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Complexes of Imidazole and some Amino-acid Anions with Chromium(II)

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The chromium(II) complexes $Cr(iz)_4X_2$, $Cr(gly)_2\cdot H_2O$, $Cr(met)_2$, $Cr(mcys)_2$, and $Cr(his)Cl\cdot H_2O$, in which iz is imidazole, X is Cl, Br, I or 1/2 SO_4, and gly, met, mcys, and his are respectively the anions of glycine, methionine, S-methylcysteine, and histidine, have been prepared. The imidazole complexes are high-spin with reflectance spectra suggesting trans-*octahedral structures with tetragonal distortion increasing in the order: $SO_4 < Cl < Br < I$. The sulphate and iodide are isomorphous with analogous copper(II) complexes of known* trans-*structures. The first three amino-acid complexes are weakly antiferromagnetic and their reflectance spectra indicate that the environment of the chromium(II) ion is similar in each case so that polymeric, carboxyl-bridged structures are likely. The histidine compound is antiferromagnetic, and is believed to be chloride-bridged.*

Introduction

This paper describes the preparation and investigation of some complexes of imidazole (iz), and of several amino-acids with bivalent chromium. The complexes are $Cr(iz)_4X_2$, where X is Cl, Br, I and 1/2 SO_4, and $Cr(gly)_2\cdot H_2O$, $Cr(met)_2$, $Cr(mcys)_2$, and $Cr(his)Cl\cdot H_2O$, where gly, met, mcys, and his are the anions of glycine, methionine, S-methylcysteine and histidine respectively.

During the course of our work the preparation of $Cr(iz)_4Cl_2$ and $Cr(iz)_4Br_2$ was reported by Mani and Scapacci [1] who also obtained a series of chromium (II) complexes of pyrazole and N-methylimidazole. The preparation of $Cr(gly)_2\cdot H_2O$ has been reported [2], and there is a comment in a recent review [3] on metal complexes of sulphur-containing amino-acids that attempts to prepare chromium(II) complexes of methionine produced a binuclear, oxygen-bridged chromium(III) complex; otherwise little is known of complexes of chromium(II) with amino-acids.

Experimental

The ligands were obtained commercially from Koch-Light Ltd and used without further purification.

Preparation of Complexes

All preparations and investigations were carried out under nitrogen or *in vacuo.* The imidazole complexes were obtained by the addition of an excess of the base dissolved in warm absolute ethanol to a solution (halides) or suspension (sulphate) of the appropriate hydrated chromium(II) salt [4] in the same solvent. The use of hydrated salts did not appear to lead to the hydrolysis or oxidation of the product which sometimes occurs [5] with chromium (II) compounds. The crystals, which separated after the flask had been shaken for some minutes, were filtered off, washed several times with absolute ethanol, and dried by pumping on them for three hours. The solids were then sealed under vacuum in pyrex tubes as they quickly turned brown in air. Attempts to prepare compounds of 6:1 or 2:1 imidazole-to-chromium ratios by using respectively a large excess or a deficiency of the base at room temperature were unsuccessful; 4:1 complexes were always obtained. This behaviour is similar to that of copper(II) [6]. The copper(II) complex $Cu(iz)_6I_2$, however, crystallised when a solution of $Cu(iz)_4I_2$ in a minimum of ethanol containing a 3:1 molar excess of imidazole was allowed to stand overnight at 0 °C [6]. Attempts to prepare an analogous chromium(II) complex by this method were unsuccessful. Copper (II) complexes needed for comparison of X-ray powder photographs with those of the chromium(II) complexes were prepared by literature methods [6].

Bis(glycinato)chromium(II) monohydrate was earlier prepared by the reaction of chromium(II) sulphate with glycine previously neutralised with sodium hydroxide. Our attempts to use this method led to the precipitation of brown chromium(II) hydroxide so the compound was obtained as follows. To glycine (1.30 g), dissolved in water (10 cm^3), was added lithium hydroxide monohydrate (0.66 g), and the mixture was heated at 60 °C and stirred until all the hydroxide had dissolved. Hydrated chromium (II) chloride (1.90 g), dissolved in ethanol (60 cm^3), was then added to the warm solution of lithium glycinate. Pale violet crystals separated and the suspension was heated at 80 °C for about 1 hr. After cooling, the solid was filtered off, washed with ethanol, and dried. Bands found in the infrared spectrum at 3320, 3270, and 3160 cm^{-1} are assigned to $\nu(NH_2)$ and $\nu(OH_2)$ vibrations. The corresponding deformations were obscured by a very broad antisym. $\nu(CO_2^-)$ absorption with peaks at 1605 and 1590 cm^{-1} and several shoulders.

