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The Preparation and Properties of some Substituted Pyridine Complexes of Chromium(II) Thiocyanate

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Abstract

The new chromium(II) complexes $[CrL_2(NCS)_2]$, where L = pyridine or 2-, 3- or 4-methylpyridine, have been prepared by the addition of an aqueous mixture of $CrBr_2$ and NH_4NCS to a solution of the pyridine. The diffuse reflectance and infrared spectra and the antiferromagnetic behaviour of the complexes suggest that they are thiocyanato-bridged linear polymers.

Introduction

Although thiocyanato complexes of the first-row transition metals generally are well documented [1], less is known about complexes of chromium(II). The preparation [2, 3] of $Na_3[Cr(NCS)_5]\cdot xH_2O$ has been confirmed and a number of tetrathiocyanatochromate(II) salts isolated [4], e.g. $[A]_2[Cr(NCS)_4]$, where A = NMe_4, NEt_4, NPr^n_4 or NBu^n_4. The NBu^n_4 salt has been obtained in two forms, one red–brown and magnetically-dilute, and the other blue and antiferromagnetic, and these have unusual structures. Single crystal X-ray investigations have shown that the red–brown polymorph contains planar $[Cr(NCS)_4]^{2-}$ ions, and the blue form dinuclear $[Cr_2(NCS)_8]^{4-}$ ions in which there are two –NCS– bridges and the metal ions are in approximate trigonal–bipyramidal coordination [5]. Some mixed ligand, thiocyanato–chromium(II) complexes are $[CrL_2(NCS)_2]$, L = 2,2′-bipyridyl or 1,10-phenanthroline [6], $[Cr(2\text{-methylimidazole})_2(NCS)_2]$ [7], $[CrL(NCS)]BPh_4$, L = (1-pyrazolylethyl)amine [8], (3,5-dimethyl-1-pyrazolylethyl)amine [9] or tetramethylcyclam [10] and the thiocyanato adducts of chromium(II) acetate and propionate [11]. In this paper the preparation and properties of another type of thiocyanato–chromium(II) complex $[CrL_2(NCS)_2]$, where L = pyridine (py) or 2-, 3- or 4-methylpyridine (mepy), are reported.

Results and Discussion

Since a simple chromium(II) thiocyanate cannot be isolated [4], the complexes (Table I) were prepared by the addition of an aqueous solution containing $CrBr_2\cdot 6H_2O$ and NH_4NCS in 1:2 molar ratio to a solution containing a stoichiometric quantity of the pyridine. Attempts to obtain products of the general formula $[CrL_4(NCS)_2]$ were unsuccessful (see 'Experimental').

The complexes exhibit antiferromagnetic behaviour. Their effective magnetic moments are below the spin-only value (4.90 BM for $3d^4$, high-spin) at room temperature and decrease still further as the temperature is lowered (Table II). The shapes of the reciprocal susceptibility *versus* absolute temperature plots are typical of antiferromagnetic behaviour, and can be reproduced (Fig. 1) by substitution of the values of the exchange integral J and g given in Table II in eqn. (1) which has been derived by Smith and Friedberg [12] to describe antiferromagnetic

TABLE I. Analyses[a] and Reflectance Spectra

Compound	Colour	C	H	N	Cr	Reflectance spectra (cm^{-1})	
$[Cr(py)_2(NCS)_2]\cdot H_2O$	greyish yellow	41.2(41.85)	3.06(3.51)	16.4(16.3)	15.1(15.1)	RT[b]	18000m,br 14800w
$[Cr(2\text{-mepy})_2(NCS)_2]$	greyish violet	47.4(47.4)	4.06(3.98)	15.4(15.8)	14.6(14.7)	RT	18200m,br
						LT	18500m,br 15500sh
$[Cr(3\text{-mepy})_2(NCS)_2]$	pale violet	46.9(47.4)	4.01(3.98)	15.4(15.8)	14.5(14.7)	RT	18200m,br
						LT	18600m,br
$[Cr(4\text{-mepy})_2(NCS)_2]$	greyish green	46.4(47.4)	3.95(3.98)	15.7(15.8)	14.5(14.7)	RT	17500m 14700sh 13000sh

[a] Calculated values in parentheses. [b] RT = room temperature, LT = liquid nitrogen temperature.

