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The δ -Bond in Binuclear Complexes of Copper(II). An Approximate Molecular Orbital Treatment

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The nature of the copper-copper interaction in copper(II) acetate dihydrate has been reconsidered from the molecular orbital viewpoint. The proposed bonding scheme appears to be adequate for explaining the magnetic and spectral properties of the complex. These results are interpreted to be consistent with the previously proposed bonding models, although a more sophisticated treatment would tend to favor the δ -bond model.

Introduction

It is common knowledge that many chelate complexes of Cu(II) occur as dimeric species which display unique spectral and magnetic properties; for example, abnormally low magnetic moments are found which can be attributed to a spin-exchange mechanism resulting from the close proximity of copper atoms. The copper acetate complex, $\text{Cu}_2(\text{O}_2\text{C}_2\text{H}_3)_4 \cdot 2\text{H}_2\text{O}$, has been well characterized and its magnetic and spectral properties have been subjected to both experimental and theoretical investigation. The complex exhibits antiferromagnetism that has been attributed to a Cu-Cu interaction in which a δ -bond is involved.¹ Theoretical treatments incorporating both valence bond and molecular orbital (MO) techniques have been advanced.^{2,3} While the former² supports the existence of a δ -bond, the latter³ suggests that a σ -bond may be involved. In this treatment the problem of the Cu-Cu bond shall be reconsidered using the LCAO-MO method which in this respect is analogous to the Forster and Ballhausen treatment,⁴ but includes some small yet important differences.

MO Description

The structure of $\text{H}_2\text{O} \cdot (\text{H}_3\text{C}_2\text{O}_2)_2\text{Cu}-\text{Cu}(\text{O}_2\text{C}_2\text{H}_3) \cdot \text{OH}_2$ has been studied by X-rays⁵ and is found to have bond distances: Cu-Cu, 2.64 Å.; Cu-O, 1.97 Å.; and Cu-OH₂, 2.20 Å. Each of the monomeric $\text{Cu}(\text{O}_2\text{C}_2\text{H}_3)_2 \cdot \text{OH}_2$ units has square-pyramidal symmetry with respect to the Cu^{2+} ion and thus belongs to the point group C_{4v} . The over-all binuclear complex, on the other hand, contains two mononuclear entities (symmetry C_{4v}) and thus is square-planar (D_{4h}). In the F.B. scheme the relative splitting of the $3d^9$ configuration of Cu^{2+} is given as: $E(d_{xz}, d_{yz}) = 0$, $E(d_{xy}) \approx 10,000 \text{ cm.}^{-1}$, $E(d_{z^2}) \approx 13,000 \text{ cm.}^{-1}$, and $E(d_{x^2-y^2}) \approx 14,000 \text{ cm.}^{-1}$, which is estimated from the spectral data for $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ after Holmes and McClure.⁶ However, both

X-ray⁷ and spectral⁸ studies show that the Cu^{2+} ion in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is very nearly in a ligand field of D_{4h} symmetry, while the Cu^{2+} ion in each of the $\text{Cu}(\text{O}_2\text{C}_2\text{H}_3)_2 \cdot \text{OH}_2$ units of the binuclear copper acetate complex is subjected to a field of C_{4v} symmetry. Inasmuch as the orbital splitting patterns for these two symmetries are different, the use of the above orbital energy assignments to estimate the relative molecular orbital energies for the Cu-Cu bond is questionable. The ligand field splitting patterns for a d^9 configuration (in the "hole" formalism) in D_{4h} and C_{4v} fields, in order of increasing energy, are^{8,9}: (a) $d_{x^2-y^2} < d_{xy} < d_{z^2} < d_{xz} = d_{yz}$; (b) $d_{x^2-y^2} < d_{z^2} < d_{xz} = d_{yz} < d_{xy}$; and (c) $d_{x^2-y^2} < d_{z^2} < d_{xy} < d_{xz} = d_{yz}$, for D_{4h} , C_{4v} , and D_{4h} distorted toward C_{4v} fields, respectively. Unfortunately, it does not appear that any adequate spectral data for C_{4v} complexes of Cu(II) are available from which orbital energy assignments can be made. Nevertheless, a reasonable estimate can be obtained by using the spectral data of Holmes and McClure⁶ only to establish the over-all magnitude of the splitting, and then calculating the energy contributions for each of the orbitals from the relative splitting parameters for C_{4v} symmetry as given by Ballhausen and Jørgensen.⁸ In effect the experimental data for $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (D_{4h} symmetry) is used only to fix the "baricenter" of the levels. A classical crystal field calculation in C_{4v} symmetry is then performed, and the energy of each of the derived levels gaged by its splitting parameter so that the magnitude of the splitting is established relative to the determined zero of energy. The results of this procedure are given in Fig. 1.