Bis(methionato)chromium(II) was obtained as follows. DL-Methionine (1.93 g) was added to a solution of $LiOH{\cdot}H_2O$ in water (0.39 g, 10 cm^3). To this was added about 70 cm^3 of ethanol and the mixture was heated at 60 °C with stirring for about 20 m. Then it was filtered to remove any undissolved methionine. To the filtrate was added a solution of $CrCl_2{\cdot}4H_2O$ in ethanol (1.10 g, 20 cm^3). The pale violet precipitate was filtered off, washed with an ethanol/water mixture and then ethanol, and dried. The complex was very finely divided and difficult to filter off, as were all the amino-acid complexes, particularly if precipitated from entirely aqueous media. The use of aqueous ethanolic solutions gave a slightly more filterable product. The i.r. spectrum of the complex in nujol showed $\nu(NH_2)$ vibrations at 3300 and 3230, $\delta(NH_2)$ at 1570, and antisym. $\nu(CO_2^-)$ at 1605 cm^{-1}.

To prepare bis(S-methyl-L-cysteinato)chromium (II) the amino-acid (4.09 g) was dissolved in methanol (60 cm^3), and heated with $LiOH{\cdot}H_2O$ (1.22 g) at 60 °C with stirring for 30 m. After cooling to room temperature, $CrCl_2{\cdot}4H_2O$ (3.50 g) in ethanol (20 cm^3) was added, and the pale violet precipitate which formed was filtered off, washed with methanol, and dried. This compound blackened and smouldered on exposure to air. The complex had $\nu(NH_2)$ vibrations at 3295 and 3225, $\delta(NH_2)$ at 1570, and antisym. $\nu(CO_2^-)$ at 1605 cm^{-1}.

Although a 2:1 ratio of L-histidine to metal ion was used in attempts to prepare bis(histidinato) chromium(II) complex the compound $Cr(his)Cl{\cdot}H_2O$ was obtained. Histidine (3.00 g) was dissolved in warm water (20 cm^3) and $LiOH{\cdot}H_2O$ (0.92 g) added. After the mixture had been heated at 80 °C for 30 min, ethanolic $CrCl_2{\cdot}4H_2O$ (1.20 g in 30 cm^3) was added to the warm solution. The finely-divided, bluish-violet precipitate which formed was filtered off, washed with a mixture of water and ethanol, and then dried.

Attempts to isolate a cysteine–chromium(II) complex from ethanolic or aqueous solution under nitrogen produced a black precipitate which was not air-sensitive and did not give satisfactory analyses.

Physical Measurements

Chromium was determined by direct combustion of the complex to Cr_2O_3. Magnetic measurements were carried out by the Gouy method down to liquid nitrogen temperature on a Newport Instruments Ltd. apparatus. The samples were contained in sealed tubes. Diffuse reflectance spectra were recorded on a Unicam SP 700C spectrophotometer, with lithium fluoride as reference and the samples in sealed cells. X-ray powder photographs were recorded on a Philips PW1024/00 camera of radius 114.6 mm with copper Kα radiation and a nickel filter. The samples were sealed in Lindemann capillaries or well-drawn-out Pyrex capillaries.

Results and Discussion

Complexes of Imidazole

The imidazole compounds (Table I) obeyed the Curie law over the temperature range investigated, with effective magnetic moments slightly below the spin-only value of 4.90 BM as expected [4] for magnetically-dilute high-spin chromium(II) compounds. The absence of magnetic interaction suggests that these are monomeric compounds. The effective magnetic moments (and the reflectance spectra) for $Cr(iz)_4Cl_2$ and $Cr(iz)_4Br_2$ agree well with those recently reported [1].

