but when N-bonded, it lies between H\(_2\)O and NH\(_3\).\(^{131,132}\)

**METAL COMPLEXES OF ORGANIC ISOCYANATES, THIOCYANATES AND ISOTHIOCYANATES**

There is little possibility of comparing the (iso)cyanate and (iso)thiocyanate groups between them because nearly all of the examples of metal complexes are from the thio groups. From the few data on (iso)cyanates it appears that they are rather difficult to prepare, hence the -NCO group may be considered as less stable than the (iso)thiocyanato group (-NCS).

One of the interesting questions from the point of view of coordination chemistry is how the change from the free ions to the organic derivatives influences the ligand properties. Lacking directly determined thermodynamic quantities, the spectrochemical and nephelauxetic parameters should be the most relevant to this question. Only data on Cr(III) and Co(II) complexes obtained by AHMED\(^{10}\) are available and they are reproduced in Table I.2a. From infrared data and, in fact, in agreement with the nitrogen position in both series N-coordination is present in all these complexes. The difference between the ionic and covalently bonded isothiocyanate is surprisingly small. The 10 D\(_q\) and \(\beta\) values place both somewhere near the middle of the nephelauxetic and spectrochemical series and may taken as indicative of significant \(\pi\) propensity.
Table I.2a. Spectroscopic parameters of nitrogen coordinated species in carbon tetrachloride solutions

<table>
<thead>
<tr>
<th>Species</th>
<th>$10D_q^a$ (kK)</th>
<th>$\beta^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cr(allyl-NCS)$_6$]Cl$_3$</td>
<td>10.18</td>
<td>0.5</td>
</tr>
<tr>
<td>[Cr(NCS)$_6$]$^{3-}$</td>
<td>17.80</td>
<td>0.6</td>
</tr>
<tr>
<td>[Co(allyl-NCS)$_4$]Cl$_2$</td>
<td>5.10</td>
<td>0.65-0.67</td>
</tr>
<tr>
<td>[Co(NCS)$_4$]$^{2-}$</td>
<td>4.55</td>
<td>0.69</td>
</tr>
</tbody>
</table>

*a*, Crystal field splitting;

*b*, Ratio of Racah's $B$ values for the complexes and free ion (nephelauxetic ratio).
Table I.2b. Shifts in uranyl asymmetric stretching vibration in the spectra of complexes $R_4N[\text{UO}_2\text{Cl}_3L]$ ($\nu_3 = 943 \text{ cm}^{-1}$) and $R_4N[\text{UO}_2\text{Br}_3L]$ ($\nu_3 = 944 \text{ cm}^{-1}$) ($R_4N^+ = \text{tetradecylammonium ion}$) in benzene solvent

<table>
<thead>
<tr>
<th>Ligand L</th>
<th>$[\text{UO}_2\text{Cl}_3L]^{-}$ $\Delta \nu_3$</th>
<th>$[\text{UO}_2\text{Br}_3L]^{-}$ $\Delta \nu_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeCN</td>
<td>-12</td>
<td>-10</td>
</tr>
<tr>
<td>MeSCN</td>
<td>-13</td>
<td>-10</td>
</tr>
<tr>
<td>$(\text{C}_4\text{H}_9\text{O})_2\text{O}$</td>
<td>-14</td>
<td>-10</td>
</tr>
<tr>
<td>MeNCS</td>
<td>-15</td>
<td>-</td>
</tr>
<tr>
<td>$(\text{C}_4\text{H}_9\text{O})_3\text{PO}$</td>
<td>-16</td>
<td>-14</td>
</tr>
<tr>
<td>ClO$_4^-$</td>
<td>-17</td>
<td>-15</td>
</tr>
<tr>
<td>$(\text{C}_4\text{H}_9\text{O})_3\text{PO}$</td>
<td>-21</td>
<td>-18</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>-25</td>
<td>-23</td>
</tr>
<tr>
<td>I$^-$</td>
<td>-26</td>
<td>-24</td>
</tr>
<tr>
<td>SCN$^-$</td>
<td>-26</td>
<td>-25</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>-29</td>
<td>-26</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>-31</td>
<td>-26</td>
</tr>
</tbody>
</table>
The effect of the ligands on the asymmetric stretching vibration $\gamma_3$ of the uranyl group in equitorially bonded complexes can be interpreted in terms of stronger donating ability of the $\text{SCN}^-$ ion, but the perturbation of the $\text{U}-\text{O}$ bonds might be also connected with the overall charge as obvious from the data in Table I.2b. The higher formation enthalpy of the thiocyanate ion in charge transfer complexes with iodine (Table I.2c) may reasonably be attributed to the lower ionization potential of $\pi$-electrons in the ion. The difference in this sense appears at least in the MO calculation$^{133}$ on the $\text{HNCO-NC}^-$ pair and may be expected also for the corresponding sulphur pair.

