

Complexes of Imidazoline (1,3H)-2-thione with Co(II) and Zn(II) Salts

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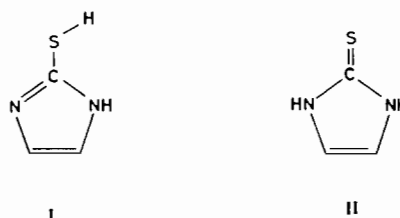
Complexes of imidazoline-2(1,3H)-thione (*ImT,L*), have been prepared with Co(II) and Zn(II) salts. Stoichiometries of the complexes, ML_2X_2 , for the halides and ML_4X_2 for the nitrates and perchlorates, have been established by chemical analysis. Thermal analysis has revealed the extent of hydration among the cobalt complexes. The solid complexes have been further characterised by means of magnetic susceptibility data, infrared and visible spectral measurements. The soluble complexes have been studied by means of electrolytic conductance measurements and their visible spectra have also been recorded. Ligand field parameters have been determined and probable structures assigned. The ligand coordinates by means of its exocyclic sulphur atom and one of its ring nitrogen atoms in the solid complexes. For the soluble complexes coordination involves the sulphur atom only.

Introduction

The coordination chemistry of the N-methyl derivatives of imidazoline-2-thione with transition and other metals has been previously described [1–4]. The monodentate thione-S donating character of the N(1)-methyl (*MImT*) [5–7] and the N,N(1,3) di-methyl (*DMTmT*) [2] derivatives have been established by means of spectroscopic and single-crystal X-ray diffraction methods.

The impetus for this and similar work arises from the wide ranging applications of heterocyclic S,N-containing molecules in industry and medicine [8].

In addition, such molecules invariably possess diverse coordinating potential. The parent molecule of this series, imidazoline (1,3-H)-2-thione (*ImT*) is capable of existing in thiol and thioketonic (thione) tautomeric forms (I–II) and clearly possesses a variety of coordinating possibilities.



The eventual outcome of a particular interaction will be decided by the character of the acceptor cation, the reaction conditions as well as other factors which are known to affect the behaviour of ambidentate ligands [9].

In a previous article we reported that the result of reacting *ImT* with Ni(II) salts in neutral media was a series of tetragonal paramagnetic complexes with the ligand behaving as a monodentate thione-S donor [4].

We now report the behaviour of *ImT* with Co(II) and Zn(II) salts in neutral media.

Results

General Comments

The analytical data (Table I) show that the stoichiometries of the halo complexes are ML_2X_2 and those of the nitrate and perchlorate complexes are ML_4X_2 . While the calculated and observed analytical data for the zinc complexes show excellent agreement some discrepancies occur among those of the cobalt complexes; these have been shown, by means of thermal analysis, to be due to varying degrees of solvent retention by the solid complexes.

In general, the complexes are sparingly soluble in common organic solvents. Only CoL_2I_2 and $CoL_4(ClO_4)_2$ dissolve in nitromethane to any significant extent ($10^{-3} M$). The resultant electrolytic conductivities were consistent with non-electrolytic behaviour for the iodo complex ($\Lambda_m = 20 \text{ mhos cm}^2 \text{ mol}^{-1}$) and a 1:2 electrolyte for the perchlorate complex ($\Lambda_m = 196 \text{ mhos cm}^2 \text{ mol}^{-1}$) [10].

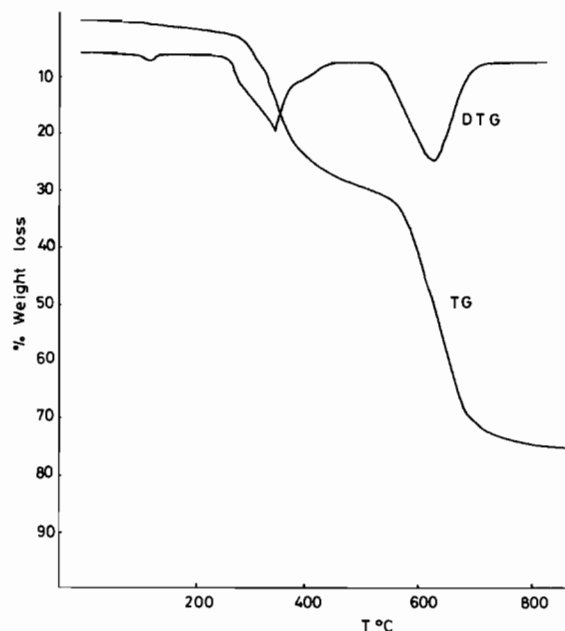
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TABLE I. Analytical Data.