The reflectance spectra (Table I) are as commonly found for tetragonally-distorted, six-coordinate chromium(II) compounds. Each spectrum comprises a band in the region of 18000 cm^{-1} with a shoulder to lower frequency. The band is assigned to superimposed $^5B_{1g} \rightarrow {}^5B_{2g}$ and $^5B_{1g} \rightarrow {}^5E_g$ transitions and the shoulder to the $^5B_{1g} \rightarrow {}^5A_{1g}$ transition (D_{4h} symmetry). The band near 18000 cm^{-1} moved slightly to higher frequency, and the shoulder considerably to higher frequency, in the order $SO_4 < Cl < Br < I$ as would be expected if the anions were coordinated and the tetragonal distortion were increasing in the same order. Similar behaviour was found [7] with the bis(ethylenediamine) complexes, $Cr(en)_2X_2$, in which X = Br, I and $1/2SO_4$, and in the pyrazole and N-methyl-imidazole complexes [1].

The infrared spectra of the complexes were similar. The sulphate exhibited apparent slight splittings of the ν_3 sulphate [8] absorption with bands at 1150, 1100, and 1060 cm^{-1}, suggesting weak bidentate coordination of the anion. However, comparison with the spectra of the halides showed that the imidazole ligands absorbed strongly in this region so that no definite conclusions were possible. Ligand bands similarly obscured the ν_4 region (*ca.* 620 cm^{-1}), although the ν_1 sulphate band appeared weakly at 975 cm^{-1}.

Imidazole does not absorb in the range 600–200 cm^{-1}, and the complexes showed anion-independent bands (cm^{-1}) at 330 w–m, 310m, 235m (Cl), 330vs, 250s (Br), 320mb (SO_4). The bands above 300 cm^{-1} are assigned to the (Cr–N) stretching vibration and the other bands to the (N–Cr–N) deformation. The ν(Cr–N) vibrations for the chloride and bromide are as reported recently [1] {320–310s (Cl) and 325s (Br)}, but only broad absorption with no definite bands was found in the (N–H) stretching region.

TABLE I. Analytical, Magnetic and Reflectance Data.

Compound	Analyses[a]				T/K	$\mu_{eff}{}^b$/BM	θ^b/°	$\chi_L{}^c$	Reflectance Spectra/cm^{-1}	
	C	H	N	Cr						
$[Cr(iz)_4Cl_2]$	36.3 (36.5)	4.0(4.1)	28.4(28.35)	12.7 (13.15)	295	4.87	0	139	17500	13000sh
violet purple					90	4.86			17800	13200sh
$[Cr(iz)_4Br_2]$	29.9 (29.8)	3.4(3.3)	23.1(23.1)	10.5 (10.7)	295	4.84	0	162	19300vb[d]	16400sh
pale purple					90	4.87			20000	17200sh
$[Cr(iz)_4I_2]$	24.85(24.9)	2.8(2.8)	19.3(19.4)	8.85(9.0)	295	4.78	0	194	19000vb[d]	
violet					90	4.77			19800	17400sh
$[Cr(iz)_4SO_4]$	34.3 (34.3)	3.8(3.8)	26.7(26.65)	12.6 (12.4)	295	4.77	0	133	17200	12400sh
blue–violet					90	4.75			17800	13000sh
$[Cr(gly)_2H_2O]$	21.4 (22.0)	4.4(4.6)	12.3(12.8)	23.4 (23.8)	295	4.61	6	87	16300	12000sh
pale violet					90	4.52			16400	12000
$[Cr(met)_2]$	34.8 (34.5)	5.7(5.8)	7.6(8.0)	14.5 (14.9)	295	4.76	11	196	17000	12100sh
pale violet					90	4.61			17000	12000
$[Cr(mcys)_2]$	29.3 (30.0)	5.0(5.0)	8.5(8.7)	16.1 (16.2)	295	4.67	8	153	16800	13100sh
pale violet					90	4.54			17000	13000sh
$[Cr(his)Cl]\cdot H_2O$	27.4 (27.8)	3.6(3.9)	15.5(16.2)	20.2 (20.0)	295	3.70	24	110	18000vb[d]	12700sh
blue violet					90	3.38			18500vb[d]	13300sh

[a] Calculated values are given in parentheses.