Since we shall resort to the standard overlap criterion to estimate the relative order of MO energies, Slater orbitals are employed rather than self-consistent field (SCF) orbitals, for overlap integrals for the former are available from the literature. Furthermore, in the region of the "tail" the overlaps are essentially the same for both types of orbitals. In the present treatment, like that of the F.B. scheme, we shall ignore the effect of the ligands as far as the Cu-Cu bond is concerned

(1) (a) B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 3837 (1956); (b) R. L. Martin and H. Waterman, *ibid.*, 2545 (1957).

(2) (a) I. G. Ross, *Trans. Faraday Soc.*, **55**, 1057 (1959); (b) I. G. Ross and J. Yates, *ibid.*, **55**, 1064 (1959).

(3) L. S. Forster and C. J. Ballhausen, *Acta Chem. Scand.*, **16**, 1385 (1962).

(4) Hereafter referred to as the F.B. scheme.

(5) J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst.*, **6**, 227 (1953).

(6) O. G. Holmes and D. S. McClure, *J. Chem. Phys.*, **26**, 1686 (1957).

(7) C. A. Beevers and H. Lipson, *Proc. Roy. Soc. (London)*, **A146**, 570 (1934).

(8) C. J. Ballhausen and C. K. Jørgensen, *Kgl. Danske Videnskab. Selskab, Mat. fys. Medd.*, **29**, No. 14 (1955).

(9) L. Belford, M. Calvin, and G. Belford, *J. Chem. Phys.*, **26**, 1165 (1957).

