Inorganica Chimica Acta, 41 (1980) 145–149
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Nickel(II) Complexes of 1-methylimidazoline-2(3H)-thione

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Received December 5, 1979

Complexes of 1-methylimidazoline-2(3H)-thione (MImT = L) and Ni(II) have been prepared. Various physical techniques, including infrared, proton nuclear magnetic resonance and electronic spectroscopy, have been used to study the structures of these complexes and have shown that NiL_4X_2 (X^- = Cl, Br, I and NO_3) are tetragonal; $NiL_2(SCN)_2$ is polymeric and tetragonal; NiL_4X_2 (X^- = ClO_4 and BF_4) are square-planar. Only NiL_4Cl_2 and $NiL_2(SCN)_2$ are paramagnetic at room temperature.

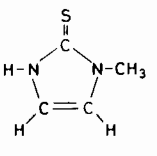
The ligand is monodentate and S-bonded to the metal in all cases, in both the solid as well as in solution.

TABLE II. Principal Infrared Bands in the Complexes (cm^{-1}).

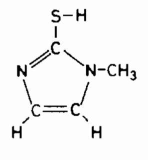
Compound	ν(Ni–L)	Anion bands
NiL_4Cl_2	417w	240w
NiL_4Br_2	375w	
NiL_4I_2	348w	
$NiL_2(SCN)_2$	360w	2085s 2170s; 820w, 470/455w
$NiL_4(ClO_4)_2$	350w	1175–1025s, 825w, 625m
$NiL_4(NO_3)_2$	345w	1470m, 1385s, 1290m, 1025w
$NiL_4(BF_4)_2$	360w	1130–1020s, 520w

Introduction

Interactions of monodentate S-donors with Ni(II), in particular thiourea [1], substituted thioureas [2], ethylenethiourea [3] and heterocyclic-thiones [4], have produced a range of complexes involving all the commonly observed stereochemical environments of Ni(II). The factors governing the structure which is adopted by a particular ligand are still being explored. Previous research has demonstrated that MImT coordinates to Co(II) and Zn(II) with its thione-S(I) rather than its pyridino-N atom (II) in neutral media [5].



(I)



(II)

TABLE I. Analytical and other Physical Data.

Compound	Colour	Found %			Calculated %			μ(B.M.)	Λ_m mhos cm^2 mol^{-1}	M.P. (°C)
		C	H	N	C	H	N			
NiL_4Cl_2	Orange	32.92	4.23	19.04	32.78	4.13	19.11	3.26	2.46	150
NiL_4Br_2	Green	29.00	3.57	16.61	28.46	3.58	16.60	–	4.58	132
NiL_4I_2	Brown	26.02	3.58	13.14	24.98	3.15	14.57	–	17.18	142
$NiL_2(SCN)_2$	Orange	27.47	2.40	19.77	29.79	3.00	20.84	3.09	–	226
$NiL_4(ClO_4)_2$	Green	27.43	3.55	16.04	26.91	3.39	15.69	–	96.43	–
$NiL_4(NO_3)_2$	Green	30.11	3.77	21.39	30.06	3.78	21.91	–	11.02	152
$NiL_4(BF_4)_2$	Green	27.65	3.82	16.16	27.89	3.51	16.26	–	103.06	209

TABLE III. NMR Chemical Shift Values (δ) in ppm for the Nickel Complexes in DMSO, using TMS as an Internal Standard.

Compound	N^3–H	N^1–CH_3	–C^4H=C^5H–	
Ligand	11.72	3.43	6.77,	6.91
NiL_4Cl_2	11.96	3.99	6.82,	7.05
NiL_4Br_2	11.66	3.34	6.75,	6.93
NiL_4I_2	12.00	3.50	6.90,	7.15
$NiL_4(ClO_4)_2$	11.60	3.00	6.50,	6.65
$NiL_4(NO_3)_2$	11.50	2.80	6.29,	6.45
$NiL_4(BF_4)_2$	11.95	3.36	6.82,	7.00

TABLE IV. Electronic Spectra (kK).

