Inorganica Chimica Acta, 20 (1976) L9 - L10

Ferromagnetic Behaviour of Diethylenetriammonium Chlorochromate(II)

L. F. LARKWORTHY and A. YAVARI

Joseph Kenyon Laboratories, Department of Chemistry, University of Surrey, Guildford GU2 5XH, U.K.

(Received July 21, 1976)

There has been considerable discussion of the structure and properties of the compound diethylenetriammonium chlorocuprate(II), $[(NH_3CH_2CH_2)_2NH_2][CuCl_4]Cl$, first [1] believed to contain the trigonal bipyramidal anion $[CuCl_5]^{3-}$ but now known from its crystal structure [2] to contain square planar $[CuCl_4]^{2-}$ units and discrete chloride ions. Additional chlorides from neighbouring $[CuCl_4]^{2-}$ units complete an elongated octahedral about each copper ion, and give a two-dimensional network of $[CuCl_4]^{2-}$ units linked along their four-fold axes with approximately linear Cu–Cl····Cu bridges, the Cu–Cu distance being 5.1 Å. The networks are well separated by intervening amine cations and chloride ions. This compound has interesting magnetic properties [3] in that it behaved as a Heisenberg two-dimensional ferromagnet when the temperature was reduced considerably below that of liquid nitrogen, but antiferromagnetic interactions became important at still lower temperatures.

Compounds of high-spin chromium(II), S = 2, are often structurally analogous to those of copper (II), S = 1/2. The greenish-grey chromium(II) compound, $[(NH_3CH_2CH_2)_2NH_2][CrCl_4]Cl$, crystallized when hydrogen chloride was passed briefly through a solution of the amine and chromium(II) chloride [4] in concentrated hydrochloric acid. All manipulations were carried out under nitrogen or in vacuum because the dry compound* absorbs moisture and turns green in air. The chromium(II) and copper(II) compounds were found to be isomorphous, *d*-spacings and relative intensities being given in the Table. Thus, the chromium compound can be assumed to have a two-dimensional network of $[CrCl_4]^{2-}$ units giving an elongated octahedral configuration about the chromium(II) ion with a Cr–Cl···Cr separation of approximately 5.1 Å.

The effective magnetic moment, μ_e, at 295 °K, determined by the Gouy method, was 5.36 B.M., much greater than the spin-only value of 4.90 B.M. which the moments of magnetically-dilute, high-spin chromium(II) compounds are always [4, 5] close to. The magnetic moment increased markedly to over 8 B.M. at 90 °K. Least squares extrapolation of the Curie–Weiss plot between 135° and 300 °K gave a θ value of –68 °C [Curie–Weiss law taken as $\chi_A^{-1} \propto (T + \theta)$]. Therefore, the two-dimensional network leads to ferromagnetic interactions as found recently for the related chromium(II) compounds: M_2CrCl_4 (M = NH_4, K, Rb, Cs) [5–7] and Cs_2CrBr_4 [8]. The Curie point lies below the lower limit of our measurements. Neutron diffraction has confirmed [9] ferromagnetic ordering below about 58 °K in Cs_2CrCl_4. The magnetic behaviour of the diethylenetriammonium compound can be fitted approximately with J = 6 cm^{-1} and g = 1.98 to the series expansion expression [10] for a two-dimensional Heisenberg ferromagnet well above the Curie point, as has been found [6] for Cs_2CrCl_4.

TABLE. X-Ray Powder Diffraction Data for $[(NH_3CH_2CH_2)_2NH_2][MCl_4]Cl$ (Cu K_α radiation). Relative intensities I_{rel} were estimated visually.

