Chromium(II) Chemistry. Part 13.[1] Thiocyanates

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Chromium(II) forms the pentathiocyanatochromate(II), $Na_3[Cr(CNS)_5]\cdot9H_2O$, which from magnetic, diffuse-reflectance, and i.r. data contains a square-pyramidal arrangement of *N*-bonded thiocyanates. Attempts to prepare similar salts of other metal cations have been unsuccessful, and organic cations give a series of tetrathiocyanatochromates(II), $[A]_2[Cr(CNS)_4]$ [A = NMe_4, NEt_4, NPr^n_4, NBu^n_4, Hhex, Hpy, $\frac{1}{2}H_2en$, or $\frac{1}{2}H_2L$; hex = hexamine (hexamethylenetetramine), py = pyridine, en = ethylenediamine, and L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene]. In general these complexes show antiferromagnetic behaviour, and are believed to have thiocyanato-bridged structures. Monoethanol adducts of the $[NEt_4]^+$ and $[NPr^n_4]^+$ salts have also been isolated, and found to be magnetically normal. The $[NBu^n_4]^+$ salt is isolated in two forms, one brown and magnetically normal, and the other blue and antiferromagnetic.

THIOCYANATO-COMPLEXES of later metals of the first transition series are well known,[2] and where thiocyanate is the only ligand the stoicheiometry of the complex anion is usually $[M(NCS)_4]^{2-}$ or $[M(NCS)_6]^{3-}$. Few investigations of chromium(II) thiocyanates have been reported. Sand and Burger[3] believed that tetrathiocyanates such as $[NH_4]_2[Cr(CNS)_4]$ were present in solutions of chromium(II) chloride to which ammonium thiocyanate in amyl alcohol had been added. However, Koppel[4] isolated the dark blue, highly air-sensitive, pentathiocyanate $Na_3[Cr(CNS)_5]\cdot11H_2O$ from aqueous solution containing sodium thiocyanate in excess, and Asmussen[5] obtained a value of 4.77 B.M.† at 291 K for its magnetic moment. Hume and Stone[6] found a magnetic moment of 4.90 B.M. for aqueous chromium(II) chloride containing an excess of potassium thiocyanate, and Barbieri and Tettamanzi[7] isolated a chromium(II) thiocyanate formulated as $Cr(CNS)_2\cdot2\,hex\cdot2HCNS$; hex is hexamine (hexamethylenetetramine), $C_6H_{12}N_4$.

The chromium(II)–thiocyanate system has been reinvestigated because of the unusual pentathiocyanato- and hexamine compounds, and to confirm that it is not possible to isolate complexes of uranium(III) as the hexathiocyanatochromate(III) salts[8] because of reduction[9] of the anion by uranium(III) to chromium(II) thiocyanate species.

RESULTS AND DISCUSSION

Pentathiocyanates.—The unique[2] pentathiocyanato-formulation of the sodium salt has been confirmed, but elemental analyses do not establish the precise degree of hydration (Table 1), and on thermal analysis the compound lost hydrogen sulphide as well as water. An acetone adduct $Na_3[Cr(CNS)_5]\cdot CH_3COCH_3\cdot6H_2O$ has been obtained but no ammonium, potassium, caesium, or barium salts could be isolated, and the use of large organic cations produced tetrathiocyanates (see below).

All investigations of $Na_3[Cr(CNS)_5]\cdot9H_2O$ were carried out on freshly prepared solids or solutions because of slow decomposition (see Experimental section). The effective magnetic moment (Table 1) is 4.5 B.M., somewhat below the value of 4.9 B.M. expected for high-spin chromium(II); the low value could arise because of the considerable uncertainty in the degree of hydration, *e.g.* if it were a decahydrate the moment would be 4.6 B.M., and because of slight decomposition, although none was apparent. However, since the compound obeys the Curie law over the temperature range studied, the magnetic data establish that the compound is unlikely to be polymeric. This is confirmed by the i.r. spectrum (Table 2) which shows that no bridging or *S*-bonded but only *N*-bonded thiocyanate is present. The CS stretching frequency is well within the range[2] ascribed to *N*-bonding, and, in confirmation, the CN stretching absorption is below 2 100 cm^{-1} and broad and asymmetric. There are no bands assignable to unco-ordinated NCS^-; thus a possible structure is a square-pyramidal arrangement of isothiocyanato-groups with the remaining octahedral position occupied by a water molecule. The presence of two absorption bands in the region where the water deformation occurs, with the higher-frequency band (1 673 cm^{-1}) of lesser intensity, suggests that co-ordinated and lattice water may be present.