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TABLE II. Exchange integrals (J) and Temperature Variation of Molar Susceptibility (χ_A)[a] and Effective Magnetic Moment (μ_{eff})[b]

$[Cr(py)_2(NCS)_2]\cdot H_2O$ ($J = -9.55°$, $g = 2.03$)								
T (K)	295.0	262.5	230.0	198.5	166.5	135.5	103.5	89.5
$10^6\chi_A$ ($cm^3\ mol^{-1}$)	8093	8678	9708	10740	11730	13120	14660	15300
μ_{eff} (BM)	4.37	4.27	4.23	4.13	3.95	3.77	3.48	3.31
$[Cr(2\text{-mepy})_2(NCS)_2]$ ($J = -12.25°$, $g = 2.14$)								
T (K)	295.0	262.5	230.0	198.5	166.5	135.5	103.5	89.5
$10^6\chi_A$ ($cm^3\ mol^{-1}$)	8220	8826	9832	10720	11760	12810	13640	13650
μ_{eff} (BM)	4.40	4.30	4.25	4.13	3.96	3.73	3.36	3.13
$[Cr(3\text{-mepy})_2(NCS)_2]$ ($J = -7.45°$, $g = 1.97$)								
T (K)	293.0	262.5	230.0	198.5	166.5	135.5	103.5	89.5
$10^6\chi_A$ ($cm^3\ mol^{-1}$)	8133	8809	9725	10870	12330	13940	16190	16900
μ_{eff} (BM)	4.37	4.30	4.23	4.15	4.05	3.89	3.66	3.48
$[Cr(4\text{-mepy})_2(NCS)_2]$ ($J = -10.35°$, $g = 2.00$)								
T (K)	291.5	262.5	230.0	198.5	166.5	135.5	103.5	89.5
$10^6\chi_A$ ($cm^3\ mol^{-1}$)	7654	8274	9131	10040	11070	12360	13440	13900
μ_{eff} (BM)	4.22	4.17	4.10	3.99	3.84	3.66	3.34	3.15

[a] Corrected for diamagnetism: $[Cr(py)_2(NCS)_2]\cdot H_2O$, 173×10^{-6} $cm^3\ mol^{-1}$, $[Cr(mepy)_2(NCS)_2]$, 190×10^{-6} $cm^3\ mol^{-1}$, and for T.I.P. 100×10^{-6} $cm^3\ mol^{-1}$. [b] Calculated from $\mu_{eff} = 2.828\ (\chi_A T)^{1/2}$ BM.

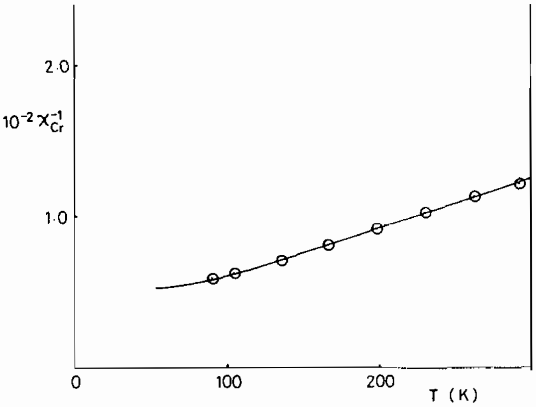

Fig. 1. Plot of reciprocal molar susceptibility χ_{Cr}^{-1} against absolute temperature for $[Cr(3\text{-mepy})_2(NCS)_2]$. The lines are calculated by substitution in eqn. (1) of the J and g values in Table II. The other complexes show similar behaviour.

interaction in a linear chain of paramagnetic atoms. From the shapes of the $1/\chi_{Cr}$ *versus* T plots there are Neel points near 60 K, below the limit of our measurements.