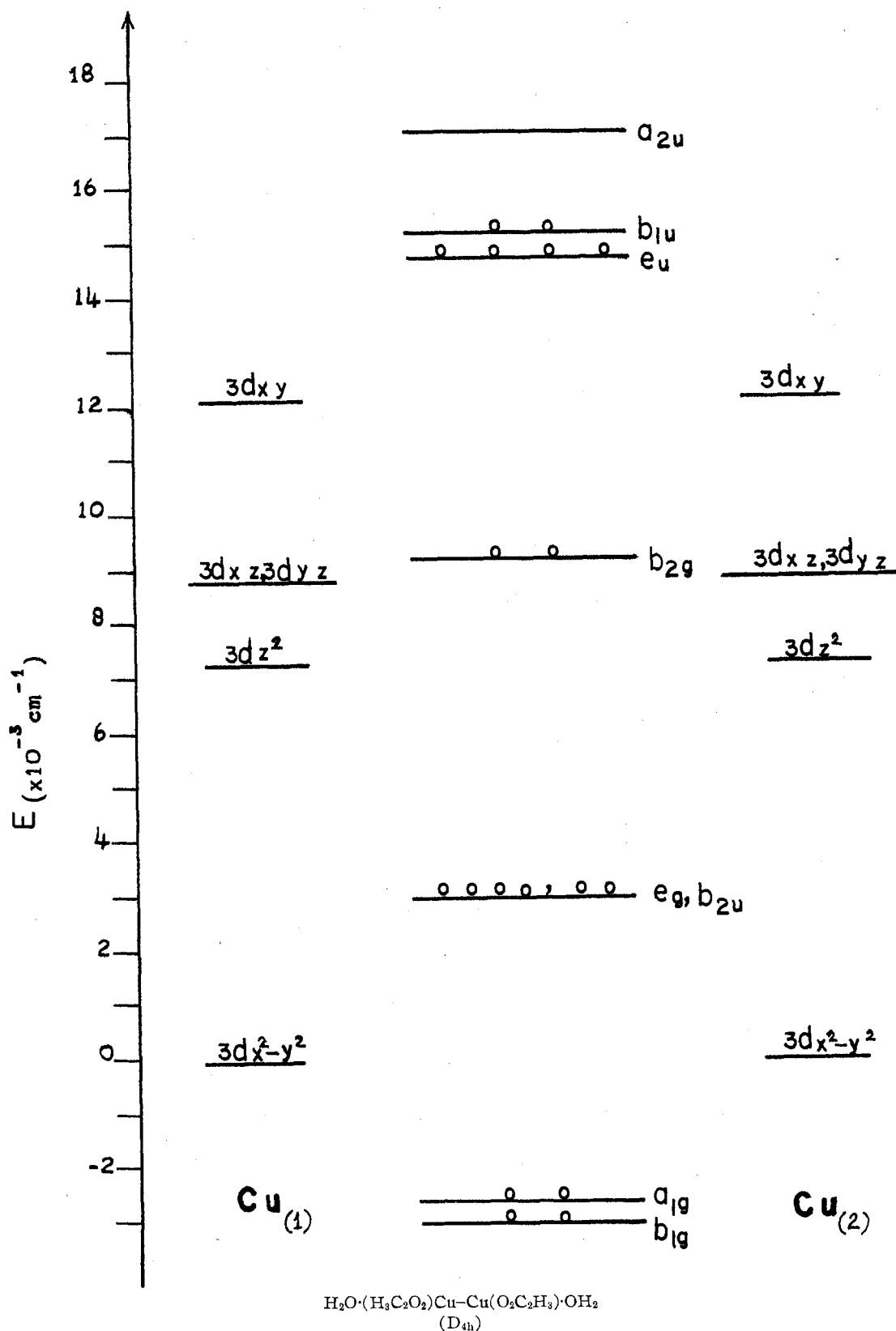


Fig. 1.—Proposed MO scheme for the Cu–Cu interaction in $\text{Cu}_2(\text{O}_2\text{C}_2\text{H}_3)_4 \cdot 2\text{H}_2\text{O}$. The symmetries of the ligand fields associated with each of the separated copper ions is C_{4v} , while that for the total complex is D_{4h} . The relative MO energy splittings are obtained from eq. 1.

and thus derive the relative energies of the molecular orbitals from symmetry and Cu–Cu overlaps. In computing the overlaps given in Table I a more realistic value for the effective charge ($Z_{\text{eff}} = 6.3$) has been as-

signed to the copper ion rather than the value of 7.8 derivable from the usual Slater screening constants. This result was established from a rather detailed study of the variation of Z_{eff} as a function of the exchange

energy, $-J$, for both Slater and SCF orbitals.^{2b} The value $Z_{\text{eff}} = 6.3$ corresponds to that which gives the correct experimental value of $-J$.

The relative energy separation, ΔE , between a given bonding orbital and its antibonding component is given approximately by

$$\Delta E = \frac{2H_{11}S_{12} - 2H_{12}}{1 - S_{12}^2} \quad (1)$$

where H_{11} and H_{12} are the coulomb and resonance integrals, respectively, and S_{12} is the overlap integral. The resonance integral is approximated by $H_{12} = -(H_{11}H_{22})^{1/2}S_{12}$, where for a Cu(1)-Cu(2) bond $H_{11} = H_{22}$. In eq. 1 H_{11} is assigned a value of -13.5 e.v. as estimated from valence state ionization potentials of copper¹⁰ with allowances having been made for a certain amount of charge neutralization due to the presence of the ligands.¹¹ The latter effect results in an effective charge of $+0.46$ on each copper atom, thus raising the ionization energy above that of the neutral atom. Values of ΔE are given in Table I together with the overlaps. The resulting MO scheme for the $\text{H}_2\text{O} \cdot (\text{H}_3\text{C}_2\text{O}_2)_2\text{Cu}-\text{Cu}(\text{O}_2\text{C}_2\text{H}_3)_2 \cdot \text{OH}_2$ complex is given in Fig. 1. It remains to be shown that this scheme is consistent with the spectral and magnetic properties of the complex.

