

Pressure in Coordination Chemistry. II.¹ Antiferromagnetic Complexes of Copper(II)

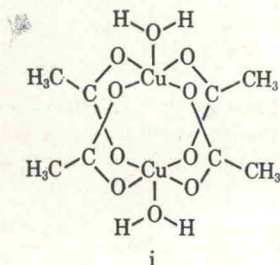
BY A. H. EWALD AND E. SINN

Received July 22, 1968

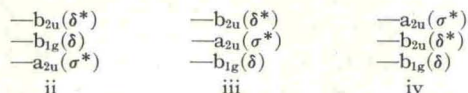
The effect of high pressure (1–3000 atm) on the magnetic properties of binuclear carboxylate complexes of copper(II), all of which exhibit pairwise antiferromagnetic interactions, is found to be surprisingly small, when the measurements are made on solutions in aprotic solvents or on the solids milled in inert media. This indicates that there is little reduction in volume in going from the "triplet state" dimer (with one unpaired electron per copper) to the "singlet state" dimer (diamagnetic). The polymeric copper(II) oxalate behaves similarly. This result is best explained in terms of a weak copper–copper interaction, in the form of a δ bond or a superexchange mechanism. In solutions containing "structure-breaking" solvents, such as ethanol or pyridine, there is an increase in magnetic susceptibility with increasing pressure, which is attributed to the dissociation of the bimolecular complexes.

Introduction

Since the first observation of the unusually low magnetic susceptibility of copper(II) acetate monohydrate,² postulates of the bonding responsible for the lowering in the magnetism in the binuclear complex³ (i) have varied from a weak δ bond,^{4,5} or superexchange interactions between isolated copper ions,⁶ to a strong σ bond, or a strong δ -bonding interaction.^{7,8}



The molecular orbitals $a_{2u}(\sigma^*)$ derived from the copper d_{z^2} orbitals, which lie along the Cu–Cu axis in i, and $b_{1g}(\delta)$ and $b_{2u}(\delta^*)$ derived from the $d_{x^2-y^2}$ orbitals, which lie normal to the Cu–Cu axis in i, are most likely to be the three highest energy molecular orbitals and should therefore be responsible for the copper–copper interaction.^{4,6–8} Arguments have been presented for three different relative energies—ii,⁴ iii,⁷ and iv⁸—of these molecular orbitals



The complete orbital schemes are then

$$a_{1g}(\sigma)^2 e_u(\pi)^4 e_g(\pi^*)^4 b_{2g}(\delta')^2 b_{1u}(\delta'^*)^2 a_{2u}(\sigma^*)^2 b_{1g}(\delta)^2 \quad (\text{ii})$$

$$[a_{1g}(\sigma)^2, e_u(\pi)^4] e_g(\pi^*)^4 b_{2g}(\delta')^2 b_{1u}(\delta'^*) b_{1g}(\delta)^2 a_{2u}(\sigma^*)^2 \quad (\text{iii})$$

$$e_u(\pi)^4 a_{1g}(\sigma)^2 e_g(\pi^*)^4 b_{2g}(\delta')^2 b_{1u}(\delta'^*) b_{1g}(\delta)^2 b_{2u}(\delta^*)^2 \quad (\text{iv})$$

for the singlet state of the molecule and

$$a_{1g}(\sigma)^2 e_u(\pi)^4 e_g(\pi^*)^4 b_{2g}(\delta')^2 b_{1u}(\delta'^*)^2 a_{2u}(\sigma^*)^2 b_{1g}(\delta)^2 b_{2u}(\delta^*)^1 \quad (\text{ii})$$

$$[a_{1g}(\sigma)^2, e_u(\pi)^4] e_g(\pi^*)^4 b_{2g}(\delta')^2 b_{1u}(\delta'^*)^2 b_{1g}(\delta)^2 a_{2u}(\sigma^*)^1 b_{2u}(\delta^*)^1 \quad (\text{iii})$$

$$e_u(\pi)^4 a_{1g}(\sigma)^2 e_g(\pi^*)^4 b_{2g}(\delta')^2 b_{1u}(\delta'^*)^2 b_{1g}(\delta)^2 b_{2u}(\delta^*)^1 a_{2u}(\sigma^*)^2 \quad (\text{iv})$$

for the triplet state. The orbitals are labeled according to their symmetries with respect to their tetragonal axes, *i.e.*, $d_{z^2} = \sigma$, $d_{x^2-y^2} = \pi$, $d_{x^2-y^2} = \delta$, and $d_{xy} = \delta'$.

