

Complexes of Chromium(II) with Some Neutral Oxygen-Donor Ligands

L. F. LARKWORTHY and M. H. O. NELSON-RICHARDSON

The Joseph Kenyon Laboratory, University of Surrey, Guildford, GU2 5XH, U.K.

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Some chromium(II) complexes of urea (ur), methylurea (mur), and biuret (bi) have been isolated. These are $\text{Cr(ur)}_4\text{X}_2$, $\text{Cr(mur)}_4\text{X}_2$, where $\text{X} = \text{Cl}$ or Br , $\text{Cr(bi)}_2\text{Cl}_2$, and $\text{Cr(ur)}_2\text{Cl}_2$. All except the last compound, which is antiferromagnetic and halide-bridged, are high-spin. The reflectance spectra indicate trans-octahedral structures, with oxygen coordination which is confirmed by the infrared spectra. The far infrared spectra are complicated by ligand absorptions but, where the chloride and bromide were available, no halide-dependent bands were detected near 300 cm^{-1} and this suggests that the halide ions are along the elongated tetragonal axis. X-ray powder data show that $\text{Cr(bi)}_2\text{Cl}_2$ is isomorphous with $\text{Cu(bi)}_2\text{Cl}_2$ which is known to have a trans structure with "long" Cu–Cl bonds and oxygen-donor biuret.

Introduction

Known complexes of chromium(II) with neutral oxygen-donor ligands are the hydrated salts [1], and various complexes of some phosphine oxides [2], triphenylarsine oxide [3], dimethylsulphoxide [4], and tetrahydrofuran [5]. The preparation and investigation of complexes of bivalent chromium with the neutral oxygen-donor ligands urea (ur), N-methylurea (mur), and biuret (bi) are reported here.

Results and Discussion

Magnetism

The magnetic results are shown in Tables I and II. The tetrakis (urea) complexes and $\text{Cr(bi)}_2\text{Cl}_2$ obeyed the Curie law over the temperature range investigated, and have temperature-independent magnetic moments slightly below the spin-only value (4.90 B.M.) for high-spin chromium(II). The absence of antiferromagnetic interaction suggests that the complexes are monomeric and, in agreement with the formulae, six-coordinate. Biuret is presumably bidentate in $\text{Cr(bi)}_2\text{Cl}_2$.

Dichlorobis(urea) chromium(II) has a room temperature magnetic moment (Table II) below the spin-

only value which decreased with decreasing temperature, but the Curie–Weiss law was not obeyed. The graph showing the variation of the reciprocal of the atomic susceptibility with temperature curves upwards at low temperature typical of a compound in which antiferromagnetic interaction is present. This compound is therefore likely to have a chloride-bridged polymeric structure.

Reflectance Spectra

The reflectance spectra are shown in Table I. The spectra of all the urea, methylurea and biuret complexes resemble those usually found for tetragonally distorted chromium(II) compounds [6]. At low temperatures two or even three bands are resolved in some of the spectra, indicating that lower symmetry fields than tetragonal (D_{4h}) may be present. Several of these compounds exhibit weak, sharp bands between $15,000$ and $30,000\text{ cm}^{-1}$, particularly at liquid nitrogen temperatures. Such bands are often observed in the spectra of chromium(II) compounds when charge transfer bands do not obscure this region, and are attributed to spin-forbidden transitions to triplet states. The bands are especially obvious in the spectrum of $\text{Cr(ur)}_2\text{Cl}_2$ presumably because of enhancement through the antiferromagnetic interaction.

Infrared Spectra

Infrared data have been used by Penland *et al.* [7] to determine whether urea or substituted ureas are coordinated through oxygen or nitrogen. A decrease in the N–H stretching frequency of the complex compared to the free ligand is considered to indicate N-coordination, while a decrease in the C–O stretching frequency and an increase in the C–N stretching frequency indicate O-coordination. The reduction in N–H stretching frequencies on N-coordination was found to be of the order of 100 cm^{-1} . For the C–O and C–N stretching frequencies, shifts of $5\text{--}50\text{ cm}^{-1}$ were found according to the mode of coordination.

For the urea, methylurea, and biuret complexes described in this paper, although the solids often did not mull well, the infrared data indicate that metal–oxygen coordination only is present. In the N–H

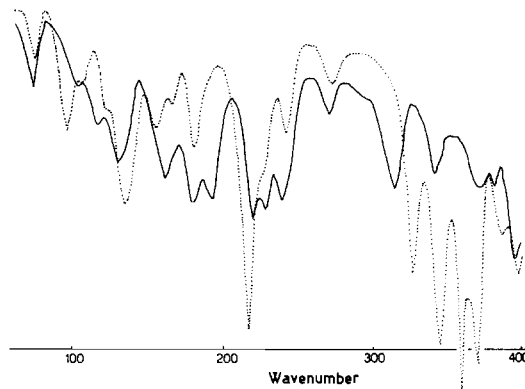
TABLE I. Analytical, Magnetic, and Reflectance Data.