TABLE I
OVERLAPS AND RELATIVE MO ENERGY SEPARATIONS FOR Cu-Cu
IN $\text{Cu}_2(\text{O}_2\text{C}_2\text{H}_3)_4 \cdot 2\text{H}_2\text{O}$

Atomic orbitals	S_{12}^a	Molecular orbitals ^b	ΔE , cm. ^{-1c}
$3d_{z^2}-3d_{z^2}$ ($d_\sigma-d_\sigma$)	0.030	a_{1g}, a_{2u}	19,664
$3d_{xz}-3d_{xz}$ ($d_\pi-d_\pi$)	0.018	e_g, e_u	11,766
$3d_{yz}-3d_{yz}$ ($d_\delta-d_\delta$)	0.009	b_{2g}, b_{1u}	5,911
$3d_{x^2-y^2}-3d_{x^2-y^2}$ ($d_\delta-d_\delta$)	0.009	b_{1g}, b_{2u}	5,911

^a Obtained from the literature [D. P. Craig, *et al.*, *J. Chem. Soc.*, 332 (1954)], as calculated for $Z_{\text{eff}} = 6.3$. ^b These are the orbitals derivable relative to the symmetry of the entire complex, point group D_{4h} . ^c The values represent the MO separations calculated from eq. 1.

Results

(A) **Absorption Spectrum.**—The experimental crystal spectrum of $\text{Cu}_2(\text{O}_2\text{C}_2\text{H}_3)_4 \cdot 2\text{H}_2\text{O}$ reveals a rather intense band at $14,300 \text{ cm.}^{-1}$ strongly polarized in the x, y direction, and in solution it has a molar extinction coefficient of about 400 based on a dimer concentration.¹² A second somewhat less intense band occurs at $27,000 \text{ cm.}^{-1}$, strongly polarized in the z direction, and a molar extinction coefficient of 100 is observed in solution. Lastly, a band appears at $33,700 \text{ cm.}^{-1}$ strongly x, y polarized and also at $35,000 \text{ cm.}^{-1}$, which is z polarized. Although the origin of these latter two bands is virtually unknown, they are probably associated with charge-transfer transitions specifically involving the ligands. The $14,300$ and $27,000 \text{ cm.}^{-1}$ bands, on the other hand,

are attributed to ligand field transitions involving the metal atom.

According to the MO scheme given in Fig. 1, the ground state of the complex with respect to the Cu-Cu bond, in order of increasing energy, is $(b_{1g})^2(a_{1g})^2-(e_g)^4(b_{2u})^2(b_{2g})^2(e_u)^4(b_{1u})^2$. There are a total of eighteen electrons (nine from each copper ion) filling all of the orbitals with the exception of the a_{2u} , which is vacant. The ground state is thus ${}^1A_{1g}$. The electric vectors transform like A_{2u} for parallel and E_u for perpendicular components relative to the fourfold symmetry axis. Thus an allowed transition would involve the promotion of a single electron from the e_g to the a_{2u} orbital leading to the transition ${}^1A_{1g} \rightarrow {}^1E_u$. From Fig. 1 it appears that the energy of this transition is about $14,000 \text{ cm.}^{-1}$, which agrees well with the $14,300 \text{ cm.}^{-1}$ band in the observed spectrum. Similarly, the allowed transition ${}^1A_{1g} \rightarrow {}^1A_{2u}$ with the promotion of an electron from the a_{1g} to the a_{2u} orbital is about $20,000 \text{ cm.}^{-1}$. Here again it is reasonable to associate this with the $27,000 \text{ cm.}^{-1}$ band in the observed spectrum. The transition moment for this excitation may be expressed as

$$\bar{P} = \int \psi({}^1A_{1g}) \sum_i \vec{r}_i \psi({}^1A_{2u}) d\tau \quad (2)$$

where $\psi({}^1A_{1g})$ and $\psi({}^1A_{2u})$ are the complete, normalized, determinantal wave functions for the ground and excited states, respectively. Thus on neglecting overlaps we get the result

