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Complexes of Chromium(II) Halides with Thiourea and Substituted Thioureas

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The new chromium(II) complexes: $CrCl_2 \cdot 2tu$, its acetone adduct, $CrBr_4 \cdot 4tu$, $CrI_2 \cdot 6tu$; $CrCl_2 \cdot 2etu$, $CrBr_2 \cdot 5etu$, $CrI_2 \cdot 4etu$; $CrCl_2 \cdot dctu$, $CrBr_2 \cdot 5dctu$, and $CrI_2 \cdot 6dctu$, where tu, etu, and dctu are respectively thiourea, N,N'-ethylenethiourea, and N,N'-dicyclohexylthiourea, have been isolated from a weakly-donating solvent mixture. The chlorides are antiferromagnetic and are believed to be linear polymers. The other complexes are high-spin and magnetically-dilute.

Introduction

No complexes of chromium(II) with neutral sulphur-donor ligands have been reported. Chromium(II) is expected, from its position in the Periodic Table, to show predominantly Class a behaviour, and most known complexes are of O- and N-donor ligands. However, we have found that complexes of chromium(II) halides and thiourea (tu), N,N'-ethylenethiourea (etu), and N,N'-dicyclohexylthiourea (dctu) can be isolated from a weakly-donating solvent mixture [1] of acetone and small amounts of 2,2-dimethoxypropane and methanol. The new complexes (Table I) are: $CrCl_2 \cdot 2tu$ and its mono-acetone adduct, $CrBr_2 \cdot 4tu$, $CrI_2 \cdot 6tu$, $CrCl_2 \cdot 2etu$, $CrBr_2 \cdot 5etu$, $CrI_2 \cdot 4etu$; $CrCl_2 \cdot dctu$, $CrBr_2 \cdot 5dctu$, and $CrI_2 \cdot 6dctu$. The magnetic behaviour down to liquid nitrogen temperature and some spectroscopic properties of these complexes are reported.

Experimental

All manipulations of chromium(II) compounds were carried out under nitrogen or in vacuum. Physical measurements were carried out as before [2].

Attempts to isolate complexes of chromium(II) halides [3] with thioureas from water, dimethylformamide, and the lower alcohols were unsuccessful because these solvents are more powerful donors than the thioureas. Anhydrous chromium(II) chloride was prepared by the reaction between hydrogen chloride and anhydrous chromium(II) acetate in diethyl ether [4], and by thermal dehydration of $CrCl_2 \cdot 4H_2O$, but it was insoluble in weak donor solvents such as acetone and ethyl acetate and so was not suitable for reactions with the thioureas. It was then found that hydrated chromium(II) bromide and iodide dissolve readily in a mixture of acetone and just more than sufficient 2,2-dimethoxypropane to react with all the water of hydration to give methanol and acetone. When $CrCl_2 \cdot 4H_2O$ was similarly treated it was found necessary to add extra methanol (10 cm^3) to dissolve all the $CrCl_2 \cdot 4H_2O$ (prepared from 3 g of the metal) in 150 cm^3 of solution. These halide solutions are referred to as 'acetone' solutions in the preparations described below, but they contain variable and small amounts of methanol which did not prevent the isolation of the complexes of thioureas. The weights of chromium(II) halide recorded in the preparations refer to the weight of hydrated halide from which the 'acetone' solution was prepared. The complexes were obtained in good yield.

To prepare $CrCl_2 \cdot 2tu$ a suspension of thiourea in acetone (2.5 g, 30 cm^3) was added to an 'acetone' solution of chromium(II) chloride (3.4 g). After shaking, the yellow-green solid (the mono-acetone adduct) which separated was filtered off, washed with acetone, and dried by pumping on it at room temperature for two hours, and at 130 °C for a further five hours. The dry solid was bright yellow, and it turned brown almost instantaneously on exposure to air. The yellow-green mono-acetone adduct was obtained by drying at room temperature. Its infra-red spectra contained bands at 1675 cm^{-1} (s) and 1240 cm^{-1} (m) assigned to the ν(CO) and coupled ν(CO) and ν(CC) vibrations of acetone.

The complexes $CrBr_2 \cdot 4tu$ and $CrI_2 \cdot 6tu$ were similarly prepared, but it was necessary to concentrate the solution and add ethyl acetate in excess to induce crystallisation.

The complex $CrCl_2 \cdot 2etu$ was prepared as follows. A suspension of N,N'-ethylenethiourea (3.1 g in 30 cm^3) was added to an 'acetone' solution of chromium(II) chloride (3.0 g). A very pale blue solid separated. The mixture was boiled for 10 minutes and then cooled. The solid was filtered off, washed with acetone, and dried by pumping on it for three hours at room temperature and at 90 °C for one hour. The bromide $CrBr_2{\cdot}5etu$ and the iodide $CrI_2{\cdot}4etu$ were prepared similarly.

