Inorganica Chimica Acta, 25 (1977) L131–L132

Magnetic Properties of Cu(pyrr:2-amino-2-methyl propanol

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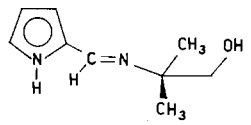
Received October 20, 1977

Syamal and Kale have recently reported [1] the synthesis and magnetic properties of two copper(II) Schiff base complexes derived from pyrrole-2-aldehyde and isopropanolamine or 2-amino-2-methyl propanol. Cu(pyrr:isopropanolamine) has previously been reported from this laboratory [2]. The second



complex, Cu(pyrr:2-amino-2-methyl propanol), has been characterised as a dimer and involved in antiferromagnetic interactions [1]. This complex contains a five membered chelate ring in the alcohol-amine part of the ligand and all complexes of this type have been reported to be tetrameric. The difference in properties was attributed to the presence of steric factors arising from the two methyl groups in this complex [1]. Cu(sal:2-amino-2-methyl propanol) has been reported to be tetrameric [3] and the two methyl groups do not hinder formation of a tetramer in this case. We therefore decided to re-investigate the properties of Cu(pyrr:2-amino-2-methyl propanol).

Experimental

Cu(pyrr:2-amino-2-methyl propanol) was prepared as reported with the exception that equimolar copper (II) nitrate trihydrate and Schiff base were used rather than 1:2 described. The complex was recrystallized from chloroform and ethanol mixtures. The shining dark green crystals were dried in vacuum. Analyzed for $CuC_9H_{12}N_2O$: Calcd: C, 47.46; H, 5.27; N, 12.30; Cu, 27.92. Found: C, 47.29; H, 5.39; N, 12.01; Cu, 27.86%. The molecular weight was determined in chloroform at 37 °C using a Mechrolab Model 301A Osmometer calibrated with benzil. Magnetic susceptibility data was collected on a Faraday balance [4] using $HgCo(NCS)_4$ as the standard. The magnetic data was computed on a IBM 360/50 computer. The experimental susceptibility data was fitted to theoretical susceptibility equations derived from the HDVV-model for appropriate symmetry employing a non-linear least square fitting program utilizing $\Sigma_i(\chi_M(exp)_i - \chi_M(calcd)_i)^2 T_i^2$ as the fitting criterion [5].

Results and Discussion

Repeated molecular weight measurements in chloroform solutions indicate that the complex Cu(pyrr:2-amino-2-methyl propanol) is tetrameric. The nujol mull spectrum exhibits a band centered around 16,000 cm^{-1} which does not change in chloroform solution. The electronic spectrum is not consistent with a dimeric structure with copper(II) in a planar environment.

Magnetic data is presented in Table I. The magnetic moments drop quite appreciably with decrease in temperature suggesting a singlet ground state. The magnetic behavior could not be approximated by treating the compound as a dimer [6] (Table II).

TABLE I. Magnetic Susceptibility Data for Cu(pyrr:2-amino-2-methyl propanol).

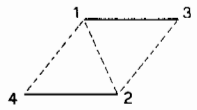
Temp, °K	μ_{eff}, BM	$\chi_M \times 10^{-6}$ cgs emu experimental	$\chi_M \times 10^{-6}$ cgs-emu calculated
298.9	1.70	1203	1190
254.3	1.64	1328	1335
222.4	1.61	1455	1459
203.7	1.57	1523	1540
173.0	1.52	1688	1683
151.7	1.48	1800	1787
129.0	1.39	1876	1886
98.8	1.24	1940	1955
76.8	1.08	1907	1888
52.2	0.80	1532	1536
26.7	0.33	508	507

TABLE II. Estimated Parameters.

Model	J (cm^{-1})	g	Residual sum of Squares
Bleaney–Bowers	$J = -48.1$	1.94	1.3×10^{-7}
T_d	$J = -46.1$	2.25	4.8×10^{-8}
D_{2d}	$J_S = -48.1$	1.94	1.3×10^{-7}
	$J_L = 0.3$		
C_{2v}	$J_{13} = J_{24} = -32.1$	2.40	4.4×10^{-9}
	$J_{34} = 0$		
	$J_{23} = J_{14} = +31$		
	$J_{12} = -31.6$		
C_2	$J_1 = -45$	2.07	2.0×10^{-9}
	$J_2 = -55$		
	$J_3 = +22$		

$N\alpha$ is fixed at 60×10^{-6} cgs-emu

The tetrameric treatment involves the various approximate symmetries for the core *viz.*: T_d, D_{2d}, C_{2v} and C_2. These equations were tested [7, 8, 9] and the best fit was obtained with the arrangement shown below.



Based on a spin-only isotropic Heisenberg–Dirac–van Vleck model a general susceptibility equation for 4-centers of 1/2 spin system has been described by Sinn [10]. The Hamiltonian is $H = -2\Sigma_{j>i=1}^{4} J_{ij}\hat{S}_i\hat{S}_j$ and the general susceptibility equation is given by

$$\chi_M = \frac{Ng^2\beta^2}{4kT} \frac{10e^{-E_2/kT} + 2(e^{-E_1^a/kT} + e^{-E_1^b/kT} + e^{-E_1^c/kT})}{5e^{-E_2/kT} + 3(e^{-E_1^a/kT} + e^{-E_1^b/kT} + e^{-E_1^c/kT}) + e^{-E_0^\alpha/kT} + e^{-E_0^\beta/kT}} + N\alpha \quad (1)$$

where E_2, $E^{a,b,c}$ *etc.* are the energies of the total spin states S_T = 2,1,1,1,0,0.

A simple equation appropriate for the arrangement of copper ions as in the above drawing (C_2 symmetry; J_{34} = 0 since the atoms are far apart) can be obtained. The Hamiltonian describing this system is then given by

$$H = -2J_1(\hat{S}_1\hat{S}_2) - 2J_2(\hat{S}_2\hat{S}_4 + \hat{S}_1\hat{S}_3) - 2J_3(\hat{S}_1\hat{S}_4 + \hat{S}_2\hat{S}_3)$$

and the sixteen energy levels corresponding to the various S^T values are as follows.

	S^T	E_{S^T}	
(5)	2	$-J_1/2 - J_2 - J_3$	E_2
(3)	1	$-J_1/2 + J_2 + J_3$	E_1^a
(3)	1	$J_1/2 + A$	E_1^b
(3)	1	$J_1/2 - A$	E_1^c
(1)	0	$J_1/2 + J_2 + J_3 + B$	E_0^α
(1)	0	$J_1/2 + J_2 + J_3 - B$	E_0^β

(16)

$$A = \{J_1^2 + (J_3 - J_2)^2\}^{1/2}$$

$$B = (J_1^2 + 4J_2^2 + 4J_3^2 - 2J_1J_2 - 2J_1J_3 - 4J_2J_3)^{1/2}$$

The energy levels thus obtained can be substituted into equation 1 to obtain the appropriate expression. This expression when applied to the data for Cu(pyrr: 2-amino-2-methyl propanol) gave an excellent fit between experimental and calculated values with parameters J_1 = –45 cm^{-1}, J_2 = –55 cm^{-1}, J_3 = +22 cm^{-1}, g = 2.07 and the sum of the squares of the residuals was 2.0×10^{-9}. The best fit in favor of the C_2 arrangement seems unusual. In the absence of X-ray data this cannot be pursued further.

Acknowledgment

This research was supported by The Robert A. Welch Foundation and the North Texas State University Faculty Research Fund. We wish to thank Professor W. A. Baker, Jr. and Dr. R. C. Dickinson for the magnetic measurements.

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