$$\bar{P} = \sqrt{2} \int a_{1g} \vec{r} a_{2u} d\tau \quad (3)$$

where

$$a_{1g} = 1/\sqrt{2} [\psi_{(z^2)}^{(1)} + \psi_{(z^2)}^{(2)}]$$

$$a_{2u} = 1/\sqrt{2} [\psi_{(z^2)}^{(1)} - \psi_{(z^2)}^{(2)}]$$

with

$$\psi_{(z^2)} = \alpha(3d_{z^2}) + \sqrt{1-\alpha^2} \sum_i \phi_i$$

where $\alpha \approx 1$, and ϕ_i are ligand wave functions associated with one mononuclear unit of C_{4v} symmetry. The net result is

$$\bar{P} \approx 1/\sqrt{2} [\alpha^2 \bar{R}_{(\text{Cu})}] \quad (4)$$

where $R_{(\text{Cu})}$ is the observed Cu-Cu distance (2.64 \AA). From eq. 4 and the above calculated value for the ${}^1A_{1g} \rightarrow {}^1A_{2u}$ transition, the calculated oscillator strength, f , is found to be

$$f = 4.704 \times 10^{-7} \nu_{\text{max}} \bar{P}^2 = 0.033 \quad (5)$$

Experimentally the oscillator strength is given by the well-known expression

$$f = 1.35 \times 10^{-8} \epsilon (\bar{\nu}_{\text{max}} - \bar{\nu}_{1/2}) \quad (6)$$

With the values $\epsilon = 100$, $\bar{\nu}_{1/2} \approx 8 \times 10^3 \text{ cm.}^{-1}$, and $\bar{\nu}_{\text{max}} = 27,000 \text{ cm.}^{-1}$, the experimental value of f is found to be 0.026. It is thus apparent that the agreement between theory and experiment is good, and hence the assignments of the observed transitions seem to be in order as far as the present approximations are concerned.

(10) C. E. Moore, "Atomic Energy Levels," U. S. National Bureau of Standards Circular 467, Vol. 11, 1952.

(11) R. G. Pearson and H. B. Gray, *Inorg. Chem.*, **2**, 358 (1963).

(12) S. Yamada, H. Nakamura, and R. Tsuchida, *Bull. Chem. Soc. Japan*, **30**, 953 (1957).

(B) **Magnetic Characteristics.**—Magnetic susceptibility studies¹ on $\text{Cu}_2(\text{O}_2\text{C}_2\text{H}_3)_4 \cdot 2\text{H}_2\text{O}$ show that the complex is antiferromagnetic, having an exchange energy of $-J \approx 300 \text{ cm.}^{-1}$. It has been suggested that these characteristics can be explained by a low-lying excited triplet state.¹³ From Fig 1, the lowest lying singlet-triplet transition is ${}^1\text{A}_{1g} \rightarrow {}^3\text{B}_{2g}$, resulting from an electron being transferred from the b_{1u} to the vacant a_{2u} orbital. The approximate splitting between this singlet-triplet level may be estimated from¹⁴

$$\Delta E({}^1\text{A}_{1g} - {}^3\text{B}_{2g}) \approx \frac{[E(a_{2u}) - E(b_{1u})]^2}{2K_{12}} \quad (7)$$

where a rough estimate of K_{12} may be obtained from the overlap criterion from which the approximation may be made

$$K_{12} \approx 2(H_{11}) \left[\frac{S(d_{xy} - d_{xy})}{S(d_x^2 - d_x^2)} \frac{S(d_{xy} - d_{xy})}{S(d_x^2 - d_x^2)} + \frac{S(d_x^2 - d_x^2)}{S(d_x^2 - d_x^2)} \left\{ 1 - \frac{S(d_{xy} - d_{xy})}{S(d_x^2 - d_x^2)} \right\} \right] \approx 5324 \text{ cm.}^{-1}$$

Hence $\Delta E({}^1\text{A}_{1g} - {}^3\text{B}_{2g}) \approx 339 \text{ cm.}^{-1}$, which compares very favorably with the observed value $-J \approx 300 \text{ cm.}^{-1}$. This result is obtained, however, with complete disregard for the spin-orbit coupling energy which is greater than the inter-copper exchange energy by some factor of two. Consequently a more sophisticated calculation should include the spin-orbit terms. On the other hand, the inter-exchange energy will be far exceeded before the spin-orbit coupling is significantly altered; hence the latter may be essentially the same for both of the states involved. Under such conditions (7) is a reasonable estimate for the relative energy separation.¹⁵ The only conclusion to be drawn from this is that the association of the observed antiferromagnetism with a low-lying triplet level is at least energetically feasible.