Compound (L = H ₄ C ₃ N ₂ S)	Colour	Found % (Calculated %)		
		C	H	N
CoL ₂ Cl ₂	Blue-green	20.4(21.8)	2.54(2.42)	16.0(17.0)
CoL ₂ Br ₂	Emerald green	14.2(17.2)	2.0 (1.91)	11.1(13.4)
CoL ₂ I ₂	Dark green	14.3(14.0)	1.61(1.56)	10.9(10.9)
CoL ₄ (NO ₃) ₂	Emerald green	25.0(24.7)	2.78(2.74)	24.1(24.0)
CoL ₄ (ClO ₄) ₂	Dark green	18.3(21.9)	2.36(2.43)	14.0(17.0)
ZnL ₂ Cl ₂	Colourless	21.5(21.4)	2.49(2.38)	16.7(16.7)
ZnL ₂ Br ₂	Colourless	17.1(16.9)	1.98(1.88)	13.3(13.3)
ZnL ₂ I ₂	Colourless	13.9(13.9)	1.64(1.54)	10.8(10.8)
ZnL ₄ (NO ₃) ₂	Colourless	24.5(24.4)	2.74(2.71)	23.9(23.8)
ZnL ₄ (ClO ₄) ₂	Colourless	21.7(21.7)	2.50(2.41)	17.2(16.9)

TABLE II. Thermal Analysis Data.

Compound	Mr	Decomposition Range (°C)	Observed	Calculated
CoL ₂ Cl ₂	330.2	269–840	76.8	75.8
CoL ₂ Br ₂ ·2.5H ₂ O	464.9	51–697	82.0	82.9
CoL ₂ I ₂	512.9	285–836	84.0	84.4
CoL ₄ (NO ₃) ₂	583.3	204–830	86.0	86.3
ZnL ₂ Cl ₂	336.7	258–697	81.0	75.9
ZnL ₂ Br ₂	425.6	270–690	92.0	81.0
ZnL ₂ I ₂	519.4	300–763	86.8	84.4
ZnL ₄ (NO ₃) ₂	589.8	226–812	85.8	87.3
H ₄ C ₃ N ₂ S	100.1			

Fig. 1. Thermal analysis curves of Co(*MmT*)₂Cl₂.

Thermal Analysis

The major features of the thermal analysis of these complexes are summarised in Table II; TG and DTG curves for CoL₂Cl₂ are shown in Fig. 1. No results are reported for the perchlorate complexes because of their inherently explosive nature.

The TG and DTG curves of the CoL₂X₂ complexes show slight (2–3%) initial weight losses indicative of the presence of small traces of occluded solvent. In the case of CoL₂Br₂ solvent retention is significant and corresponds to 2.5 molecules of water which are removed in two stages in the temperature range 51 to 157 °C. The zinc complexes, as well as CoL₄(NO₃)₂, show no trace of solvent retention which is to be expected from their chemical analysis (Table I).

With the exception of CoL₂Br₂·2.5H₂O thermal decomposition commences at rather higher temperatures than has been previously observed for the cobalt complexes of *MmT* [11]. In the temperature range

TABLE III. Room Temperature Magnetic Moments Reflectance Spectra and Ligand Field Parameters.

