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Octahedral Nickel(II) Dithiocarboxylates

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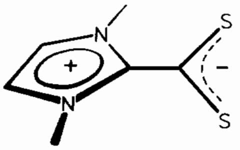
Abstract

Two nickel(II) complexes, NiL_2Cl_2 and $NiL_2(NO_3)_2 \cdot 0.3EtOH$, with the ligand 1,3-dimethylimidazoliumdithiocarboxyalato (L) have been synthesized and characterized by infrared and electronic spectroscopy and magnetic susceptibilities. The complexes exhibit the normal paramagnetism characteristic of octahedral nickel(II). The magnetic moments decrease with falling temperature, indicative of antiferromagnetic coupling, which is greater for the chloride than for the nitrate adduct. Columnar structures with chloro and nitrato bridging are proposed.

Introduction

Dithiocarboxylates have been less widely investigated as ligands than other well-known dithio anions such as xanthates, dithiocarbamates and dithiophosphates [1–7]. Several recent review articles [8–10] have discussed the variety of metal complexes prepared with the 1,1-dithiolato ligands. Nickel(II) complexes of dithiocarboxylates are of interest because they form perthio-carboxylate complexes which are 'sulfur-rich' and differ markedly, both in stereochemistry and electronic spectra, from the nickel complexes of other 1,1-dithiolato ligands [11].

We report the preparation and characterization of two octahedral nickel(II) complexes of the heterocyclic dithiocarboxylate zwitter ion, 1,3-dimethylimidazoliumdithiocarboxylate (I). This has a dithiocarboxylic group joined at the 2-position to an orthogonally oriented dimethylimidazolium cation.



I

Experimental

Preparation of Dichlorobis(1,3-dimethylimidazolium-dithiocarboxylato)nickel(II), NiL_2Cl_2

The ligand was prepared by the general procedure of Forkey and Keihl [12]. $[NEt_4]_2[NiCl_4]$ (0.345 g), prepared according to the procedures of Gill and Taylor [13], was refluxed with the ligand (0.637 g) in acetonitrile (50 ml) overnight. A black finely divided powder was collected by vacuum filtration. Melting point (m.p.) 248–249 °C. Conductivity: 49 ohm^{-1} cm^2 mol^{-1} for a 1×10^{-4} M aqueous solution. *Anal.* Calc. for $Ni(C_6H_8N_2S_2)_2Cl_2$: C, 30.57; H, 3.4; N, 11.8; S, 27.05; Cl, 14.97; Ni, 12.38. Found: C, 30.57; H, 3.5; N, 11.8; S, 27.15; Cl, 15.02; Ni, 12.29%. Refluxing anhydrous $NiCl_2$ (0.113 g) with the ligand (0.300 g) in acetonitrile gives the same product, as determined by the infrared spectrum, melting point and magnetic properties.

Preparation of Dinitrobis(1,3-dimethylimidazolium-dithiocarboxylato)nickel(II), $NiL_2(NO_3)_2$

Hydrated nickel(II) nitrate (0.169 g) was dissolved in 10 ml of triethyl orthoformate and heated. The ligand (0.2 g) was dissolved in 10 ml of acetonitrile and added to the hot metal ion solution. A black precipitate formed immediately and was collected by vacuum filtration. m.p. 167–168 °C. *Anal.* Calc. for $Ni(C_6H_8N_2S_2)_2(NO_3)_2 \cdot 0.3C_2H_5OH$: C, 27.97; H, 3.4; N, 15.5. Found: C, 27.86; H, 3.4; N, 15.2%.

Spectroscopy

All UV–Vis. spectra were taken on a Beckman model 25 spectrophotometer. All IR spectra were obtained on a Perkin-Elmer model 598 IR spectrophotometer. Solid samples were run from 300–4000 cm^{-1} as KBr pellets and from 200–400 cm^{-1} as mineral oil smears on polystyrene plates.

Electrical Conductivity

Electrical conductivity measurements were performed using a Chemtrix type 60A pH meter and Lazar Cond-156 conductivity probe.

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Magnetic Measurements

Magnetic susceptibilities (4–320 K) were measured on a SQUID magnetometer. The calibration and method of operation are as described elsewhere [14, 15].

Results and Discussion

There is precedent for polymeric structure in nickel(II) dithiocarboxylate (aryl and alkyl) complexes of Ni(II) [8–10]. Bonamico *et al.* [16] have reported a nickel–nickel bond in a bridging acetate-cage binuclear complex of bis(dithiophenylacetato)nickel(II). The two nickel atoms are in a square planar arrangement with a Ni–Ni distance of 2.56 Å. They have also reported the structure of the trimeric bis(dithiobenzoato)nickel(II) [17], which contains two types of planar nickel, A and B, with Ni–S bonds of 2.2 Å. Weak (Ni–S = 3.109 Å) bridging bonds make A a tetragonally very distorted octahedron. Type B nickel is pentacoordinate.