The broad, asymmetric, reflectance band (Table 3), which was resolved at liquid-nitrogen temperature into a band with a lower-frequency shoulder, is typical of distorted octahedral chromium(II). The main band has a frequency between those[10] of $[Cr(en)_3]Br_2$ (15 700 cm^{-1}, en = ethylenediamine) and $[Cr(en)_2Br_2]$ (17 900 cm^{-1}), and similar to that of $[Cr(NH_3)_5]I_2$ (17 600 cm^{-1}),[11] as would be expected if *N*-bonded thiocyanate were present. The high frequency of the shoulder (the distortion band) suggests considerable distortion from octahedral symmetry in agreement with the structure proposed above. The complex $[CrCl\{N(CH_2CH_2NMe_2)_3\}]Cl$ is trigonal bipyramidal,[12] but it absorbs at a much lower frequency than the pentaisothiocyanate. The complexes $Cr(thiourea)_4Br_2$ and $Cr(thiourea)_6I_2$, which contain *S*-bonded thiourea, have[13] main bands much lower in frequency at *ca.* 13 000 cm^{-1} so this confirms that the thiocyanate ions are *N*-bonded.

The *X*-ray powder pattern of $Na_3[Cr(NCS)_5]\cdot9H_2O$ can be indexed in terms of a tetragonal unit cell (a = 8.20, c = 12.2 Å).

In ethanol and in aqueous solution the shoulder in the electronic spectrum was no longer resolved and the main

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† Throughout this paper: 1 B.M. ≈ 9.27×10^{-24} A m^2; 1 Oe ≃ 79.58 A m^{-1}.

TABLE 1

Analyses and magnetic data

Complex [a] and colour	Analysis (%) [b]							
	C	H	N	Cr	T/K	$\mu_{eff.}$[c]/ B.M.	θ[c]/°	χ_L[c]
$Na_3[Cr(NCS)_5]\cdot 9H_2O$	10.5 (10.5)	2.5 (3.1)	12.2 (11.7)	8.9 (9.1)	295 90	4.5 [d] 4.5	0	292
$Na_3[Cr(CNS)_5]\cdot CH_3COCH_3\cdot 6H_2O$	16.6 (16.6)	2.3 (3.1)	12.3 (12.1)	8.8 (9.0)	295 90	4.31 3.55	77	299
$[H_2en][Cr(CNS)_4]$ grey-blue	20.8 (20.8)	3.1 (2.9)	23.5 (24.3)	15.3 (15.0)	295 90	4.24 3.36	80 [e]	222
$[Hhex]_2[Cr(CNS)_4]$ blue	33.6 (33.9)	4.7 (4.6)	29.1 (29.7)	9.2 (9.2)	295 90	4.75 4.75	0	357
$[Hhex]_2[Cr(CNS)_4]\cdot EtOH$ blue	35.9 (35.3)	5.1 (5.3)	27.3 (27.4)	8.4 (8.5)	295 90	4.74 3.92	70	391
$[H_2L][Cr(CNS)_4]$ [f] blue	41.3 (42.4)	6.0 (6.05)	19.6 (19.8)	9.0 (9.2)	295 90	4.29 3.27	90 [e]	317
$[Hpy]_2[Cr(CNS)_4]$ green-brown	36.9 (37.8)	2.7 (2.7)	18.7 (18.9)	11.65 (11.7)	295 90	3.78 3.36	35	213
$[NMe_4]_2[Cr(CNS)_4]$ pale blue	33.2 (33.3)	5.7 (5.6)	19.1 (19.4)	12.0 (12.0)	295 90	3.81 2.98	90 [e,g]	254
$[NEt_4]_2[Cr(CNS)_4]$ mauve	44.0 (44.1)	7.3 (7.2)	15.3 (15.4)	9.5 (9.5)	295 90	4.38 3.91	38	348
$[NEt_4]_2[Cr(CNS)_4]\cdot EtOH$ blue	44.4 (44.7)	8.0 (7.85)	14.4 (14.3)	8.8 (8.8)	295 90	4.63 4.63	0	383
$[NPr^n{}_4]_2[Cr(CNS)_4]$	50.75 (51.2)	8.8 (8.6)	12.7 (12.8)	7.9 (7.9)	295 90	4.47 3.47	82	443
$[NPr^n{}_4]_2[Cr(CNS)_4]\cdot EtOH$ mauve	51.2 (51.25)	9.05 (8.9)	11.85 (11.95)	7.4 (7.4)	295 90	4.69 4.66	0	477
$[NBu^n{}_4]_2[Cr(CNS)_4]$ brown	55.8 (56.2)	9.5 (9.4)	10.8 (10.9)	6.75 (6.8)	295 90	4.76 [g] 4.75	0	538
blue	56.0 (56.2)	9.5 (9.4)	10.9 (10.9)	6.7 (6.8)	295 90	4.30 [g] 3.36	90 [e]	538

[a] Complexes soon become dark grey in air except $[Hhex]_2[Cr(CNS)_4]$ which is stable when dry. [b] Calculated percentages in parentheses. [c] Calculated from $\mu_{eff.} = 2.828\,(\chi_A T)^{\frac{1}{2}}$ and Curie–Weiss law $\chi_A{}^{-1} \alpha (T + \theta)$; $10^{-6}\chi_L$ is the diamagnetic correction in cm^3 mol^{-1}. [d] Calculated assuming $9H_2O$; analyses do not precisely fix degree of hydration. [e] Obtained by extrapolation of upper linear part of Curie–Weiss plot. [f] L = $C_{16}H_{32}N_4$ macrocycle. [g] Magnetic moments in solution: $[NMe_4]^+$, 4.8 B.M.; brown $[NBu^n{}_4]^+$, 4.90 B.M.; blue $[NBu^n{}_4]^+$, 5.1 B.M.