Table I.2c. Formation enthalpies of charge transfer complexes with iodine.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{SCN}^- + \text{I}_2$ $^a$</td>
<td>-8.1</td>
</tr>
<tr>
<td>$\text{MeSCN} + \text{I}_2$ $^b$</td>
<td>-2.2</td>
</tr>
<tr>
<td>$\text{MeNCS} + \text{I}_2$ $^b$</td>
<td>-3.3</td>
</tr>
<tr>
<td>$\text{EtNCS} + \text{I}_2$ $^c$</td>
<td>-3.9</td>
</tr>
<tr>
<td>$\text{Allyl-NCS}$ $^c$</td>
<td>-3.6</td>
</tr>
</tbody>
</table>

$^a$, from reference 134; $^b$, from reference 135; $^c$, from reference 136.

In the above mentioned investigation and also in connection with the charge-transfer complexes studied by WAYLAND & GOLD$^{135}$ the concept of 'hard' and 'soft' bases is involved which brings
us to the problem of the site of complexing. In the charge-transfer complexes with iodine, sulphur as the 'soft' base was supposed to be the donor atom towards iodine.\textsuperscript{135} Again, MeNCS turns out to yield a larger enthalpy of interaction with the softer palladium whereas the harder base MeSCN has a higher enthalpy on interacting with the harder nickel\textsuperscript{137} (Table I.2d).

Table I.2d. Estimated enthalpies, in kcal/mol of interactions in methyl isothiocyanate and methyl thiocyanate with bis(methyl-n-octylglyoxime)metal(II)\textsuperscript{137}

<table>
<thead>
<tr>
<th></th>
<th>Ni(II)</th>
<th>Pd(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeNCS</td>
<td>0</td>
<td>1.03 ± 0.36</td>
</tr>
<tr>
<td>MeSCN</td>
<td>0.79 ± 0.21</td>
<td>0.71 ± 0.35</td>
</tr>
</tbody>
</table>

The gas-chromatographic technique was used in the determinations of enthalpies with metal glyoximates as stationary phase. However, absolute enthalpy values of the axial coordination were not determined because of the lack of data on the strength of the metal-metal bonds (of the order of 1 kcal/mol) which are replaced by the ligand bonds. Unfortunately, the known enthalpy (2.2 kcal/mol) of formation of the corresponding mono-thiocyanate nickel(II) complex in solution\textsuperscript{138} cannot be used for comparison because it includes the solvation effects.
Coordination through sulphur of EtNCS to the aluminium ion was assumed by HARAGUCHI and FUJIWARA. These authors have measured the chemical shifts and line width in the magnetic resonance of the Al nucleus of aluminium halides in a series of organic solvents. In particular, the existence of the complex of [Al(EtNCS)]$^{3+}$ was noted in the solution of AlI$_3$ in EtNCS.

From these results a sequence of the strength of interaction could be established as follows: H$_2$O $>$ C$_2$H$_5$OH, C$_3$H$_7$OH $>$ Cl$^-$, Br$^-$, I$^-$ $>$ C$_2$H$_5$NCS $>$ C$_6$H$_5$CN $>$ CH$_2$=CHCN $>$ MeCN. This sequence corresponds to the UO$_2$ stretching shifts as shown in Table I.2b.

