Contribution from the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514, U.S.A.

The Magnetism of Di-μ-N,N'-*m*-Phenylenetetrakis-(salicylideneiminato)dicopper(II)

David Y. Jeter[1] and William E. Hatfield

Received October 26, 1971

*The magnetic susceptibility of the dimer di-μ-N,N'-*m*-phenylenetetrakis(salicylideneiminato)dicopper(II) obey the Curie-Weiss law over the temperature range 2.7-290°K yielding μ_{eff} = 1.73 B. M. The electron paramagnetic resonance spectrum gives evidence for the triplet state as well as lines which apparently arise from transitions between the singlet ground state and the excited triplet state.*

Introduction

In a recent crystal structure determination, Bear, Waters, and Waters[2] found that the complex previously formulated as N,N'-*m*-phenylenebis(salicylideneiminato)copper(II)[3] is in fact a centrosymmetric dimer composed of two bis(salicylideneiminato)copper(II) residues bridged by two *m*-phenylene groups. A chloroform molecule is hydrogen bonded *trans* to the *m*-phenylene bridges at each copper atom. The environment about copper is distorted and is best described as being intermediate between *cis*-planar and regular tetrahedral. As a part of our continuing study of bridged copper(II) complexes,[4-6] we report in this article the results of both electron paramagnetic resonance and magnetic susceptibility studies on di-μ-N,N'-*m*-phenylenetetrakis(salicylideneiminato)dicopper(II).

Experimental Section

Preparation of the Compound. The procedure described by Bear, *et al.*[2] was used for this preparation. The ligand was made by adding a small volume of salicyladehyde to a hot solution of decolorized *m*-phenylenediamine dissolved in chloroform. The yellowish solution was then allowed to stand for a few minutes, after which a hot ethanol solution of copper(II) acetate was gently filtered on to the surface of the hot ligand solution. Three layers were initially observed; blue on top (copper(II) acetate), brown in the middle (complex), and yellow on the bottom (ligand). These layers slowly diffused together. Upon slight evaporation a crystalline substance precipitated. This was collected, washed with chloroform, and dried. The resulting crystals which appear to be purple become light brown upon powdering.

Anal. Calcd for $CuC_{20}H_{14}N_2O_2 \cdot CHCl_3$: C, 50.72; H, 3.04; N, 5.63%. Found: C, 50.93; H, 3.14; N, 5.89%.

Magnetic Measurements. The magnetic susceptibilities of a powdered sample in the temperature range 77.2 to 290°K were measured using a Faraday balance.[7] A Foner-type vibrating sample magnetometer,[8] operating at a field strength of 10,000 G was used for measurements in the range 2.7° to 60°K. The magnetic susceptibility standard used was mercury tetrathiocyanatocobaltate(II).[9] The appropriate diamagnetic corrections for the substituent atoms were estimated from Pascal's constants.[10]

EPR Measurements. The EPR spectra of both a powder sample at room temperature and 77.2°K, and a frozen solution of the complex in chloroform at 77.2°K, were obtained using a Varian Model E-3 X-band spectrometer with 100 kHz modulation. The microwave frequencies used were 9.18 GHz at room temperature and 9.19 GHz at 77.2°K. Cylindrical quartz sample tubes were used with the standard Varian E-4531 cavity. A quartz dewar which fitted into the cavity was used at the low temperature.

Results

Electron paramagnetic resonance spectra were recorded at room temperature using a polycrystalline sample. A very strong unsymmetrical absorption was seen near 3200 G with additional weak lines at about 1500, 4700, and 6100 G as shown in Figure 1. At 77°K these resonances still may be seen although the line near 6100 G increased in relative intensity,

---

[1] NSF Trainee 1968-71.

[2] C.A. Bear, J.M. Waters, and T.N. Waters, *J. Chem. Soc. (A)*, 1494 (1970).

[3] P. Pfeiffer and H. Pfitzner, *J. Prakt. Chem.*, *145*, 246 (1936).