TABLE 2

Infrared absorptions (cm^{-1}) of thiocyanato-groups

Compound	ν(CN)	ν(CS)	2 × δ(NCS)	δ(NCS)	ν(MN)
$Na_3[Cr(NCS)_5]\cdot 9H_2O$ [a]	2 085vs, vb	810w	960w, b	480vw	327m
$Na_3[Cr(CNS)_5]\cdot 6H_2O$ (acetone adduct)	2 118s, sh 2 085vs	810m 724m	960w 940w	480w 420 (sh)	335m
$[H_2en][Cr(CNS)_4]$	2 118vs, b 2 070 (sh)	(800w) (770s)	958w 945w	482s 469m	(343s) [b]
$[Hhex]_2[Cr(CNS)_4]$	2 090vs, b 2 050 (sh)	(786m) [b] (830vs) [820 (sh)] (848s)	(978s) [970 (sh)]	479m	330m, b 366vw
$[Hhex]_2[Cr(CNS)_4]\cdot EtOH$	2 080vs, b 2 050 (sh)	(814s) (782w)	(958s)	485m	345m, vb
$[H_2L][Cr(CNS)_4]$	2 130 (sh) 2 115s 2 105vs 2 075vs	(815m) [800 (sh)]	(938m)	478m	342m, b
$[Hpy]_2[Cr(CNS)_4]$	[2 120 (sh)] 2 050vs, vb	810vw	(965w, b)	485m	370s 330s
$[NMe_4]_2[Cr(CNS)_4]$	2 095vs, vb	810w 793vw	(965vw) (951s) (942vs)	480w 472w	367w 333m
$[NEt_4]_2[Cr(CNS)_4]$	2 080vs, vb	(780s, b) (722m)	965m 950m	482m	365s 345s
$[NEt_4]_2[Cr(CNS)_4]\cdot EtOH$	2 080vs, b	(790s, b)	972m 958m	487m	365m 345 (sh)
$[NPr^n{}_4]_2[Cr(CNS)_4]$	2 115s, sp 2 075vs, b	808m 795 (sh)	945 (sh)	479m	(322s, b)
$[NPr^n{}_4]_2[Cr(CNS)_4]\cdot EtOH$	2 060vs, vb	826m	(968s)	482m	(355m, b)
$[NBu^n{}_4]_2[Cr(CNS)_4]$ brown	2 075vs, b	(832m) (800 m) (773w)	965m	488m	355s, vb
blue	2 126vs, sp 2 090 (sh) 2 070vs, b	812m [790 (sh)]	955m 970m	480m	364m 326m

[a] Water absorptions: $\nu(OH_2)$ at 3 580s, 3 420vs, vb, and 3 200vw (sh); $\delta(OH_2)$ at 1 673m and 1 610s, b cm^{-1}. [b] Assignments of bands shown in parentheses are uncertain because counter-ion absorptions occur in the same regions.

bands were at lower frequency: 15 300 ($\varepsilon = 41$ cm^2 mol^{-1}) and 15 200 cm^{-1} respectively, the bathochromic shift suggesting some solvolysis. In agreement, the addition of an excess of sodium thiocyanate increased the absorption frequencies respectively to 16 700 and 16 600 cm^{-1}, close to the reflectance value. The spectrum of the ethanolic solution was similar to that[9] of the solution obtained from the reaction of $[NH_4][UCl_4]\cdot5H_2O$ with $K_3[Cr(NCS)_6]$, thus confirming that reduction of the hexathiocyanatochromate(III) by the uranium(III) had occurred, so it is unlikely that uranium(III) salts of the chromate(III) anion can be isolated in spite of a report[8] to this effect.

TABLE 3

Reflectance and solution spectra (cm^{-1})

Compound	Reflectance bands	Solution bands[a]
$Na_3[Cr(NCS)_5]\cdot9H_2O$ normal high-spin	16 800vb, 17 200sb,[c] 13 500 (sh)	15 300 (41),[b] 15 200[d]
$[H_2en][Cr(CNS)_4]$	17 700mb	
$[Hhex]_2[Cr(CNS)_4]$ normal high-spin	16 800sb, 12 000m	
$[Hhex]_2[Cr(CNS)_4]\cdot EtOH$	17 000vb, 17 400sb,[c] 16 600 (sh)	
$[H_2L][Cr(CNS)_4]$	15 000vb	
$[Hpy]_2[Cr(CNS)_4]$	17 400mb	
$[NMe_4]_2[Cr(CNS)_4]$	16 700mb	17 700 (52), 16 900 (sh), 16 500,[b] 15 400 (sh)
$[NEt_4]_2[Cr(CNS)_4]$	18 000mb	17 900 (52), 16 800 (sh)
$[NEt_4]_2[Cr(CNS)_4]\cdot EtOH$ normal high-spin	17 000mb	16 700 (48), 15 200 (sh)
$[NPr^n{}_4]_2[Cr(CNS)_4]$	15 800s	18 000 (60), 16 800 (sh)
$[NPr^n{}_4]_2[Cr(CNS)_4]\cdot EtOH$ normal high-spin	19 200s	17 800 (70), 16 800 (sh)
$[NBu^n{}_4]_2[Cr(CNS)_4]$ brown normal high-spin	18 000mb, 15 000 (sh)	17 500 (66), 16 600 (sh)
blue	14 500s	17 900 (82), 16 800 (sh)