M = Cu		M = Cr	
d_{hkl} (Å)	I_{rel}	d_{hkl} (Å)	I_{rel}
11.60	vs	11.51	vs
5.94	s	5.92	s
5.18	m	5.18	m
4.64	vs	4.69	vs
3.87	m	3.87	m
3.61	s	3.66	s
3.55	s	3.56	s
3.40	vw	3.41	vw
3.26	m	3.25	m
3.15	vw	3.14	vvw
3.04	vw	3.03	vvw
2.96	s	2.98	s
2.85	w	2.86	w
2.55	vs	2.55	vs

The isomorphism of the copper(II) and chromium (II) compounds indicates that the ferromagnetic interactions in the latter must be transmitted via the Cr–Cl····Cr elongated four-fold axis. Ferromagnetic Cs_2CrCl_4 has a K_2NiF_4 structure [9] in which two-dimensional networks of planar $[CrCl_4]^{2-}$ units, bridged by four linear Cr–Cl–Cr bonds, are separated by double layers of caesium and chloride ions. The six-fold coordination of the chromium(II) ion is completed by axial chloride ions within the CsCl layers 2.399 Å away, but the planar Cr–Cl bond lengths are all 2.609 Å, *i.e.* the octahedron is compressed, and the magnetic interaction is not transmitted along the four-fold axis. Thus, bridging along this axis is not necessary for ferromagnetism, but since the

---

**Anal.* Calcd for $C_4H_{16}Cl_5Cr$: C, 14.31; H, 4.77; N, 12.52; Cl, 52.90; Cr, 15.49. Found: C, 14.45, H, 4.98; N, 12.76; Cl, 52.91; Cr, 15.14%.

Cr–Cl–Cr distance is similar in each case (5.1 Å as above and 5.2 Å in Cs_2CrCl_4) it may be that the separation of the Cr ions is critical. The bridging angle is also important since compounds $MCrCl_3$ in which this is close to 90° are antiferromagnetic [5, 6].

The reflectance spectrum exhibits the unusually intense and sharp bands at 18,550 and 15,700 cm^{-1} found [5, 7, 8] in the spectra of other ferromagnetic chromium(II) compounds. These have been assigned [7] to spin-forbidden transitions intensified by magnetic exchange. The absorptions at 11,200 cm^{-1} and 8000 cm^{-1} constitute the usual pattern [5] for tetragonally-distorted chromium(II), and are assigned respectively to superimposed $^5B_{1g} \rightarrow {}^5B_{2g}$, ^5E_g transitions, and the $^5B_{1g} \rightarrow {}^5A_{1g}$ transition.

The related compounds $[C_2H_5NH_3]_2[CrCl_4]$, $[H_3NCH_2CH_2NH_3][CrCl_4]$, and $[CH_3NH_3]_2[CrCl_4]$ have similar unusual properties, but $[(CH_3)_2NH_2]_2$-$[CrCl_4]$ is antiferromagnetic, and its reflectance spectrum does not contain any intense "spin-forbidden" bands.

Acknowledgment

We thank the Ministry of Science and Higher Education of Iran for a scholarship (A.Y.).

References

1 G. C. Allen and N. S. Hush, *Inorg. Chem.*, *6*, 4 (1967); M. Mori and S. Fujiwara, *Bull. Chem. Soc. Japan*, *36*, 1636 (1963).

2 B. Zaslow and G. Ferguson, *Chem. Commun.*, 822 (1967); G. Ferguson and B. Zaslow, *Acta Crystallogr., Sect. B*, *27*, 849 (1971).

3 D. B. Losee and W. E. Hatfield, *J. Am. Chem. Soc.*, *95*, 8169 (1973).

4 A. Earnshaw, L. F. Larkworthy and K. S. Patel, *J. Chem. Soc.*, 3267 (1965).

5 L. F. Larkworthy, J. K. Trigg and A. Yavari, *J. Chem. Soc. Dalton*, 1879 (1975).

6 D. H. Leech and D. J. Machin, *J. Chem. Soc. Dalton*, 1609 (1975).

7 A. K. Gregson, P. Day, W. E. Gardner, D. H. Leech, and M. J. Fair, *J. Chem. Soc. Dalton*, 1306 (1975).

8 L. F. Larkworthy and A. Yavari, *Chem. Commun.*, 632 (1973).

9 M. T. Hutchings, A. K. Gregson, P. Day and D. H. Leech, *Solid State Commun.*, *15*, 313 (1974).

10 M. E. Lines, *J. Phys. and Chem. Solids*, *31*, 101 (1970).