Compound	Reflectance		Solution	
NiL_4Cl_2	13.3;	8.0, 6.9sh	15.6;	14.4
$NiL_2(SCN)_2$	14.3;	8.3, 6.5sh		
NiL_4Br_2	13.9;	8.7, 6.1	14.8,	14.1
NiL_4I_2	14.3;	7.9, 6.1	13.7	
$NiL_4(NO_3)_2$	15.6;	8.8, 6.9	13.8	
$NiL_4(ClO_4)_2$	13.0;	9.5, 6.5	13.4	
$NiL_4(BF_4)_2$	14.7;	8.6, 6.2	15.9	

We now report the behaviour of MImT towards Ni(II) and discuss the factors governing the structures and other properties of the complexes.

Results

The stoichiometries of the complexes have been determined by chemical (C,H,N) analyses (Table I). Room-temperature magnetic moments have been performed on NiL_4Cl_2 and $NiL_2(SCN)_2$, the remaining complexes are diamagnetic at room temperature (Table I). Selected infrared spectra (Table II), proton nuclear magnetic resonance spectra (Table III) and electrolytic conductivities in non-aqueous media (Table I) have been used to identify the coordinating atom in the ligand and to establish the role of the anion in the complex, in the solid as well as in solution. The structures of the complexes have been deduced from diffuse reflectance spectra (Table IV); some representative reflectance spectra are shown in Fig. 1.

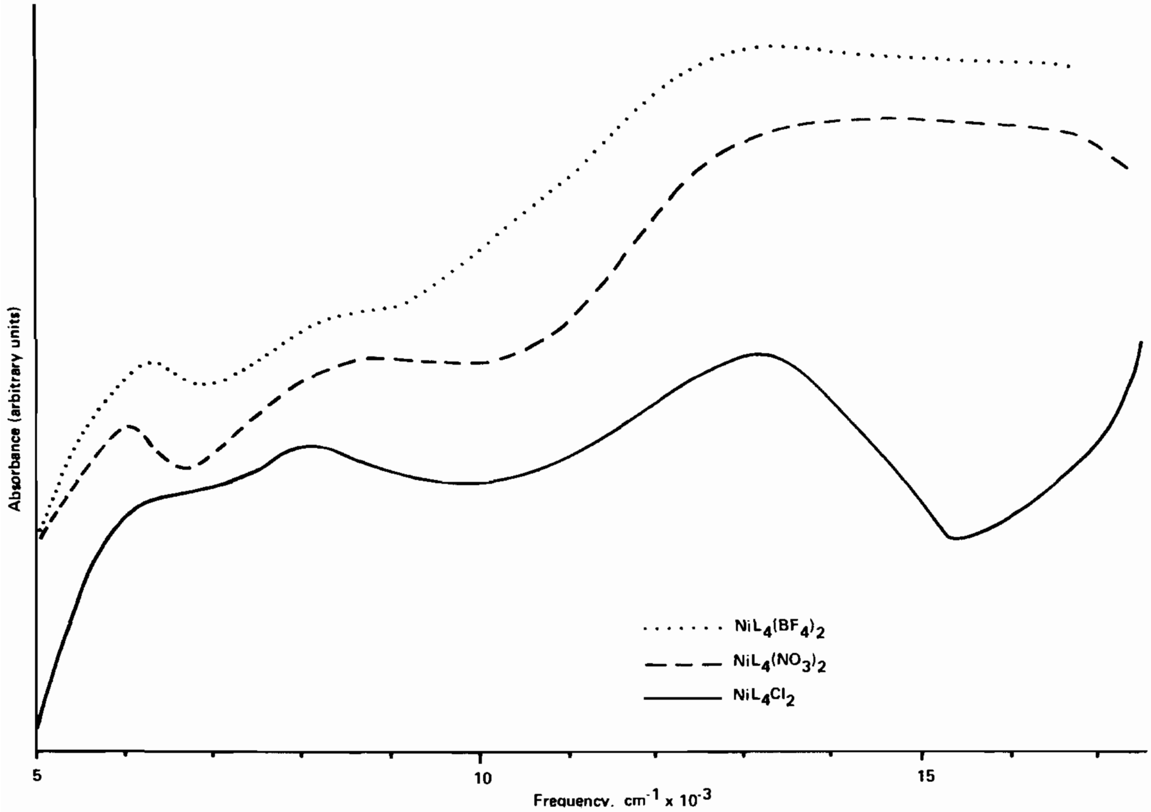


Fig. 1. Selected diffuse reflectance spectra; L = MImt.