(C) **E.s.r. Characteristics.**—The experimentally determined g factors for the binuclear copper acetate complex are¹³ $g_{\parallel} = 2.42 \pm 0.03$ and $g_{\perp} = 2.08 \pm 0.03$. The quantities can be evaluated theoretically by considering the spin-orbit interaction of the ${}^3\text{B}_{2g}$ state with the ${}^3\text{B}_{1g}$, ${}^3\text{E}_{u(1)}$, and ${}^3\text{E}_{u(2)}$ states. The latter two states may be included if it is maintained that vibronic coupling of the e_g and a_{2u} orbitals *via* the ϵ_u vibrational mode can cause the $\text{A}_{1g} \rightarrow \text{E}_u$ transition to become magnetically allowed. However, when such vibronic mixing is involved one obtains wave functions of the form $\Phi = (\psi_{a_{2u}} + \gamma Q \psi_{e_g}) \phi_{\text{vib}}$. Thus the extent of mixing will be dependent on the mixing factor, γ , the vibrational expectation value, $\langle 0|Q|1 \rangle$, and the Boltzmann vibrational population. Consequently it is expected that such mixing will by no means be complete, and hence the calculated g_{\perp} values should actually be considerably lower than what is indicated by experiment. The only

alternative is to conclude that the magnetic dipole selection rules for some nonobvious reasons are not stringent, and hence the $\text{A}_{1g} - \text{E}_u$ transition is sufficiently magnetically allowable. In addition, the obvious deduction that mixing must occur with ${}^3\text{E}_g$ states arising from the magnetically allowed $(b_{1u})^2(a_{2u})^1$ excitations (see Fig. 1) is evidently also in error, for this gives calculated g_{\perp} values that are much too high. Thus, on neglecting overlap, it may be construed that the g factors are given by

$$g_{\parallel} = 2 \left[1 - \frac{4\lambda}{E({}^3\text{B}_{1g}) - E({}^3\text{B}_{2g})} \right]$$

$$g_{\perp} = 2 \left[1 - \frac{\lambda}{E({}^3\text{E}_{u(1)}) - E({}^3\text{B}_{2g})} - \frac{3\lambda}{E({}^3\text{E}_{u(2)}) - E({}^3\text{B}_{2g})} \right] \quad (8)$$

By incorporating the above results together with the data in Fig. 1, the pertinent energy separations are estimated to be $({}^3\text{B}_{1g} - {}^3\text{B}_{2g}) \approx 13,700 \text{ cm.}^{-1} \approx ({}^3\text{E}_{u(1)} - {}^3\text{B}_{2g}) \ll ({}^3\text{E}_{u(2)} - {}^3\text{B}_{2g})$, the latter inequality being due to the large delocalization effects and high state repulsion energies from which it is expected that the energy of ${}^3\text{E}_{u(2)}$ should be very much greater than that of ${}^3\text{E}_{u(1)}$. Consequently, the last energy term in g_{\perp} of eq. 8 may be neglected. If a value of about 625 cm.^{-1} is assigned to λ ,¹⁶ the spin-orbit coupling constant, the calculated values of g_{\parallel} and g_{\perp} from eq. 8 are $g_{\parallel} \approx 2.36$, $g_{\perp} \approx 2.09$, which compare very favorably with the previously cited observed values.

Discussion

The apparently good agreement between the experimental and calculated results suggests that the proposed MO scheme is indeed reasonable. Although the presently proposed scheme is at variance in some respects with the F.B. scheme, all in all, in view of the approximations used, the agreement between the calculated and experimental data for both MO schemes is essentially the same. The most important feature wherein the present treatment differs from the F.B. scheme is in the order of the splitting of the d^9 configuration (C_{4v} for the former as opposed to D_{4h} for the latter) of copper in the mononuclear $\text{H}_2\text{O} \cdot (\text{H}_3\text{C}_2\text{O}_2)_2\text{Cu}$ species. This leads to an MO description for the binuclear complex in which the b_{1g} orbital is lowest and b_{1u} highest in energy while the F.B. scheme gives the e_g lowest and the b_{2u} highest.

