$ClOClO_3$ was estimated as approximately +43. This value is reasonable, in view of the heats of formation of ClO^{29} (+24) and $ClO_3{}^{28}$ (+37), since the formation of the $ClO-ClO_3$ bond should be somewhat exothermic.

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Antiferromagnetism in Transition Metal Complexes. III. The Ground and Low-Lying Excited States of Cupric Acetate[1]

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The effects of the crystalline field and of electron repulsion on the energies of the low-lying electronic states of cupric acetate are discussed. These states, in order, are ${}^1A_{1g}$, ${}^3A_{2u}$, and ${}^1A_{1g}$, the lowest ${}^1A_{1g}$ and ${}^3A_{2u}$ states most probably arising from the occupation of $d_{x^2-y^2}$ orbitals and the other ${}^1A_{1g}$ arising from d_{z^2} orbitals. This leads to excellent agreement with the observed temperature dependence of the susceptibility.

It has been known for over 50 years that the molar susceptibility of cupric acetate monohydrate is appreciably less than that commonly found for copper(II) salts.[2a] The susceptibility of single crystals reaches a maximum at *ca.* 255°K and probably obeys the Curie–Weiss law at temperatures well above this,[2b] although the thermal decomposition of the compound has prevented this being observed experimentally, data being available up to 390°K. The explanation of this antiferromagnetic behavior undoubtedly lies in the existence of the compound as dimeric molecules both in the crystal state and in solution, the copper–copper separation[3] being *ca.* 2.64 Å (*cf.* metallic copper in which the separation is 2.56 Å), leading to a coupling between the unpaired electrons formally associated with each copper atom.

Dimeric copper(II) carboxylates, for which cupric acetate is the prototype, have attracted considerable attention, both experimentally and theoretically.[4] Experimentally, a wide range of stable species may readily be prepared which are susceptible to investigation by a range of techniques. Theoretically, the two copper atoms may be treated as a diatomic molecule, the resulting two-hole problem having strong analogies with that of the H_2 molecule. In this approach, which we follow in this paper, the effects of the bridging acetate groups (Figure 1) are manifest in the ligand field splitting of the d orbitals in zeroth order and in the parameterization of the spin–orbit coupling constant λ.

The crystal structure of cupric acetate was to some extent anticipated by Bleaney and Bowers in their interpretation of the esr spectrum of the compound by their inclusion of a $-JS_1 \cdot S_2$ term in their spin Hamiltonian.[5] This term leads to a splitting J (an intrinsically negative integral with the dimensions of energy) between the spin singlet and triplet states, obtained from two electrons constrained to different orbitals, of *ca.* 280 cm^{-1} such that, in this model, the coupling is antiferromagnetic. It is readily shown that this treatment leads to the prediction that the magnetic susceptibility of the dimer will have a temperature variation given by eq 1.[5] The experimental data may be fitted to this equation indicating that the pattern of energy levels is, indeed, quite well represented by a ground-state singlet with a low-lying triplet which may be thermally populated. It should be noted that this equation is, strictly, applicable only to a gaseous system and is not dependent upon the explicit form of the orbital wave functions. In the crystal, as in solution, the magnetic centers of adjacent dimeric molecules are well separated and so the assumption of a gaseous system is not unrealistic, as there are no chemical bridges between the dimers.

$$\chi_M' = \frac{2g^2N\beta^2}{kT}\left(3 + \exp\left(\frac{-J}{kT}\right)\right)^{-1} + N\alpha \qquad (1)$$

The value of J in (1) is best obtained by susceptibility measurements (from the value of Θ, the Weiss constant). Commonly, an alternative expression, due to Figgis and Martin, may be used.[6] This states that $J \simeq -1.6 \cdot kT_N$ where T_N is the Néel temperature (J may also be obtained, less accurately, from the temperature variation of the esr spectrum).[5] It is found that if an experimental value of J is used in eq 1, then the g

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value may (for most copper carboxylate derivatives) have to be given a value substantially different from that obtained by esr measurements. The esr peaks are often broad, and it is difficult to obtain accurate g parameters from them. Even so, the values used in eq 1 are commonly incompatible with the observed spectra.[4,7,8] Alternatively, if the experimental g is used, then the value of J needed in eq 1 differs from that found experimentally. This or related ambiguities have led to a wide variety of explanations. A C_{2v}, rather than the commonly assumed C_{4v}, local symmetry for the copper atoms has been assumed by Kokoszka, *et. al.*,[9] and Bagchi and Sengupta,[10] while a temperature-dependent crystal field has been suggested by Bose, Mitra, and Dutta.[11] The possibility that J is temperature dependent has been discussed by Bleaney and Bowers,[5] Abe and Shimada,[12] and Mookherji and Mathur.[13] The possible existence of an interdimer coupling has been suggested by Matsuura and Kawamori;[14] however, this idea is not in accord with the data of Kondo and Kubo,[15] who found a close similarity between the magnetic properties of the solid and solutions of dimeric cupric acetate. It must be noted, however, that the two groups studied rather different temperature ranges.