Compound	μ_{eff} (B.M.)	Reflectance Spectra ($\text{cm}^{-1} \times 10^{-3}$)	Assignments	Ligand Field Parameters ^a
CoL ₂ Cl ₂	4.60	12.1 20.4	${}^4T_{2g} \leftarrow {}^4T_{1g}(\text{F})$ ${}^4T_{1g}(\text{P}) \leftarrow {}^4T_{1g}(\text{F})$	Dq 1322 B' 635 β 0.66
CoL ₂ Br ₂	4.93	10.9, 11.6 19.2, 20.4	${}^4T_{2g} \leftarrow {}^4T_{1g}(\text{F})$ ${}^4T_{1g}(\text{P}) \leftarrow {}^4T_{1g}(\text{F})$	Dq 1214 B' 662 β 0.69
CoL ₂ I ₂	4.68	11.9, 13.2 18.8, 19.7	${}^4T_{2g} \leftarrow {}^4T_{1g}(\text{F})$ ${}^4T_{1g}(\text{P}) \leftarrow {}^4T_{1g}(\text{F})$	Dq 1294 B' 528 β 0.55
CoL ₄ (NO ₃) ₂	4.87	11.1, 12.1 19.2, 20.4	${}^4T_{2g} \leftarrow {}^4T_{1g}(\text{F})$ ${}^4T_{1g}(\text{P}) \leftarrow {}^4T_{1g}(\text{F})$	Dq 1287 B' 586 β 0.61
CoL ₄ (ClO ₄) ₂	4.63	12.2 18.5, 19.6	${}^4T_{2g} \leftarrow {}^4T_{1g}(\text{F})$ ${}^4T_{1g}(\text{P}) \leftarrow {}^4T_{1g}(\text{F})$	Dq 1312 B' 544 β 0.56

^aCalculated values [16] and B for the free Co(II) ion is 967 cm^{-1} .

TABLE IV. Solution Electronic Spectra.^a

Compound	Band Positions ($\text{cm}^{-1} \times 10^{-3}$)	Assignments	Ligand Field ^b Parameters
CoL ₂ I ₂	8.00, 6.94 14.7, 15.6, 17.2	${}^4T_1(\text{F}) \leftarrow {}^4A_2$	Dq 452.1 B' 650 β 0.67
CoL ₄ (ClO ₄) ₂	8.00, 7.14 13.3, 14.7, 15.6sh	${}^4T_1(\text{F}) \leftarrow {}^4A_2$ ${}^4T_1(\text{P}) \leftarrow {}^4A_2$ ${}^4T_1(\text{P}) \leftarrow {}^4A_2$	Dq 449.6 B' 588 β 0.60

^a $10^{-3} M$ solutions in nitromethane. ^bCalculated values [17] and B for the free Co(II) ion is 967 cm^{-1} .

involved (200–830 °C, Table II) observed and calculated weight losses show excellent agreement for the cobalt complexes whose end-product is Co₃O₄. The discrepancies observed for the zinc complexes are due to sublimation of ZnO.

All the complexes decompose in a two-stage process (Fig. 1) with the second stage invariably greater than the first. The absence of any clear distinction between loss of the heterocyclic molecules and conversion of the resultant halide to the oxide suggests that the decompositions are complicated in character and most likely involve thermal breakdown of the ligand as has also been suggested for the cobalt complexes of *MImT* [11].

Magnetic Moments and Electronic Spectra

Room temperature magnetic moments and diffuse reflectance spectral band energies, with their assignments, as well as derived ligand field parameters, are listed in Table III. Solution electronic spectra together with their band assignments and ligand field parameters are listed in Table IV. Reflectance spectra are illustrated in Fig. 2.

The magnetic moments of the bromo and nitrate complexes occur in the range associated with octahedral Co(II) whereas the remaining values occur in the upper portion of the range observed for tetrahedral Co(II) [12]. However, room temperature magnetic moments of the order of 4.5 to 4.6 B.M.

TABLE V. Major Infrared Bands and their Assignments.^a

Ligand	Halides	Nitrates	Perchlorates	Assignments
3100s	3160–3250s	3220s	3250s	$\nu(\text{N-H})$
1580s	1575–1580s	1575–1580s	1575–1580s	$\nu(\text{C=C}) + \nu(\text{C=N})$
1480s	1430–1450m	1450–1455m	1455m	Thioamide I
1230s	1210–1240w–m	1220m	1220m	Thioamide II
1070m	1050–1080m	1060–1070m	1060m	Thioamide III
780m	730–780m	735–750br,s	740br,s	Thioamide IV
735s	715–735s			
670m	640–670m	675m	675m	$\pi(\text{NH})$
510br,m	485–500m	490m	490–510m	$\delta(\text{C-S})$
340m	340–350m	310–335w	340w	$\pi(\text{C-S})$
	360–370w	315m	320w	$\nu(\text{M-L})$
	320–295m			$\nu(\text{Co-Cl})$
	255m			$\nu(\text{Zn-Cl})$
		1360br,s		ν_3 Ionic
		825m		ν_2 Nitrate
			1100vs	ν_3
			920m	ν_1 Ionic Perchlorate
			620s	ν_4

^aBr, broad; s, strong; m, moderate; w, weak; ν , stretching frequency.