Copper acetate monohydrate has an epr spectrum^{5,8,9} characteristic of a triplet molecule, and the spectrum is quenched at low temperatures, as is the magnetic moment, owing to mutual pairing within the dimeric molecule i of the single unpaired electrons on the two copper atoms. Thus, it is more pertinent to talk of the singlet and triplet states in molecule i than of the unpaired electron per copper atom.

If the interaction between the two copper atoms results in a strong bond formation (arrangements iii and iv of the orbitals), the molar volume of complex i in the singlet state should be smaller than that in the triplet state, and increasing external pressure is expected to raise the population in the singlet state. This would result in a decrease in the magnetic susceptibility with increasing pressure, analogous to that found in the iron(III) dithiocarbamates,^{10,11} xanthates,¹¹ and thio-xanthates,¹² where the transfer of 1 mol of complex in the sextuplet 6A_1 state to the doublet 2T_2 state is accompanied by a contraction of 5–6 cm³/mol. In nickel salicylaldimines¹ dimerization is favored by increase in pressure and leads to an increase in magnetic susceptibility. The formation of one new bond per molecule results in a contraction of 7–8 cm³/mol.

(1) Part I: A. H. Ewald and E. Sinn, *Inorg. Chem.*, **6**, 40 (1967).
 (2) J. Lifschitz and E. Rosenbohm, *Z. Elektrochem.*, **21**, 499 (1915).
 (3) J. N. van Niekerk and F. R. L. Schoenig, *Nature*, **171**, 36 (1953); *Acta Cryst.*, **6**, 227 (1953).
 (4) B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 3837 (1956).
 (5) I. G. Ross, *Trans. Faraday Soc.*, **55**, 1057 (1959); I. G. Ross and J. Yates, *ibid.*, **55**, 1064 (1959); M. L. Tonnet, S. Yamada, and I. G. Ross, *ibid.*, **60**, 840 (1964).
 (6) B. Bleaney and K. D. Bowers, *Proc. Roy. Soc. (London)*, **A214**, 451 (1952).
 (7) D. J. Royer, *Inorg. Chem.*, **4**, 1830 (1965).
 (8) L. S. Forster and C. J. Ballhausen, *Acta Chem. Scand.*, **16**, 1385 (1962).

(9) F. W. Lancaster and W. Gordy, *J. Chem. Phys.*, **19**, 1181 (1951); H. Abe and J. Shimada, *Phys. Rev.*, **90**, 316 (1953).
 (10) A. H. Ewald, R. L. Martin, I. G. Ross, and A. H. White, *Proc. Roy. Soc. (London)*, **A280**, 235 (1964).
 (11) A. H. Ewald, R. L. Martin, E. Sinn, and A. H. White, submitted for publication.
 (12) A. H. Ewald and E. Sinn, *Australian J. Chem.*, **21**, 927 (1968).

If the interaction between two copper atoms is weak (arrangement ii of the orbitals) and especially if it involves bulky nonbonding or antibonding orbitals even in the singlet state,¹³ then there may not be very much difference between the volumes of the singlet and triplet states, and the effect of pressure would be correspondingly smaller.

It is well established that the basic structural unit of copper acetate (i) is shared by copper complexes of the other alkanolic acids,¹⁴ with the exception of some copper(II) formate derivatives.¹⁵ The range of this study has thus been extended to include other alkanates measured in a variety of solvents. Copper(II) acetate is soluble only in protic solvents such as water and ethanol, while copper(II) octanoate is soluble in chloroform and ethanol, but not in water.

Experimental Section

The copper salts were prepared by standard methods.¹⁶⁻¹⁷ Saturated suspensions of copper(II) acetate monohydrate, chloroacetate, oxalate, and succinate were prepared by allowing the finely powdered complexes to stand in chloroform for several days and discarding the top layer. No appreciable further settling occurred in the limited periods of time required for measurements. The solubility of long-chain alkanates in chloroform was not as high as desirable, but measurements could be made on slightly supersaturated solutions, which remained stable for a few hours. Attempts to use strongly supersaturated solutions invariably resulted in some of the complex coming out of solution at high pressures.

The magnetic measurements were made as previously described.^{1,10} All of the measurements were made at room temperature (about 20°), which did not vary by more than 1° during any one run. The densities of the solutions and suspensions were measured at atmospheric pressure, and the densities at other pressures were estimated from their compressibility values. The compressibilities of solutions were assumed to be the same as those of the solvents;¹⁸ mixed solvents were assumed to obey the Wiedemann mixture law. The compressibilities of suspensions were estimated from the reduction in the lengths of suspensions when compressed in a tube whose cross-sectional area remained constant within experimental error. The accuracy of the solution magnetic moment values is about 3%, but the relative values for a single substance over a pressure range are accurate to within about 1%.¹ The accuracy is better (0.5%) in the mulls because of the much higher concentration.