Compound	Analyses ^a				X ^b	T/K	$\mu_{\text{eff}}^{\text{c}}/\text{BM}$	$\theta^{\text{e}}/^\circ$	$\chi_{\text{L}}^{\text{d}}$	Reflectance Spectra/cm ⁻¹
	C	H	N	Cr						
Cr(ur) ₂ Cl ₂	9.9 (9.9)	3.3 (3.3)	22.9 (23.0)	21.6 (21.4)	29.4 (29.2)	295	4.39	-	111	13300s 10800sh 13500s ^e 11000m
pale blue						90	3.50			8800sh 9400sh
Cr(ur) ₄ Cl ₂	13.3 (13.2)	4.4 (4.4)	30.4 (30.9)	14.4 (14.3)	19.4 (19.5)	295	4.78	-3	183	13000s ^f 14000sh 12700s
blue						90	4.83			10200sh 12800s
Cr(ur) ₄ Br ₂	10.4 (10.6)	3.6 (3.6)	24.7 (24.8)	11.5 (11.5)	35.3 (35.3)	295	4.85	-2	205	14400s ^f 14800sh 12600s
pale blue						90	4.90			10200sh
Cr(mur) ₄ Cl ₂	22.8 (22.9)	6.0 (5.8)	26.6 (26.7)	12.4 (12.4)	16.4 (16.9)	295	4.79	0	230	13000 ^f 14600s 12400s
pale blue						90	4.79			10200sh
Cr(mur) ₄ Br ₂	19.2 (18.9)	4.9 (4.8)	22.6 (22.1)	10.4 (10.2)	-	295	4.87	-2	253	13500
pale blue						90	4.90			10800sh
Cr(bi) ₂ Cl ₂	14.9 (14.6)	3.1 (3.1)	25.0 (25.5)	15.9 (15.8)	21.5 (21.5)	295	4.85	0	153	15000s 15200s
pale blue						90	4.86			11000sh 10800m

^a Calculated values are given in parentheses. ^b Halogen analyses. ^c Calculated from $\mu_{\text{eff}} = 2.828 (X_{\text{A}} T)^{1/2}$ B.M. and the Curie-Weiss law $\chi_{\text{A}}^{-1} \propto (T + \theta)$. ^d $10^{-6} \chi_{\text{L}}$ is the diamagnetic correction (c.g.s.u.). ^e Very weak absorptions (presumably spin-forbidden transitions to triplet levels) at 16000, 18000, 19000, 20800, 28200 and 33200 cm⁻¹. ^f Spin-forbidden bands at approximately 19100 cm⁻¹.

TABLE II. Magnetic Data for Cr(ur)₂Cl₂.

T/K	$10^6 \chi_{\text{A}}/\text{c.g.s.u.}$	$\mu_{\text{eff}}/\text{BM}$
294.5	8164	4.39
262.5	8941	4.33
230.0	9768	4.27
198.5	11000	4.18
166.5	12380	4.06
135.5	14000	3.90
104.0	16070	3.66
89.5	17070	3.50

Figure. Far infrared spectra at liquid nitrogen temperature of A, Cr(ur)₄Cl₂ (—) and B, Cr(ur)₄Br₂ (·····).

stretching region (3,100–3,500 cm⁻¹) no significant shifts were observed although there was a somewhat different pattern of absorption in the spectra of the complexes due to changes in hydrogen bonding on coordination. However, the C–N stretching frequencies at 1471 and 1001 cm⁻¹ in the spectrum of urea were increased to near 1485 and 1020 cm⁻¹ respectively in the chromium(II)-urea complexes. Also, a distinct shift to lower frequencies was apparent for bands in the C–O stretching region (1600–1700 cm⁻¹) in the spectra of all complexes.

The infrared evidence for metal-oxygen coordination is supported by the reflectance spectral data. The positions of the bands due to *d-d* transitions are within the range usually found [1] for the chromophore that would be present assuming oxygen coordination, and below the frequencies found for the analogous chromophore with nitrogen- instead of oxygen-coordination, e.g. Cr(4-methylpyridine)₄-X₂ [6].