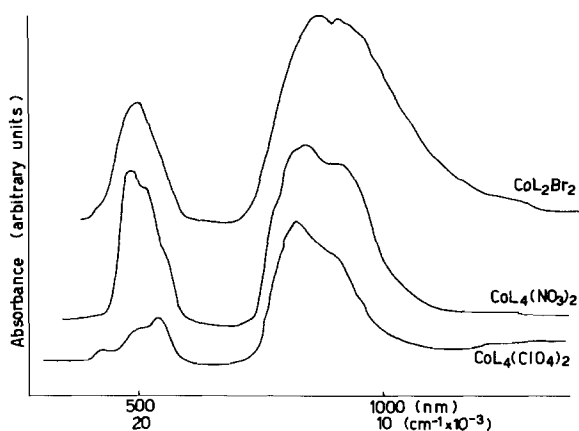


Fig. 2. Selected reflectance spectra ($L = ImT$).

have also been reported for pseudo-octahedral complexes of Co(II) with S and N-coordinating heterocyclic molecules [13, 14].

The reflectance spectra consist of two bands in the ranges 10,000–12,100 and 18,000–20,400 cm^{-1} respectively. The low energy absorption is invariably broader and more intense than that which occurs at higher energies (Fig. 2). For the halo complexes this intensity ratio is of the order of 2.1, for the perchlorate complex the ratio is 3.1 whereas for the nitrate complex the intensities are virtually equivalent. Consequently the intense colours of the solid complexes result largely from the low energy absorption. In addition, both bands in most of the complexes exhibit fine structures.

The relative positions of these two bands rules out any assignment on the basis of tetrahedral sym-

metry [15]. The most satisfactory assignment is on the basis of octahedral symmetry. Accordingly, the low energy band is assigned to the ν_1 absorption and the high energy band to the ν_3 absorption (Table III). The alternative assignment, ν_1 and ν_2 , is rejected because the resultant ratios, ν_2/ν_1 , (1.58–1.84) are too low [15]. The fine structure shown by both bands in most of the complexes is probably due to the presence of low symmetry components to the ligand field such as are expected for distorted octahedral fields. Alternatively, both the fine structure and the relatively weak intensities of the ν_3 bands may be due to some contribution from the ν_2 , (${}^4A_{2g} \leftarrow {}^4T_{1g}$), transition, which frequently lies close to ν_3 in octahedral Co(II) complexes, as well as to the presence of spin forbidden transitions.

Ligand field parameters have been calculated on the basis of the above assignments, by König's methods [16]. The Dq values are as expected, in view of the position of the various ν_1 bands, and are 10–11% greater than those reported for octahedral Co(II) complexes with monodentate N-donors [15] as well as for bridging, S,N-donating heterocyclic molecules [27]. The B' and β values, on the other hand, are indicative of substantial covalent character to the bonds such as would be expected for thione-S donors [1].

It would seem that ImT uses both a ring-N atom as well as its thione-S atom in coordinating to Co(II) in these complexes.

The solution spectra, (Table IV), of the iodo and perchlorate complexes are clearly very different from their solid state counterparts. The positions of the two bands are entirely consistent with the ν_3 and ν_2

absorptions of tetrahedral Co(II) complexes and have been assigned accordingly [15]. Both bands possess fine structure however and this suggests the symmetry to be pseudo-tetrahedral in character.

Ligand field parameters have been calculated [17] and they are indicative of CoS₄ (perchlorate) and CoS₂I₂ chromophores. The values for the perchlorate complex show D_q (449 cm⁻¹) to be in the upper end of the range (380–476 cm⁻¹) and B' (588 cm⁻¹) in the lower end of the range (559–651 cm⁻¹) reported for thione-S donors [1].