In the preparation of $CrBr_2{\cdot}5dctu$ a suspension of N,N′-dicyclohexylthiourea (5.5 g in 30 cm^3) was added to an 'acetone' solution prepared from 3.8 g of $CrBr_2{\cdot}6H_2O$. The mixture was shaken until all the substituted thiourea dissolved, and a few minutes later a light green, feathery solid began to separate. When the separation appeared complete, the solid was filtered off, washed with acetone and dried for several hours at room temperature. The chloride $CrCl_2{\cdot}dctu$ and the iodide $CrI_2{\cdot}6dctu$ were similarly prepared except that the reaction mixture was boiled for 5–10 minutes and the solids were dried at 100–120 °C.

Attempts were made to prepare bis-, tetrakis- and hexakis-thiourea complexes with each halide, but only one complex of each thiourea and halide could be isolated. The complexes of chromium(II) bromide with five molecules of N,N′-ethylene-thiourea or N,N′-dicyclohexylthiourea separated even from solutions containing 2 mol of the substituted thiourea per mole of chromium(II) bromide. Attempts to isolate complexes of N,N′-di-n-butylthiourea were also unsuccessful, possibly because this ligand is much more soluble than the other thioureas.

Results and Discussion

Magnetism

The bromides and iodides have effective magnetic moments μ_{eff} (Table I) which are essentially temperature-independent and close to the spin-only value for four unpaired electrons (4.90 E.M.) as expected for high-spin chromium(II). They obeyed the Curie law ($\theta \simeq 0$) and are therefore magnetically dilute. This magnetic behaviour and their spectroscopic properties described below show that these complexes are monomeric. Complexes $CrBr_2{\cdot}4tu$ and $CrI_2{\cdot}4etu$ are presumably *trans*-octahedral like other metal(II) complexes [5] of this stoichiometry but no X-ray data are available. The chloro-complexes, on the other hand, are antiferromagnetic. They have magnetic moments (Tables I and II) below the spin-only value at room temperature which decreased still further as the temperature was lowered. The Curie–Weiss law was obeyed at high temperatures by $CrCl_2{\cdot}2tu$ and

TABLE I. Analytical and Magnetic Data.

Compound	Analyses[a]				T/K	μ_{eff}[b]/B.M.	θ/°	$10^6\chi_L^b$
	C	H	N	Cr				
$CrCl_2{\cdot}2tu$	8.6(8.7)	2.9(2.9)	19.9(20.4)	19.1(18.9)	295	4.49	23[c]	130
yellow					90	3.94		
$CrCl_2{\cdot}2tu{\cdot}CH_3COCH_3$	17.9(18.0)	4.3(4.2)	16.9(16.8)	15.5(15.6)	295	4.41	96[c]	165
yellow-green					90	3.38		
$CrBr_2{\cdot}4tu$	9.4(9.3)	3.1(3.1)	22.2(21.7)	10.1(10.1)	295	4.86	0	237
light blue					90	4.89		
$CrI_2{\cdot}6tu$	9.6(9.5)	3.0(3.2)	21.9(22.0)	7.1(6.8)	295	4.97	0	353
blue-green					90	4.97		
$CrCl_2{\cdot}2etu$	21.9(22.0)	3.7(3.7)	16.7(17.1)	16.1(15.9)	295	4.33	[d]	167
light blue					90	3.16		
$CrBr_2{\cdot}5etu$	24.7(24.9)	4.2(4.2)	18.8(19.4)	7.2(7.2)	295	4.75	0	370
blue-green					90	4.75		
$CrI_2{\cdot}4etu$	20.5(20.2)	3.4(3.4)	15.9(15.7)	7.4(7.3)	295	4.87	0	341
light green					90	4.89		
$CrCl_2{\cdot}dctu$	42.8(43.0)	6.9(6.7)	7.7(7.7)	14.5(14.3)	295	3.83	[d]	220
yellow					90	2.45		
$CrBr_2{\cdot}5dctu$	54.9(55.2)	8.8(8.5)	9.6(9.9)	3.7(3.7)	295	4.74	0	934
light green					90	4.77		
$CrI_2{\cdot}6dctu$	53.3(53.6)	8.5(8.3)	9.3(9.6)	2.8(3.0)	295	4.77	0	1140
yellow green					90	4.76		

[a] Calculated values in parentheses. [b] Calculated from $\mu_{eff} = 2.828\,(\chi_A T)^{1/2}$ B.M., χ_L is diamagnetic correction (c.g.s.). [c] The Curie–Weiss law was taken as $\chi_A^{-1} \alpha (T + \theta)$, and as the χ_A^{-1} *versus* T graph showed upward curvature at low temperatures θ was obtained from the linear high temperature part of the graph. [d] The Curie–Weiss law was not obeyed over the temperature range available.