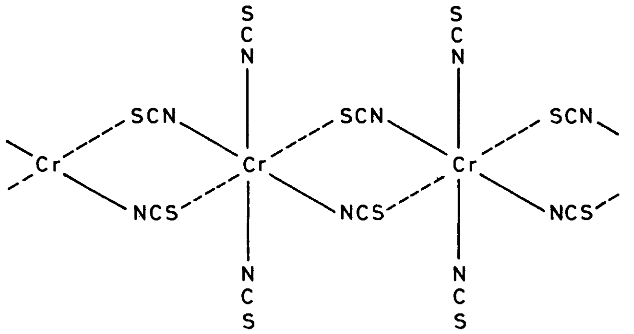
[a] The solvent was acetone unless otherwise stated. Absorption coefficients (cm^2 mol^{-1}) are given in parentheses. [b] Ethanol. [c] Reflectance spectra were recorded at room and liquid-nitrogen temperature, and only for these complexes was there increased resolution on cooling. [d] Water.

The acetone adduct (Table 1) has a magnetic moment well below the spin-only value which decreased still further as the temperature was lowered, and the compound obeyed the Curie–Weiss law with $\theta = 77°$. The reflectance spectrum was very similar to that of $Na_3[Cr(NCS)_5]\cdot9H_2O$, indicating a similar environment for the chromium(II) ion, but a shoulder at 2 118 cm^{-1} on the strong, broad, ν(CN) absorption at 2 085 cm^{-1} suggests[2] that *S*-bonded, probably bridging, as well as *N*-bonded, thiocyanato-groups are present. This, and the antiferromagnetic behaviour, indicate polymerisation of the thiocyanato-anions in the solid.

Tetrathiocyanates.—During an attempt to prepare chromium(II) complexes of the Curtis[14] macrocycle $C_{16}H_{32}N_4$ (L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene) the macrocycle dihydrobromide was added to an aqueous solution containing chromium(II) bromide and ammonium thiocyanate. The tetrathiocyanate $[H_2L][Cr(CNS)_4]$ crystallised, and this led to the preparation of the hexamine compound,[7] now more accurately formulated as a hexaminium salt, $[Hhex]_2[Cr(CNS)_4]$, and an ethylenediamine (en) salt, $[H_2en][Cr(CNS)_4]$, and similar salts of singly charged substituted ammonium cations (Table 1). These represent a new class of chromium(II) complex. Ammonium thiocyanate in excess (see Experimental section) did not give penta- or hexa-thiocyanates; tetrathiocyanates always separated, although the ion $[Cr(NCS)_6]^{4-}$ is said[15] to exist in molten potassium thiocyanate.

Magnetic behaviour. Several tetrathiocyanatochromate(II) salts (Table 1) were isolated in two forms dependent on the experimental procedure: $[NBu^n{}_4]^+$, brown or blue; and, with or without ethanol, $[Hhex]^+$ $[NEt_4]^+$, and $[NPr^n{}_4]^+$. One of each pair of complexes, and all the complexes which were obtained in one form only, were antiferromagnetic since their effective magnetic moments (Table 1) at room temperature were well below the spin-only value, decreasing still further as the temperature was lowered. They obeyed the Curie–Weiss law over the range 150—300 K, and the majority showed upward curvature of the $1/\chi_A$ plots below 150 K, indicating that Néel points lie not far below liquid-nitrogen temperature.

The antiferromagnetic behaviour could arise because of interaction between chromium(II) ions bridged by thiocyanate as in (I) in which long bonds are shown to S atoms of thiocyanato-bridges. Electronic and i.r. spectra (see below) are compatible with this type of structure. The magnetic data (Table 4), except for the $[Hpy]^+$ and $[NMe_4]^+$ salts, could be fitted to Smith and Friedberg's expression[16] for antiferromagnetic interaction in an infinite linear chain by substitution of the values of *J* and *g* given in Table 5. Examples of the fits are given in the Figure. It is not known why the data for the $[Hpy]^+$ and $[NMe_4]^+$ salts could not be fitted satisfactorily.