Infrared Spectra

The absence of $\nu(\text{SH})$ at 2500 cm⁻¹, in the spectrum of the free ligand, (Table V), together with the presence of $\nu(\text{NH})$, as well as the characteristic four 'thioamide' bands, [18], confirms the thione tautomer(II) to be the dominant form of the ligand in the solid state. This situation is similar to what has been observed for *MImT* [1] and other heterocyclic molecules [19]. Furthermore, the position and character of the $\nu(\text{NH})$ band is indicative of the formation of N–H···S bonds in the solid [20].

Among the complexes the $\nu(\text{NH})$ band displays substantial positive shifts. The resultant band among the halides is broad and complex, for the nitrate and perchlorate complexes it is a sharply defined single peak. Such shifts are usually regarded as signifying that the ligand is not N-bonded to the metal [21]. The situation however is complicated by the fact that imido groups of coordinated heterocyclic molecules, e.g. *MImT*, are known to readily H-bond with the anions within a complex [5, 6]. Thus the shifts in $\nu(\text{NH})$ most likely result from a combination of factors including electronic changes within the molecule upon coordination as well as H-bonding effects.

Of the four thioamide bands those showing the most significant changes upon coordination are I and IV. Since the shifts are all in the same direction the bonding pattern is deduced to be the same for all the complexes.

Thioamide I has major contributions from $\nu(\text{CN})$ and $\delta(\text{CH})$ and shows negative shifts ranging from 25 to 50 cm⁻¹. Thioamide IV has its greatest contribution from $\nu(\text{C–S})$ and this band also exhibits negative shifts, although, in some instances, notably CoL₂Br₂·2.5H₂O as well as the nitrates and perchlorates, the band exhibits a complex character. These observations are consistent with coordination to the metal by both N and S-atoms of the ligand [21].

Only the chloro complexes exhibit any pronounced $\nu(\text{M–X})$ activity in the range of our instrument. The band positions are in the expected ranges for tetrahedral complexes although the value for the zinc complex is rather low [22].

The infrared spectra of the perchlorate and nitrate anions are indicative of ionic rather than coordinated species [23, 24].

The presence of a $\pi(\text{C–S})$ vibration (340 cm⁻¹), in the region in which $\nu(\text{M–L})$ absorptions of various thione donor complexes are normally observed [25], complicates the low frequency infrared spectra of these complexes. However, $\nu(\text{M–L})$ bands have been observed in most cases, in the range 317–370 cm⁻¹; they are believed to be largely $\nu(\text{M–S})$ in character [1, 25]. There is no indication of any $\nu(\text{M–N})$ absorptions for these complexes in the range normally associated with imidazole-N donors [26]. Evidence for the presence of water molecules in CoL₂Br₂·2.5H₂O is inconclusive because of the presence of considerable vibrational activity in the region normally associated with $\nu(\text{OH})$ (3500 cm⁻¹) and $\delta(\text{HOH})$ (1600 cm⁻¹).

Discussion

Overall, the spectroscopic evidence suggest that *ImT* uses one of its ring-N atoms as well as its thione-S atoms in coordinating to Co(II) and Zn(II).

The infrared evidence is not entirely consistent with this picture. The absence of $\nu(\text{M–N})$ in the low frequency infrared spectra may be due to the fact that the absorption is below the range of our instrument (200 cm⁻¹) and may indicate also that the M–N bond is weak. Alternatively, the $\nu(\text{M–L})$ absorptions may themselves be combinations of $\nu(\text{M–N})$ and $\nu(\text{M–S})$ as has been reported for complexes of benzoxazoline-2-thione [19].

The involvement of N and S-atoms in the coordination of *ImT* suggests either a bridging or a chelating role for the ligand. The former is the more frequently reported behaviour for a variety of thione substituted N-containing heterocyclic molecules, largely because of the steric strain inherent in the resultant four membered chelates which are attached to five membered heterocyclic molecules [27]. Pyrimidine-2-thione (PymT) however, in Co(PymT)₂Cl₂ forms a pseudo-octahedral complex containing two irregular chelate rings with Co–N at 2.098 and Co–S at 2.960 Å [13].

