Chromium(II) Chemistry. Part X.[1] The Preparation and Properties of some Ammines

By **Leslie F. Larkworthy** * and **Javad M. Tabatabai**, The Joseph Kenyon Laboratory, University of Surrey, Guildford GU2 5XH

The first series of chromium(II) ammines has been isolated: $[Cr(NH_3)_6]X_2$ and $[Cr(NH_3)_5]X_2$ (X = Cl, Br, or I); $CrX_2(NH_3)_2$ (X = Cl or Br); $[Cr(NH_3)_4(OH_2)][SO_4]$; and $Cr(NH_3)_2(SO_4)$. The hexa-ammines, obtained by bubbling ammonia through ethanolic solutions of the chromium(II) halides, lose ammonia readily and reversibly to form penta-ammines. Thermal decomposition of the latter gives the diammine halides. The sulphates have been obtained by similar procedures. From magnetic, spectroscopic, and X-ray powder investigations, the hexa-ammines and penta-ammines have been assigned tetragonal octahedral and square-pyramidal structures respectively, and the diammines anion-bridged six-co-ordinate structures. The tetra-ammine sulphate is square pyramidal with co-ordinated water.

AMMINES of chromium(II) chloride were prepared by Peters,[2] Ephraim,[3] and Schlesinger and Hammond,[4] but no physical investigations were carried out. The only other study of chromium(II) ammines appears to be that of Lux *et al.*[5] who prepared $[Cr(NH_3)_4][SO_4]\cdot H_2O$, and reported that it was isomorphous with the corresponding copper(II) complex. This paper reports the isolation and investigation of a series (Table 1) of hexa-, penta-, tetra-, and di-ammines of Cr^{II}.

RESULTS AND DISCUSSION

Hexa-ammine Complexes.—These complexes have magnetic moments, $\mu_{eff.}$, which vary little with temperature (Table 1), and are close to the value (4.9 B.M.) † expected for magnetically dilute high-spin d^4 compounds. Samples of the hexa-ammines for magnetic, reflectance, and X-ray powder investigations were sealed in ammonia at just less than 1 atm, otherwise they readily lost ammonia to give the penta-ammines. This is apparently

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† 1 B.M. ≈ 9.27×10^{-24} A m²; 1 atm = 101 325 Pa; 1 cmHg ≈ $13.6 \times 9.8 \times 10^2$ Pa.

[1] Part IX, L. F. Larkworthy, J. K. Trigg, and A. Yavari, *J.C.S. Dalton*, 1975, 1879.

[2] V. Peters, *Chem. Ber.*, 1909, **42**, 4837.

[3] F. Ephraim, *Chem. Ber.*, 1917, **50**, 535.

[4] H. I. Schlesinger and E. S. Hammond, *J. Amer. Chem. Soc.*, 1933, **55**, 3971.

[5] H. Lux, L. Eberle, and D. Sarre, *Chem. Ber.*, 1964, **97**, 503.

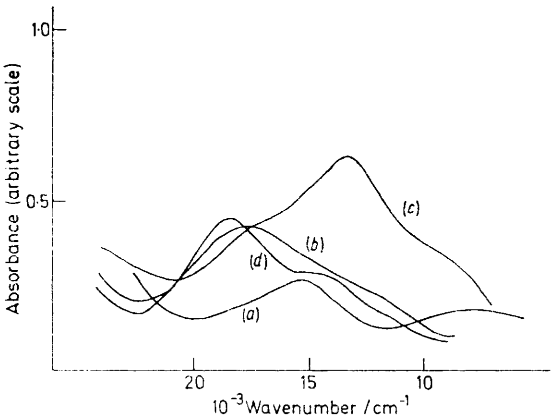
a result of the Jahn–Teller distortion of the high-spin d^4 configuration since the vanadium(II) complex, $[V(NH_3)_6]Br_2$ (d^3 configuration) in which distortion is not expected, does not lose ammonia *in vacuo* at room temperature.[6] In confirmation, although six identical ligands are present, the diffuse-reflectance spectra (Table 1 and Figure) are as expected for tetragonally distorted octahedral chromium(II) complexes. The *d–d* absorption bands occur at similar frequencies to those of the tris(ethylenediamine)chromium(II)[7] and bis(3-azapentane-1,5-diamine)chromium(II) salts,[8] and the same assignments are made, *i.e.* the more intense higher-frequency band to superimposed transitions ${}^5B_{1g}\rightarrow{}^5B_{2g}$ and ${}^5B_{1g}\rightarrow{}^5E_g$ (the main band), and the weaker band at *ca.* 8 000 cm^{-1} to the ${}^5B_{1g}\rightarrow{}^5A_{1g}$ transition (the distortion band). The very definite and rapid change from grey or pale greenish grey to violet on loss of ammonia to form the penta-ammines, which is reversed when ammonia at *ca.* 1 atm is readmitted, and the different reflectance (Table 1 and Figure) and i.r. (Table 2) spectra of the latter, show that the chromium(II) complexes contain the $[Cr(NH_3)_6]^{2+}$ ion.