[4] W.E. Hatfield, J.A. Barnes, D.Y. Jeter, R. Whyman, and E.R. Jones, *J. Amer. Chem. Soc.*, *92*, 4982 (1970).

[5] D.Y. Jeter, D.J. Hodgson, and W.E. Hatfield, *Inorg. Chim. Acta*, *5*, 257 (1971).

[6] N.T. Watkins, D.Y. Jeter, W.E. Hatfield, and S.M. Horner, *Trans. Faraday Soc.*, *67*, 2431 (1971).

[7] W.E. Hatfield, C.S. Fountain, and R. Whyman, *Inorg. Chem.*, *5*, 1855 (1966).

[8] S. Foner, *Rev. Sci. Instr.*, *30*, 548 (1959).

[9] B.N. Figgis and R.S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

[10] E. König, *Magnetic Properties of Transition Metal Compounds*, Springer-Verlag, Berlin, 1966.

thereby partially obscuring the 4700 G absorption. The spectra of the complex in a chloroform glass were much richer than those for the solid state sample. In all, seven main absorptions were observed. Of these, five lines near 1560, 2790, 3030, 3230, and 3250 G can be tentatively interpreted in terms of the spin Hamiltonian for the triplet state which is expressed as[11]

$$H = \beta HgS + DS_z^2 + E(S_x^2 - S_y^2) - \frac{2D}{3}.$$

The absorption near 1560 G, although very weak, can be assigned to the resonance field H_{min}[12] which is due to the $\Delta M_s = \pm 2$ transition. In the $\Delta M_s = \pm 1$ region, shown in Figures 2 and 3, the 2790 G absorption is assignable to the low-field parallel transition, using the notation of Wasserman, *et al.*[13] since copper hyperfine is observable on this line where the splittings is approximately 70 G. The line near 3030 G is assignable as the low-field perpendicular component. Two intense absorptions appear at 3090 and 3120 G which do not appear to be part of the triplet spectrum can likely be attributed to impurities with the spin state $S = 1/2$. On the high field side of these lines are lines at about 3230, 3300, and 3370 G which are separated by 70 G and can be assigned as the $M_I = 0, -1$, and -2 components of the high-field parallel transition. Finally, the shoulder at 3250 G is assigned to the high-field perpendicular transition. These assignments give $g_\parallel = 2.18$, $g_\perp = 2.09$ and $|D| = 0.022$ cm^{-1} with the assumption that $E = 0$. Assigning other transitions to these absorptions results in unlikely magnetic parameters. It should be mentioned that a very broad absorption comparable to the 5700 G line in the powder spectrum was observed.

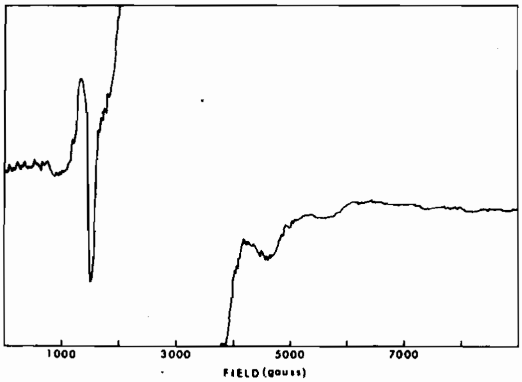

Figure 1. The powder EPR spectrum of di-µN,N'-*m*-phenylenetetrakis(salicylideneiminatodicopper(II) at room temperature in the range 0-9,000 G. The single intense absorption near 3000 G has, from necessity, been omitted here.

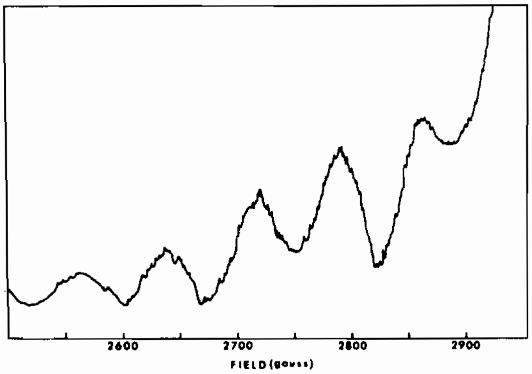

Figure 2. The chloroform glass spectrum of diµ-N,N'-*m*-phenylenetetrakis(salicylideneiminato)dicopper(II) at 77°K in the range 2500-2950 G.