Most of the evidence for the structure of complexes of the organic (iso)thiocyanates and hence of the site of bonding originates from infrared spectroscopy. This is most often used in connection with synthetic work. This high frequency shift of the 2100 cm$^{-1}$ band is usually taken as a criterion for N-coordination in thiocyanate. The S-coordination leaves this band with little change. In the isothiocyanates, the S-coordination is assumed to cause a high frequency shift whereas N-coordination causes a low frequency shift because of a reduced N-C and C-S vibrational interaction. π-Coordination to the C-S bond seems to reduce the former antisymmetric frequency to as little as 1600 cm$^{-1}$. However, the implications of the actually observed frequencies regarding the electronic changes on complexing and hence to the site of coordination should be taken with some caution in view of the mass and steric effects which are very
lucidly exposed by BELLAMY. Some of the conclusions based on infrared frequencies are fortunately also corroborated by steric considerations. For instance, in the case of chelating dithiocyanates, sulphur coordination is only possible on steric grounds. The frequency of the CN band is in agreement with this.

From the existing data it may be concluded that the soft 'b' class transition elements prefer bonding to sulphur, selenium, or the π-electron system whereas elements of the border region prefer bonding to nitrogen. However, no conclusion about the steric influence of the position of the ligating atom in organic cyanates and thiocyanates can be drawn.

1,2-Dithiocyanatoethane and 1,2-diselenocyanatoethane form the most numerous group of complexes with a surprising versatility of bonding modes. Bridging structures with ligating nitrogen atoms were proposed for a yellow moisture sensitive complex with the class 'a' metal Ti(IV) [(TiCl₄)₂.NCSCH₂CH₂SCN] (structure 8) and for a temperature unstable complex of the class 'b' metal silver(I). White crystals of [AgCl₄.NCSCH₂CH₂SCN] detonate on heating to 165°C. The crystal is presumably made up of polymeric Ag.NCSCH₂CH₂SCN- units held together by perchlorate ions. Attempts to prepare complexes with methyl, allyl or cinnamyl thiocyanates were unsuccessful.

Comparing 1,2-dithiocyanatoethane with 1,2-diselenocyanatoethane as ligands, GOODALL emphasized the similarity of behaviour
towards cobalt(II), rhodium(III) and iridium(III).\textsuperscript{144,145} Cobalt(II) halides form complexes of the type $[\text{CoX}_2L]_n$ (with $L = \text{NCSCH}_2\text{CH}_2\text{SCN}$; $X$ is Cl, Br, I and with $L = \text{NCSCH}_2\text{CH}_2\text{SeCN}$; $X$ is Cl) which are stable in dry air. Solid reflectance spectroscopy in the visible, infrared spectroscopy and magnetic measurements suggest octahedrally coordinated high-spin polymeric complexes with a non-chelating ligand in the trans form bonded through nitrogen and sulphur (selenium) and with each pseudo-halide group acting as a bridge between two cobalt atoms. Rh(III) and Ir(III) form stable dimeric diamagnetic complexes $M X_3L$ ($M = \text{Rh, Ir}$; with $L = \text{NCSCH}_2\text{CH}_2\text{SCN}$; $X$ is Cl, Br, I and $L = \text{NCSCH}_2\text{CH}_2\text{SeCN}$; $X$ is Cl). The chelating ligand should be in the gauche form, coordinated through sulphur or selenium, respectively. By splitting the chlorine bridges in (structure 9) through unidentate
ligands, monomeric complexes result (MCl₃·L·X; M = Rh, Ir; with L = NCSCH₂CH₂SCN; X is p-toluidine or pyridine and with L = NCSeCH₂CH₂SeCN; X is p-toluidine).

1,2-Dithiocyanatoethane shows no tendency to form complexes with nickel(II), but with palladium(II) products of indefinite composition were obtained. However, a complex with platinum(II) chloride (PtCl₂·L) has been described. A special type of optical isomerism in complex compounds is produced by the chelating ligand in the gauche form, coordinated through sulphur atoms. While the possible configurations were thoroughly discussed using infrared spectra, no experimental information on the complex proper was presented. On the other hand 1,2-diselenocyanatoethane yields complexes with both palladium(II) and platinum(II) (MCl₂·L). The complexes are insoluble in all common solvents and thus the molecular weight was not determined. These complexes are diamagnetic. On the basis of infrared spectra they were formulated as monomeric and square-planar. The ligand is coordinated through selenium atoms in the gauche configuration which is necessary for chelation. However, the appearance of a broad band at about 2200 cm⁻¹ suggests that some bonding may be taking place through the nitrogen atom also.