A range of models for the complex has been examined by Ross and coworkers,[16-18] using both the MO and VB approaches; they concluded that there is a weak δ bond between the two copper atoms. No model, to date, can claim to provide an unambiguous explanation for the electronic spectra of cupric acetate and its homologs,[18-20] but vibrational effects on the singlet–triplet equilibrium have been discussed by Martin.[21]

We have recently shown that it is possible to obtain a very precise fit to the experimental susceptibility data using the experimental values of g and J together with a modified form of eq 1.[22] The modification consisted, essentially, of the introduction of a spin singlet, lying above the set of four levels previously considered, which becomes appreciably thermally populated at room temperature.

Although Figgis and Martin's approximate expression for J is not strictly valid on our model, the values we obtain for the corresponding splitting (by a procedure analogous to theirs) are very similar to those found by their method. One significant difference is that, using a MO basis, the spin–spin splitting is ferromagnetic, occurring between functions different from those of the Bleaney–Bowers method, the overall pattern leading to antiferromagnetism.

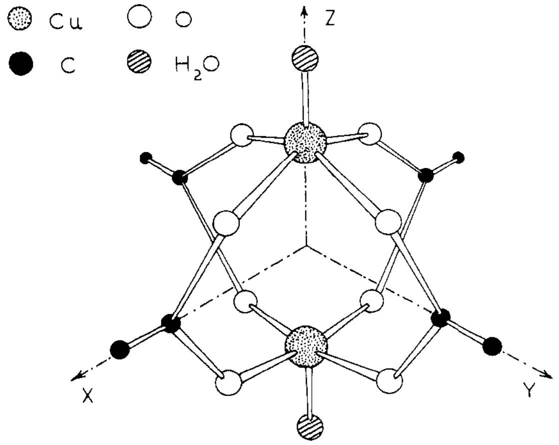

Figure 1.—Cupric acetate monohydrate.

The model we proposed is the simplest which leads to the postulated energy level sequence, the effective Hamiltonian being

$$\mathcal{H}_{\text{eff}} = X_1 + X_2 + \mathcal{H}_{\text{cov}} - JS_1\cdot S_2 + \lambda L\cdot S + \beta H(L + 2S) \qquad (2)$$

In the present paper we propose to explore the problem in greater detail; it is thus appropriate first to examine this Hamiltonian. The $\mathcal{H}_{\text{cov}}$ term is one which permits the introduction of a splitting between corresponding bonding and antibonding orbitals; it is essentially a core term. It follows that the only implicit recognition of electron repulsion lies in the $JS_1\cdot S_2$ term. Although electron repulsion is very important,[19,20,23] its main effect in the present context is merely to modify the explicit form of the singlet states.

The esr work of Kokoszka, Allen, and Gordon indicates that the copper ions in cupric acetate monohydrate behave as if only weakly coupled together,[9] a finding which had been anticipated by the theoretical work of Hansen and Ballhausen.[20] The present work is in many respects an extension of that of the latter authors. We have considered configuration interaction between all 190 states arising from the (d^9 + d^9) configuration. Such a discussion hinges on the values of the electron repulsion and overlap integrals. Most of the former were available from the work of Hansen and Ballhausen;[20] the most reliable overlap integrals appeared to be those of Forster and Ballhausen.[24] However, because of the uncertainty associated with these quantities, we have preferred to work algebraically as far as possible. For instance, the overlap integrals used by Boudreaux[25] lead to rather different conclusions from those of Forster and Ballhausen[24] (*vide infra*).

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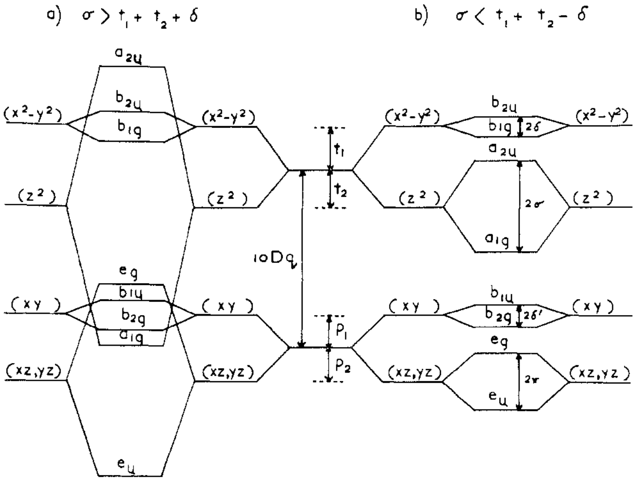

Figure 2.—Alternative molecular orbital diagrams for binuclear complexes.