General Comments

The formulae of the complexes were the same for preparations involving excess ligand as well as for those with the appropriate stoichiometric ratios. The solubility of the complexes in common organic solvents is variable. The extreme insolubility of the thiocyanato complex suggests that it is probably polymeric. The chloro complex is insoluble in ethanol but soluble in both nitromethane and dimethyl sulphoxide (DMSO) which appear to be the most effective solvents for the remaining complexes. All the complexes hydrolyse readily in water.

Electrolytic Conductance Measurements

Conductance measurements in nitromethane (Table I) show that all except the perchlorate and tetrafluoroborate are non-electrolytes.

The behaviour, in solution, of Ni(II) complexes containing heterocyclic ligands is frequently complicated and the interpretation of their conductance measurements is consequently not straightforward [3, 6].

Although the values for the perchlorate and tetrafluoroborate complexes suggest 1:1 rather than 1:2 electrolytic behaviour we deduce them to be 1:2 electrolytes with anomalously low conductance values.

Infrared and Proton Nuclear Magnetic Resonance Spectra

The infrared spectrum of the ligand shows the presence of ν(NH) at 3105 cm^{-1}, and the absence of ν(SH) at 2500 cm^{-1}. Similarly, the proton nmr spectrum demonstrates that the acidic proton resides on the N(3) atom since the chemical shift (δ 11.72) for this proton is more typical of N–H (δ 9–12) than S–H (δ 3–5) [7]. Thus the thione form (I) appears to be the predominant tautomer in both the solid as well as in solution.

Analysis of the thioamide bands [8] has been used successfully to differentiate between M–N and M–S contacts for various thione ligands [4, 9, 10]. In this instance, however, the shifts observed in the diagnostically useful thioamide I and IV bands are mostly very small and inconclusive.

The chemical shifts (Table III) for the N–H, N–CH_3 and olefinic protons of MImT remain essentially the same in the complexes as well as in the free ligand. This suggests that the exocyclic thione-S atom, rather than the pyrollic N–H, is the most likely donor atom in these complexes.

The range of ν(M–S) absorptions for monodentate sulphur in the far infrared region is well known to be extensive [11]. Of particular interest are the ν(Ni–S) values for thiourea (220 cm^{-1}) and ethylenethiourea (235 cm^{-1}) [12]. In addition, values for ν(Ni–N) absorptions occur at 261 cm^{-1} for imidazole [13] and in the range 212–250 cm^{-1} for N-bonded thiomorpholine-3-thione [14]. Table II shows that the values for ν(Ni–L) extend from 340 to 417 cm^{-1} with those for the halogen complexes exhibiting a pronounced halogen dependence. Although these values are significantly different from those noted above for similar sulphur donors, they are in the range previously reported for this ligand, as a monodentate thione donor, and are probably largely ν(M–S) in character [1, 2].

TABLE V. Assignments and Electronic Spectral Parameters for NiL_4Cl_2 and $NiL_2(SCN)_2$ (cm^{-1}).