Methyl and phenyl-isothiocyanates yield crystalline air stable complexes with platinum(II) [Pt·L·(Ph₃P)₂; L = MeNCS, PhNCS]. Infrared evidence supports the assumption that the ligands are coordinated through the C-S bond (structure 10) by
analogy with the structure of the planar CS$_2$ complex. No evidence was found for the existence of the possible cis-trans isomerism about the C=N bond. No equivalent products with phenylisocyanate were isolated. This was directly attributed to the low affinity of the metal for oxygen. But, very interesting complexes of PtO$_2$(Ph$_3$P)$_2$.2PhNCO and PtO$_2$(Ph$_3$P)$_2$.PhNCS were obtained as intermediate products in the synthesis of nitrene complexes. Infrared spectra suggest cyclic structures with the participation of the peroxo group similar to the structure of adducts of PtO$_2$(Ph$_3$P)$_2$ with aldehydes and ketones. There are

\[
\text{(10)}
\]

both \(\pi\)-bonded and \(\sigma\)-bonded ligands in the proposed (structure 11), the stable complexes of RhCl(L)$_2$(PPh$_3$)$_2$ (L = PhNCS, PhNCO). A series of iridium(I) complexes and a rhodium(I) complex with acyl-isocyanates was obtained in the course of investigating complexes which fix molecular nitrogen. \(\pi\)-Bonding of the isocyanate group to the central metal atom (structure 12) was proposed. On the other hand, metalallocyclic structures composed of M-O-C-N-C or M-S-C-N-C skeletons (structure 13) were suggested
for a number of related complexes of benzoyl and thiobenzoyl isocyanates and some organometallic compounds of rhodium(I) and palladium(0).  

An unusual structure (i.r., and n.m.r. evidence) with bridging isocyanate was assumed for the complex (structure 14) of \((\text{C}_5\text{H}_5\text{Fe}_3(\text{CO})_4\text{CH}_2\text{NCO})\).  

The structure was supported by the analogy with the carbon-carbob triple bond in acetylenes acting
as a similar bridging group in \((RC\equiv CR)CO_2^-(CO)_6\) and in \((RC\equiv CR)(NiC_5H_5)_2\). 

Both platinum and palladium form stable complexes with allyl-isothiocyanate \(\text{Pt}(C_3H_5\text{NCS})(\text{PPh}_3)_2\) and \(\text{Pd}(C_3H_5\text{NCS})_2\text{Cl}\). A critical discussion of the platinum complex (structure 15) indicates a \(\pi\)-bonded allyl group and a sulphur-bonded thiocyanate ion, dissociating in polar solvents (structure 16). It is implied that similar bonding conditions are possible in the palladium complex also.

![Chemical structures](image)

Three iron complexes of butyl- and phenyl-isocyanates were claimed. The crystal structure determination of one of them, \([\text{Fe(CO)}_3\cdot \text{PhNCO}]_2\), revealed that it is actually an adduct of diphenylurea, and one may conclude, by analogy, that the other two cognate complexes are likewise urea adducts. The only reported stable phenyl-isocyanate adduct of the border region transition elements seems to be the complex of \(\text{Ni-}(\text{PhNCO})_2(\text{PPh}_3)_2\). It was isolated as an intermediate in nickel-catalyzed trimerization reaction of phenyl-isocyanate. Nitrogen bonding was postulated, as a result of the thermal decomposition
studies, in the unstable hygroscopic adduct of VOCl₃·2PhNCO.

Some unstable phenyl-isocyanate and isothiocyanate complexes were proved to exist in solutions. Indications for nitrogen coordination were found in chromium(III) and cobalt(II) complexes with phenyl-isothiocyanate, studied by spectroscopy in the visible region. Cr/PhNCS and Co/PhNCS ratios were determined to be 1/6 and 1/4 respectively. A 3:1 complex of phenyl-isocyanate with cobalt(II) naphthenate and a 2:1 complex with manganese(II) naphthenate were postulated from electronic spectra. TaCl₅·PhNCS is stable under an inert atmosphere in hexane or heptane solutions under mild conditions.