Hansen and Ballhausen,[20] in particular, have discussed in some detail the likely errors in these data. We shall not duplicate this discussion in the present paper. Rather, we shall indicate those points at which the values given to the integrals are of crucial importance.

While recognizing the need to allow for spin–orbit coupling[5] in splitting the spin triplets, the corrections occasioned by this are small compared with the probable errors in other terms considered, and so they have not been included. The effect of λ is however included in the estimation of the gyromagnetic ratio when this is not known from experiment.

The Calculation

We consider only terms arising from the partial occupation of $d_{x^2-y^2}$ and/or d_{z^2} orbitals on the two copper atoms. All matrix elements between these states and those omitted from this discussion have little effect on the thermally populated states.

We thus consider the terms arising from the $b_{1g}{}^2$, $b_{1g}b_{2u}$, $b_{2u}{}^2$, $a_{1g}{}^2$, $a_{1g}a_{2u}$, and $a_{2u}{}^2$ configurations, where

$$(b_{1g}) = \frac{1}{\sqrt{2 + 2S_\delta}}(d_{x^2-y^2}(a) + d_{x^2-y^2}(b))$$

$$(b_{2u}) = \frac{1}{\sqrt{2 - 2S_\delta}}(d_{x^2-y^2}(a) - d_{x^2-y^2}(b))$$

$$(a_{1g}) = \frac{1}{\sqrt{2 + 2S_\sigma}}(d_{z^2}(a) + d_{z^2}(b))$$

$$(a_{2u}) = \frac{1}{\sqrt{2 - 2S_\sigma}}(d_{z^2}(a) - d_{z^2}(b))$$

Here S_δ amd S_σ are the overlap integrals between orbitals centered on copper atoms a and b

$$S_\sigma = \int d_{z^2}(a)d_{z^2}(b)\ d\tau$$

$$S_\delta = \int d_{x^2-y^2}(a)d_{x^2-y^2}(b)\ d\tau$$

These configurations give rise to the states listed in Table I.

TABLE I

Confign	States	Confign	States
$b_{1g}{}^2$	$^1A_{1g}$	$a_{1g}{}^2$	$^1A_{1g}$
$b_{1g}b_{2u}$	$^1A_{2u}$, $^3A_{2u}$	$a_{1g}a_{2u}$	$^1A_{2u}$, $^3A_{2u}$
$b_{2u}{}^2$	$^1A_{1g}$	$a_{2u}{}^2$	$^1A_{1g}$

In the present paper we replace the first four terms of the effective Hamiltonian given earlier by

$$\mathcal{H} = \mathcal{H}^c{}_{(a)} + \mathcal{H}^c{}_{(b)} + \mathcal{H}_e + \mathcal{H}_n$$

where $\mathcal{H}^c{}_{(a)}$ and $\mathcal{H}^c{}_{(b)}$ are core Hamiltonians. $\mathcal{H}_e = 1/r_{12}$ and $\mathcal{H}_n = Z^2/r$, where r is the internuclear distance (atomic units).

The diagonal matrix elements of the $^1A_{1g}$ states under $\mathcal{H}^c{}_{(a)} + \mathcal{H}^c{}_{(b)}$ are

$^1A_{1g}(b_{2u}{}^2)$	$^1A_{1g}(b_{1g}{}^2)$	$^1A_{1g}(a_{2u}{}^2)$	$^1A_{1g}(a_{1g}{}^2)$
$\dfrac{-2(G_a - \delta)}{1 - S_\delta}$	$\dfrac{-2(G_a + \delta)}{1 + S_\delta}$	$\dfrac{-2(G_A - \sigma)}{1 - S_\sigma}$	$\dfrac{-2(G_A + \sigma)}{1 + S_\sigma}$

all off-diagonal terms being zero. Here

$$G_a = \langle d_{x^2-y^2}(a)|\mathcal{H}^c{}_{(a)}|d_{x^2-y^2}(a)\rangle + \langle d_{x^2-y^2}(a)|\mathcal{H}^c{}_{(b)}|d_{x^2-y^2}(a)\rangle$$

