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Nickel(II) Complexes of 1,3-(N,N^1)-Dimethylimidazoline-2-thione

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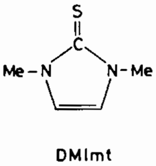
Introduction

The coordination chemistry of imidazoline-2-thione (*Imt*), its N-methyl (*MImt*), as well as its N,N^1-dimethyl (*DMImt*) derivatives towards a variety of M(II) ions, in neutral media, has been previously reported [1–8].



Both *MImt* and *DMImt* are monodentate thione-S donating under these conditions while *Imt* is either S,N-chelating or thione-S donating. The tetragonal NiL_4X_2 (X^- = Cl, Br, I, NO_3, ClO_4 and BF_4) complexes of *Imt* and *MImt* possess diverse magnetic properties and solid state electronic spectra, in addition, the soluble *MImt* complexes exhibit complex structural equilibria in solution. Since the previous report [7] on the nickel complexes of *DMImt* was limited to the halo complexes we have extended our research on these molecules to the nickel complexes of *DMImt* with SCN^-, NO_3^-, ClO_4^- and BF_4^- ions. We now report the results of this work and compare our observations with previous work in this field [4, 5].

Experimental

Preparation of the Ligand

The ligand was prepared by refluxing 1-methylimidazole (0.31 mol) and methyl iodide (21 ml) in ethyl acetate (8.3 ml) for 1.5 h. After removal of the ethyl acetate, methanol (300 ml), sulphur (11.2 g) and potassium carbonate (10.0 g) were added. The mixture was refluxed, with stirring for 24 h. Water (800 ml) was added and the product was extracted with methylene dichloride (8 × 100 ml) and dried over sodium sulphate. The solvent was removed and the pink/white crystalline product was identified by ^1H nmr, mass spectroscopy and infrared spectroscopy. The 1-methylimidazole was obtained from Emanuel Ltd., the remaining chemicals were reagent quality.

Preparation of the Complexes

(a) Complexes of the type NiL_4X_2 (X^- = NO_3, ClO_4 and BF_4) were prepared by the addition of a solution of *DMImt* (4 mmol) in anhydrous ethanol (5 cm^3) containing triethylorthoformate (1 cm^3) to a solution of the nickel salt (1 mmol) in anhydrous ethanol (6 cm^3). The product, which formed after the reactants had been heated for several minutes at 60 °C, was separated by filtration, washed with cold anhydrous ethanol, then dry diethylether and finally vacuum dried at room temperature.

(b) Preparation of $NiL_2(SCN)_2$ involved the addition of a solution of $Ni(SCN)_2$ (1 mmol) in methanol (20 cm^3) to a solution of *DMImt* (2 mmol) in methanol (10 cm^3). The reactants were heated for 1 hour when the orange product was removed by filtration washed with cold methanol and vacuum dried.

Analysis

C, H and N were analysed at I.C.I., Corporate Laboratory, Runcorn, Cheshire.

Physical Measurements

Infrared spectra were recorded as mulls and discs (CsI) in the range 4,000–200 cm^{-1} on a Perkin-Elmer 577 grating spectrophotometer. Solid state reflectance electronic spectra were recorded on a Unicam SP700 spectrophotometer. Solution electronic spectra were recorded in anhydrous nitromethane on a Cary 17D spectrophotometer, the range in both cases was 200–2000 nm. Electrolytic conductivity measurements were performed at room temperature in nitromethane (10^{-3} *M*). A Portland Electronics conductivity bridge and dip-type electrode were used. Magnetic measurements were employed at room temperature on a Gouy balance using $Hg[Co(NCS)_4]$ as standard. Molecular susceptibilities were corrected for the diamagnetism of the component atoms.

Results and Discussion

The complexes are listed in Table I with their elemental analyses and other physical data. Major infrared bands of the ligand and its complexes are in Table II; Tables III and IV contain electronic spectral data, band assignments and calculated ligand field parameters.

TABLE I. Analytical Data, Found % (Calcd. %), Room Temperature Magnetic Moments (B.M.), and Molar Conductivities Λ_M (Ω^{-1} mol^{-1} cm^2) in 10^{-3} M Nitromethane and Melting Points (°C).

Compound	Colour	C	H	N	μ (B.M.)	Λ_M	M. Pt.
$NiL_2(SCN)_2$	Orange	32.04(33.40)	3.35(3.74)	19.06(19.49)	2.88	–	176
$NiL_4(ClO_4)_2$	Green	31.14(31.18)	4.46(4.19)	14.63(14.55)	3.31	135.58	–
$NiL_4(NO_3)_2$	Green	31.27(31.76)	4.30(4.41)	14.60(14.46)	3.18	127.78	300
$NiL_4(BF_4)_2$	Green	32.28(32.24)	4.11(4.33)	15.25(15.04)	3.34	135.58	307

TABLE II. Principal Infrared Bands (cm^{-1}) of *DMImt* and Its Coordination Compounds.

Compound	ν(C–S)	ν(Ni–L)	Anion bands
Ligand	735s	–	–
$NiL_2(SCN)_2$	740m	325w	2140m, 750m, 460w
$NiL_4(ClO_4)_2$	752s	325w	1180–1080br,s; 625m
$NiL_4(BF_4)_2$	750s	350w	1130–1020br,s, 520w
$NiL_4(NO_3)_2$	750s	350w	1490m, 1385s, 1290m, 1240m, 835w

TABLE III. Electronic Spectral Data (cm^{-1} × 10^{-3}).

