

Ni(II) Complexes of Imidazoline-2(1,3H)-thione

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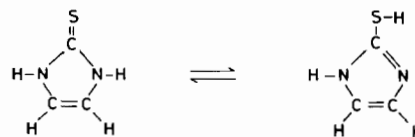
Complexes of imidazoline-2(1,3H)-thione, (ImT), with Ni(II) have been prepared. Stoichiometries of the complexes are NiL_4X_2 ($X^- = Cl, Br, I, NO_3, BF_4$ and ClO_4) and $NiL_2(SCN)_2$. Room temperature magnetic measurements, infrared spectra and electronic spectral data (Dq, Dqxy, Dqz and Dt) have shown the complexes to be paramagnetic, tetragonal species. The extent of tetragonal distortion is discussed in terms of the relative positions of the heterocyclic ligand and the coordinated anions in the spectrochemical series. The instability of the complexes in solution has precluded conductivity and proton nmr measurements.

Introduction

Complexes of the 1-methyl derivative of imidazoline-2-thione have been previously reported and shown to involve the exocyclic thione-S atom as the donor towards Co(II), Zn(II) and Ni(II) [1–3].

We now report the coordination behaviour of the parent ligand, imidazoline-2(1,3H)-thione (ImT,L), towards Ni(II). Tautomerism in the ligand produces

several possible coordination sites, thione-S, pyrrolic-N, pyridino-N and the thiol group. Thus, ImT, like its 1-methyl derivative is potentially ambidentate with thione-S and pyridino-N the most likely contenders for coordination in neutral media.



Several Ni(II) complexes have been prepared, namely, NiL_4X_2 ($X^- = Cl, Br, I, NO_3, ClO_4, BF_4$) and $NiL_2(SCN)_2$ by reacting the appropriate metal salt and the ligand in absolute ethanol. The stoichiometries of the complexes have been determined by chemical (C,H,N) analysis. Room temperature magnetic moments, infrared and diffuse electronic spectra have been used to characterise the complexes. Unfortunately, the extreme instability of these complexes in solution has precluded the use of conductivity data and proton nmr studies.

Our interest in the coordination chemistry of S and N containing heterocyclic molecules results from

TABLE I. Analytical and Other Physical Data.

Compound	Colour	Found %			Calculated %			μ B.M.	M. Pt. °C
		C	H	N	C	H	N		
NiL_4Cl_2	Orange	26.16	2.77	20.12	27.19	3.04	21.36	3.41	201
NiL_4Br_2	Brown	23.42	2.60	17.66	23.28	2.61	18.10	3.27	219
NiL_4I_2	Brown	19.94	2.19	15.25	20.21	2.26	15.71	3.34	216
$NiL_2(SCN)_2$	Orange	25.77	1.64	21.89	25.61	2.15	22.40	3.42	212
$NiL_4(ClO_4)_2$	Orange	21.56	1.85	16.72	21.90	2.45	17.02	2.97	—
$NiL_4(NO_3)_2$	Orange	23.91	2.56	23.19	24.71	2.77	24.01	2.86	199
$NiL_4(BF_4)_2$	Red	21.93	2.88	17.02	22.77	2.55	17.71	2.76	209

TABLE II. Infrared Absorption Bands (4000–200 cm^{-1}).

Compound	$\nu(\text{NH})$	Thioamide bands				$\nu(\text{M-L})$
		I	II	III	IV	
Ligand	3130s	1480s	1228m	1070s	740s	
NiL_4Cl_2	3250m	1472s	1220m	1065m	725s	340w
NiL_4Br_2	3130m	1455s	1215m	1070m	745s	300w
NiL_4I_2	3100m	1460s	1215m	1060m	720s	300w
$\text{NiL}_2(\text{SCN})_2$	3180m	1470m	1225w	1070m	740s	290w
$\text{NiL}_4(\text{ClO}_4)_2$	3120m	1480s	1220m	—	740s	340w
$\text{NiL}_4(\text{NO}_3)_2$	3130m	1480m	—	1070w	740m	295w
$\text{NiL}_4(\text{BF}_4)_2$	3130m	1480s	1220m	1065m	740s	290w

TABLE III. Infrared Absorption Bands Due to Anions.