where the former integral equals $-\alpha_0 + 6Dq + t_1$ (Figure 2) and the latter we denote as $-\alpha_a$. Similarly, $G_A = -\alpha_0 + 6Dq - t_2 - \alpha_A$, where $-\alpha_A = \langle d_{z^2}(a)|\mathcal{H}^c{}_{(b)}|d_{z^2}(a)\rangle$. The integrals δ and σ are, respectively, $\langle d_{x^2-y^2}(a)|\mathcal{H}^c{}_{(a)} + \mathcal{H}^c{}_{(b)}|d_{x^2-y^2}(b)\rangle$ and $\langle d_{z^2}(a)|\mathcal{H}^c{}_{(a)} + \mathcal{H}^c{}_{(b)}|d_{z^2}(b)\rangle$. They are, to a first approximation, proportional to the corresponding overlap integrals, which are taken to be $S_\sigma = 0.019$ and $S_\delta = 0.002$.[24] (Boudreaux[25] gave values of $S_\sigma = 0.030$ and $S_\delta = 0.009$.) The $^1A_{1g}$ core matrix elements are all positive, because we consider hole wave functions. Their effect is shown schematically in Figure 2, where we have assumed that (a) $\sigma > \delta + t_1 + t_2$ and (b) $\sigma < t_1 + t_2 - \delta$.

The values of t_1 and t_2 may, to a first approximation, be inferred from spectroscopic studies on tetragonally distorted octahedral copper(II) complexes. However, the values of σ and δ have been the subject of some controversy.[25] It is for this reason we include the two extreme possibilities in Figure 2. The matrix of the $^1A_{1g}$ states under $\mathcal{H}_e$ is given in Chart I, neglecting small terms, where

$$J_{aa} = \left\langle d_{x^2-y^2}(a,1)d_{x^2-y^2}(a,1)\left|\frac{1}{r_{12}}\right|d_{x^2-y^2}(a,2)d_{x^2-y^2}(a,2)\right\rangle$$

$$J_{ab} = \left\langle d_{x^2-y^2}(a,1)d_{x^2-y^2}(a,1)\left|\frac{1}{r_{12}}\right|d_{x^2-y^2}(b,2)d_{x^2-y^2}(b,2)\right\rangle$$

$$J_{AA} = \left\langle d_{z^2}(a,1)d_{z^2}(a,1)\left|\frac{1}{r_{12}}\right|d_{z^2}(a,2)d_{z^2}(a,2)\right\rangle$$

$$J_{AB} = \left\langle d_{z^2}(a,1)d_{z^2}(a,1)\left|\frac{1}{r_{12}}\right|d_{z^2}(b,2)d_{z^2}(b,2)\right\rangle$$

$$K_{aA} = \left\langle d_{z^2-y^2}(a,1)d_{z^2}(a,1)\left|\frac{1}{r_{12}}\right|d_{x^2-y^2}(a,2)d_{z^2}(a,2)\right\rangle$$

with values of, very approximately,[20] $J_{aa} \simeq J_{AA} = F_0 + 4F_2 + 36F_4 \simeq 145{,}000\ \text{cm}^{-1}$, $J_{ab} \simeq J_{AB} \simeq$

CHART I

$^1\mathrm{A}_{1g}(\mathrm{b}_{2u}{}^2)$	$^1\mathrm{A}_{1g}(\mathrm{b}_{1g}{}^2)$	$^1\mathrm{A}_{1g}(\mathrm{a}_{2u})^2$	$^1\mathrm{A}_{1g}(\mathrm{a}_{1g}{}^2)$
$^1/_2(1 - S_\delta{}^2)(J_{aa} + J_{ab})$	$^1/_2(1 + S_\delta{}^2)(J_{aa} - J_{ab})$	$^1/_2(1 + S_\delta + S_\sigma)K_{aA}$	$^1/_2(1 + S_\delta - S_\sigma)K_{aA}$
	$^1/_2(1 - S_\delta{}^2)(J_{aa} + J_{ab})$	$^1/_2(1 - S_\delta + S_\sigma)K_{aA}$	$^1/_2(1 - S_\delta - S_\sigma)K_{aA}$
		$^1/_2(1 - S_\sigma{}^2)(J_{AA} + J_{AB})$	$^1/_2(1 + S_\sigma{}^2)(J_{AA} - J_{AB})$
			$^1/_2(1 - S_\sigma{}^2)(J_{AA} + J_{AB})$

CHART II

$^1\mathrm{A}_{1g}(\psi_{1+})$	$^1\mathrm{A}_{1g}(\psi_{1-})$	$^1\mathrm{A}_{1g}(\psi_{2+})$	$^1\mathrm{A}_{1g}(\psi_{2-})$
$J_{aa} - J_{ab}S_\delta{}^2 - 2G_a + 2\delta S_\delta - 2G_aS_\delta{}^2$	$2\delta - 2G_aS_\delta + 2\delta S_\delta{}^2$	$(1 + S_\delta{}^2 + S_\sigma{}^2)K_{aA}$	$S_\sigma K_{aA}$
	$J_{ab} - J_{aa}S_\delta{}^2 - 2G_a + 2\delta S_\delta - 2G_aS_\delta{}^2$	$S_\delta K_{aA}$	$S_\delta S_\sigma K_{aA}$
		$J_{AA} - J_{AB}S_\sigma{}^2 - 2G_A + 2\sigma S_\sigma - 2G_AS_\sigma{}^2$	$2\sigma - 2G_AS_\sigma + 2\sigma S_\sigma{}^2$
			$J_{AB} - J_{AA}S_\sigma{}^2 - 2G_A + 2\sigma S_\sigma - 2G_AS_\sigma{}^2$

$e^2/2.64 \simeq 44{,}000$ cm^{-1}, and $K_{aA} = 4F_2 + 15F_4 \simeq 10{,}000$ cm^{-1} ($F_2 \simeq 2000$ cm^{-1}).

