CONTRIBUTION FROM THE CSIRO, DIVISION OF APPLIED CHEMISTRY,
HIGH PRESSURE UNIT, CHEMISTRY DEPARTMENT, UNIVERSITY OF SYDNEY, SYDNEY, AUSTRALIA

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

BY A. H. EWALD AND E. SINN

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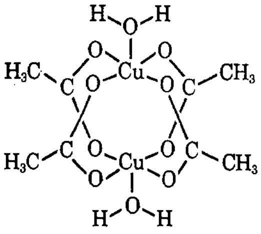
The effect of high pressure (1–3000 atm) on the magnetic properties of binuclear carboxylate complexes of copper(II), all of which exhibit pairwise antiferromagnetic interactions, is found to be surprisingly small, when the measurements are made on solutions in aprotic solvents or on the solids mulled 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 complex[3] (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]



i

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 iv[8]—of these molecular orbitals

—$b_{2u}(\delta^*)$	—$b_{2u}(\delta^*)$	—$a_{2u}(\sigma^*)$
—$b_{1g}(\delta)$	—$a_{2u}(\sigma^*)$	—$b_{2u}(\delta^*)$
—$a_{2u}(\sigma^*)$	—$b_{1g}(\delta)$	—$b_{1g}(\delta)$
ii	iii	iv

The complete orbital schemes are then

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

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

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

for the singlet state of the molecule and

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

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

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

for the triplet state. The orbitals are labeled according to their symmetries with respect to their tetragonal axes, *i.e.*, $d_{z^2} = \sigma$, $d_{x^2}d_{y^2} = \pi$, $d_{x^2-y^2} = \delta$, 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 thioxanthates,[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 cm^3/mol. In nickel salicylaldimines[1] 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 cm^3/mol.

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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 alkanoic acids,[14] with the exception of some copper(II) formate derivatives.[15] The range of this study has thus been extended to include other alkanoates 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-chan alkanoates 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 polymeric[17] 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 cm^3/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				
Alkanoate (medium)	1	500	1000	2000	3000
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_2Cl_2)	1.34	1.33	1.36	1.31	1.34
Octanoate	839	852	841	862	827
(2.3% in CH_2Cl_2)	1.36	1.37	1.36	1.38	1.35
Octanoate	1011	1038	1074	1098	1129
(2.2% in CH_2Cl_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 bond[4] or Kramer's superexchange interactions between the copper atoms.[6] In agreement with this, a recent discussion of the copper(II) alkanoate 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) alkanoates show a pressure dependence. The intensity of band I (650 mμ) 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 mμ) 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-

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vent,[14] such as pyridine, there is a strong increase in magnetic susceptibility with increasing pressure (Table I). This effect is readily explained in terms of the ionization equilibrium

$$\mathrm{Cu_2A_4} + \text{solvent} \overset{P}{\rightleftharpoons} 2\mathrm{Cu^{2+}}(\text{solvent}) + 4\mathrm{A^-}(\text{solvent}) \qquad (1)$$

where A represents an alkanoate. In pure water copper acetate appears to be almost completely ionized. In agreement with other results,[1,21,22] increasing pressure shifts the equilibrium in favor of the more solvated species. Equilibrium 1 parallels the pressure-dependent equilibria between $\mathrm{CuCl_4^{2-}}$ or $\mathrm{CoCl_4^{2-}}$ and the solvated $\mathrm{Cu^{2+}}$ and $\mathrm{Cl^-}$ or $\mathrm{Co^{2+}}$ and $\mathrm{Cl^-}$ species.[21]

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
RENSSELAER POLYTECHNIC INSTITUTE, TROY, NEW YORK 12181

Thermodynamics of Copper(I)–Cycloolefin Complex Formation[1]

BY JOSEPH M. HARVILCHUCK,[2a] DAVID A. AIKENS, AND RICHARD C. MURRAY, JR.[2b]

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A convenient and precise method for measurement of complex formation constants of Cu(I) has been developed, based on coulometric generation of Cu(I) and potentiometric measurement of the Cu(I) activity in a $\mathrm{LiClO_4}$–2-$\mathrm{C_3H_7OH}$ ionic medium. Formation constants and heat of formation values are reported for the 1:1 Cu(I) complexes of a number of cyclic olefins. The logarithmic formation constants of the Cu(I) complexes are linearly related to those of the corresponding Ag(I) complexes. The thermodynamic data for formation of model Cu(I) complexes together with thermodynamic and structural data for the corresponding Ag(I) complexes indicate that the Cu(I) complex of 2,5-norbornadiene is not chelated.

Despite continuous interest in preparation and structural characterization of copper(I)–olefin complexes, little attention has been devoted to the thermodynamics of complex formation. The principal contribution was made by Keefer, Andrews, and Kepner,[3,4] who determined the formation constants of the copper(I) complexes of 20 water-soluble unsaturated alcohols and carboxylic acids. Their value for the formation constant of the allyl alcohol complex has been confirmed by Manahan,[5] who also determined the formation constant of the copper(I)–cyclooctadiene complex.[6] The method used by Keefer, Andrews, and Kepner is based on the increased solubility of cuprous chloride in an aqueous solution of the olefin. This method is limited to water-soluble olefins, and establishment of equilibrium requires 1–2 hr. The method is applicable only to ligands which form copper(I) complexes of sufficient stability to increase the solubility of cuprous chloride substantially, and hence ligands that complex copper(I) weakly cannot be studied. The method used by Manahan is based on the shifts in polarographic half-wave potentials of the Cu(II)–Cu(I) and Cu(I)–Cu(0) waves for stepwise reduction of copper(II) perchlorate in a solution of the ligand in either water or an appropriate nonaqueous solvent. This method avoids the problems of the method of Keefer, Andrews, and Kepner, but the uncertainty of ±0.1 log unit in the formation constants is sufficiently high that estimation of heats of complex formation with reasonable accuracy is virtually impossible.

This paper describes a new approach to measurement of formation constants of copper(I) complexes that avoids the difficulties associated with the earlier methods. A known concentration of copper(I) in a nonaqueous ionic medium is generated by coulometric oxidation of a copper foil, and the copper(I) activity after addition of known concentrations of ligand is measured potentiometrically using a copper amalgam electrode. The method is applied to determination of formation constants and heats of formation of the 1:1 copper(I) complexes of a number of monocyclic and bicyclic monoolefins and diolefins in a 1 M lithium perchlorate–2-propanol medium. The results are related to the data for the corresponding silver(I) complexes and to the question of chelation in copper(I) complexes of cyclic diolefins.

Development of the Method

The formation constants of the 1:1 copper(I)–cycloolefin complexes are sufficiently high to ensure essentially complete complexation of copper(I) when free ligand concentrations are in the range 0.01–1 M. In

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