Compound	Anion bands (cm^{-1})
NiL_4Cl_2	235w
NiL_4Br_2	—
NiL_4I_2	—
$\text{NiL}_2(\text{SCN})_2$	2100m, 2085m, 810m, 485w, 470w
$\text{NiL}_4(\text{NO}_3)_2$	1480m, 1385s, 1340m, 1280m
$\text{NiL}_4(\text{ClO}_4)_2$	1145, 1100, 1090s, 915w, 626m, 420w
$\text{NiL}_4(\text{BF}_4)_2$	1120, 1060, 1035s, 740w, 520w, 340w

their ability to inhibit metallic corrosion [4, 5] and in the nature of the metal-inhibitor interaction.

Results and Discussion

The complexes are listed in Table I with their elemental analysis and other physical properties.

All of the complexes are insoluble in common organic solvents, and in more polar solvents such as methanol, dimethylsulphoxide and water they appear to dissolve with complete dissociation, hence the absence of conductivity data.

Infrared Spectra

The infrared absorptions are in Tables II and III. The predominant tautomeric form of the ligand in the solid state may be deduced from its infrared spectrum. This shows the absence of $\nu(\text{SH})$ at 2500 cm^{-1} and the presence of $\nu(\text{NH})$ at 3130 cm^{-1} , demonstrating that the thione form (I) appears to be the predominant tautomer, in the solid.

Analysis of the thioamide bands [6] has been used in the past to differentiate between M–N and M–S contacts for various thione ligands [1, 7, 8].

However, as occurred with the Ni(II) complexes of 1-methylimidazoline-2-thione [3] the shifts in the thioamide I and IV bands are also inconclusive for these complexes (Table II).

The $\nu(\text{M-L})$ absorptions range from 290 to 340 cm^{-1} and are generally in agreement with those reported earlier [3] for M–S thione contacts.

The only $\nu(\text{Ni-X})$ vibration observed in this instance is that of $\nu(\text{Ni-Cl})$ at 235 cm^{-1} which is similar to values reported for related complexes [3, 9].

The nitrate complex exhibits a strong, sharp absorption at 1385 cm^{-1} but it appears that this is only one component of a split band, the other component being a broader band of medium intensity of 1340 cm^{-1} . A similar splitting of this ν_3 band has been observed [10] in complexes where the nitrate group is weakly coordinated. The ν_1 and ν_4 absorptions of coordinated nitrate are largely obscured by the thioamide I and II bands at 1480 and 1280 cm^{-1} respectively. Thus the infrared evidence suggests that the nitrate group is coordinated in this complex.

The position of $\nu(\text{CN})$ at 2100 and 2085 cm^{-1} as well as $\nu(\text{CS})$ at 810 cm^{-1} are indicative of bridging thiocyanate [11] and strongly suggests that the complex is polymeric. The structure most likely consists of two apical N-atoms and four equatorial S-atoms octahedrally arranged around Ni(II) as has been established for $[\text{Ni}(\text{etu})_2(\text{SCN})_2]$ [12].

The infrared absorptions due to the perchlorate and tetrafluoroborate ions in the complexes are shown in Table III. In these complexes the spectra of the anions are intermediate in character between those expected of the coordinated as well as those of the free ion [13, 14]. In each spectrum the ν_3 band shows some evidence of splitting and the ν_1 and ν_2 modes occur, albeit weakly. Such spectra are typical of complexes in which these ions are weakly coordinated, as has been observed in $[\text{Cu}(\text{en})_2](\text{ClO}_4)_2$ and $[\text{Cu}(\text{en})_2](\text{BF}_4)$ [15].

TABLE IV. Reflectance Spectra (cm^{-1}).

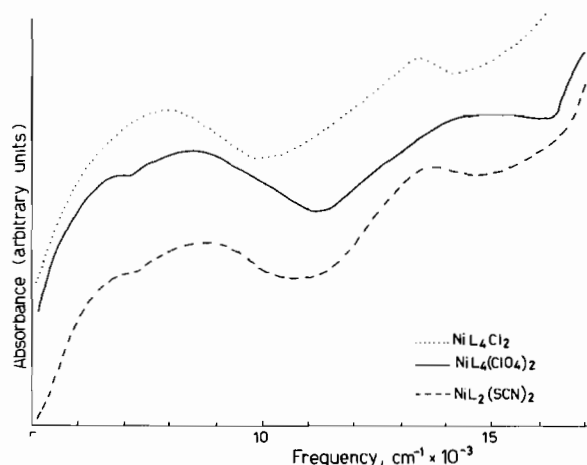
Compound	Absorption Bands		
NiL_4Cl_2	14,085	7,813	
NiL_4Br_2	13,986	8,696	6,897
NiL_4I_2	13,699	8,969	6,993
$\text{NiL}_2(\text{SCN})_2$	14,925	8,333	6,897
$\text{NiL}_4(\text{ClO}_4)_2$	13,986	8,696	6,897
$\text{NiL}_4(\text{NO}_3)_2$	13,986	8,333	6,993
$\text{NiL}_4(\text{BF}_4)_2$	13,699	8,621	6,897