Because of the large off-diagonal terms in the electron repulsion matrix the terms $^1\mathrm{A}_{1g}(\mathrm{b}_{2u}{}^2)$ and $^1\mathrm{A}_{1g}(\mathrm{b}_{1g}{}^2)$ are mixed (as, approximately, $\psi_{1\pm} = (1/\sqrt{2})(^1\mathrm{A}_{1g}(\mathrm{b}_{2u}{}^2) \pm {}^1\mathrm{A}_{1g}(\mathrm{b}_{1g}{}^2))$ as also are $^1\mathrm{A}_{1g}(\mathrm{a}_{1g}{}^2)$ and $^1\mathrm{A}_{1g}(\mathrm{a}_{2u}{}^2)$, to give $\psi_{2\pm}$. The partially diagonalized matrix resulting is given in Chart II

It is evident that the two lowest lying $^1\mathrm{A}_{1g}$ levels are $^1\mathrm{A}_{1g}(\psi_{1-})$ and $^1\mathrm{A}_{1g}(\psi_{2-})$; the matrix element between them is small, but there are off-diagonal core terms between ψ_{1+} and ψ_{1-} and between ψ_{2+} and ψ_{2-}. These latter may be allowed for by second-order perturbation theory, to give the final energies of the lowest lying $^1\mathrm{A}_{1g}$ states.

The only other low-lying state of interest from the point of view of magnetism is the $^3\mathrm{A}_{2u}$ arising from the $\mathrm{b}_{1g}\mathrm{b}_{2u}$ configuration. Although this is mixed with the $^3\mathrm{A}_{2u}$ levels arising from other configurations, such mixing is in fact small and will be neglected here. The separation between the lowest $^3\mathrm{A}_{2u}$ and $^1\mathrm{A}_{1g}(\psi'_{1-})$ levels is given by

$$(J_{ab} + J_{aa})S_\delta{}^2 + \frac{(-2\delta + 2G_aS_\delta)^2}{J_{aa} - J_{ab}}$$

Approximate values for many of the integrals in this expression are given by Hansen and Ballhausen;[20] it is probable that explicit allowance for molecular orbital formation involving the acetate groups would significantly alter their values. However, *faut de mieux*, we have used their data, whence, for example, the first terms in the above expression will be of the order of 1 cm^{-1}. Using their data, the value of G_a is approximately $-100{,}000$ cm^{-1} so that $2G_aS_\delta \simeq -400$ cm^{-1}. Experimentally the $^3\mathrm{A}_{2u}$–$^1\mathrm{A}_{1g}(\psi'_{1-})$ separation is found to be *ca.* 300 cm^{-1}, so that, with $J_{aa} - J_{ab} \simeq 100{,}000$ cm^{-1}, $(-2\delta - 400)^2$ is *ca.* 3×10^7 cm^{-2}, giving a value of δ of *ca.* -3×10^3 cm^{-1}. Dubicki and Martin have reported a similar value.[19] The δ-bond energy, *ca.* 6×10^3 cm^{-1}, is therefore quite large—it is of the same order of magnitude as the crystal field. The σ bond energy will be approximately S_σ/S_δ times the δ-bond energy. Using Forster and Ballhausen's[24] overlap integrals, we obtain a value for σ of *ca.* 2.8×10^4 cm^{-1}, while Boudreaux's[25] data give a value of *ca.* 9.9×10^3 cm^{-1}. In the former case the energy level diagram shown in Figure 2a is presumably appropriate. This is not to say that this σ-bonded model leads to a $^1\mathrm{A}_{1g}$ ground state derived from d_{z^2} orbitals, because Figure 2a is appropriate for a single hole and electron repulsion is not included.