The complexes with alkyl esters are more stable. Thus, the isomerization equilibria of the crystalline niobium(V) and tantalum(V) complexes in melt were studied.

\[
\begin{align*}
\text{TaCl}_5\cdot\text{MeNCS} & \xrightarrow{175^\circ \text{C}} \text{TaCl}_5\cdot\text{MeSCN} \\
\text{NbCl}_5\cdot\text{MeNCS} & \xrightarrow{165^\circ \text{C}} \text{NbCl}_5\cdot\text{MeSCN}
\end{align*}
\]

These are the only reported isomerization equilibria between the sulphur and nitrogen coordinated species that we are aware of. There are well-defined 1:1 solid complexes of methyl-thiocyanate with MeMCl₄ and Me₂MCl₃ (M = Nb, Ta). Indications for a mixture of sulphur and nitrogen bonded isomers were presented. The complexes, with the exception of Me₂NbCl₃·MeSCN, slowly disproportionate in organic solvents. The complexes of
ethyl-thiocyanate with titanium(IV) and tin(IV) halides are remarkably stable. It is possible to purify them by sublimation. Coordination through sulphur is suggested. A great difference in colour, melting point and infrared spectra between TiCl$_4$.EtSCN and TiCl$_4$.EtNCS is stressed. The second one has a spectrum very different from that of the pure ligand. It was concluded that this indicates a great change in the electron distribution of the ligand in the complex. The same is true of the TiCl$_4$.2EtNCO. However, this complex exhibits, in CH$_2$Cl$_2$ solutions, both the original peaks and the new peaks indicating considerable dissociation. This was taken as evidence that the molecular changes occurring in the ligand on bonding are reversible if the ligand is liberated. An oily, unstable product of the composition of TiCl$_4$.2Allyl-SCN was isolated. A very unstable, air-sensitive t-butyl-isocyanate complex with nickel of the formula Ni(t-BuNCO)(t-BuNCS) was isolated at low temperature (-40°C) from a reaction mixture involving Ni(t-BuNCS)$_2$ and (t-BuNCO)$_2$. Its instability prevented characterization. Coordination was proved by the shifted infrared bands due to the isocyanate group and by the reaction of the complex with excess t-BuNCS in toluene at room temperature, giving Ni(t-BuNCS)$_4$ and 98% of coordination t-BuNCO. Last to be mentioned are actually the first reported - in 1934 and 1939 - complexes with these ligands. These are Co(SCN)$_2$(MeSCN)$_2$ and Co(SCN)$_2$(EtSCN)$_2$, which were obtained during solubility studies of metal salts in MeSCN and EtSCN. The complexes lose coordinated esters when exposed to air.

<table>
<thead>
<tr>
<th>Complex(es) (1)</th>
<th>Structural information (2)</th>
<th>Reference (3)</th>
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<tbody>
<tr>
<td>Co(II), Ni(II), Cu(II) &amp; Hg(II)</td>
<td>Ni possesses octahedral, Co tetragonal, Cu[D_{2h}], and Cd &amp; Hg tetrahedral geometry in the complexes.</td>
<td>B. SINGH et al., Inorg. Chem., 8, 2341 (1969).</td>
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<tr>
<td>complexes of Quinazoline(1H,3H)-2,4-dithione</td>
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<tr>
<td>Ligand</td>
<td>Simple salt</td>
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<tr>
<td>Cu(II) complexes of thiourea.</td>
<td>In the complexes Cu(dipyrindyl)$_2$-Tu(ClO$_4$)$_2$H$_2$O and Cu(1,10-phenanthroline)$_2$tu(ClO$_4$)$_2$H$_2$O etc., Cu is stabilized in oxidation state two. [tu = thiourea].</td>
<td>A. MONTENERO &amp; C. PELIZ Inorg. Chem. Acta, 6, 644 (1972).</td>
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![Ni(II) complex](image)

'Table I.3 (contd.)'

Ligand is bidentate in all the complexes with coordination through N & S. Metal-Cl bridges are present in Ru & Rh complexes. Except that of Ru, all the complexes are diamagnetic, Pt(II) & Pd(II) complexes are square-planar; All others are octahedral.