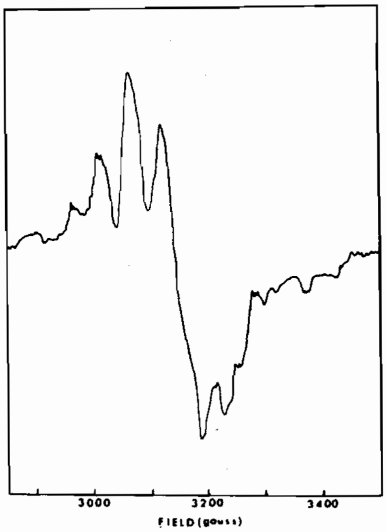

Figure 3. The chloroform glass spectrum of di-µ-N,N'-*m*-phenylenetetrakis(salicylideneiminato)dicopper(II) at 77°K in the range 2850-3500 G.

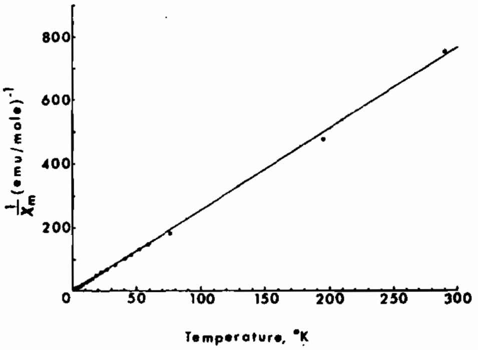

Figure 4. The temperature variation of the inverse susceptibility for di-µ-N,N'-*m*-phenylenetetrakis(salicylideneiminato)-dicopper(II) in the temperature range 2.7-2.90°K.

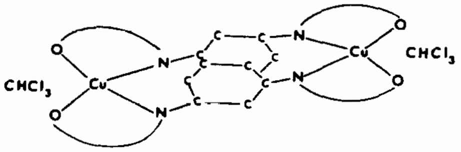

Figure 5. A schematic representation of the structure of di-µ-N,N'-*m*-phenylenetetrakis(salicylideneiminato)dicopper(II). The two salicylideneiminato residues have been abbreviated.

---

[11] B. Bleaney and K.D. Bowers, *Proc. Roy. Soc., Ser., A, 214,* 451 (1952).
[12] P. Kottis and R. Lefebvre, *J. Chem. Phys.,* 39, 393 (1963).
[13] E. Wasserman, L.C. Snyder, and N.A. Yager, *J. Chem. Phys., 41,* 1763 (1964).

Table I. Magnetic Susceptibility Data for Di-μ-N,N′-*m*-phenylenetetrakis(salicylideneiminato)dicopper(II).

Temperature (°K)	$\chi_m^{corr}(\times 10)$ c.g.s.	$1/\chi_m^{corr}$	μ_{eff}(B.M.)
2.7	0.99180	10.1	1.46
3.0	0.95620	10.5	1.51
3.4	0.87910	11.4	1.54
3.6	0.84910	11.8	1.56
4.2	0.78250	12.8	1.62
4.6	0.77270	12.9	1.68
4.9	0.73550	13.6	1.69
5.1	0.71620	14.0	1.70
5.4	0.68190	14.7	1.71
6.1	0.61890	16.2	1.73
6.9	0.55470	18.0	1.75
7.5	0.51380	19.5	1.75
8.5	0.46270	21.6	1.77
9.9	0.40180	24.9	1.78
11.6	0.35040	28.5	1.80
14.0	0.28770	34.8	1.79
16.2	0.24560	40.7	1.78
19.5	0.19800	50.5	1.75
23.0	0.16530	60.5	1.74
27.5	0.14590	68.5	1.79
34.0	0.11670	85.7	1.78
42.0	0.09478	105.5	1.78
47.0	0.08662	115.4	1.80
53.0	0.07258	137.8	1.75
60.0	0.06550	152.7	1.77
77.2	0.05358	186.6	1.81
195.0	0.02062	485.0	1.79
290.0	0.01292	774.0	1.73