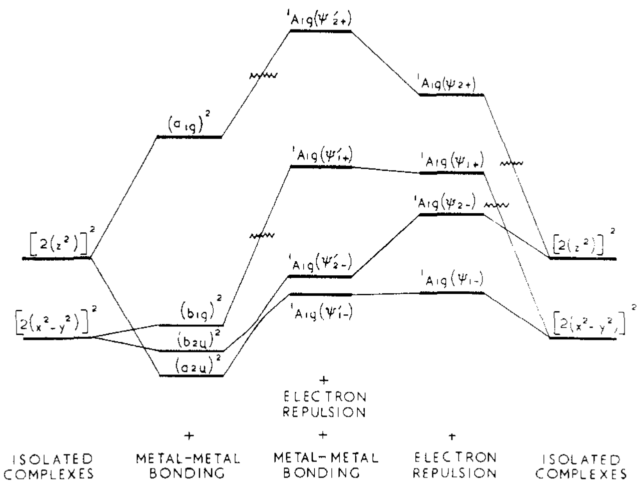

Figure 3.—Low-energy $^1\mathrm{A}_{1g}$ states of binuclear Cu(II) complexes.

The inclusion of electron repulsion has the effect that the core terms become less significant. Instead of appearing as diagonal terms, they become off diagonal and are allowed for by second-order perturbation theory. The result is that their effect on the final energy levels is much reduced. This sequence may be followed in the matrices given earlier and is illustrated diagrammatically in Figure 3, which should be compared with Figure 2a. We now return to the problem of the magnitude of the $^1\mathrm{A}_{1g}(\psi^1{}_{1-})$–$^1\mathrm{A}_{1g}(\psi^1{}_{2-})$ separation. This is given by

$$2(t_2 + t_1) + (J_{AB} - J_{ab}) + 2(\alpha_A - \alpha_a) - \frac{(2\sigma + 2G_AS_\sigma)^2}{J_{AA} - J_{AB}} + \frac{(-2\delta + 2G_aS_\delta)^2}{J_{aa} - J_{ab}} + b$$

TABLE II

COMPARISON OF EXPERIMENTAL AND CALCULATED MOLAR SUSCEPTIBILITIES (CGSU)

	Temp, °C															
	93.5	100.1	120.2	143.5	160.5	181.0	200.9	220.0	239.7	258.6	277.9	294.2	300.3	321.3	349.5	396.5
(a) Experimental Values (Eq 1)																
$10^6\chi_{\mathrm{M}}'(\mathrm{exptl}^{6})$	532	604	902	1224	1424	1574	1674	1746	1786	1796	1790	1778	1756	1752	1708	1594
$10^6\chi_{\mathrm{M}}'(\mathrm{calcd}^{a})$	614	707	1041	1361	1541	1697	1796	1851	1877	1883	1873	1863	1849	1817	1770	1678
(b) The Bleaney and Bowers Method[5] (Eq 1)																
$10^6\chi_{\mathrm{M}}'(\mathrm{exptl})$	532	604	902	1224	1424	1574	1674	1746	1786	1796	1790	1778	1756	1752	1708	1594
$10^6\chi_{\mathrm{M}}'(\mathrm{calcd}^{b})$	487	575	874	1191	1380	1551	1667	1738	1780	1798	1800	1792	1787	1766	1726	1647
$10^6\chi_{\mathrm{M}}'(\mathrm{calcd}^{c})$	518	611	906	1217	1400	1565	1675	1742	1781	1797	1797	1788	1782	1760	1720	1642
(c) The Figgis and Martin Method[6] (Eq 1)																
$10^6\chi_{\mathrm{M}}'(\mathrm{exptl})$	532	604	902	1224	1424	1574	1674	1746	1786	1796	1790	1778	1756	1752	1708	1594
$10^6\chi_{\mathrm{M}}'(\mathrm{calcd}^{d})$	566	668	983	1294	1468	1617	1713	1765	1791	1795	1786	1770	1762	1732	1686	1598
$10^6\chi_{\mathrm{M}}'(\mathrm{calcd}^{e})$	588	688	997	1303	1474	1620	1714	1765	1791	1795	1786	1770	1762	1733	1688	1601
(d) This work (Eq 3)																
$10^6\chi_{\mathrm{M}}'(\mathrm{exptl})$	532	604	902	1224	1424	1574	1674	1746	1786	1796	1790	1778	1756	1752	1708	1594
$10^6\chi_{\mathrm{M}}'(\mathrm{calcd}^{f})$	524	617	915	1226	1408	1573	1680	1745	1780	1793	1789	1776	1770	1742	1696	1609
$10^6\chi_{\mathrm{M}}'(\mathrm{calcd}^{g})$	528	622	921	1234	1416	1579	1687	1751	1786	1798	1794	1781	1774	1747	1701	1613