Pijovesona [11] concludes that Ni(II) dithio- and perthio-carboxylates are low spin nickel(II) chromophores, with the paramagnetism observed in some compounds resulting from ferromagnetic impurities. Pyridine adducts, however, such as $Ni(PhCSS)_2(py)_2$ (PhCSS = dithiobenzoates) are paramagnetic in solution, though no solid complexes have been isolated [18].

Recently several nickel–triad metal(II) derivatives of dithiocarboxylic acids, RCSSH, where R is an alkyl group, have been found to have a columnar structure [19]. Several of these compounds have been found to react with halogens. An example of this linear-chain type compound is $[Ni_2(CH_3CS_2)_4]I$, formed from the reaction of the binuclear dithiocarboxylate with iodine [20].

The ligand used in this study is a neutral zwitter ion. It forms metal complexes easily with the large soft acids such as Pt(II), Pd(II) and Au(I) [21], but nickel complexes are more difficult to obtain. Hydrated nickel salts could not be used for the synthesis in ordinary organic solvents; evidently water binds more tightly to the nickel than the sulfur donors of the zwitter ion. It was necessary to use $[NEt_4]_2[NiCl_4]$ to obtain anhydrous conditions in the presence of chloride, and triethyl orthoformate to remove water with nitrate ion. The triethyl orthoformate reaction also works with chloride, but was not used because of the risk of contamination of the product with the insoluble anhydrous nickel chloride.

TABLE I. Infrared Absorptions (cm^{-1}) for Ligand (L), NiL_2Cl_2 and $NiL_2(NO_3)_2$

Ligand (L)	NiL_2Cl_2	$NiL_2(NO_3)_2$	Band assignment
		1385s	NO_3^-
1240s	1240s	1240s	Ar-CSS
1100m	1090m(sh)	1100m(sh)	
1050–1070s,b	1050s,b	1050s,b	
1030(sh)	1030(sh)	1030(sh)	
900s	925m	930m	ν_aCSS
840s	885m	840w	ν_bCSS
750s	760–780m	760–780m,b	
740s	745m		
700s	700s	700s	

s = strong, m = medium, b = broad, sh = shoulder.

The infrared spectra of the two nickel complexes are compared to the ligand in Table I. The symmetric and assymmetric stretch of the CSS unit shifts relative to the ligand, indicating sulfur chelation to the metal. The UV–Vis. absorptions (Table II) are observed in similar regions in the complexes and the ligand, indicating that the ligand charge transfer bands are not strongly affected by chelation. The n-π* band at 520 nm in the dithiocarboxyl group is responsible for the red color of the ligand and its complexes.

Both complexes are paramagnetic, indicating octahedral nickel environments. Magnetic susceptibility and moment data are given for the two compounds from 10.9–320 K in Table III. The fact that the moment varies from 2.1 BM to 3.6 BM indicates an interaction between octahedral nickel atoms in NiL_2Cl_2. The data fails to conform to Heisenberg exchange dimer, trimer or other models containing small groups of nickel atoms. The data appears more like the values for a large group of nickel atoms; thus, strings of polymeric molecules are proposed. The moment for $NiL_2(NO_3)_2$ remains essentially constant with temperature. The moment of 2.54–2.88 BM denotes two unpaired electrons and a weaker antiferromagnetic interaction. Since the data is different for two compounds, polymerization through Ni–S bonding such as is observed in bis-

TABLE II. UV–Vis. Data (ν is in nm and log E_{mol} is given in parentheses)

	n-π*(CSS) [22]		π-π*(CSS)	π-π* (aromatic ring)
Ligand	523 (2.23)	434 (2.45)	360 (4.34)	271 (4.13)
NiL_2Cl_2	520 (2.66)	438(2.96)		267 (4.32)
$NiL_2(NO_3)_2$	520 (2.30)	435 (2.40)	358 (4.28)	268 (3.97)

TABLE III. Temperature Dependence of Effective Magnetic Moments (BM)