Magnetism and Electronic Spectra

Room temperature magnetic measurements (Table I) show that all the Ni(II) complexes have paramagnetic moments in the range 2.76–3.42 B.M. These are normal values for such complexes.

The paramagnetic nature of the complexes requires that the electronic spectral data (Table IV) be interpreted by means of assignments between triplet states; specimen spectra are shown in Fig. 1. The electronic spectrum of octahedral Ni(II) with a ${}^3A_{2g}$ ground state normally consists of three absorptions. In these complexes the ν_3 absorption is obscured by a charge transfer band, a common occurrence for complexes with Ni–S bonds; the electronic spectra thus consist of two d–d bands. In all but the chloro complex the ν_1 absorption has a shoulder on the low-energy side, a clear indication of tetragonal distortion. Consequently the two absorptions in the chloro complex may be assigned in octahedral symmetry to the ${}^3T_{2g} \leftarrow {}^3A_{2g}$ (ν_1) and ${}^3T_{1g} \leftarrow {}^3A_{2g}$ (ν_2) transitions respectively. With $\Delta \sim 7813 \text{ cm}^{-1}$ the position of ImT in the spectrochemical series appears to be close to, but slightly above that of Cl^- (Δ_o for NiCl_6^{4-} is $6600\text{--}7200 \text{ cm}^{-1}$ [16]). Thus the chloro complex possesses a virtually symmetrical ligand field, which probably accounts for the absence of any detectable level of tetragonal distortion in the visible spectrum. Calculation of B' , inhibited by the absence of the ν_3 absorption, has been obtained by the Tanabe–Sugano method using the less reliable ν_2/ν_1 ratio ($B = 1030 \text{ cm}^{-1}$). The resultant B' value, 446 cm^{-1} , is lower than might have been reasonably expected and probably suggests a greater degree of covalent character in the Ni–S bonds than actually exists.

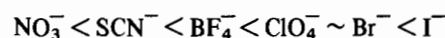
The absorptions for the remaining complexes may be assigned in tetragonal symmetry [17, 3]. For such a system the ground state is ${}^3B_{1g}$, the shoulder on the ν_1 absorption is assigned to the ${}^3E_g \leftarrow {}^3B_{1g}$ transition, with a separation of $35/4$ Dt [18]. The bulk of the absorption corresponds to the ${}^3B_{2g} \leftarrow {}^3B_{1g}$ transition whose separation corresponds to 10 Dqxy, the in-plane field strength. The

Fig. 1. Selected diffuse reflectance spectra ($L = \text{ImT}$).TABLE V. Electronic Spectral Parameters (cm^{-1}).

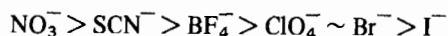
Compound	Dt	Dqxy	Dqz
NiL_4Br_2	206	870	510
NiL_4I_2	226	870	502
$\text{NiL}_2(\text{SCN})_2$	164	833	546
$\text{NiL}_4(\text{ClO}_4)_2$	206	870	510
$\text{NiL}_4(\text{NO}_3)_2$	153	833	565
$\text{NiL}_4(\text{BF}_4)_2$	197	862	517

out-of-plane field strength, Dqz is obtained from $Dt = 4/7 (Dqxy - Dqz)$ (Table V). The ν_2 absorption arises from a transition involving ${}^3B_{1g}$ and the unresolved components ${}^3A_{2g}(\text{F})$, ${}^3E_g(\text{F})$, of the transformed orbital triplet, ${}^3T_{2g}(\text{F})$, in octahedral symmetry.