TABLE II. Exchange Integrals (J) and Temperature Variation of Magnetic Properties of Chloro-complexes.

$CrCl_2 \cdot 2tu$ (J = 3.26 cm^{-1}, g = 1.96)								
T(K)	294.5	262.5	230.0	198.5	166.5	136.0		
$10^6\chi_A$ (c.g.s.)	8535	9344	10620	12040	13990	16330		
μ_{eff}(B.M.)	4.49	4.43	4.42	4.38	4.32	4.22		
T(K)	104.0	89.5						
$10^6\chi_A$ (c.g.s.)	19660	21640						
μ_{eff}(B.M.)	4.05	3.94						
$CrCl_2 \cdot 2tu \cdot CH_3COCH_3$ (J = 6.19 cm^{-1}, g = 2.03)								
T(K)	295.0	262.8	230.0	198.5	166.5	135.0	103.5	89.5
$10^6\chi_A$ (c.g.s.)	8251	8966	9861	10900	12160	13570	15240	15960
μ_{eff}(B.M.)	4.41	4.34	4.26	4.16	4.02	3.83	3.55	3.38
$CrCl_2 \cdot 2etu$ (J = 7.70 cm^{-1}, g = 2.07)								
T(K)	295.0	262.5	230.5	198.5	166.5	136.0	104.0	89.5
$10^6\chi_A$ (c.g.s.)	7937	8662	9492	10460	11530	12630	13710	13980
μ_{eff}(B.M.)	4.33	4.27	4.18	4.08	3.92	3.71	3.38	3.16
$CrCl_2 \cdot dctu$ (J = 12.5 cm^{-1}, g = 1.99)								
T(K)	294.5	262.5	230.0	198.5	166.5	135.0	104.0	89.5
$10^6\chi_A$ (c.g.s.)	6221	6595	7029	7444	7838	8178	8334	8294
μ_{eff}(B.M.)	3.83	3.73	3.60	3.44	3.23	2.98	2.64	2.44

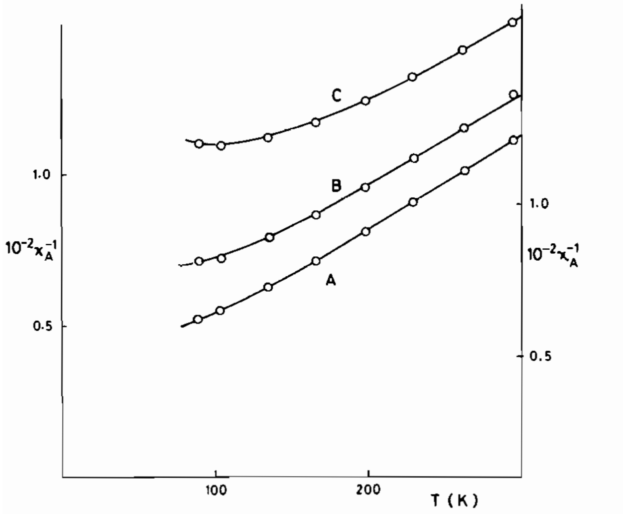

Fig. 1. Plots of reciprocal molar susceptibility χ_A^{-1} against absolute temperature for $CrCl_2 \cdot 2tu \cdot CH_3COCH_3$(A), $CrCl_2 \cdot 2etu$(B), and $CrCl_2 \cdot dctu$(C). The scale at the left hand side applies to B. The lines are calculated by substitution in equation (1) of the J and g values in Table II.

$CrCl_2 \cdot 2tu \cdot CH_3COCH_3$, but there was upward curvature of the χ_A^{-1} *versus* T graph at low temperatures (Fig. 1). The complexes $CrCl_2 \cdot dctu$ and $CrCl_2 \cdot 2etu$ did not obey the Curie–Weiss law over the temperature range studied: the former has a broad Néel point at 100 K, and the latter appears to have a Néel point just below the lower limit of the magnetic measurements (Fig. 1). Thus the chlorides have bridged structures, perhaps analogous to those of the pyridine halides [2], which lead to the antiferromagnetic interaction. Presumably the failure to isolate complexes of the type $CrX_2 \cdot 2$thiourea when X is bromide or iodide reflects the weaker bridging ability of these halides.

The antiferromagnetic behaviour of the chlorides can be reproduced (Fig. 1) by substitution of the values of J (exchange integral) and g given in Table II in equation (1):

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

where u(K) = cothK – (1/K) and K = 2JS(S + 1)/kT. Equation (1) has been derived by Smith and Friedberg [6] to describe antiferromagnetic interaction in a linear chain of paramagnetic metal ions.