TABLE 1

Analyses and magnetic and diffuse-reflectance data

Complex	Colour	Analysis (%) [a]		$\mu_{eff.}$/B.M.		θ[b]/°	10^6 Diamagnetic correction c.g.s. units	Reflectance spectra,[c] ν/cm^{-1}		
		Cr	X	295 K	90 K					
$CrCl_2(NH_3)_2$	Pale blue	32.9 (33.1)	45.5 (45.2)	4.57	4.05	40	−83	17 000 (sh) 17 000 (sh)	14 000 svb 14 100svb	11 300 (sh) 11 000 (sh)
$[Cr(NH_3)_5]Cl_2$	Violet	25.3 (25.0)	33.6 (34.1)	4.77	4.74	0	−137	17 800svb [d] 18 200s	 14 500 (sh)	 11 400 (sh)
$[Cr(NH_3)_6]Cl_2$	Grey	23.7 (23.1)	30.9 (31.5)	4.85	4.78	0	−155	16 000svb 17 300svb		8 500m 8 500m
$CrBr_2(NH_3)_2$	Pale blue	21.9 (21.1)	64.9 (65.0)	4.33	4.09	23	−67	17 500 (sh) 17 400 (sh)	13 200s 13 700s	9 500 (sh) 9 500 (sh)
$[Cr(NH_3)_5]Br_2$	Violet	17.7 (17.5)	53.3 (53.8)	4.76	4.80	0	−159	17 500svb [d] 18 200s	 14 500 (sh)	 11 300 (sh)
$[Cr(NH_3)_6]Br_2$	Greenish grey	17.0 (16.6)	50.4 (50.9)	4.87	4.90	0	−177	15 400sb 15 700sb		7 500m 7 700m
$[Cr(NH_3)_5]I_2$	Violet	13.1 (13.3)	64.7 (64.9)	4.87	4.87	0	−191	17 600s 18 100s	12 800 (sh) 14 000(sh)	 11 200(sh)
$[Cr(NH_3)_6]I_2$	Greenish grey	13.1 (12.7)	61.9 (62.2)	4.88	4.91	0	−209	15 200s 15 400s		7 600m 7 800m
$Cr(NH_3)_2(SO_4)$	Pale blue	29.0 (28.9)	51.8 (52.7)	4.69	4.26	32	−76	14 000vb 14 000s	 11 500 (sh)	 9 800 (sh)
$Cr(NH_3)_4(SO_4)\cdot H_2O$	Violet	22.2 (22.2)	41.2 (41.0)	4.89	4.74	8	−125	18 000vb [d] 18 400vb	 15 000 (sh)	

[a] Calculated values are given in parentheses; X = anion. [b] Curie–Weiss law taken as $\chi_A^{-1} \propto (T + \theta)$. [c] Spectra at room (first line) and liquid-nitrogen (second line) temperatures. [d] Very broad and asymmetric to low wavenumbers.



Reflectance spectra at room temperature of $[Cr(NH_3)_6]Br_2$ (*a*), $[Cr(NH_3)_5]Br_2$ (*b*), and $CrBr_2(NH_3)_2$ (*c*); (*d*) spectrum of $[Cr(NH_3)_5]Br_2$ at liquid-nitrogen temperature

The *X*-ray powder patterns are similar to those reported for the corresponding copper(II) hexa-ammines.[9,10] It has been possible to index the lines of the chloride and bromide in terms of tetragonal unit cells with dimensions close to those of the copper(II) complexes (Table 3), although the departures from cubic symmetry are not large. The iodide is essentially cubic, the copper(II) complex being variously reported as tetragonal[9] or cubic.[10] There is controversy[9,10] concerning the nature of the copper(II) hexa-ammines: some[9] workers believe that these contain the $[Cu(NH_3)_6]^{2+}$ ion, while others consider that the hexa-ammines[10] and penta-ammines[10b] have such similar unit-cell dimensions, and electronic, e.s.r., and i.r. spectra that the hexa-ammines should be formulated as $[Cu(NH_3)_5\cdot NH_3]^{2+}$. The sixth ammonia molecule is not co-ordinated, but held in the lattice. Our preparative and spectroscopic evidence, outlined earlier, is that the sixth ammonia molecule is co-ordinated in the chromium(II) hexa-ammines. Additionally, the unit-cell dimensions of the chromium(II) hexa-ammines and penta-ammines, though similar, are not identical (Table 3). Unlike the chromium(II) complexes, the copper(II) hexa-ammines do not undergo obvious colour or spectral changes[9,10] on loss of ammonia; it is therefore possible that although copper(II) hexa-ammines were isolated,