The Dqxy values are very similar to one another and between 6 and 10% greater than the Dq value for the NiL_4Cl_2 complex. This suggests a fairly uniform NiS_4 entity within these complexes. The Dt values, with the possible exception of the iodo complex, are in the range normally associated with heterocyclic S-bonds rather than heterocyclic N-bonds, a useful diagnostic test [18, 19]. The extent of the distortion in the tetragonal complexes may also be assessed by means of the Dt values. Consequently, arranging the anions in order of increasing Dt produces the sequence:



Alternatively, increasing tetragonality should be accompanied by a decrease in the Dqz parameter, thus:



In addition, a decrease in the Dqz component of the ligand field strength is accompanied by an increase in the Dqxy contribution (Table V).

Although too much reliance can not be placed on these derived electronic spectral parameters the overall trend suggests that the extent of tetragonal distortion is not entirely what would have been predicted from the relative positions of these anions in the spectrochemical series [20]. However, the Dqz values do support the infrared spectra and the magnetic measurements in indicating that the ClO_4^- and BF_4^- ions are coordinated in these complexes. Comparable Dqz values, at least for the ClO_4^- ion, have been reported for other tetragonal complexes of Ni(II) with heterocyclic molecules [18].

Conclusions

In its complexes with Ni(II), ImT behaves as a soft ligand, coordinating in all cases by means of its exocyclic thione-S atom. The maximum number of coordination sites occupied by the ligand is four, producing square-planar NiS_4 entities. Attempts to prepare 1:6 complexes were unsuccessful. It is possible that the excellent π -accepting properties of the S-atom is the major reason for this, by lowering the charge on the cation and enabling the apical coordination sites to be occupied by various anions, at the expense of the heterocyclic ligand.

The observed increase in tetragonal distortion, expressed in terms of increasing Dqz:



differs from that predicted on the basis of the relative positions of the anions in the spectrochemical series [20]:



The juxtaposition of ImT and Cl^- in the spectrochemical series precludes any detectable tetragonality in the NiL_4Cl_2 complex and accounts for the position of Cl^- in the above. Inversion of the positions of NO_3^- and SCN^- is most likely due to the fact that the latter is bridging in character whereas the former is monodentate. While the remainder of the observed sequence is unexpected it must be noted that their Dqz values differ by no more than 3% and therefore are probably not significantly different from one another. The general observation however that the BF_4^- , ClO_4^- , Br^- and I^- complexes represent the most tetragonally dis-

torted group, within this series, agrees with the prediction. Although we have equated spectral data with tetragonal distortion, a steric phenomenon, we are aware that such spectral variations are not necessarily accompanied by comparable bond length variations in the solid state.

In contrast to the behaviour of its 1-methyl derivative [3] ImT does not generate sufficient ligand field strength to cause spin-pairing in Ni(II), not even in the most tetragonally distorted environments. This supports the general observation concerning thione donors in direct contrast to the behaviour of other S-donors such as thiols, monothio- β -diketonates and diethyldithiophosphates [21].

Experimental

Starting Materials

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

Analysis

C, H and N were analysed by ICI Corporate Laboratory, Runcorn.

Physical Measurements

The infrared and electronic spectral measurements and magnetic susceptibility of the complexes were measured as described previously [1].

Preparation of the Complexes

(i). Complexes of the type NiL_4X_2 ($\text{X}^- = \text{Cl}, \text{Br}, \text{I}, \text{NO}_3, \text{BF}_4, \text{ClO}_4$) were prepared by dissolving 1 mmol of the appropriate nickel salt in 6 cm^3 hot anhydrous ethanol containing 1 cm^3 triethylorthoformate as a dehydrating agent. To this hot solution 4 mmol of the ligand dissolved in 15 cm^3 hot anhydrous ethanol containing 5 cm^3 triethylorthoformate, was added. The resultant solution was heated on a steam bath for up to six hours until the precipitation of the powdery product seemed to be complete. Occasionally the product formed as a dark oil, and the complex was shaken out of solution using dry ether. The product was separated by filtration, washed with cold anhydrous ethanol and then *vacuum* dried at room temperature. Product yields were less than 50% of the theoretical.

(ii). $\text{NiL}_2(\text{SCN})_2$, was prepared by dissolving 1 mmol $\text{Ni}(\text{SCN})_2$ in 25 cm^3 hot methanol, and adding 2 mmol ligand dissolved in 15 cm^3 hot methanol. The resultant solution was refluxed for 3 hrs until the precipitate of the yellow powder seemed to be complete. This was removed by filtration, washed with cold methanol and *vacuum* dried at room temperature.

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