Discussion

Increasing pressure is seen (Table I) to have very little effect on the magnetic properties of the solid binuclear copper(II) acetate, chloroacetate, and succinate complexes, or on the polymeric¹⁷ oxalate. There is an over-all decrease of magnetic susceptibility with increasing pressure, but the effect is very slight and the calculated volume difference (*cf* ref 1) between the singlet and triplet forms is very small (<0.5 cm³/

mol). No pressure dependence is observed for the magnetic properties of copper(II) octanoate and decanoate in chloroform solution. As the concentration of complex was much lower than in the mulls, the accuracy available from the solution measurements is lower, and a very small pressure effect would therefore be obscured by experimental error.

TABLE I
MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS^a
OF COPPER(II) ALKANOATES^b

	Pressure, atm				
	1	500	1000	2000	3000
Alkanoate (medium)					
Acetate	861	844	842	833	824
(82.5% in CHCl ₃ mull)	1.38	1.37	1.36	1.35	1.35
Chloroacetate	904	887	882	873	867
(79.5% in CHCl ₃ mull)	1.41	1.40	1.39	1.38	1.38
Oxalate	562	552	550	543	636
(86.8% in CHCl ₂ mull)	1.09	1.08	1.08	1.07	1.06
Succinate	794	781	783	769	760
(83.7% in CHCl ₃ mull)	1.32	1.31	1.31	1.30	1.29
Acetate	1367	1364	1348	1375	1399
(6.1% in water)	1.76	1.75	1.74	1.76	1.78
Hexanoate	821	801	837	789	815
(1.6% in CH ₂ Cl ₂)	1.34	1.33	1.36	1.31	1.34
Octanoate	839	852	841	862	827
(2.3% in CH ₂ Cl ₂)	1.36	1.37	1.36	1.38	1.35
Octanoate	1011	1038	1074	1098	1129
(2.2% in CH ₂ Cl ₂ + ethanol (35%))	1.50	1.52	1.55	1.57	1.59
Decanoate	9.67		1017	1051	1108
(2.5% in CHCl ₃ + pyridine (13.1%))	1.46		1.50	1.53	1.57

^a The magnetic moments are corrected for a temperature-independent paramagnetism of 60×10^{-6} cgsu. ^b The first line for each complex gives $10^6 \chi_M$ in cgsu; the second line gives μ_{eff} in BM.

The pressure results seem reasonable in terms of a weak δ bond⁴ or Kramer's superexchange interactions between the copper atoms.⁶ In agreement with this, a recent discussion of the copper(II) alkanate spectra presents a "multiple-doughnut" representation of the acetate π system, which allows for both of these types of interaction between the coppers,¹⁹ while stressing that the δ bond "is so weak that the configuration of the binuclear molecule can only be maintained by the four bridging acetate groups."^{4,19} The results are not compatible with a strong copper-copper interaction.^{7,8}

The electronic spectra of copper(II) alkanates show a pressure dependence. The intensity of band I (650 m μ) increases with rising pressure, an effect compatible with the assignment of this band as an asymmetry-allowed d-d transition, probably $\delta' \rightarrow \delta$ (or ${}^2B_1 \rightarrow {}^2E$).^{5,19,20} The intensity of band II (370 m μ) decreases with rising pressure as would be expected, since this band is believed to be vibronically allowed.^{19,20}

In the presence of some aprotic solvents such as water or ethanol, or other "structure-breaking" sol-

(13) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press Inc., New York, N. Y., 1964.

(14) M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, **64**, 99 (1964).

(15) R. L. Martin and H. Waterman, *J. Chem. Soc.*, 1359 (1959).

(16) R. L. Martin and H. Waterman, *ibid.*, 2545 (1957).

(17) L. Dubicki, C. M. Harris, E. Kokot, and R. L. Martin, *Inorg. Chem.*, **5**, 93 (1966).

(18) P. W. Bridgman, "Physics of High Pressure," G. Bell and Sons, London, 1949 [chloroform: *Proc. Am. Acad. Arts Sci.*, **74**, 411 (1942); ethanol: *ibid.*, **49**, 1 (1913); **74**, 404 (1942); water: *ibid.*, **66**, 219 (1931)].

(19) L. Dubicki and R. L. Martin, *Inorg. Chem.*, **5**, 2203 (1966); L. Dubicki, A. H. Ewald, R. L. Martin, and E. Sinn, to be submitted for publication.

(20) H. G. Drickamer and J. C. Zahner, *Advan. Chem. Phys.*, **4**, 161 (1962).