It is also of interest to consider the formation of the binuclear complex in terms of molecular orbitals for the single-ion components. The distribution of molecular orbitals for a complex of C_{4v} symmetry has recently been treated in some detail, for which the preferred arrangement is¹⁷: $1a_1, 2a_1, 1e, 1b_1, 1b_2, 3a_1, 2e, 2b^*_1, 1a_2$, etc., in order of increasing energy. On considering that the electronic structure of each mononuclear $\text{H}_2\text{O} \cdot (\text{H}_3\text{C}_2\text{O}_2)_2\text{Cu}$ species may be represented with a total of nineteen electrons (nine from copper and two

(13) B. Bleaney and K. D. Bowers, *Proc. Roy. Soc. (London)*, **A214**, 451 (1952).

(14) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, New York, N. Y., 1962, p. 208.

(15) What has been estimated is the energy for the singlet-triplet separation and not $-J$. Any direct computation of this latter quantity must obviously include matrix elements for the spin-spin and spin-orbit interactions.

(16) E. A. Boudreaux, *Trans. Faraday Soc.*, **59**, 1055 (1963).

(17) J. S. Selbin, L. H. Holmes, Jr., and S. P. McGlynn, *J. Inorg. Nucl. Chem.*, **25**, 1359 (1963).

from each of the acetate and water oxygens) the ground state is given as: $(1a_1)^2(2a_1)^2(1e)^4(1b_1)^2(1b_2)^2(3a_1)^2(2e)^4(2b^*_1)^1$ with a single unpaired electron in a b^*_1 orbital essentially localized on the copper atom (*i.e.*, a $3d_{x^2-y^2}$ orbital). Thus the formation of the binuclear complex *via* Cu-Cu bonding of the two mononuclear species will require the overlap of two $3d_{x^2-y^2}$ orbitals or d_δ - d_δ overlap. In fact this latter approach toward rationalizing the metal-metal bonding in copper acetate dihydrate is probably much more realistic from

MO viewpoint than either the F.B. scheme or the present treatment, but is unfortunately considerably more difficult to treat quantitatively.

Lastly, the main aspect of this work is that an approximate MO calculation of the Cu-Cu interaction in binuclear complexes of Cu(II) can lead to results that are not in opposition to either of the previously proposed δ -bond or σ -bond models. The actual theoretical solution apparently lies in a detailed programmed MO treatment of the entire complex.

CONTRIBUTION FROM THE CENTRAL BASIC RESEARCH LABORATORY
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Tricarbonyl-(1,1'-bicycloalkenyl)iron(0) Complexes

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Tricarbonyliron(0) complexes of 1,1'-bicyclopentenyl, 1,1'-bicyclohexenyl, and 1,1'-bicycloheptenyl have been prepared, and their nuclear magnetic resonance spectra have been interpreted to favor structures involving 1,4-addition of the iron atom across the dienic system.

Introduction

The formation of π -complexes between metal carbonyls and unsaturated hydrocarbons continues to be of interest,¹ as do rearrangements in such systems.^{2,3} It is of interest to know whether or not isomerization of a once-formed tricarbonyl(diene)iron(0) complex can occur, or whether a conjugated diene can form a complex derived from an isomeric diene in which the double bonds have migrated. To secure information bearing on these questions, we have investigated the reactions of iron carbonyls with 1,1'-bicyclopentenyl, 1,1'-bicyclohexenyl, and 1,1'-bicycloheptenyl.^{4,5}

Experimental

General.—Infrared spectra, except as otherwise noted, are of cyclohexane solutions, recorded on a Perkin-Elmer Model 421 instrument, with resolution of one wave number. Nuclear magnetic resonance spectra are of carbon disulfide solutions containing tetramethylsilane as internal standard, recorded on a Varian A-60 instrument. Ultraviolet spectra are of cyclohexane solutions recorded on an Optica CF-4 spectrophotometer. Gas chromatography utilized a 300-ft. capillary column coated with polypropylene glycol, operated at 150° with helium at 35 p.s.i. as carrier gas. Microanalyses and molecular weights (osmometric, in benzene) were obtained from the Analytical Research Division of this company and from Galbraith Laboratories, Inc., Knoxville, Tennessee. The 1,1'-bicycloalkenyls were prepared according to published methods.^{4,5}