![Rh(III), Ru(III), Pt(II), Pt(IV), Pd(II) & Pd(IV) complexes of 2,4-dithioureacil.](image)

[Pt(Tu)₂Cl₂]
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<tr>
<td>Pt(IV), Pd(IV), Pt(II), Pd(II), Pt(0) &amp; Pd(0) complexes of Quinazoline(1H,3H)-2,4-dithione.</td>
<td>Pt(HL)(_2)(PPh(_3))(_2) &amp; Pd(HL)(_3)(PPh(_3)) are tetrahedral; Pt(L)(_2), Pd(L)(_2), PtH(L)(_2)NO(_3) &amp; PtH(L)(_2)I are square-planar; Pt(L)(_2)Cl(_2) &amp; Pd(L)(_2)Cl(_2) are octahedral. (LH = ligand molecule).</td>
<td>U. AGARWALA &amp; LAKSHMI, J. Inorg. Nucl. Chem., 34, 2255 (1972).</td>
</tr>
<tr>
<td>Rh(I), Rh(II), Rh(III), Ru(II) &amp; Ru(III) complexes of Quinazoline(1H,3H)-2,4-dithione.</td>
<td>Ligand is monodentate in Rh(I) Rh(III) and Ru(III) complexes, and bidentate in Rh(II) &amp; Ru(II) complexes. Ru(II), Ru(III) and Rh(III) complexes are octahedral while Rh(I) complex is square-planar. In Rh(II) a direct metal to metal bond has been suggested.</td>
<td>U. AGARWALA AND LAKSHMI ibid., 34, 241 (1972)</td>
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Ru(II) complex

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<tr>
<td><strong>Metal complexes of 1,2,3,4-thiatriazole-5-thiolate, CS$_2$N$_3$</strong></td>
<td><strong>Complex formation of 1,2,3,4-thiatriazole-5-thiolate with Tl, Cd, Pb, Cu and Zn was studied polarographically in a supporting electrolyte of Na-1,2,3,4-thiatriazole-5-thiolate of constant ionic strength. The anion is in the thiol form and co-ordinates through sulphur.</strong></td>
<td><strong>F.A. NEVES &amp; D.W. FRANCO, <em>J. Inorg. Nucl. Chem.</em>, 37, 277 (1975).</strong></td>
</tr>
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</table>

36 Mixed ligand complexes of Ag(I) of the type Ag(stu)$_x$ and Ag(stu)AMX, where stu = thiourea, naphtylthiourrea or diphenylthiourea; AM = pyridine, 2,2'-dipyridyl or o-phenanthroline and X = Cl$^-$, Br$^-$, I$^-$.

The molar conductances of these complexes are in the range of 3.4 - 22.6, 6.42 - 20.74 and 3.89 - 12.45 ohm$^{-1}$cm$^2$ mole$^{-1}$ for the thiourea, napthylthiourea and diphenylthiourea complexes respectively. Molar conductances at this concentration in acetone are generally 100-140, 160-200, about 270 and about 360 ohm$^{-1}$cm$^2$mole$^{-1}$ for 1:1, 2:1 and 4:1 electrolytes. It may be concluded that these complexes are non-electrolytes.

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<td><img src="image1.png" alt="Chemical Structure" /></td>
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All the complexes are colourless, amorphous and have 1:2 stoichiometry \([\text{ML}_2\text{Cl}_2]\); (ii) metal-ligand coordination is through sulphur; (iii) All the complexes are tetrahedral.