$$\chi_A(T) = \frac{Ng^2\mu_B S(S+1)}{3kT} \times \frac{1+u(K)}{1-u(K)} \qquad (1)$$

$u(K) = \coth K - (1/K)$; $K = 2JS(S+1)/kT$; for high spin chromium(II) $S = 2$

The antiferromagnetic behaviour of the complexes $[CrL_2(NCS)_2]$ suggests that they are polymers containing bridging thiocyanate groups. The analogous complexes $[Co(py)_2(NCS)_2]$ and $[Cu(py)_2(NCS)_2]$ have been reported [13] to have a pseudo octahedral coordination geometry with linear NCS bridges. In $[Cu(py)_2(NCS)_2]$ the coordination sphere bond distances are Cu–N = 2.10 Cu–N(py) = 2.12, and Cu–S = 3.00 Å. The angle $M\text{–}\hat{N}CS$ is approximately 160° and $M\text{–}\hat{S}CN$ is about 140°. Since copper(II) and high-spin chromium(II) are both subject to Jahn–Teller distortion, and frequently form complexes with the same structure, the X-ray powder diffraction patterns of the complexes $[ML_2(NCS)_2]$, M = Cr, Cu, L = py, 3-mepy have been obtained (Table III). The similarities in the d-spacings, particularly for the pyridine complexes, suggest that the structures are similar, if not isomorphous.

Electronic and Infrared Spectra

The electronic spectra of six coordinate chromium(II) complexes frequently consist of one band ascribed, in D_{4h} symmetry, to superimposed $^5B_{1g} \rightarrow {}^5B_{2g}$ and $^5B_{1g} \rightarrow {}^5E_g$ transitions, and a weaker band at lower wave number assigned to the $^5B_{1g} \rightarrow {}^5A_{1g}$ transition. In some complexes both bands merge to give one very broad band asymmetric to low wave number. The diffuse reflectance spectra (Table I) follow the general pattern, indicative of six coordinate Cr(II), but the spectra (and colours) differ more than might be expected for this series of apparently similar complexes. It is assumed that packing requirements of the pyridines and the thiocyanato ligands cause considerable variation in the detailed

TABLE III. X-ray Powder Diffraction Data

$[Cr(py)_2(NCS)_2]$ d_{hkl} (A)	$[Cu(py)_2(NCS)_2]$ d_{hkl} (A)	$[Cr(3\text{-}mepy)_2(NCS)_2]$ d_{hkl} (A)	$[Cu(3\text{-}mepy)_2(NCS)_2]$ d_{hkl} (A)
7.07vs	7.07vs	8.89w	9.12w
5.21vs	5.24s	7.55vs	7.69vw
5.03vs	4.98s	5.46m	5.45s
4.22vs	4.21s		5.13w
4.07vs	4.02vs	4.56m	4.61m
	3.83vs	4.34m	4.35m
	3.72m		4.19m
3.62vs	3.59s	4.10m	4.03s
3.38w	3.39w	3.87m	3.90w
3.23w		3.70s	3.69w
3.04m	3.07m	3.48m	3.48m
2.86s	2.93s	3.21s	3.21s
2.77vw	2.84vw	3.07m	3.10s
2.66s	2.72s	2.90m	2.90m
	2.62w	2.48m	2.47s
	2.49w	2.07vw	2.06w
2.43m	2.40m	1.91vw	1.94m
2.38w	2.34m	1.83vw	1.83vw
2.26vw	2.28m	1.80vw	1.79vw

