MAGNETIC BEHAVIOUR OF SOME COPPER(II) COMPLEXES OF BENZOXAZOLE

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Duff and Hughes[1] have recently described dichlorobis(benzoxazole)copper(II) and dibromobenzoxazolecopper(II) and reported their magnetic moments as 1·57 and 0 B.M. respectively.

In this work a series of benzoxazole complexes of the general formula CuL_2X_2 was prepared where X = chloride, bromide, and nitrate and L is benzoxazole. The nitrate was also obtained as the dihydrate. The bromide and the nitrate are described for the first time. Attempts to prepare dibromobenzoxazolecopper(II) ($CuLBr_2$) were unsuccessful.

TABLE 1

ROOM TEMPERATURE MAGNETIC DATA

Complex	T (K)	$10^6\chi'_M$	μ (B.M.)	Physical description
CuL_2Cl_2	294	1500	1·89	pale blue needles, dec. $\geqslant$140°C
CuL_2Br_2	293	1460	1·86	olive green needles, dec. $\geqslant$150°C
$CuL_2(NO_3)_2$	294	1510	1·89	purple plates, dec. $\geqslant$160°C
$CuL_2(NO_3)_2,2H_2O$	292	1560	1·92	pale blue powder, dehydrates with dec.

The magnetic moments at room temperature (see Table 1) are well above the spin-only value and lie in the range $1·89\pm0·03$ B.M. The variation of the magnetic susceptibility with temperature (Table 2) follows without exception Curie–Weiss law with $\theta = -14\pm1$ K over the temperature range 80–350 K. It is possible that the magnitude of θ reflects a weak antiferromagnetic interaction which may be directed through long-range halogen (or nitrate) bridging between discrete monomer units in the solid state. Further low-temperature work in the liquid helium range might resolve this point.

The simple magnetic behaviour of the complexes probably reflects a monomeric structure. The ready solubility of the compounds in alcohol, water, acetone,

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[1] Duff, E. J., and Hughes, M. N., *J. chem. Soc.* (A), 1968, 2144.

and warm ethyl acetate also indicates a monomeric structure. From its electronic spectra (both solid and solution) Duff and Hughes conclude that CuL_2Cl_2 is square-planar.

TABLE 2

TEMPERATURE VARIATION MAGNETIC DATA

T in K, μ in B.M.

CuL_2Cl_2			CuL_2Br_2			$CuL_2(NO_3)_2$			$CuL_2(NO_3)_2,2H_2O$		
T	$10^6\chi'_M$	μ	T	$10^6\chi'_M$	μ	T	$10^6\chi'_M$	μ	T	$10^6\chi'_M$	μ
80·5	5111	1·82	79·4	4928	1·78	78·0	5054	1·78	82·0	5054	1·83
90·0	4728	1·85	90·0	4343	1·78	88·0	4480	1·78	92·0	4402	1·81
100·0	4251	1·85	100·0	3947	1·78	98·5	4028	1·79	105·0	3924	1·82
115·0	3735	1·86	115·0	3481	1·80	120·0	3369	1·81	120·0	3471	1·83
140·0	3146	1·88	140·0	2941	1·82	150·0	2757	1·83	150·0	2834	1·85
180·0	2464	1·89	180·0	2325	1·84	190·0	2236	1·85	191·5	2277	1·88
220·0	2032	1·90	220·0	1917	1·84	230·0	1852	1·85	230·0	1908	1·88
260·0	1736	1·91	260·0	1638	1·85	270·0	1625	1·88	270·0	1644	1·89
300·0	1491	1·90	300·0	1427	1·86	310·0	1433	1·89	310·0	1467	1·91
350·0	1369	1·97	340·0	1301	1·89	350·0	1229	1·86			
θ −14 K			θ −15 K			θ −13 K			θ −14 K		

The anhydrous $CuL_2(NO_3)_2$ is strongly hygroscopic and on exposure to air is converted within 2 hr into the dihydrate $CuL_2(NO_3)_2,2H_2O$. Owing to its hygroscopic nature, an electronic reflectance spectrum of anydrous $CuL_2(NO_3)_2$, uncontaminated by water, was not obtained. The electronic reflectance spectrum of $CuL_2(NO_3)_2,2H_2O$ is indicative of a square-pyramidal structure (15100, 11800sh cm^{-1}). The complex may be better formulated $[CuL_2(NO_3)_2H_2O]H_2O$, dinitratoaquobis(benzoxazole)-copper(II) monohydrate.

The discrepancy in the value of the magnetic moment for dichlorobis(benzoxazole)copper(II) in this work and that of Duff and Hughes is surprising in that the compound described here was prepared by the method quoted by Duff and Hughes and it is of the same colour.

It is possible that the differing magnetic moments reflect structurally different compounds. Structural isomerism is known to result in differences in magnetic behaviour for the various modifications of copper(II) formate.[2]

Experimental

Preparations

The complexes were prepared by the method described by Duff and Hughes.[1] Dibromobis-(benzoxazole)copper(II) crystallized when the temperature of the reaction mixture was kept below 20°C. The product was washed in dry ether and excess washing solvent was removed over paraffin wax at room temperature.

Attempted recrystallization from ethanol and ethyl acetate–ethanol mixtures gave black decomposition products of variable composition. Copper was determined volumetrically using EDTA and murexide indicator. Halogen was determined potentiometrically. Carbon, hydrogen,

[2] Martin, R. L., and Waterman, H., *J. chem. Soc.*, 1959, 1359.

and nitrogen analyses were determined in the Microanalytical Laboratory of the University of New South Wales. Analytical data are collated in Table 3.

TABLE 3

ANALYSES

Complex	Found (%)					Calc. (%)				
	C	H	Cu	N	Hal	C	H	Cu	N	Hal
CuL_2Cl_2	45·4	3·1	17·2	8·0	19·7	45·1	2·7	17·0	7·5	19·1
CuL_2Br_2	36·5	2·5	14·0	6·0	34·3	36·4	2·2	13·8	6·1	34·6
$CuL_2(NO_3)_2$	38·9	2·5	15·2	13·2	—	39·5	2·4	14·9	13·2	—
$CuL_2(NO_3)_2,2H_2O$	36·6	3·2	14·0	12·1	—	36·2	3·1	13·8	12·1	—

Magnetic Measurements

Magnetic moments at room temperature were determined by the Gouy method and calculated from the expression $\mu = 2{\cdot}839(\chi'_M T)^{1/2}$. The diamagnetic corrections, Δ, were obtained from Pascal's constants. Apparatus similar to that described by Figgis and Nyholm[3] was used to measure susceptibilities at various temperatures.

Electronic Reflectance Spectra

Electronic reflectance spectra were run on a Zeiss PMQ-II spectrophotometer with an RA-3 reflectance attachment.

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