Magnetic Behaviour of Some Copper(II) Nitrate Complexes of Benzimidazolylalkanols

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Abstract

Complexes of the type $CuL_2(NO_3)_2(H_2O)_n$ were prepared where L is benzimidazolylalkanol. When n is 1 or 2, the magnetic behaviour follows the Curie–Weiss Law. On dehydration, antiferromagnetism is observed.

In an earlier paper[1] we have described the magnetic properties and probable structures of complexes $Cu_2L_2X_2$ where L is a deprotonated benzimidazolylalkanol and X is chloride, bromide or acetate. Attempts to prepare analogous nitrate complexes led to the preparation of compounds of general formula $CuL_2(NO_3)_2(H_2O)_n$ where L is the neutral benzimidazolylalkanol and n is 1 or 2. The magnetic moments at room temperature (Table 1) are above the spin-only value. The variation of magnetic susceptibility with temperature (Table 2) for the hydrated complexes follows the Curie–Weiss law with Weiss constants, $\theta = -15 \pm 1$ K, over the temperature range 80–350 K. The complexes are sparingly soluble in warm nitrobenzene. The electrical conductivities of the nitrobenzene solutions are negligible and indicate the complexes are molecular.

Table 1. Room temperature magnetic data of complexes $CuL_2(NO_3)_2(H_2O)_n$

Ligand L	n	T (K)	$10^{10}\chi'_M$ (m^3 mol^{-1})	μ (B.M.)
Benzimidazol-2-ylmethanol	1	293	193	1·91
1-(Benzimidazol-2-yl)ethanol	2	293	177	1·83
N-Methylbenzimidazol-2-ylmethanol	1	295	173	1·81
Benzimidazol-2-ylmethanol	0	295	175	1·82

The anhydrous complex bis(benzimidazol-2-ylmethanol)dinitratocopper(II) is an antiferromagnet. The $\mu(T)$ plot is markedly curved and the magnetic moment falls below the spin-only value to 1·67 B.M. at 79 K (Table 2). The Weiss constant ($\theta = -27$ K) is larger than for the hydrated parent compound ($\theta = -14$ K). The magnetic data can be satisfactorily fitted on the basis of an infinite chain of Ising spins from Fisher's[2] expression

$$\chi = \tfrac{1}{3}\chi_{\parallel} + \tfrac{2}{3}\chi_{\perp} + N\alpha$$

[1] Hamilton, G. J., and Kokot, E., *Aust. J. Chem.*, 1973, **26**, 997.
[2] Fisher, M. E., *J. Math. Phys.* (N.Y.), 1963, **4**, 124.

where

$$\chi_{\parallel} = (Ng^2\beta^2/4k_BT)\exp(2J/k_BT)$$

and

$$\chi_{\perp} = (Ng^2\beta^2/8|J|)[\tanh(J/k_BT)+(J/k_BT)\,\mathrm{sech}^2(J/k_BT)]$$

The parameters $g = 2{\cdot}15$, $-J = 20\ \mathrm{cm}^{-1}$ and $N\alpha = 7{\cdot}5\times10^{-10}\ \mathrm{m^3\ mol^{-1}}$ give the curves in Fig. 1.

Table 2. Temperature-variation magnetic data

Bis(benzimidazol-2-ylmethanol)dinitratocopper(II) monohydrate												
T (K)	78·5	91·6	107·0	126·7	152·0	188·0	225·8	269·7	313·5			
$10^{10}\chi'_M$ ($m^3\ mol^{-1}$)	626	542	469	402	341	282	238	200	176			
μ (B.M.)	1·78	1·79	1·79	1·81	1·82	1·85	1·86	1·86	1·88			
Weiss constant $\theta = -14$ K												
Bis[1-(benzimidazol-2-yl)ethanol]dinitratocopper(II) dihydrate												
T (K)	75·7	87·5	97·6	112·0	130·0	155·5	184·5	208·0	247·0	280·0	309·0	346·5
$10^{10}\chi'_M$ ($m^3\ mol^{-1}$)	624	542	492	437	381	325	276	243	209	187	173	155
μ (B.M.)	1·74	1·74	1·75	1·77	1·78	1·80	1·81	1·80	1·82	1·83	1·85	1·86
Weiss constant $\theta = -16$ K												
Bis(*N*-methylbenzimidazol-2-ylmethanol)dinitratocopper(II) monohydrate												
T (K)	78·5	88·5	98·0	110·8	123·0	140·2	168·5	196·5	235·5	280·5	318·5	
$10^{10}\chi'_M$ ($m^3\ mol^{-1}$)	663	593	537	483	435	390	331	284	240	206	184	
μ (B.M.)	1·83	1·83	1·84	1·85	1·85	1·87	1·89	1·89	1·90	1·92	1·94	
Weiss constant $\theta = -15$ K												
Bis(benzimidazol-2-ylmethanol)dinitratocopper(II)												
T (K)	79·0	90·0	102·0	110·5	131·5	160·7	202·0	247·0	300·5	339·8	373·6	
$10^{10}\chi'_M$ ($m^3\ mol^{-1}$)	552	503	452	426	367	310	249	210	180	164	142	
μ (B.M.)	1·67	1·70	1·72	1·74	1·76	1·79	1·80	1·82	1·87	1·89	1·85	
Weiss constant $\theta = -27$ K												