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| Ru(II) complexes of the type RuHCO\(\text{PPh}_3\)_3Cl \((L = 1\text{-phenyl-}, 1\text{-p-methoxyphenyl-}, 1\text{-p-chlorophenyl-}, 1\text{-o-methoxyphenyl-}
| The Cl atom is covalently bonded in all these complexes and ligands are co-ordinated through sulphur. | B.R. SINGH & M. CHANDRA, Indian J. Chem., 14A, 676 (1976). |
| \(\text{N} - \text{C} = \text{S} - \text{NH} \) | The ligand coordinates through nitrogen in Cd(II) complex and through the exo-cyclic thia-carbonyl group in other complexes. Chloride ions are co-ordinated to the metals. Ni(II) complex is octahedral; Cd(II) is polymeric with bridging chloride groups; Hg(II) complex is tetrahedral; Cu(II) complex is square-planar or octahedral. (It may be polymeric with bridging chloride ions.) | ...contd. |
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<tr>
<td>Zn(II)-, Cd(II)- &amp; Hg(II)-chloride complexes of substituted thioureas.</td>
<td>Complexes of the ML₂Cl type are formed. In Hg(II) complex of ethylenethiourea hexacoordination is obtained which is less-common for Hg(II) complexes. A polymeric halogen-bridged pseudo-octahedral structure has been proposed. Coordination through nitrogen as well as sulphur is reported.</td>
<td>A.C. HIREMATH &amp; A.S.R. MURTHY, <em>Indian J. Chem.</em>, 15A, 55 (1977).</td>
</tr>
<tr>
<td>VO(II), Co(II), Ni(II) &amp; Cu(II) complexes of 1-isonicotinyl-4-phenyl-3-thiosemicarbazide</td>
<td>(i) VO(II) forms VO(L-2H) complex in which metal is N &amp; O co-ordinated; (ii) In VOSO₄L complex metal is linked to S of sulphato group; (iii) CoCl₂ complex is tetrahedral, CoL is octahedral Cu(L-2H)Cl is square planar, and Cu(L-2H) complex is highly distorted octahedral.</td>
<td>R.C. AGGARWAL &amp; R.B.S. YADAV, <em>Indian J. Chem.</em>, 15A, 50 (1977).</td>
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<tr>
<td><strong>Hg(II) complex of thiosalicylic acid with thiourea.</strong></td>
<td>The complex Hg$_2$L$_2$Cl$_2$tu$_2$ has tetrahedral configuration. (L = thiosalicylic acid; tu = thiourea)</td>
<td>B.B. MAHAPATRA et al., J. Indian Chem. Soc., 54, 361 (1977).</td>
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<tr>
<td><strong>Pt(IV) complex of 2,2'-diaminodiphenyldisulphide</strong></td>
<td>In platinum(IV) diaminodiphenyldisulphide complex, metal to ligand ratio is 1:2.</td>
<td>S.P. BAG &amp; S.K. CHATURVEDI, Talanta, 24, 128 (1977).</td>
</tr>
<tr>
<td><strong>Pd(II), Pt(II) and Cu(I) complexes of isoperthiocyanic acid (L)</strong></td>
<td>MCl$_2$(L)$_2$ (M = Pd(II) and Pt(IV)) and CuCl(L)$_2$ are formed. Pd(II) and Pt(II) complexes are cis-square-planar. Cu(I) complex is a chlorine-bridged tetrahedral. Ligand acts as a monodentate using exocyclic thione sulphur.</td>
<td>D.A. EDWARDS et al., Inorg. Chem. Acta, 23, 215 (1977).</td>
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<tr>
<td>The crystal structure of Bi(III) in chlorothiourea complexes</td>
<td>Crystals are rhombohedral. The structure consists of ([\text{Bi}{\text{tu}}<em>{1.5}\text{Cl}</em>{1.5}\text{Cl}_3])^{3/2-}</td>
<td>L.P. BATTAGLIA et al., J. Chem. Soc. (Dalton Trans.), No. 12, 1141</td>
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<tr>
<td>([\text{Bi}(\text{tu})<em>6][\text{Bi}{\text{tu}}</em>{1.5}\text{Cl}_{1.5}\text{Cl}_3])_2</td>
<td>in which there is disorder involving thiourea and chlorine atoms, and ([\text{Bi}(\text{tu})_3]^{3+}) cations. In both ions bismuth atoms bond octahedrally to thiourea and (or) chlorine ions. Bismuth chloride and thiourea have been reported to give two adducts of molar ratio 3:7 (yellow form) and 1:3 (red form).</td>
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<tr>
<td>(tu = thiourea)</td>
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<td>(1977)</td>
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<tr>
<td>Ni(II), Cd(II) &amp; Hg(II) complexes of 1,3-dithiobiuret and Ni(II) &amp; Cd(II) complexes of 2,4-dithiomalonamide.</td>
<td>In all these complexes, ligands are acting as bidentate co-ordinating through both sulphur atoms. DTB has -cis CS-NH-CS group. These ligands are in (C_{2v}) symmetry</td>
<td>A. RAY &amp; D.N. SATHYANARAYANA, Indian J. Chem., 15A, 591 (1977).</td>
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<tr>
<td>Hg(II) complexes with substituted dithioureas (=L) of the type HgLX₂, where X = Cl⁻, I⁻, SCN⁻.</td>
<td>The complexes are octahedral involving a halogen or pseudohalogen bridge.</td>
<td>B.B. MOHAPATRA, et al., Indian J. Chem., 15A, 746 (1977).</td>
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<tr>
<td>Pd(II) complexes of N-aryl, N'-2(5-halopyridyl)thioureas</td>
<td>In all the complexes, metal is coordinated through thiocarbonyl sulphur. The chlorine atoms are also in coordinated form.</td>
<td>R.P. BHATNAGAR &amp; S.K. BANERJI, J. Indian Chem. Soc., 55, 297 (1978).</td>
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<tr>
<td>[PdCl₂L₂]</td>
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<tr>
<td>Co(II), Ni(II), Cu(II), Zn(II)</td>
<td>Co and Ni complexes show the presence of 3 and 2 unpaired electrons respectively, hence they are having a high-spin o₃ configuration. The Cu complex has 1 unpaired electron, thus having square-planar geometry.</td>
<td>B.B. MOHAPATRA et al., J. Indian Chem. Soc., 55, 229 (1978).</td>
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<tr>
<td>Cd(II) &amp; Hg(II) complexes of following thioureas:</td>
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<tr>
<td>N-o-Hydroxyphenyl-N'-phenylthiourea, N,N'-di(o-hydroxyphenyl)thiourea</td>
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<tr>
<td>N-(o-hydroxyphenyl)thiourea, N-(o-carboxyphenyl)thiourea, [MLCl] (M = Cu, Zn, Cd, Hg)</td>
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<tr>
<td>[MLCl(H₂O)₂] (M = Ni)</td>
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<td>[ML₂] (M = Co)</td>
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<tr>
<td>Mercury(II) complexes with substituted aminobenzothiazoles</td>
<td>Complexes of the type [HgL₂X₂] were prepared, where L = 2-amino-6-methylbenzothiazole and 2-amino-6-chlorobenzothiazole, and X = Cl⁻, Br⁻, I⁻, NO₃⁻, SCN⁻, or OAc⁻. On the basis of analytical and conductance data the complexes have tetrahedral configuration around the metal ion.</td>
<td>R.P. MISRA et al., J. Ind. Chem. Soc., 56, 832 (1979).</td>
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Complexes of zinc(II) and cadmium(II) with 2-pyridine ethanol