Compound	Solid reflectance	Solution (10^{-3} M in nitromethane)
$NiL_2(SCN)_2$	13.4, 8.0, 6.2	–
$NiL_4(ClO_4)_2$	13.2, 9.6, 6.8	17.5, 13.3
$NiL_4(BF_4)_2$	16.0, 9.7, 6.6	17.5, 13.3
$NiL_4(NO_3)_2$	14.0, 9.1, 6.5	17.5, 13.3

TABLE IV. Electronic Spectra: Band Assignments and Spectrochemical Parameters (cm^{-1}).

	$NiL_2(SCN)_2$	$NiL_4(ClO_4)_2$	$NiL_4(BF_4)_2$	$NiL_4(NO_3)_2$
$^3E_g \leftarrow {}^3B_{1g}$	6200	6800	6600	6500
$^3B_{2g} \leftarrow {}^3B_{1g}$	7950	9600	9700	9100
$\left.\begin{matrix} ^3A_{2g}(F) \\ ^3E_g(F) \end{matrix}\right. \leftarrow {}^3B_{1g}$	13400	13200	16000	14000
$Dqxy$	795	960	970	910
Dqz	426	400	353	390
Dt	211	323	354	297

All except the thiocyanate complex were sufficiently soluble in nitromethane to permit electrolytic conductivity measurements. Their behaviour in other organic solvents was similar. The general insolubility of the thiocyanate complex suggests it may be polymeric like those of *Imt* and *MImt* [4, 5]. The remaining complexes are all 1:2 electrolytes in nitromethane [9], the room temperature magnetic moments of the solid complexes are consistent with paramagnetic six-coordinate species. This contrasting behaviour suggests that the anions are coordinated in the solid but are readily removed in solution.

The infrared spectrum of the thiocyanate complex wih ν(CN) at 2140 and ν(CS) at 750 cm^{-1} is indicative of bridging bidentate behaviour for this anion [10]. The absence of splitting in the ν_3 (ionic nitrate) band (1385 cm^{-1}) coupled with the presence of the ν_1 (coordinated nitrate) band (1240 cm^{-1}) suggests the anion to be weakly coordinated [11]. Similarly, slight splitting of the ν_3 (1020–1180 cm^{-1}) and ν_4 (520–625 cm^{-1}) bands of the perchlorate and tetrafluoroborate complexes suggest them to be weakly coordinated.

The absorption at 735 cm^{-1} in the ligands is considered to be largely ν(C–S) in character [8, 12] and shows a small positive shift upon coordination. This is not typical of a thione-S donor, however, the value for the metal-ligand absorptions are in the range previously observed for imidazoline thione-S donors [1, 4, 5, 8] and are considered to be largely Ni–S in character.

The reflectance spectra consist of two d–d bands as well as a charge transfer band. Fine structure, on the low energy side of the ν_1 absorption, signified the tetragonal character of these complexes in the solid [13] and implies that all of the anions are coordinated. Among tetragonal complexes the ground state term is $^3B_{1g}$ and the orbital triplets, in octahedral symmetry, transform to ^3E_g, $^3B_{2g}$ and $^3A_{2g}$(F), ^3E_g(F) respectively [13]. Band assignments involving these terms and the derived ligand field parameters [13] are listed in Table IV.

The ligand field parameters for the thiocyanate complex are similar to those reported for Ni(*MImt*)$_2$(SCN)$_2$ [4]. This, together with the infrared spectral data, confirms the bridging nature of the thiocyanate anion and suggests a structure for the complex similar to that which has been found, by X-ray methods, for Ni(etu)$_2$(SCN)$_2$ [14] as well as for those of *Imt* and *MImt*.

For the remaining complexes the magnetic moments and electronic spectral data are consistent with six coordinate, tetragonal structures in the solid [5]. The extent of tetragonality among these complexes, as indicated by the Dq*xy* and D*t* parameters, increases in the sequence:

$$SCN^- < NO_3^- < ClO_4^- < BF_4^-$$

and is consistent with the relative positions of both ligand and anions in the spectrochemical series. The Dq*z* values decrease in essentially the same order.

In nitromethane the soluble complexes lose their apically coordinated anions and produce electronic spectra consistent with square-planar species. This contrasts with the corresponding Ni(*MImt*)$_4$X$_2$ complexes which exhibit tetragonal–tetrahedral structural equilibria in solution [4].

The character of these complexes is intermediate between those of the corresponding *Imt* and *MImt* complexes. The Dq*xy* values for the nitrate, perchlorate and tetrafluoroborate complexes of *DMImt* are slightly larger than those of *Imt* but not so large as to cause the d^8 system to spin-couple as in the case of the relevant *MImt* complexes.

Steric factors are probably responsible for the fact that the Ni(*DMImt*)$_4^{2+}$ ions adopt square-planar configurations in solution and do not undergo complex structural equilibria as has been observed for the corresponding *MImt* complexes as well as for some complexes of imidazolidine-2-thione (etu) [15]. This compares with substituted thiourea complexes where retention of solid-state tetragonal structures in solution is restricted to those ligands with very large substituents on the N-atoms [16].

The structures of the *DMImt* complexes in the solid are governed primarily by electronic factors. These limit the number of coordinated ligands to four, the balance between the σ-donor and π-acceptor properties of the ligand leaves a resultant positive charge on the Ni(II) ion which is balanced by rather long range apical contacts to the counter ions [17]. In contrast, the structures of the pseudo-tetrahedral halo complexes of *DMImt* [7] are determined by steric factors, which operate to give diminishing stability in the order tetrahedral > square-planar > octahedral (tetragonal), and also by the charge on the ion, which is lowered due to coordination by a halide ion [17].

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