(I)

Surprisingly, the complexes $[Hhex]_2[Cr(CNS)_4]$,

$[NEt_4]_2[Cr(CNS)_4]\cdot EtOH$, $[NPr^n_4]_2[Cr(CNS)_4]\cdot EtOH$, and brown $[NBu^n_4]_2[Cr(CNS)_4]$ were not antiferromagnetic; their magnetic moments, although somewhat below the spin-only value, did not vary with temperature ($\theta = 0°$). The magnetically dilute behaviour of $[Hhex]_2[Cr(CNS)_4]$, crystallised from water, is probably due to the absence of bridging thiocyanates. The hexaminium ion has three unprotonated tertiary amine groups through which it could weakly co-ordinate. A tetragonal configuration of four equatorial thiocyanate and two axial hexaminium ions is consistent with the stoicheiometry and the magnetic behaviour. Recrystallisation from ethanol produced antiferromagnetic $[Hhex]_2[Cr(CNS)_4]\cdot EtOH$ which presumably has a thiocyanato-bridged structure. On the other hand the ethanolates of the $[NEt_4]^+$ and $[NPr^n_4]^+$ salts are magnetically normal. This may be because co-ordination of EtOH produces $[Cr(NCS)_4\cdot EtOH]^{2-}$ anions, or the bridging system is modified by its presence so that the magnetic interaction is not possible.

TABLE 4

Variation with absolute temperature of atomic susceptibilities (c.g.s. units) and magnetic moments (B.M.) of the antiferromagnetic complexes

$[NMe_4]_2[Cr(CNS)_4]$								
T	297.5	262.5	230.0	198.5	166.5	135.5	103.5	89.5
$10^6\chi_A$	6 097	6 728	7 359	8 161	9 115	10 204	11 792	12 439
$\mu_{eff.}$	3.81	3.76	3.70	3.60	3.48	3.33	3.12	2.98
$[NEt_4]_2[Cr(CNS)_4]$								
T	295.0	262.5	230.0	198.5	166.5	135.5	103.5	89.5
$10^6\chi_A$	8 133	8 899	10 230	11 320	13 320	15 440	19 040	21 340
$\mu_{eff.}$	4.38	4.32	4.34	4.24	4.21	4.09	3.97	3.91
$[NPr^n_4][Cr(CNS)_4]$								
T	295.0	262.5	230.0	198.5	166.5	135.5	103.5	89.5
$10^6\chi_A$	8 453	9 132	10 210	11 330	12 770	14 250	16 100	16 640
$\mu_{eff.}$	4.47	4.38	4.34	4.24	4.12	3.93	3.65	3.45
$[NBu^n_4]_2[Cr(CNS)_4]$								
T	293.5	263.0	230.0	198.5	166.5	135.5	103.5	89.5
$10^6\chi_A$	7 851	8 706	9 451	10 580	11 800	13 180	14 750	15 760
$\mu_{eff.}$	4.29	4.28	4.17	4.10	3.96	3.78	3.49	3.36
$[Hhex]_2[Cr(CNS)_4]\cdot EtOH$								
T	291.5	262.5	230.0	198.5	166.5	135.5	103.5	89.5
$10^6\chi_A$	9 451	10 110	11 440	12 690	14 460	16 620	17 780	21 450
$\mu_{eff.}$	4.69	4.65	4.59	4.49	4.39	4.24	4.06	3.92
$[H_2L][Cr(CNS)_4]$								
T	295.0	262.5	230.0	198.5	166.5	135.5	103.5	89.5
$10^6\chi_A$	7 816	8 519	9 456	10 420	11 600	12 900	14 030	14 880
$\mu_{eff.}$	4.29	4.23	4.17	4.07	3.93	3.74	3.41	3.26
$[H_2en][Cr(CNS)_4]$								
T	293.0	262.5	230.0	198.5	166.5	135.5	103.5	89.5
$10^6\chi_A$	7 606	8 321	9 189	10 171	11 496	13 022	14 895	15 703
$\mu_{eff.}$	4.23	4.81	4.11	4.02	3.91	3.76	3.51	3.35
$[Hpy]_2[Cr(CNS)_4]$								
T	295.5	262.5	230.0	198.5	166.5	135.5	103.5	89.5
$10^6\chi_A$	6 046	6 815	7 599	8 645	9 995	11 748	14 084	15 798
$\mu_{eff.}$	3.78	3.78	3.74	3.70	3.65	3.57	3.41	3.36

TABLE 5

Exchange integrals (J) for antiferromagnetic linear chain (ref. 16)

Compound	J/cm^{-1}	g
$[NEt_4]_2[Cr(CNS)_4]$	3.80	1.93
$[NPr^n_4]_2[Cr(CNS)_4]$	5.56	2.03
$[NBu^n_4]_2[Cr(CNS)_4]$	5.60	1.96
$[H_2L][Cr(CNS)_4]$	6.12	1.98
$[Hhex][Cr(CNS)_4]\cdot EtOH$	3.34	2.02
$[H_2en][Cr(CNS)_4]$	5.91	1.96

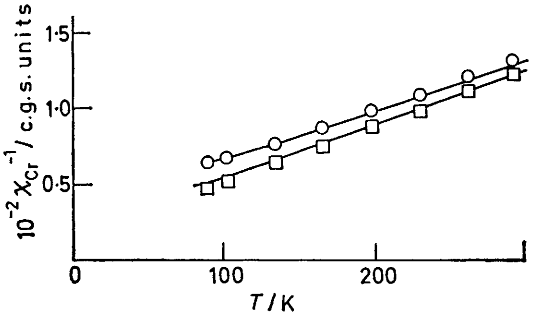
The magnetically dilute, brown complex $[NBu^n_4]_2$-$[Cr(CNS)_4]$ cannot contain tetrahedral anions since a first-order orbital contribution to the magnetic moment would be expected giving rise to a temperature-dependent moment greater than the spin-only value at room temperature. The reflectance spectrum is that of a highly distorted, six-co-ordinate, chromium(II) compound. It is thus suggested that this complex is bridged, but with greater bridging dimensions than in the blue form.