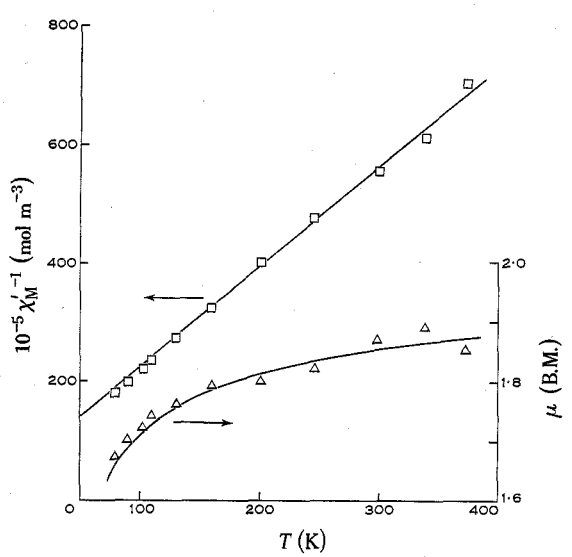

Fig. 1. Experimental values of χ'^{-1}_M (□) and μ (△) for bis(benzimidazol-2-ylmethanol)-dinitratocopper(II) superimposed on the curves calculated with parameters g 2·15, $-J$ 20 cm^{-1} and $N\alpha$ $7{\cdot}5\times10^{-10}\ \mathrm{m^3\ mol^{-1}}$.

Bridging bidentate nitrate groups are a feasible pathway for the observed antiferromagnetic exchange interaction. Similar magnetic behaviour was observed for anhydrous copper(II) nitrate.[3] The hydrated compounds may be structurally similar

[3] Kokot, E., and Martin, R. L., *Chem. Commun.*, 1965, 187.

to the anhydrous complex. Increased interlayer distance resulting from the presence of water molecules may have reduced antiferromagnetic exchange sufficiently to make it inobservable in the investigated temperature range.

Experimental

Preparations

The hydrated complexes were prepared by a common method. A solution of the ligand in ethanol was added to an aqueous ethanol solution of copper(II) nitrate. The reaction mixture was allowed to stand for 1–2 days at 0–5°C until green crystals appeared. These were collected, washed with cold alcohol and dried at room temperature.

The anhydrous complex was prepared by dehydrating the parent monohydrate at 100°C over P_4O_{10} at slightly reduced pressure. The green crystals of the monohydrate crumbled to a light green powder. Dehydration of the remaining complexes resulted in decomposition. Analytical data for the compounds are listed in Table 3. Copper was estimated volumetrically with H_4edta and murexide indicator. Carbon, hydrogen and nitrogen were determined in the Microanalytical Laboratory of the University of New South Wales.

Table 3. Elementary analyses

Copper complex	Found (%)				Calculated (%)			
	C	H	Cu	N	C	H	Cu	N
$C_{16}H_{16}CuN_6O_8,H_2O$[A]	38·5	3·5	12·8	15·7	38·4	3·6	12·7	16·8
$C_{16}H_{16}CuN_6O_8$	40·1	3·8	12·8	17·5	39·8	3·3	13·1	17·4
$C_{18}H_{20}CuN_6O_8,2H_2O$	40·0	4·3	11·2	15·0	39·5	4·4	11·6	15·3
$C_{18}H_{20}CuN_6O_8,H_2O$	40·9	4·1	11·9	15·9	40·8	4·2	12·0	15·9

[A] Weight loss on dehydration 3·8%; calc. for monohydrate 3·6%.

Magnetic Measurements

Magnetic moments at room temperature were determined by the Gouy method and calculated from the expression $\mu = 800(\chi'_M T)^{1/2}$ B.M. The diamagnetic corrections Δ were obtained from Pascal's constants. Apparatus similar to that described by Figgis and Nyholm[4] was used to measure susceptibilities at various temperatures.

Manuscript received 3 September 1974

[4] Figgis, B. N., and Nyholm, R. S., *J. Chem. Soc.*, 1959, 331.