The magnetic susceptibility data for the complex are listed in Table I. As can be seen in Figure 4, the data obey the Curie-Weiss law, $\chi = C/(T+\theta)$ to low temperatures with $C = 0.374$, $\theta = -0.5°$, and $\mu_{eff} = 1.73$ B.M.

Discussion

A schematic representation of the structure[2] of this dimeric complex is shown in Figure 5. The coordination environment about each copper(II) ion is intermediate between *cis*-planar and tetrahedral with the two Cu–O bonds being 1.9 Å long and the two Cu–N bonds about 1.97 Å. The angle between the two salicylideneiminato residues is 43.6°. Each of the coordination centers is bridged by two *m*-phenylene groups with Cu–Cu internuclear separation of approximately 8.5 Å. It is also calculated that the distance between copper ions in neighboring dimers is about 8.4 Å. Exchange interaction if present in such a complex would necessarily be small due to both the wide separation of the metals and the relatively great length of the bridges.

The magnitude of the exchange energy can be estimated from the magnetic susceptibility data using the expression[14]

$$\chi = \frac{\frac{N}{H}\Sigma[\mu_n \exp(-E_n/kT)]}{\Sigma[\exp(-E_n/kT]}$$

where $\mu = \partial E/\partial H$. At zero field the energy levels in a singlet-triplet equilibrium can be approximated by those values shown in Table II where D is the zero field splitting parameter and 2J is the energy separation between the singlet and triplet spin states. Using the EPR average g-value of 2.12 and the measured susceptibility at a field of 10,000 G, it is found that $-2J$ is of the order of 1.0 cm^{-1}. Entering $-2J$ of this magnitude into the Van Vleck dimer equation[15]

$$\chi = \frac{g^2\beta^2 N}{3kT}[1+\frac{1}{3}\exp(\frac{-2J}{kT})]^{-1}$$

one can reasonably approximate the experimentally observed data.

Table II. Singlet-Triplet Energy Levels.

$S=0$	$E=0$
$S=1$	$E_1=g\beta H+2J+D/3$
	$E_2=2J-2D/3$
	$E_3=g\beta H+2J+D/3$

In an $S = 1$ system, such as this copper(II) dimer, the presence of the singlet energy level only a wave number in energy below the triplet spin state leads to the possibility of $\Delta M_s = \pm 1$ transition between the two electronic states in addition to those normally observed in the triplet alone.[16,17] For any transition probability to exist, however, the selection rule $\Delta S = 0$ must be at least partially relaxed. It seems likely that the mixing of energy levels which would undoubtedly result in such an arrangement described above would be sufficient to cause such. This apparently is the case in the complex under study as reflected by the EPR absorption observed clearly in the powder spectra at 4700 and 6100 G. These lines are tentatively assigned as perpendicular and parallel resonance fields respectively. This conclusion further means that the analysis of the usual triplet absorption cannot be accurate due to the impurity of the wave functions involved, although it is probably a good initial approximation.

---

(14) See, for example, C.J. Ballhausen, *Introduction to Ligand Field Theory*, McGraw-Hill Book Co., Inc., New York, 1962, p. 139 ff.

(15) J.H. Van Vleck, The Theory of Electric and Magnetic Susceptibilities, Oxford University Press, London, Chapter IX, 1932.

(16) H.R. Falle, G.R. Luckhurst, H. Lemaire, Y. Marechal, A. Rassat, and P. Rey, *Mol. Phys.*, *11*, 49 (1966).

(17) R.H. Dunhill and M.C.R. Symons, *Mol. Phys.*, 15, 105 (1968).