Assignment and spectral parameter	NiL_4Cl_2	$NiL_2(SCN)_2$
$^3E_g \leftarrow {}^3B_{1g}$	6,896	6,452
$^3B_{2g} \leftarrow {}^3B_{1g}$	8,000	8,333
$^3A_{2g}(F)$, $^3E_g(F) \leftarrow {}^3B_{1g}$	13,000	14,285
Dqxy	800	833
Dqz	579	457
Dt	126	215

The only ν(Ni–X) vibration observed in this instance is that of ν(Ni–Cl) at 240 cm^{-1} which is similar to that reported for a related complex with pyridine-2-thiol [15]. The presence of the ν_2 (1025 cm^{-1}), ν_1 (1290 cm^{-1}) and ν_4 (1470 cm^{-1}) bands of the coordinated nitrate ion [16] supports the conductivity data for this complex. The observed bands for the thiocyanate ion suggest it to be bidentate bridging [17] with a structure probably similar to that observed in $[Ni(etu)_4(SCN)_2]$ [18] in which the anion provides equatorial-S and apical-N bonds. The infrared spectrum of the perchlorate and tetrafluoroborate complexes consist of the ν_3 and ν_4 absorptions of the free ion and are indicative of ionic [19, 20] rather than coordinated [21] species. Thus they support the conductivity data in suggesting the complexes to be 1:2 electrolytes.

Magnetism and Electronic Spectra

Room temperature magnetic moments (Table I) show that NiL_4Cl_2 (μ = 3.26 B.M.) and $NiL_2(SCN)_2$ (μ = 3.09 B.M.) are the only paramagnetic species. These values are in the range expected of octahedral Ni(II) complexes (2.80–3.40 B.M.) with $^3A_{2g}$ ground states. The electronic spectra of such complexes normally consist of three absorptions. The ν_3 absorptions for the above complexes are obscured by a charge transfer band; the remaining absorptions are broad and ν_1 possesses a shoulder on the low energy side. This suggests that the complexes have tetragonal structures. The ground state becomes $^3B_{1g}$ in tetragonal symmetry and the orbital triplets, in octahedral symmetry, transform to ^3E_g, $^3B_{2g}$ and $^3A_{2g}$, ^3E_g respectively [22]. Band assignments involving these terms are shown in Table V with the derived spectrochemical parameters.

The Dqxy parameters are comparable in these two complexes and also compare very well with the value (802 cm^{-1}) for Ni(thiourea)$_4$Cl$_2$ [22]. This suggests that all three complexes have similar [NiS$_4$] environments in the equatorial plane, a result of some significance considering the bridging role of the thiocyanate ion. The Dqz value for the chloride ion compares favourably with values from other heterocyclic NiL$_4$Cl$_2$ systems [22, 23]. The smaller Dqz value for the thiocyanate anion suggests a greater degree of tetragonal distortion in this complex, relative to the chloro complex, which may also be another consequence of the bridging role of this ion. The Dt values for these complexes are also significant. The value for the chloro complex is identical to that reported for Ni(thiourea)$_4$Cl$_2$ [22]. The significantly higher value for the thiocyanato complex reflects the contribution from the N-atom since Dt values for N-containing systems are invariably greater than 200 cm^{-1}.

The remaining complexes are diamagnetic and have very similar spectra (Table IV). This is not surprising since the distinction between tetragonal diamagnetic and square diamagnetic is very difficult to make spectroscopically [24].

In addition to the bands listed in Table IV all the complexes exhibit an intense charge transfer band which protrudes well into the visible range. Several workers have taken the appearance of such a band as an indication of M–S bonding [25, 26]. The visible spectra of these complexes are most unusual, however. Instead of the single broad absorption above 10,000 cm^{-1}, typical of square-planar Ni(II), we observe three bands in the ranges 13,000–15,600; 7800–9500 and 6100–6900 cm^{-1}. The band in the highest energy range we assign to the $^1B_{1g} \leftarrow {}^1A_{1g}$ transition and the absorption in the middle energy range we assign to $^1A_{2g} \leftarrow {}^1A_{1g}$ [27]. The remaining absorption is sharp but weak and we suggest this to be a spin-forbidden transition involving a triplet state close to the $^1A_{1g}$ ground state. However, in view of the inherent uncertainty among the term diagrams of square-planar Ni(II) [24] these assignments must remain tentative. The major factor responsible for these unusual visible spectra is probably the presence of π-bonding among the four Ni–S bonds [28].