TABLE IV. Infrared Absorptions (cm^{-1}) of Thiocyanato Groups

Compound	ν(C–N)	2δ(CNS)	ν(C–S)	δ(NCS)	ν(Cr–NCS)	ν(Cr–py)
$[Cr(py)_2(CNS)_2]\cdot H_2O$	2100sh 2078vs,br 2045sh	967m 953w 945w	823m	490m	387m,br 343m,br	298m
$[Cr(2\text{-}mepy)_2(CNS)_2]$	2100s,sp 2070s,br	960w,br	834w (800w)[a]	480sh (470s)[a]	(390s)[a] 345s,br	280s
$[Cr(3\text{-}mepy)_2(CNS)_2]$	2085s,br 2045sh	950w,br	820s (794s)[a]	(486sh)[a] (482s) (475s)	352m 343s	294s
$[Cr(4\text{-}mepy)_2(CNS)_2]$	2090vs,br	(960w)[a]	(806s)[a] (814s)[a]	(500s)[a] 488m 480sh	370s 346s	296s 285sh

[a] Assignments uncertain because of what may be pyridine absorptions shown in parentheses.

structure. The position of the stronger band at *ca.* 18000 cm^{-1} suggests that as in the structure of $[Cu(py)_2(NCS)_2]$ the 2S atoms are in *trans* positions along the elongated distortion axis.

The infrared spectra are similar to those of the corresponding copper(II) complexes except in the 400–200 cm^{-1} region where metal–ligand vibrations are found. In general the bands of the chromium(II) complexes are about 30 cm^{-1} to higher wave number compared with the copper(II) complexes as might be expected from the presence of a lighter metal atom. The assignment of ν(Cr–py) vibrations to bands near 290 cm^{-1} (Table IV) agrees with the similar assignments for the halide complexes $[Cr(mepy)_2X_2]$, X = Cl, Br [14]. The ν(Cr–NCS) vibrations are assigned to bands in the 390–340 cm^{-1} region. The assignments are consistent with recent results obtained on ^{15}N-substituted $[Cu(py)_2(NCS)_2]$ [15]. The absorptions of the NCS^- group can provide information [1] about whether it is terminal N- or terminal S-bonded, or bridging, but the ranges assigned to the various vibrations in the different coordination modes overlap. However, the breadth and position of the ν(C–N) bands in particular are consistent with bridging thiocyanate.

Experimental

Chromium(II) bromide hexahydrate was prepared by dissolving the metal in acid [16]. The pyridines (Aldrich) were used as received, but they, and all solvents, were deoxygenated before use. Owing to their air-sensitivity all chromium(II) complexes were handled in the absence of air. Physical measurements were carried out as before [4].

Preparation of Complexes

To prepare dithiocyanatobis(2-methylpyridine)-chromium(II) a solution containing chromium(II) thiocyanate was first prepared by mixing aqueous solutions of chromium(II) bromide hexahydrate (2.58 g, 0.0081 moles; 25 cm^3) and ammonium thiocyanate (1.23 g, 0.0162 moles; 25 cm^3). The deep blue solution (the solution decomposes on standing) was then added slowly with shaking to 2-methylpyridine (1.50 g, 0.0161 moles) dissolved in water (20 cm^3). The violet solid which separated was filtered off, washed with water, and recrystallized from warm 75% methanol.

Similar molar quantities were used in the preparation of the other three complexes, minor differences in procedure being that the amines were dissolved in 25% ethanol and the products recrystallized from aqueous acetone. Analyses are in Table I.

Needle-like crystals were formed when $[Cr(3\text{-}mepy)_2(CNS)_2]$ was crystallized slowly from acetone. Unfortunately, they were unsuitable for single crystal X-ray investigation.

Attempts were made to prepare complexes of the general formula $[CrL_4(CNS)_2]$ by the addition of the deep blue chromium(II) thiocyanate solution dropwise to a large excess of a solution of the amine. With pyridine, 2-methyl-, and 3-methyl-pyridine, complexes $[CrL_2(CNS)_2]$ were always obtained, even when neat amine was used. With 4-methylpyridine, a brown precipitate, probably the tetra-amine complex, was formed. However, when washed or during drying, it easily lost amine to give a green product apparently mainly the bis(amine) complex.

The copper(II) complexes $[Cu(py)_2(CNS)_2]$ and $[Cu(3\text{-}mepy)_2(CNS)_2]$ were prepared as described [17] for the former.

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