Few deductions can be made from the far infrared spectra (40–400 cm⁻¹) because of the large number of ligand absorptions. There is a medium-intensity band at 193 cm⁻¹ in the spectrum of Cr(ur)₄Cl₂ which is not found for the corresponding bromide (Figure). It is possible that this corresponds to a long-bonded $\nu(\text{Cr}-\text{Cl})$ vibration. The chloride also has a

TABLE III. X-ray Powder Data.

θ_{hkl} (degree)	d_{hkl} (Å)	I*	θ_{hkl} (degree)	d_{hkl} (Å)	I ^a
Cu(bi) ₂ Cl ₂			Cr(bi) ₂ Cl ₂		
6.38	6.94	S	6.43	6.89	S
7.66	5.78	S	7.60	5.83	S
8.25	5.37	S	8.18	5.42	S
8.81	5.03	W	8.84	5.02	W
9.36	4.74	M	9.21	4.82	VW
10.05	4.42	M	9.91	4.48	M
11.09	4.01	W	10.98	4.05	VVW
11.54	3.85	W	11.75	3.79	VVW
12.23	3.64	S	12.16	3.66	S
12.71	3.50	VVW	—	—	—
13.43	3.32	VW	—	—	—
13.95	3.20	VS	14.08	3.17	VS
14.39	3.10	S	14.73	3.03	S

*Relative intensities were estimated visually.

medium band at 315 cm⁻¹ but this is unlikely to be due to a short $\nu(\text{Cr}-\text{Cl})$ vibration because the bromide exhibits a band nearby at 328 cm⁻¹. Similarly, there are bands at 321 cm⁻¹ and near 200 cm⁻¹ in the spectrum of Cr(mur)₄Cl₂ which are not found for Cr(mur)₄Br₂, but definite assignments cannot be made because of the complexity of the spectra. The analogous methylpyridine complexes [6], Cr(mepy)₄X₂, showed no halogen-dependent bands above 200 cm⁻¹ so that in CrL₄X₂ complexes the halide ions are likely to be along the elongated tetragonal axis. The copper(II) complex of biuret Cu(bi)₂Cl₂ is known from X-ray investigations [9] to have a *trans*-structure with O-donor biuret and long Cu-Cl bonds which do not absorb above 200 cm⁻¹. As X-ray powder data (Table III) show the complexes Cu(bi)₂Cl₂ and Cr(bi)₂Cl₂ to be isomorphous the latter can be assigned the same tetragonally-elongated six coordinate structure.

Experimental

Solid hydrated chromium(II) halides were prepared by the dissolution of spectroscopically pure chromium pellets in AnalaR acids under nitrogen, as described previously [1]. The manipulation of all compounds of chromium(II) was carried out under nitrogen or vacuum. Physical measurements were carried out as described in the preceding paper.

The complexes Cr(ur)₂Cl₂, Cr(ur)₄Cl₂, Cr(ur)₄Br₂, and Cr(bi)₂Cl₂ crystallised when a solution of the ligand in ethanol was added to a solution of the hydrated chromium(II) halide in ethanol (an ethanol/2,2-dimethoxypropane mixture in the case of Cr-

(ur)₄Cl₂). After filtration, the solids were washed with ethanol and dried by pumping on them for several hours at room temperature except for the biuret complex which was dried at 90 °C.

The complexes of methylurea would not crystallise from ethanol as this solvent is apparently too powerful a donor. It was also necessary to remove the water of crystallisation from the hydrated chromium(II) halides. This was done by dissolving the halides in a mixture of acetone and 2,2-dimethoxypropane. The methanol produced by reaction of the latter with the water of crystallisation did not prevent the crystallisation of the complexes. When a solution of methylurea in acetone was added to an "acetone" solution of chromium(II) chloride a viscous blue oil formed immediately. The complex Cr(mur)₄Cl₂ crystallised on vigorous shaking. It was filtered off, washed with acetone, and dried at 90 °C. The corresponding bromide was similarly obtained, but it did not form an oil and was dried at room temperature.

Four further compounds, apparently of composition Cr(mur)₂Cl₂, Cr(bi)₂Br₂, Cr(ur)₂Br₂ and Cr(ur)₇I₂, were obtained, the last two by addition of ethyl acetate to concentrated reaction mixtures, but although analyses for chromium and halide were satisfactory, the microanalyses were several per cent in error.

Attempts to prepare complexes of methylurea with chromium(II) iodide, and complexes of NN'-diphenylurea with chromium(II) chloride, bromide, and iodide were unsuccessful. Copper(II) forms complexes in which anionic biuret is coordinated via nitrogen [8], but when biuret in alkaline solution was added to an aqueous solution of chromium(II) chloride, immediate oxidation of the chromium(II) occurred.

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