[b] Calculated from $\mu_{eff} = 2.828\,(\chi_A T)^{1/2}$ and the Curie–Weiss law $\chi_A{}^{-1} \propto (T+\theta)$.

[c] 10^{-6} χ_L is the diamagnetic correction (c.g.s.u.).

[d] Very broad and asymmetric to low frequencies so that the positions of shoulders are uncertain.

TABLE II. X-ray Powder data for Imidazole Complexes

θ_{hkl} (degree)	d_{hkl} (Å)	I	θ_{hkl} (degree)	d_{hkl} (Å)	I
$Cr(iz)_4SO_4$			$Cu(iz)_4SO_4$		
4.96	8.91	vs	4.96	8.91	vs
5.41	8.18	w	5.42	8.16	w
6.53	6.78	vs	6.66	6.65	vs
7.05	6.32	s	7.03	6.63	s
9.68	4.58	m	9.82	4.51	m
10.31	4.30	vs	10.26	4.33	vs
10.86	4.09	w	10.91	4.07	w
11.06	4.03	vs	11.48	3.88	vs
11.88	3.74	w	11.87	3.74	w
12.53	3.55	w	12.52	3.52	m
13.13	3.39	m	13.35	3.33	m
14.12	3.15	m	14.13	3.15	s
15.08	2.98	vw	15.36	2.91	vw
15.83	2.83	w	15.71	2.85	w
16.58	2.70	vw	16.26	2.75	vw
17.33	2.59	vw	16.80	2.67	m
17.78	2.52	vw	17.52	2.52	w
18.28	2.46	vw	18.23	2.46	w
$Cr(iz)_4Cl_2$			$Cu(iz)_4Cl_2$		
6.25	7.08	m	5.90	7.50	s
6.73	6.58	s	6.55	6.76	s
			7.17	6.17	s
			8.30	5.33	s
8.77	5.05	m	8.85	5.01	w
10.16	4.39	m	10.53	4.22	s
11.34	3.90	s	11.17	3.97	s
11.91	3.73	m	11.95	3.72	vs
12.42	3.58	m	12.77	3.49	vs
12.73	3.49	vw			
13.07	3.41	s			
13.41	3.31	w	13.71	3.25	vw
14.60	3.06	vw	14.27	3.12	m
15.08	2.96	vw			
15.58	2.86	vw	15.61	2.86	m
16.61	2.68	vw	16.33	2.74	w
$Cr(iz)_4Br_2$			$Cu(iz)_4Br_2$		
5.96	7.42	m	5.92	7.47	w
6.95	6.37	m	7.03	6.29	vs
7.51	5.90	m	7.58	5.85	vw
10.46	4.24	m	10.36	4.27	m
11.58	3.84	vw			
11.93	3.73	vs	11.85	3.75	vs
12.27	3.63	vs	12.65	3.52	vs
12.91	3.45	vw	12.98	3.44	vvw
13.72	3.25	vw	13.93	3.20	w
14.48	3.08	vvw	14.28	3.12	w
15.21	2.94	s	15.47	2.89	s
15.87	2.81	w	15.92	2.81	w
16.66	2.68	m	16.71	2.68	m
17.58	2.55	s	17.57	2.55	s
19.21	2.34	w	19.38	2.32	s
19.77	2.27	vw	20.38	2.21	w
20.81	2.16	vw	21.03	2.14	w
$Cr(iz)_4I_2$			$Cu(iz)_4I_2$		
5.76	7.68	m	5.40	8.19	s
6.83	6.48	m	6.40	6.92	s
			7.17	6.17	s
			7.90	5.02	s
			8.52	5.20	w
10.08	4.40	w	9.90	4.48	s
11.11	4.00	vw	10.97	4.05	vs
11.60	3.83	s	11.38	3.90	vs
12.06	3.69	s	12.33	3.62	s
13.50	3.30	vvw	13.77	3.22	s
14.71	3.03	w	14.45	3.08	s
15.11	2.96	w	14.96	2.99	s
15.40	2.90	w	16.03	2.79	w
16.52	2.71	w	16.73	2.67	w
16.95	2.64	m	16.70	2.53	m
17.38	2.58	vvw			
18.52	2.42	w	18.51	2.42	m