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[6] L. F. Larkworthy and J. M. Tabatabai, unpublished work.

[7] A. Earnshaw, L. F. Larkworthy, and K. C. Patel, *J. Chem. Soc.* (*A*), 1969, 1339.

[8] A. Earnshaw, L. F. Larkworthy, and K. C. Patel, *J. Chem. Soc.* (*A*), 1969, 2276.

[9] T. Distler and P. A. Vaughan, *Inorg. Chem.*, 1967, **6**, 126.

[10] (*a*) A. A. G. Tomlinson and B. J. Hathaway, *J. Chem. Soc.* (*A*), 1968, 1905; (*b*) H. Elliott and B. J. Hathaway, *Inorg. Chem.*, 1966, **5**, 885.

ammonia had been lost by the time measurements were completed in spite of the precautions taken.[10]

Penta-ammines.—The magnetic behaviour shows that the penta-ammines are also magnetically dilute high-spin chromium(II) complexes. Compared with the hexa-ammines, the most intense band in their diffuse-reflectance spectra is at considerably higher wavenumber (*ca.* 18 000 cm^{-1}) and there are two lower wavenumber bands resolved at low temperature (*ca.* 14 500 and 11 200 cm^{-1}) instead of one. Increased tetragonal distortion on the loss of a ligand, or replacement by a weaker-field ligand, has been found to lead to movement of bands to higher frequency in other copper(II) and chromium(II) systems. Since the spectra of the penta-ammines are independent of halide it seems that the anions are not co-ordinated and five-co-ordinate ions $[Cr(NH_3)_5]^{2+}$ are present. The only known trigonal-bipyramidal chromium(II) complex, $[CrCl\{N(CH_2CH_2\cdot NMe_2)_3\}]Cl$, in which the donor atoms would produce approximately the same ligand field, has a different spectrum[11] with an absorption band at 11 000 cm^{-1} and a shoulder at 14 500 cm^{-1}. The presence of three bands in the spectra of the penta-ammines therefore suggests a square-pyramidal structure (C_{4v}), and on this basis the assignments of these bands in order of increasing frequency are: $^5B_1 \rightarrow {}^5A_1$, $^5B_1 \rightarrow {}^5B_2$, and $^5B_1 \rightarrow {}^5E$.

X-Ray powder photographs of the chromium(II) penta-ammines show them to be isomorphous with the corresponding complexes of Cu^{II} which are believed[10] to be square pyramidal. The type of unit cell and its dimensions are given in Table 2. The powder photographs of the chromium(II) hexa-ammines and penta-ammines are very similar, but the unit-cell dimensions are greater for the former. Since the loss of ammonia from the hexa-ammines is reversible and accompanied by changes in colour and reflectance spectra, it is supposed that the loss of ammonia from a long-bonded tetragonal position leaving a square-pyramidal cation has little effect on the unit-cell dimensions. This seems no less likely than the suggestion[10] that the copper(II) hexa-ammines and penta-ammines have identical powder photographs because the additional ammonia molecule occupies a position along the side of the unit cell.

TABLE 2

Infrared spectra (cm^{-1}) of hexa-ammines and penta-ammines

	$[Cr(NH_3)_6]X_2$			$[Cr(NH_3)_5]X_2$		
X =	Cl	Br	I	Cl	Br	I
$\nu(NH_3)$ [a]	3 310s 3 180s [b]	3 310s 3 200 (sh)	3 310s 3 200 (sh)	3 300s 3 180s 1 620 (sh)	3 300s 3 190 (sh)	3 280s 3 210 (sh)
$\delta_d(NH_3)$	1 600s 1 310w	1 600s 1 310w	1 600s 1 310w	1 610s 1 295 (sh)	1 600s 1 300w	1 595s 1 310w, 1 275m 1 245 (sh)
$\delta_s(NH_3)$	1 200s 1 040m	1 207s 1 055m	1 220s 1 080m	1 235svb 1 095w	1 235svb	1 230s
$\rho_r(NH_3)$	675s	675s	660s	710svb 675 (sh)	730 (sh) 700s	715 655

[a] Symbols as in ref. 15. [b] Minor splittings of the bands in this region of all the spectra have been ignored.