Temperature	NiL_2Cl_2 (μ)	$NiL_2(NO_3)_2$ (μ)
10.9	2.101	2.638
12.0	–	2.650
14.7	2.357	2.682
17.0	2.360	2.702
21.2	2.509	2.727
24.5	2.507	2.748
27.6	2.539	2.763
33.0	2.681	2.777
39.5	2.633	2.789
43.2	2.679	2.798
51.9	2.779	2.808
59.9	2.856	2.829
64.1	2.894	2.831
72.5	2.956	2.838
79.0	2.998	2.837
86.5	3.046	2.840
94.0	3.088	2.848
100.0	3.119	2.852
125.2	3.241	2.873
150.2	3.321	2.894
175.1	3.382	2.898
200.4	3.434	2.916
220.7	3.464	2.937
240.2	3.489	2.949
260.4	3.529	2.959
280.2	3.551	2.968
299.2	3.553	2.979

(dithiobenzoato)nickel(II) can be ruled out. Chloro bridging forming a columnar structure is postulated for NiL_2Cl_2, with $Ni_2L_2Cl^+$ cationic chains and Cl^- anions. The cationic chain is shown in Fig. 1. Due to potential steric interference, the dimethylimidazolium groups are not likely to retain their orientation orthogonal to the CS_2 groups of the parent ligand (I), nor are they required to be coplanar with NiS_4.

The solubility properties of the chloro complex also support an ionic polymer structure since the complex fails to dissolve in solvents which do not destroy it. Solvents which act as ligands and can compete successfully with the Cl and S donor atoms bring the complex into solution. The complex is soluble in water and gives a conductivity measurement of 49 ohm^{-1} cm^2 mol^{-1}. With time, the Ni–Cl bonds in the chain and the Ni–S bonds to the zwitter ion are broken and all ligands are replaced by H_2O and the ligand can be recovered in crystalline form from the solution. The polymer also comes apart in pyridine and in time, $[Ni(py)_6]^{+2}$ can be isolated from the solution thereby indicating that pyridine is also a better ligand than the dithiocarboxylate.

A similar structure is suggested for the nitrato complex. Bridging nitrato groups would be consistent with the absence of strong antiferromagnetic interaction and would also lead to weaker intermolecular bonds, thereby making it easier to bring the complex into solution.

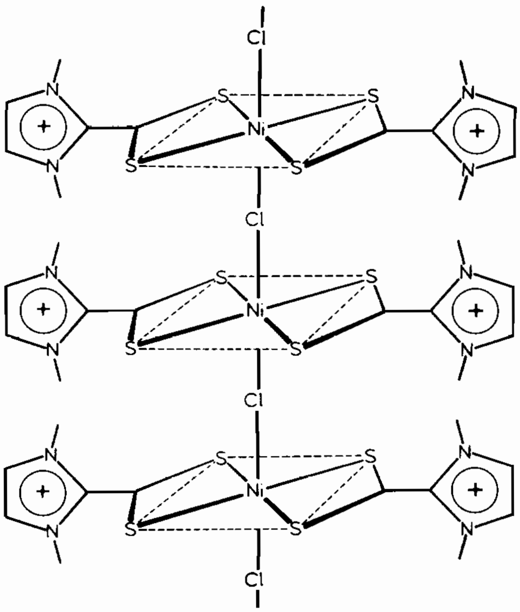

Fig. 1. Postulated structure of the $NiL_2Cl]^+$ cationic chain.

Although the infrared properties are useful in characterizing the complexes by determining the presence of ligand, they are not very informative on the intermolecular bonding. In general, νNi–Cl is expected to occur in the region 200–300 cm^{-1}. The Ni–Cl bond in $Ni(py)_4Cl_2$ is at 207 cm^{-1} and any Ni–Cl stretching frequency in an intermetallic bridging bond should be even lower, beyond the accessible frequency range [23]. It is not possible to distinguish monodentate, bidentate or bridging NO_3^- groups since only a split peak at 1385 cm^{-1} is observed. A separation of about 100 cm^{-1} is expected in unidentate coordination and about 200 cm^{-1} for bidentate bonding.

A further interesting anomaly is in the high temperature magnetism of the chloro complex in which the magnetic moment rises towards the rather large value of 3.6 BM. Such a large value would be characteristic for distorted tetrahedral nickel(II) which, however, is not compatible with the other properties of the complex nor with the general properties observed with such dithiochelate ligands. Given the rather large moment value for this complex, microanalysis was performed for every constituent element of the complex, which confirmed the formulation. The reproducibility of the moment was very closely confirmed by running another sample over the same temperature range. Zero-field splitting could cause a slight but not large elevation of the moment, while intramolecular ferromagnetism could have a similar effect. The latter model could contain antiferromagnetic coupling along chloride-bridged chains of binuclear Ni_2L_4 species. However, if the binuclear fragments were analogous to the literature Pt_2L_4 complexes, the nickel may well be low spin. In the absence of crystallographic data these possibilities cannot be explored further.

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