X-Ray powder data (Table II) show that $Cr(iz)_4SO_4$ and $Cu(ix)_4SO_4$ are isomorphous. The latter has [9] a distorted octahedral structure with planar coordination of four nitrogen atoms of imidazole ligands, and oxygen atoms of different weakly-bridging sulphato ions above and below the plane. The bond distances are Cu–N, 2.000 and 2.021Å, and Cu–O, 2.574Å. This type of structure is suggested by the reflectance and i.r. spectra for the chromium(II) complex and confirmed by the isomorphism. The sulphato-bridges do not lead to magnetic interaction presumably because the metal–metal distance is too long.

Similarly, the complex $Cu(iz)_4I_2$ is essentially planar [10] with two distant iodide ions (3.42 and 3.87Å) completing a very distorted octahedron. The reflectance spectrum of $Cr(iz)_4I_2$ shows it to be the most tetragonally-distorted of the chromium(II) complexes, and the same type of structure can be assigned. Powder data suggest that the copper(II) and chromium(II) iodides are similar, but not isomorphous. The bromides $Cu(iz)_4Br_2$ and $Cr(iz)_4Br_2$ are isomorphous, but the chlorides $Cu(iz)_4Cl_2$ and $Cr(iz)_4Cl_2$ do not exhibit such close resemblances in their powder patterns. No single crystal investigations have been carried out on these complexes but it seems reasonable to assume that they have the same configuration as the iodides.

Complexes of Amino-acids

The complexes, $Cr(gly)_2 \cdot H_2O$, $Cr(met)_2$, and $Cr(mcys)_2$ have magnetic moments at room temperature a little below 4.90 B.M. which decreased slightly at lower temperatures presumably due to some minor antiferromagnetic interactions. Bridged structures of the type suggested [11] for most $M(met)_2$ and $M(mcys)_2$ complexes generally (M = bivalent metal) would not provide pathways for extensive interaction but could account for the small reduction of effective magnetic moments.

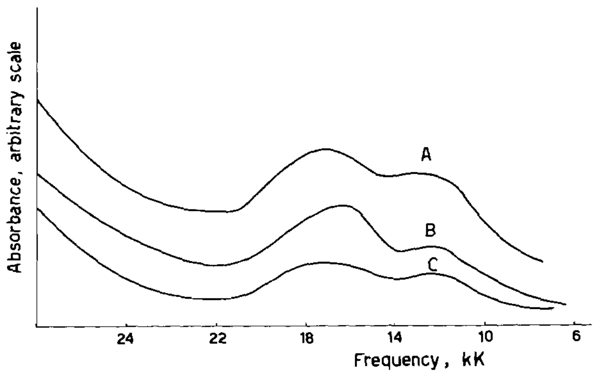

Figure. Reflectance spectra at liquid nitrogen temperature of A, Cr(mcys)$_2$, B, Cr(gly)$_2$·H$_2$O, and C, Cr(met)$_2$.

Their reflectance spectra (Figure) are very similar, with the same pattern of an absorption band with a shoulder at lower frequency as found with the imidazole complexes. The general similarity suggests that the environment of the metal ion is the same in each complex, *i.e.* the $-NH_2$ and $-CO_2^-$ groups are coordinated and not the $-SMe$ groups of the methionato- or S-methylcysteinato-ligands. As chromium(II) is a Class A acceptor, coordination through N and O rather than S is to be expected. It seems that in complexes M(met)$_2$ generally [11] the S atom is not coordinated.

Unexpectedly, the compounds Cr(gly)$_2$·H$_2$O and Cu(gly)$_2$·H$_2$O are not isomorphous so that structural analogies based on powder patterns are not possible.

The complex Cr(his)Cl·H$_2$O has a much reduced magnetic moment which decreased considerably as the temperature was reduced. It presumably has a bridged structure, permitting considerable antiferromagnetism. The breadth and asymmetry of the band in its reflectance spectrum suggest that considerable distortion from octahedral symmetry is present as might be expected from the nature of the ligands.

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