TABLE 3

X-Ray powder data

Complex	Unit cell	*a* (Å)	*c* (Å)	*c*/*a*	Ref.[a]
$[Cr(NH_3)_6]Cl_2$	Tetragonal	10.63	9.82	0.924	
		(10.38)	(9.48)		9
$[Cr(NH_3)_6]Br_2$	Tetragonal	10.70	9.91	0.926	
		(10.74)	(9.67)		9
$[Cr(NH_3)_6]I_2$	f.c.c.[b]	10.96			
		(11.20)	(10.29)		9
$[Cr(NH_3)_5]Cl_2$	Tetragonal	10.29	9.87	0.959	
		(10.29)	(9.37)		10
$[Cr(NH_3)_5]Br_2$	f.c.c.	10.45			
		(10.34)			10
$[Cr(NH_3)_5]I_2$	f.c.c.	10.76			
		(10.76)			10
$CrCl_2(NH_3)_2$	f.c.c.	3.98			
		(3.91)			*c*
$CrBr_2(NH_3)_2$	f.c.c.	4.13			*c*
		(4.07)			

[a] Values for copper(II) complexes to which these references apply are given in parentheses. [b] Face-centred cubic. [c] F. Hanic and I. A. Cakajdova, *Acta Cryst.*, 1958, **11**, 610.

Diammines.—Unlike the hexa-ammines and penta-ammines, the diammines obey the Curie–Weiss law, and have magnetic moments somewhat below the spin-only value at room temperature which decreased still further as the temperature was reduced. Since no first-order

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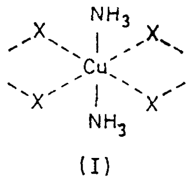
[11] M. Ciamplini, *Chem. Comm.*, 1966, 47.

orbital contribution to the moment is expected[12] for high-spin d^4 systems, this behaviour can be ascribed to antiferro-magnetic interactions in halide-bridged structures. The halide-bridged structures are confirmed by the reflectance spectra which are again typical of tetragonal six-co-ordinate Cr^{II}, except for the appearance of a high-frequency shoulder at *ca.* 17 000 cm^{-1}. Except for this shoulder, the spectra are very similar to the spectra of β-$Cu(NH_3)_2Cl_2$ and β-$Cu(NH_3)_2Br_2$ which have been assigned 'reversed' tetragonal structures, (I), with short Cu–N and long, but equal, Cu–X bonds.[13] The chromium(II) and copper(II) diammines are isomorphous and the *X*-ray powder patterns can be indexed on the assumption of cubic unit cells (Table 3).



(I)

A reversed tetragonal structure would mean that the reflectance bands should be assigned, in order of increasing energy, to the transitions ${}^5A_{1g}\rightarrow{}^5B_{1g}$, ${}^5A_{1g}\rightarrow{}^5E_g$, and ${}^5A_{1g}\rightarrow{}^5B_{2g}$. Apparently, in the chromium(II), although not in the copper(II) complexes,[13] inversion of the splitting pattern has allowed resolution of a third band. This would suggest that in the spectra[13] of the copper(II) complexes, β-$Cu(NH_3)_2X_2$, the band at lowest frequency (9 600 cm^{-1}) should be assigned to the ${}^5A_{1g}\rightarrow{}^5B_{1g}$ transition, and that the ${}^5A_{1g}\rightarrow{}^5B_{2g}$ transition is unresolved within the more intense band at *ca.* 14 200 cm^{-1} due to the ${}^5A_{1g}\rightarrow{}^5E_g$ transition.

Ammine Sulphates.—The reflectance spectra of $Cr(NH_3)_4SO_4{\cdot}H_2O$ and the penta-ammines are very similar so that an essentially square-pyramidal structure involving co-ordinated water or sulphate would be expected for this complex. This has been confirmed since it is isomorphous, as found previously,[5] with $[Cu(NH_3)_4(OH_2)][SO_4]$ in which[14] oxygen atoms from water molecules are 2.59 and 3.37 Å from planar $[Cu(NH_3)_4]^{2+}$ units.