Dissolved in acetone, both $[NBu^n_4]^+$ salts, and the $[NMe_4]^+$ salt, gave high-spin magnetic moments (Table 1, footnote *g*), indicating that the reduced moments of the solids arise from intermolecular antiferromagnetism.

Infrared spectra. Thiocyanate absorptions (Table 2) have been assigned by comparison with the spectra of the cation halides. The bands corresponding to the stretching vibration, ν(CN), are very broad and often complex, with sharp components above 2 100 cm^{-1} in some cases. There is also considerable variation in spite of the identical stoicheiometry of the anions, and, since there is considerable overlap of the ranges characteristic [2] of ν(CN) vibrations of *N*-bonded, *S*-bonded, and bridging thiocyanate, identification of the bonding mode is difficult. The position, complexity, and breadth of the bands suggest that bridging and *N*-bonded thiocyanate groups are present.

The deformation band, δ(NCS), was found in the range 470—490 cm^{-1}, which would be expected for *N*-bonded and bridged thiocyanate. Unfortunately, counter-ion absorptions confuse the regions where the ν(CS) stretching vibration and the δ(NCS) overtone occur, although where assignments are possible they suggest *N*-bonded and bridging thiocyanate. Two bands (or one broad one) in the range 320—370 cm^{-1} have been assigned to ν(Cr–NCS) vibrations.

Electronic spectra. Since the ^5D ground term of chromium(II) is split in a weak octahedral field into upper $^5T_{2g}$ and lower ^5E_g terms one spin-allowed transition is expected. However, because of the orbital degeneracy of the ^5E_g term, the spectra of chromium(II) compounds, even with six identical ligands, consist of a main band, usually of greater intensity, and a weaker distortion band or shoulder at lower frequency. In some cases, where the axial field is weak because of ligand inequivalence, as in $[Cr(en)_2I_2]$,[10] the distortion band merges with the main band to give one very broad band asymmetric to low frequencies. The main band is ascribed (D_{4h} symmetry) to superimposed $^5B_{1g} \rightarrow {}^5B_{2g}$ and $^5B_{1g} \rightarrow {}^5E_g$ transitions, and the distortion band to the $^5B_{1g} \rightarrow {}^5A_{1g}$ transition. The diffuse-reflectance spectra (Table 3) fall into this general pattern, but there are greater variations than would be expected among anionic complexes of the same stoicheiometry. For example, in the series of chloride-bridged complexes, $M_2[CrCl_4]$ (M = NH_4, K, Rb, or Cs), the main and distortion bands were found[17] in the narrow ranges 10 900—11 000 and 7 500—8 000 cm^{-1} respectively.



Temperature variation of calculated (——) and experimental reciprocal molar susceptibilities of $[NEt_4]_2[Cr(CNS)_4]$ (O) and $[H_2en][Cr(CNS)_4]$ (□)

It is difficult to see any pattern in the spectra of the $[Cr(CNS)_4]^{2-}$ salts, particularly because most spectra consist of one very broad band asymmetric to low frequencies, and no better resolution was obtained at liquid-nitrogen temperature. However, the spectrum of $[Hhex]_2[Cr(CNS)_4]$ contains a main band at 16 800 cm^{-1} and a distortion band at 12 000 cm^{-1}; this is consistent with a tetragonal arrangement of four *N*-bonded thiocyanate ions and weak axial co-ordination of two hexaminium ions, and would explain the magnetically dilute behaviour. The antiferromagnetic ethanol adduct has one reflectance band (with a shoulder resolved at liquid-nitrogen temperature), and possibly substitution of S atoms of thiocyanate bridges for axial hexaminium ions to give structure (I) has increased the distortion and caused the distortion band to merge with the main band. The spectra of the magnetically dilute ethanol adducts of the $[NEt_4]^+$ and $[NPr^n{}_4]^+$ salts also contain one band although the absorption maxima are at very different frequencies, 17 000 and 19 200 cm^{-1} respectively. Possibly, in the former complex the ethanol is co-ordinated to give a square-pyramidal anion $[Cr(CNS)_4(HOEt)]^{2-}$, while in the latter, with a spectrum indicating still greater distortion, the anions are essentially planar. The brown high-spin $[NBu^n{}_4]^+$ salt does not contain ethanol, and its spectrum, with the main band at 18 000 cm^{-1} and the distortion band as a shoulder at 15 000 cm^{-1}, indicates considerable distortion. It is possible that the complex has a chain structure like (I), but the steric requirements of the bulky counter ions located between the chains lead to Cr–S distances too large to permit antiferromagnetic behaviour.