The solution spectra of the complexes (Table IV) in nitromethane suggests that the behaviour of the complexes, even with weak donor solvents, may be complex, as has been observed for Ni(II) complexes with other S-donor ligands [2, 3]. The ν_2 band is shifted appreciably and is, in some instances, split. In addition, the extinction coefficients, (ν_2), which are otherwise not reported, were generally greater than 200 l mol^{-1} cm^{-1}. This behaviour suggests that a change from tetragonal to tetrahedral structures occurs in solution. Similar behaviour has been observed for ethylenethiourea and some substituted thiourea complexes of Ni(II) [3].

Discussion

In some respects MImT coordinates to Ni(II) in a manner similar to that of other heterocyclic thione donors, particularly in the formation of paramagnetic, tetragonal NiL$_4$Cl$_2$ and NiL$_2$(SCN)$_2$ complexes [3, 15, 22].

The most unusual aspects of its behaviour are the formation of spin-paired, tetragonal, NiL$_4$X$_2$ (X^- = Br, I and NO$_3$) and square-planar, [NiL$_4$]X$_2$ (X^- = BF$_4$ and ClO$_4$) complexes.

Rationalisation of varied magnetic behaviour among Ni(II) complexes has been achieved for imidazole N-donors [6] by means of a comparison of the ligand-field strengths of the heterocyclic donor with those of the other species, in the complexes.

Tetragonal, paramagnetic complexes are usually formed when the equatorial and apical ligands are close to one another in the spectrochemical series. For MImT this situation cccurs with the chloro and thiocyanate complexes, even though the thiocyanate ion is bridging, rather than exclusively S-bonded. When the tetragonal component of the ligand field is significantly less than that of the equatorial ligands, diamagnetic complexes may be formed. This situation exists in the bromo, iodo and nitrato complexes, since these ions are significantly separated from MImT in the spectrochemical series. Similarly, the relatively weak coordinating ability of the perchlorate and tetrafluoroborate anions is the most likely reason for the diamagnetic character and square-planar geometry in these complexes.

It is likely that, with the increase in the degree of tetragonality experienced in the diamagnetic complexes, the equatorial ligands are able to approach the Ni(II) ion more closely and generate sufficient ligand field strength to cause spin-pairing, a relatively rare event for a heterocyclic-thione donor. The factors involved in such processes are clearly very finely balanced however, as is shown by the existence of a temperature dependent magnetic moment in dichlorotetrakis(N,N'-diethylthiourea)nickel(II) [29]. The presence of a spin-forbidden, triplet ← singlet, transition in the visible spectra of the diamagnetic complexes of MImT suggests that a thermally accessible triplet state may exist for these complexes also.

Finally, the unusual visible spectra of the diamagnetic complexes suggests that some degree of π-bonding exists within the NiS$_4$ entities of these complexes.

Experimental

Starting Materials

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

Analysis

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

Physical Measurements

The infrared and electronic spectral measurements, electrolytic conductivity and magnetic susceptibility of the complexes were measured as described previously [1]. The proton nmr spectra were obtained on a Perkin-Elmer R12A 60 MHz spectrometer.

Preparation of complexes

(i) Complexes of the type NiL_4X_2 (X^- = Cl, Br, I, NO_3, BF_4, 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. This solution was then cooled in ice–water. To this solution 4 mmol of the ligand dissolved in 5 cm^3 anhydrous ethanol similarly cooled, was added. The resultant solution was allowed to stand for up to 24 hrs in ice water until the formation of crystalline product seemed to be complete. This was removed by filtration, washed with a small amount of ice cold anhydrous ethanol, then dry ether and finally dried at room temperature. Product yields were in the range 35–55% of the theoretical.

(ii) $NiL_2(SCN)_2$ was prepared by dissolving 1 mmol $Ni(SCN)_2$ in 25 cm hot methanol, and adding 2 mmol ligand dissolved in 5 cm hot methanol. The resultant solution was refluxed for 3 hours until the precipitation of the yellow powder seemed to be complete. This was removed by filtration, washed with methanol and vacuum dried at room temperature.

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