The weak antiferromagnetism (θ = 8°) probably arises through weak interaction between the paramagnetic metal ions in a hydrogen-bonded water-bridged structure as in the copper tetra-ammine. The i.r. spectrum shows a broad unsplit band (ν_3) at 1 100 cm^{-1}, indicating that the anion is not co-ordinated.[15] The considerable magnetic interaction (θ = 32°) and the stoicheiometry indicate that sulphato-bridges are present in $Cu(NH_3)_2(SO_4)$. These properties, and the fact that the reflectance spectrum has its strongest band at a frequency similar to that[12] of the hydrated chromium(II) ion, suggest that the structure comprises sulphato-bridged chains of metal ions with axially co-ordinated ammonia molecules. The ν_3 sulphate vibration[15] at *ca.* 1 100 cm^{-1} shows little splitting presumably because the sulphato-bridges are bidentate to adjacent metal ions and their symmetry remains close to T_d even on co-ordination.

EXPERIMENTAL

Preparations.—When dry ammonia was passed through a solution of a chromium(II) halide, $CrX_2{\cdot}nH_2O$ (X = Cl, Br, or I),[12] in deoxygenated absolute ethanol, heat was evolved and pale blue, violet, and then greyish precipitates successively appeared. The final product, the grey (X = Cl) or pale greenish grey (X = Br or I) *hexa-ammine*, was filtered off, washed with absolute ethanol, and dried *in vacuo* at room temperature. Unfortunately, as well as being very air-sensitive, the hexa-ammines always lost ammonia rapidly *in vacuo*, and became bluish violet because of the formation of some penta-ammine. To obtain the pure hexa-ammine, ammonia at *ca.* 75 cmHg pressure was admitted to the vessel containing the bluish violet material. Absorption occurred with evolution of heat and the colour changed to that of the hexa-ammine. To ensure that the reaction was complete, the hexa-ammines were exposed to ammonia for 6—8 h. After all apparent absorption had ceased, the hexa-ammines were sealed in glass tubes for susceptibility measurements, *etc.* under ammonia at just less than 1 atm pressure. Mulls for i.r. spectra were made up in a plastic bag through which ammonia was passed. The mulls of the hexa-ammines did not change to the colour of the penta-ammines while the spectra were being recorded.

Hexa-amminechromium(II) chloride was said[2,3] to be grey by some workers, but others have reported it to be deep blue,[4] and the grey colour was ascribed to ammonolysis following absorption of more than $6NH_3$ at ammonia pressures greater than *ca.* 35 cmHg. However, our grey products gave good analyses for hexa-ammines, and the grey colour was discharged reversibly on reduction of the ammonia pressure.

The *penta-ammines* were obtained by evacuation of the vessel containing the hexa-ammine. The pump was stopped as soon as the colour changed to violet to avoid further loss of ammonia. The pale blue *diammines* were prepared from the penta-ammines by heating them for 2 h at 50—90 °C under continuous pumping. The penta-ammines and diammines were sealed in glass tubes *in vacuo* to prevent aerial oxidation.

In some earlier experiments acetone was used as solvent and a dark brown product separated instead of the required ammines. Its nature has not been investigated, but it could be a chromium complex of a ligand formed by condensation of ammonia and acetone. Attempts to prepare chromium(II) ammines from aqueous ammonia were unsuccessful. When 0.880 s.g. ammonia was added to a concentrated aqueous solution of a chromium(II) salt a deep blue solution was obtained but before any ammine could be isolated a brown precipitate of chromium(II) hydroxide usually appeared. Nevertheless, the use of dry, but hydrated, chromium(II) salts in the preparation of the ammines from ethanol as above did not have any deleterious

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[12] A. Earnshaw, L. F. Larkworthy, and K. S. Patel, *J. Chem. Soc.*, 1965, 3267.

[13] A. A. G. Tomlinson and B. J. Hathaway, *J. Chem. Soc. (A)*, 1968, 2578.

[14] F. Mazzi, *Acta Cryst.*, 1955, **8**, 137; B. Morosin, *ibid.*, 1969, **B25**, 19.

[15] K. Nakamoto, 'Infrared Spectra of Inorganic and Co-ordination Compounds,' 2nd edn., Wiley–Interscience, New York, 1970.

effect on the products. Inability to use aqueous solution has reduced the range of preparative methods compared with copper(II) systems.[16]

The complex $Cr(NH_3)_4(SO_4)\cdot H_2O$ was prepared according to a published method.[5] On heating at 80—90 °C under continuous pumping for 1—2 h pale blue $Cr(NH_3)_2(SO_4)$ was obtained.

[5/1735 *Received, 10th September,* 1975]

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[16] B. J. Hathaway and A. A. G. Tomlinson, *Co-ordination Chem. Rev.*, 1970, **5**, 1.