[a] $g = 2.167$ (esr value[12]), $-J = 284$ cm^{-1} (calculated from Néel temperature), $10^6N\alpha = 150$ cgsu,[22] and $10^6\Sigma = 98$.[h] [b] $g = 2.193$ (esr value[5]), $-J = 300$ cm^{-1} (best-fit value), $10^6N\alpha = 120$ cgsu,[5] and $10^6\Sigma = 22.5$ cgsu.[h] [c] $g = 2.167$ (esr value[12]), $-J = 299$ cm^{-1} (best-fit value), $10^6N\alpha = 150$ cgsu, and $10^6\Sigma = 11.8$ cgsu.[h] [d] $g = 2.128$ (best-fit value), $-J = 284$ cm^{-1} (calculated from Néel temperature), $10^6N\alpha = 120$ cgsu, and $10^6\Sigma = 29.0$ cgsu.[h] [e] $g = 2.109$ (best-fit value), $-J = 284$ cm^{-1} (calculated from Néel temperature), $10^6N\alpha = 150$ cgsu, and $10^6\Sigma = 33.1$ cgsu.[h] [f] $g = 2.167$ (esr value[12]), $-J = 298$ cm^{-1} (best-fit value), $-\Delta = 832$ cm^{-1} (best-fit value), $10^6N\alpha = 150$ cgsu, and $10^6\Sigma = 7.7$ cgsu.[h] [g] $g = 2.167$ (esr value[12]), $-J = 297$ cm^{-1} (simultaneous equations[i]), $-\Delta = 847$ cm^{-1} (simultaneous equations[i]), $10^6N\alpha = 150$ cgsu, and $10^6\Sigma = 8.8$ cgsu.[h] [h] $\Sigma = \Sigma_{T_1}{}^{T_n}|\chi(\mathrm{calcd}) - \chi(\mathrm{exptl})|/n$. [i] Values of $-J$ and $-\Delta$ obtained by solving the simultaneous equations in χ and $\partial\chi/\partial T_{\mathrm{N}} = 0$.

where the last term (*ca.* 1000 cm^{-1}) is a sum of several minor terms. It is difficult to place numerical values on the quantities appearing in this expression. Hansen and Ballhausen have taken $2(t_2 + t_1)$ to equal 20,000 cm^{-1},[20] which roughly cancels the term in $(-2\sigma + 2G_{\mathrm{A}}S_{\sigma})^2/(J_{\mathrm{AA}} - J_{\mathrm{AB}})$ if Forster and Ballhausen's overlap integrals are used.[24] The net contributions from two other terms involve differences between large quantities. In view of our ignorance of the extent of molecular orbital formation with the ligands and relevant radial functions, it is impossible to reach any firm conclusion about their effect. We note, however, that Hansen and Ballhausen's data,[20] which were based on Pople's point charge approximation,[26] give $J_{\mathrm{AB}} - J_{\mathrm{ab}} = 0$. Similarly, in zeroth order $\alpha_{\mathrm{A}} - \alpha_{\mathrm{a}} = 0$.

The term $(-2\delta + 2G_{\mathrm{a}}S_{\delta})^2/(J_{\mathrm{aa}} - J_{\mathrm{ab}})$ is undoubtedly much smaller than $(-2\sigma + 2G_{\mathrm{A}}S_{\sigma})^2/(J_{\mathrm{AA}} - J_{\mathrm{AB}})$ and may therefore reasonably be neglected in this context.

We conclude that it is entirely feasible that there should be a relatively low-lying $^1\mathrm{A}_{1g}$ excited state in dimeric cupric acetates, although either $^1\mathrm{A}_{1g}(\psi'_{1-})$ or $^1\mathrm{A}_{1g}(\psi'_{2-})$ could be the ground state—magnetically it is impossible to distinguish. We have assumed the former because a small separation between $^3\mathrm{A}_{2u}$ and $^1\mathrm{A}_{1g}(\psi'_{2-})$ would be accidental, whereas $^1\mathrm{A}_{1g}(\psi'_{1-})$ must lie unambiguously just below the $^3\mathrm{A}_{2u}$, on the basis of our calculation. The pattern of thermally populated energy levels is shown in Figure 4 for cupric acetate monohydrate, where an esr value of g has been used in interpreting the experimental susceptibility data; using the data of Abe and Shimada[12] we obtain a value of 2.17 by averaging g_z^2, g_x^2, and g_y^2. The results shown in Figure 4 were obtained (a) by a least-squares fit of eq 3 to the experimental susceptibility data[6] and (b) by solving equations in χ and its derivative with respect to temperature at the Néel point.

$$\chi_{\mathrm{M}}' = \frac{2g^2N^2}{kT}(3 + \exp(-J/kT) + \exp(-\Delta/kT))^{-1} + N\alpha \quad (3)$$

A comparison of the calculated and observed susceptibilities is given in Table II. The agreement obtained is within the experimental error over the whole temperature range. It should be noted that the anisotropy of the gyromagnetic ratio observed for Cu–Zn pairs in zinc-doped cupric acetate monohydrate places the single electron unambiguously in the b_{2u} orbital.[9] Nevertheless the results of copper-63 quadrupole magnetic resonance experiments have been interpreted[27] as indicating that the electron density along the Cu–Cu axis is greater in the singlet state than in the triplet state and therefore decreases with increasing temperature. This is in agreement with our suggestion that the $^1\mathrm{A}_{1g}$ state arising from d_{z^2} orbitals is significantly populated above room temperature. For example, our calculations indicate that 1% of the paramagnetic electron density is in d_{z^2} orbitals at 300°K.