The remaining salts are all antiferromagnetic, with one broad reflectance band, and structures like (I) are suggested for those with band maxima near 17 000 cm^{-1} or higher. However, the complexes $[NPr^n{}_4]_2[Cr(CNS)_4]$ and blue $[NBu^n{}_4]_2[Cr(CNS)_4]$ have reflectance bands at such low frequency compared to the other complexes that terminal *S*-bonded thiocyanate may be present, or N atoms of the bridges may lie along the elongated tetragonal axis to reduce the net ligand field.

Unfortunately, no detailed *X*-ray structural data are available for these or related copper(II) complexes. The *d* spacings of $[NEt_4]_2[Cu(CNS)_4]$[18] and $[NEt_4]_2[Cr(CNS)_4]$ are similar, although not identical, so that the complexes are likely to have the same general structure. The copper(II) ion is believed,[18] from spectroscopic studies, to be surrounded by 4 N and 2 S atoms, *i.e.* it contains bridging thiocyanate, but with weaker bridges than in $[NMe_4]_2[Ni(CNS)_4]$. With large counter ions, copper(II) forms tetrahedral thiocyanato-anions,[18] but this has not been found with chromium(II) The powder photograph of the blue form of $[NBu^n{}_4]_2[Cr(CNS)_4]$ showed little resemblance to that of the brown form, confirming the considerable structural differences adduced from other evidence.

Dissolved in acetone, the $[NMe_4]^+$, $[NEt_4]^+$, $[NPr^n{}_4]^+$, and $[NBu^n{}_4]^+$ salts gave similar spectra (Table 3) indicating that the same species, presumably $[Cr(CNS)_4]^{2-}$ with axially co-ordinated solvent molecules, was present. However, the spectrum of the ethanol adduct of the $[NEt_4]^+$ salt in acetone was similar to its diffuse-reflectance spectrum, and the main band was at a frequency approaching that of a saturated solution of the $[NMe_4]^+$ salt in ethanol. This agrees with the suggestion that ethanol is co-ordinated in the magnetically normal $[NEt_4]^+$ salt. The molar absorption coefficients are accurate only to 5—10% because of the difficulties in handling these highly air-sensitive solutions, but they are too low for tetrahedral anions to be present in solution and are of the order found for six-co-ordinate chromium(II) complexes, *e.g.* for[19] $[Cr(dien)_2]I_2$ (dien = diethylenetriamine), $\varepsilon = 19$ cm^2 mol^{-1}.

EXPERIMENTAL

Preparation of $Na_3[Cr(NCS)_5]\cdot9H_2O$.—Chromium(II) chloride tetrahydrate (3.05 g) in water (7 cm^3) was added under nitrogen to a saturated solution of sodium thiocyanate monohydrate in excess (18 g, 25 cm^3). The deep blue solution was cooled in ice and the beautiful deep lilac-blue needles which separated were filtered off as soon as possible because the aqueous solution became dark green in a few hours, even under nitrogen.

The crystals were then washed with a very small amount of cold ethanol in which they are highly soluble, and dried on the pump for several hours. The compound is hygroscopic and air-sensitive, and in sealed tubes darkens in a few weeks. It is very soluble in acetone and ethyl acetate, solutions in organic solvents being much more stable than those in water. When the compound was dissolved in acetone, the solution filtered, and the solvent removed completely, pale blue, hygroscopic, and air-sensitive crystals of a monoacetone *adduct* were obtained. The carbonyl stretching frequency of acetone was lowered to 1 690 cm^{-1} in the complex.

Deep blue solutions were obtained when potassium, ammonium, or barium thiocyanates were used as above, but no crystals separated on cooling or on the addition of ethanol, and after a few hours or on concentration the solutions decomposed. When saturated aqueous lithium chloride was added to the deep blue aqueous solution containing an excess of ammonium thiocyanate, and the mixture was cooled in ice, pale violet crystals separated. They were contaminated with lithium and/or ammonium salts since extraction with acetone left a white residue. Chromium analysis of the soluble portion corresponded approximately to $Li_3[Cr(CNS)_5]$, but because of the difficulty in obtaining this material no further investigations were carried out.

Preparation of Tetrathiocyanates.—An aqueous solution of chromium(II) bromide hexahydrate (1.60 g, 15 cm^3) in water was treated under nitrogen with an aqueous solution of ammonium thiocyanate (1.52 g, 15 cm^3; 1 : 1 mol ratio). To the very deep blue solution was added an aqueous solution (2.20 g, 25 cm^3; 1 : 1 mol ratio) of the Curtis[14] macrocycle dihydrobromide dihydrate $L\cdot2HBr\cdot2H_2O$ in which $L = C_{16}H_{32}N_4$. A bright blue precipitate of the *complex* $[H_2L][Cr(CNS)_4]$ formed immediately. This was filtered off, washed with water, and dried *in vacuo*.