(1) **Tricarbonyl-(1,1'-bicyclopentenyl)iron(0).** (a).—A mixture of 1.34 g. (10 mmoles) of 1,1'-bicyclopentenyl, 2.0 g. (4 mmoles) of triiron dodecacarbonyl, and 50 ml. of cyclohexane was stirred under nitrogen in an oil bath at 95° for 18 hr. The

mixture was cooled to room temperature and chromatographed on alumina. Pentane eluted a yellow band, evaporating to an orange oil; from this was distilled (25° (0.05 mm.)) to a surface cooled to -78°) 380 mg. of a pale yellow liquid, shown by infrared and v.p.c. analysis to be starting material plus a trace of the iron carbonyl complex. Crystallization (pentane, -78°) of the undistilled portion yielded 400 mg. (15% yield) of golden crystals, m.p. 33°.

(b).—A mixture of 2.0 g. (15 mmoles) of 1,1'-bicyclopentenyl, 14.6 g. (75 mmoles) of iron pentacarbonyl, and 40 ml. of ethylcyclohexane was stirred under nitrogen in an oil bath at 130° for 66 hr. The mixture was cooled and chromatographed on alumina. Pentane eluted a yellow band, evaporating to an orange oil. After removal by distillation of 240 mg. of oil, shown by infrared and v.p.c. analysis to be unchanged starting material with a trace of complex, crystallization (pentane, -78°) yielded 2.9 g. (71% yield) of golden needles, m.p. 34-35° (I, $n = 1$).

Anal. Calcd. for $C_{13}H_{14}O_3Fe$: C, 56.96; H, 5.14; mol. wt., 274. Found: C, 56.59, 56.97; H, 5.36, 5.22; mol. wt., 280.

A 2:1 pentane-dichloromethane mixture eluted a red band, evaporating to a red-violet solid, recrystallized (pentane, -78°) to 60 mg. of violet solid, m.p. 109-110° (IV).

Anal. Calcd. for $C_{24}H_{26}O_4Fe_2$: C, 58.80; H, 5.34; mol. wt., 490. Found: C, 58.35; H, 5.33; mol. wt., 400.

(c).—A solution of 0.78 g. of tricarbonyl-(1,1'-bicyclopentenyl)iron(0) in 22 ml. of ethylcyclohexane was heated under nitrogen in an oil bath at 130° for 66 hr. Only the carbonyl bands of the starting material were seen in the infrared spectrum of the product after cooling and removal of solvent. The recovered complex was mixed with 3 ml. of iron pentacarbonyl and 25 ml. of ethylcyclohexane; after an additional 67 hr. in an oil bath at 130°, no sign of IV was seen in the infrared spectrum.

(2) **Tricarbonyl-(1,1'-bicyclohexenyl)iron(0).** (a).—A mixture of 2.5 g. (15 mmoles) of 1,1'-bicyclohexenyl and 4.0 g. (8 mmoles) of triiron dodecacarbonyl in 50 ml. of cyclohexane was heated under nitrogen in an oil bath at 95° for 20 hr. The cooled mixture was chromatographed on alumina. Pentane eluted a yellow band, evaporating to an oil, from which crystallization (pentane, -78°) yielded 500 mg. (11% yield) of orange crystals, m.p. 33° (I, $n = 2$).

(1) M. A. Bennett, *Chem. Rev.*, **62**, 611 (1962).

(2) R. Pettit and J. E. Arnet, *J. Am. Chem. Soc.*, **83**, 2954 (1961).

(3) T. A. Manuel, *J. Org. Chem.*, **27**, 3941 (1962).

(4) E. B. Barnett and C. A. Lawrence, *J. Chem. Soc.*, 1104 (1935).

(5) D. S. Greidinger and D. Ginsburg, *J. Org. Chem.*, **22**, 1406 (1957).