Complexes of the type $ML_2X_2$ were formed, where $M = Zn(II)$ or $Cd(II)$, $L = 2$-pyridine ethanol and $X = Cl^-$, $Br^-$, $I^-$, $NO_3^-$, $SCN^-$ and $OAc$. The i.r. studies showed that the ligand is bonded to metal ions through N.

Complexes of Cr(III), Mn(III), Fe(III) and Co(III) with triazolinethiones

Complexes of Cr(III), Mn(III), Fe(III) and Co(III) with 3-(o-hydroxyphenyl)-1,2,4-triazoline-5-thione and 3-(o-hydroxybenzylidene)-1,2,4-triazoline-5-thione have been prepared and characterized on the basis of elemental analysis, spectral (infrared and electronic) and magnetic susceptibility data. All the complexes are octahedral.


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<tr>
<td>Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) complexes of dithiooxamide</td>
<td>Complexes of the type $ML_2X_2$ were prepared ($X=\text{Cl}$ or $\text{SCN}^-$). All complexes were having non-electrolytic nature. Complexes of Mn, Co, and Cu were paramagnetic, and their $\mu_{\text{eff}}$ values suggested octahedral geometry. Nickel complex was diamagnetic, hence square-planar. Bonding in all the complexes was through $N$ and $S$.</td>
<td>B.B. MAHAPATRA et al., J. Ind. Chem. Soc., 58, 75 (1981).</td>
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</tbody>
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    F.P. DWYER & D.P. MELLOR, Academic Press, New York, p. 51,
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    143 (1958).