A similar procedure with ethylenediamine dihydrochloride gave a pale blue product which left a white residue of ammonium chloride when treated with acetone or ethanol. The blue product was too soluble to be extensively washed with water to remove the ammonium chloride. Thus, to prepare the *complex* $[H_2en][Cr(CNS)_4]$, the barium sulphate obtained when an equivalent amount of aqueous barium thiocyanate (2.53 g, 20 cm^3) was added to aqueous chromium(II) sulphate pentahydrate (2.38 g, 20 cm^3) was filtered off as quickly as possible, and the resulting solution of chromium(II) thiocyanate treated with aqueous ethylenediammonium dithiocyanate (1.78 g, 20 cm^3). The pale blue solid which separated was filtered off, washed with a little ice-cold water, and dried. The ethylenediammonium dithiocyanate was prepared by crystallisation from an aqueous solution of ethylenediamine to which dilute hydrochloric acid and then ammonium thiocyanate had been added in 1 : 2 mol ratio.

The pyridinium, $[NMe_4]^+$, $[NEt_4]^+$, $[NPr^n_4]^+$, and hexaminium (Hhex = $C_6H_{13}N_4$) *tetrathiocyanatochromates*(II) were prepared from aqueous solution analogously to $[H_2L][Cr(CNS)_4]$, except that the last was prepared from the hexaminium thiocyanate and not the bromide. The blue *ethanolates* $[NEt_4]_2[Cr(CNS)_4]\cdot EtOH$, $[NPr^n_4]_2[Cr(CNS)_4]\cdot EtOH$, and $[Hhex]_2[Cr(CNS)_4]\cdot EtOH$ were obtained when the aqueous products were recrystallised from warm 96% ethanol. The dark purple complex $[NPr^n_4]_2[Cr(CNS)_4]\cdot EtOH$ lost ethanol under reduced pressure at 40 °C forming the blue unsolvated complex. The other complexes lose ethanol less readily.

The tetrabutylammonium salt $[NBu^n_4]_2[Cr(CNS)_4]$ can be obtained in brown and blue forms. When aqueous $[NBu^n_4]Br$ was added to an aqueous solution of chromium(II) bromide and ammonium thiocyanate a sticky blue precipitate separated immediately. After a few minutes the solid started turning brown and the change was complete after 10—15 min. The brown solid was then shaken from the sides of the flask, filtered off, and washed with small portions of water. It was then dissolved in a minimum of absolute ethanol, and left to stand. *Crystals* of the brown form of $[NBu^n_4]_2[Cr(CNS)_4]$ separated from the blue solution after a few hours. To obtain the blue form chromium(II) sulphate was used instead of the bromide, and the mother-liquor was quickly decanted from the sticky blue solid before it could change completely to brown. The solid was quickly washed twice with water by decantation, dissolved in 96% ethanol, and left to crystallise. Blue *crystals* separated slowly. If crystallisation took place too quickly brown crystals appeared but these reverted to the blue form on standing. Preparations from chromium(II) sulphate or iodide almost invariably gave the blue form, but attempts to obtain this from the chloride or bromide were unsuccessful. This behaviour is not understood.

The tetrathiocyanatochromates(II) show different solubility behaviour from the pentaisothiocyanate. They are insoluble in water, almost insoluble in ethanol, and very soluble in acetone. In general, they are stable under nitrogen. With the exception of the ethanol-free hexaminium salt, which seemed unchanged after some months, the complexes quickly turn dark grey in air.

Attempts to isolate a simple chromium(II) thiocyanate were unsuccessful. On concentration under reduced pressure or on standing the deep blue solutions obtained from chromium(II) salts and ammonium or barium thiocyanates became dark green and hydrogen sulphide was evolved.

The complexes $[NEt_4]_2[Cu(CNS)_4]$ and $[NEt_4][Co(NCS)_4]$ were obtained by the methods of Forster and Goodgame.[18]

Analyses and Physical Measurements.—To determine chromium the sodium salts were dissolved in water, nitric acid added, and the solution boiled until it became dark green. The chromium was precipitated as the hydroxide by the addition of concentrated ammonia until the solution was alkaline to Methyl Red. The hydroxide was then filtered off and ignited to Cr_2O_3. All other complexes were ignited directly to Cr_2O_3.

Magnetic measurements on solids were carried out by the Gouy method from room to liquid-nitrogen temperature on samples sealed *in vacuo* in Pyrex tubes. The apparatus, calibrated with $Hg[Co(NCS)_4]$, was supplied by Newport Instruments, Newport Pagnell, Bucks. The Evans method[20] was used to determine the magnetic susceptibility of complexes dissolved in acetone. The solutions were prepared under nitrogen from redistilled acetone. Reflectance spectra were recorded on a Unicam SP 700C spectrophotometer provided with a SP 735 diffuse-reflectance attachment and a lithium fluoride reference. Solution spectra were recorded on a Beckman Acta MIV spectrophotometer. The samples were sealed in cells under nitrogen. Infrared spectra of Nujol mulls (KBr discs) made up in a nitrogen bag were recorded on a Perkin-Elmer 577 spectrophotometer.

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