One striking feature of our model is that it gives a distinct improvement of fit at higher temperatures, where the earlier models tend to predict too high a value for the susceptibility. This is illustrated in Table II where we compare the experimental values of χ with values calculated from eq 1 using the experi-

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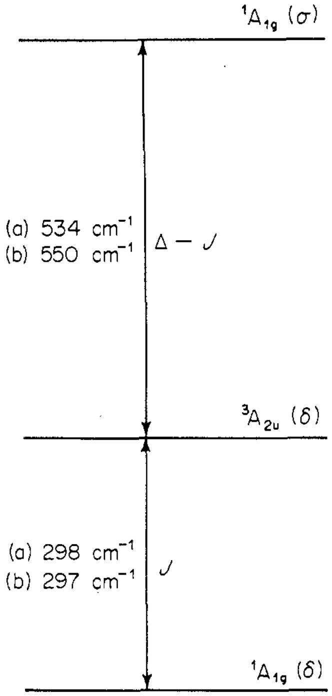

Figure 4.—Thermally populated states of cupric acetate monohydrate: (a) least-squares fit of susceptibility; (b) solving equations in χ and $\partial\chi/\partial T$.

mental values of g and J (Table IIa), values calculated from eq 1 using experimental values of g and the best-fit values of J (Table IIb), values calculated from eq 1 using experimental values of J and best-fit values of g (Table IIc), and finally values calculated from eq 3 by least-squares procedures. Method IIb was originally used by Bleaney and Bowers[5] and method IIc by Figgis and Martin.[6] The value of 2.193 used for g in early work[5] has been revised to 2.167 as a result of more accurate esr measurements,[12] and the commonly used value of $N\alpha$ for two Cu(II) ions was revised[22] from 0.000120 to 0.000150 on the basis of the electronic spectrum. For each calculation, the closeness of fit is indicated by an average deviation. The most successful calculation based on eq 1 is the case where only J was allowed to vary freely in the fitting procedure. The effect of varying J on the calculated susceptibility is much more profound than that of varying g, so that when both are allowed to vary freely for a series of cupric acetate homologs the values obtained for g vary more widely than the J values.[4] As neither g nor $N\alpha$ are expected to vary greatly for binuclear Cu(II) complexes,[22] we would suggest that the practice of treating these as free parameters should be discontinued. When an experimental value is not available for g, its value might well be constrained within the limits $g = 2.17 \pm 0.02$. Likewise $N\alpha$ may usually be estimated from the electronic spectrum.[22]

We emphasize that, as a result of the large electron repulsion energies (which may normally be neglected when discussing the magnetic properties of Cu(II) systems), the metal–metal bonding energies contribute very little to the overall stability of the dimeric complex. This view correlates with the relative positions of the metal atoms with respect to the coordinated oxygen atoms in dimeric copper and molybdenum acetates.[28,29]

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Thermochemistry of Liquid Borates. II. Partial Enthalpies of Solution of Boric Oxide in Its Liquid Mixtures with Lithium, Sodium, and Potassium Oxides

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The partial enthalpies of solution of B_2O_3 in its liquid mixtures with Li_2O, Na_2O, and K_2O have been measured at 940° (Li_2O–B_2O_3, $0.4 < N_{B_2O_3} < 1.0$) and at 985° (Na_2O–B_2O_3, $0.5 < N_{B_2O_3} < 1.0$; K_2O–B_2O_3, $0.7 < N_{B_2O_3} < 1.0$). In all these systems the partial enthalpy of B_2O_3 is slightly positive in the high B_2O_3 range ($N_{B_2O_3} > 0.85$–0.90) but becomes negative at lower B_2O_3 contents, the exothermic character increasing in the sequence Li_2O–B_2O_3 < Na_2O–B_2O_3 < K_2O–B_2O_3. The results are discussed in terms of recent observations of subliquidus immiscibility in alkali borate glasses and of attempts to derive structural information on the nature of borate species in the melts from phase diagram data.

Introduction

During the past several years we have developed calorimetric methods which allow detailed and precise thermochemical studies of ionic melts at temperatures up to about 1000°. Recently these methods were applied for a thermochemical investigation of the liquid system PbO–B_2O_3 at 800°.[1] At this temperature the viscosity of B_2O_3 is still quite high. Therefore, we were unable to study the concentration range between 65 and 100% B_2O_3.

In the present communication we report an extension

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