We suggest that *ImT* also forms irregular chelates with Co(II) and Zn(II) but that the major donor is the thione-S atom with a ring-N atom playing a subsidiary role at a somewhat greater distance. The visible spectra of the soluble cobalt complexes support this suggestion since they indicate that the Co–N contact is broken in solution leaving the ligand S-bonded to the metal.

The structures of the solid complexes are of two types. Those of formula ML₂X₂ are pseudo-octahedral with, presumably, *trans*-chelating *ImT* mole-

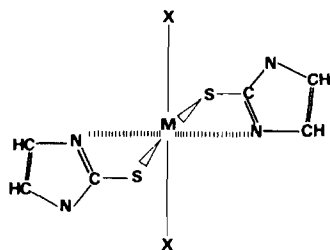


Fig. 3. Proposed structure for the ML_2X_2 complexes.

cules. The position of the terminal $\nu(M-Cl)$ absorptions testifies to the distortion in the resultant structures. For the ML_4X_2 complexes the anions are not coordinated and only two of the *ImT* molecules will be needed for chelation, the remaining two ligands will be S-bonded only, in order to complete the distorted octahedral arrangements.

The fact that M-S-C angles, in complexes of thione donating ligands, range from 101 to 105° [5-7] probably facilitates chelation. Furthermore, the H-atom of one of the imido groups, in each ligand molecule, will necessarily be replaced by the M-N bond. The proposed structure of the ML_2X_2 complexes (Fig. 3) indicates that the M-N bond is weak as a result of a long M-N distance and an unfavourable orientation of the lone pair of electrons on the ring-N atom.

Chelating behaviour has also been proposed for Pd(II) complexes of *ImT* in acid solution [28]. This contrasts with the exclusive S-donating character of the ligand among the tetragonal Ni(II) complexes [4].

Experimental

Starting Materials

The ligand was used as supplied by Koch Light Laboratories Ltd., Hydrated metal salts of reagent quality were obtained from BDH Ltd and Alpha Chemicals.

Chemical Analysis

C, H and N were analysed by Butterworths Micro-analytical Services Ltd, Teddington, Middlesex.

Spectral Measurements

Infrared spectra of the ligand and its complexes were recorded on a Perkin-Elmer 577 grating spectrophotometer. The samples were run as CsI discs in the range 4000-200 cm^{-1} and also as Nujol mulls between polyethylene plates in the same range. Solid state electronic reflectance spectra were run on a Unicam SP1700 spectrophotometer in the range 200-850 nm and on a Unicam SP700 in the range 200-2,000 nm (Sheffield City Polytechnic). The solution electronic spectra, in nitromethane, were run

in the range 350-2,000 nm on a Cary 17D spectrophotometer.

Thermal Analysis

A Stanton Redcroft TG 750 machine, with DTG facility, was used to record the TG and DTG curves in flowing air. Sample sizes were in the range 2-5 mg and open Pt crucibles were also used. The heating rate was 10° cm^{-1} . End-products were identified by X-ray powder diffraction [1].

Magnetic susceptibility and electrolytic conductivity measurements were recorded as described previously [1].

Preparation of Complexes

Halo Complexes (ML_2X_2)

These were prepared by dissolving 1 mmol of the appropriate metal halide (hydrated) in a minimum volume of hot absolute ethanol containing 5-10% (volume) of triethylorthoformate as dehydrating agent. To this solution 2 mmol of *ImT* was added in the minimum volume of hot absolute ethanol. The resultant solution was warmed for several minutes then left until precipitation was complete. The product was removed by filtration, washed with a small volume of cold anhydrous EtOH, then vacuum dried at room temperature. Product yields were in the range 50-70%.

Perchlorate and Nitrate Complexes ML_4X_2

These were obtained by the addition of 4.00 mmol of *ImT* in hot ethyl acetate to a solution of the appropriate metal salt (1 mmol) in hot ethyl acetate containing 5-10% (volume) of triethylorthoformate. The resultant solution was warmed for several minutes; cooling to room temperature was accompanied by formation of the product which was removed by filtration then washed and dried as above. Product yields were in the range 75-90%.

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