Electronic and Infrared Spectra

The diffuse reflectance spectra (Table III) generally consist of a main band in the range 11000 to 14000 cm^{-1}, (ν_2) and a less intense band or shoulder (ν_1) at lower frequency. This is the usual pattern [2] of bands for distorted six coordinate, high-spin chromium(II) complexes. The main band is assigned, in D_{4h} symmetry, to superimposed transitions $^5B_{1g} \rightarrow {}^5B_{2g}$, $^5E_g(\nu_2)$ and the weaker band to the transition

TABLE III. Reflectance Spectra.

					$\bar{\nu}$/cm^{-1}	
					ν_2	ν_1
$CrCl_2 \cdot 2tu$[a]	RT[b]		17150vw	14950vw	11600s	8000msh
	LT		17000vw	14950vw	11700s	7400m
$CrCl_2 \cdot 2tu \cdot CH_3COCH_3$	RT		17800vw		11900s	8400msh
	LT		17800vw		12500s	8300m
					11800sh	
$CrCl_2 \cdot 2etu$	RT	21400vw	17600vw		11400s	
			17200vw			
	LT	21200vw	17600vw		11600s	9000msh
		20100vw	17150w			
			16700vw			
$CrCl_2 \cdot dctu$	RT		18200vw	15300vw	11000s	6700m
	LT		18200vw	15300vw	11400s	6700m
			17300vw			
$CrBr_2 \cdot 4tu$	RT				12200s	8000msh
	LT				14000ssh	9000msh
					12600s	
					11400s	
$CrBr_2 \cdot 5etu$	RT				13900s	11000msh
	LT		17200vw		14500s	9800msh
					11000m	
$CrBr_2 \cdot 5dctu$	RT		19800vw		12800s	9600msh
	LT		19800vw		13000s	10200msh
$CrI_2 \cdot 6tu$	RT	22600vw	20200w		13300vs	
			19200vw			
	LT	22500vw	20200w		13600vs	11200msh
			19200w			
$CrI_2 \cdot 4etu$	RT	21000w	17400vw		11400vs	
	LT	20700w	17200w		11700vs	10200vs
$CrI_2 \cdot 6dctu$	RT				14000m	
					11600msh	
	LT				14300m	6000w
					11800w	

[a] All complexes have strong absorption in the region of 30000 cm^{-1}. [b] RT = room temperature, LT = liquid nitrogen temperature.

$^5B_{1g} \rightarrow {}^5A_{1g}(\nu_1)$. In the spectra of $CrCl_2 \cdot 2tu \cdot CH_3COCH_3$, $CrBr_2 \cdot 5etu$ and $CrI_2 \cdot 6dctu$ at liquid nitrogen temperature the ν_2 band appears to be resolved into two components, and in the low temperature spectrum of $CrBr_2 \cdot 4tu$ there are three strong bands indicating some splitting of the E_g term. The weak bands to higher frequency than ν_2 are presumably due to spin forbidden absorptions.

The position of the main band ν_2 is an approximate indication of the ligand field splitting 10Dq, and since ν_2 is well below the values found for analogous complexes of N-donor ligands [$Cr(mepy)_4X_2$ [2], $\nu_2 \simeq 17000$ cm^{-1}; $Cr(NH_3)_4(OH_2)SO_4$ [7], $\nu_2 \simeq 18000$ cm^{-1}, and $Cr(mepy)_2X_2$, $\nu_2 \simeq 14500$ cm^{-1}, where mepy is 3- or 4-methyl-pyridine and X is halide] the thioureas are acting as S-donors rather than N-donors. Coordination through nitrogen would also be expected to decrease the N–H stretching frequencies of the complexes relative to the free ligands, but only minor differences were found in the 3300 cm^{-1} region, arising from changes in the degree of hydrogen bonding.

The complexes $CrBr_2 \cdot 5etu$ and $CrBr_2 \cdot 5dctu$ may be five coordinate. Their reflectance spectra indicate considerable distortion but do not establish the coordination number or stereochemistry. A suitable solvent could not be found for conductance measurements. The far infrared spectra (400–70 cm^{-1}) of these complexes did not contain any prominent bands which were not also present in the free ligand, thus no bands which could be assigned to ν(Cr–Br) could be found, but this is not conclusive.

The far infrared spectra (400–250 cm^{-1}) of the chlorides contained bands at 320 cm^{-1} ($CrCl_2 \cdot 2tu$ and $CrCl_2 \cdot 2etu$) and 315 cm^{-1} ($CrCl_2 \cdot dctu$) which can be assigned to Cr–Cl stretching vibrations. The chloride-bridged, linear polymers $Cr(mepy)_2Cl_2$ absorb in the same region [2].

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