experiments. Thermodynamic functions for the formation of the three binary fluorides have been derived from the equilibrium constant data, and a correlation of the temperature dependence of the equilibrium constants with molecular data has been made by least-squares analysis. The average bond energies are found to be nearly identical for XeF_2 and XeF_4 at 31 kcal, while the last two bonds in XeF_6 can be taken as 3.6 kcal weaker. Previously reported bond energies for these molecules gave a more irregular pattern.

The reliability of the data can be judged in terms of the constancy of the values of ΔH°_0. For the k_4 data (eq 13), $\Delta H^\circ_0 = 24{,}850 \pm 90$ cal mole^{-1}. There were not sufficient measurements to make a similar assessment of the reliability of ΔH°_0 for k_2. The values derived for the two missing vibrational frequencies of XeF_4 are $\nu_4 = 237$ and $\nu_7 = 250$ cm^{-1}. Their average value of 246 cm^{-1} is probably good to ± 10 cm^{-1}. Claassen's[23] value of $\nu_4 = 232$ cm^{-1} derived from force constant calculations is in agreement, but his value of $\nu_7 = 183$ cm^{-1} is significantly different from our derived value. The value of $S^\circ = 75.6$ cal deg^{-1} mole^{-1} at 298.16°K that we calculate for XeF_4 from the molecular data agrees with the experimental value of 75.3 cal deg^{-1} mole^{-1}.

Statistically there is not a significant difference in fit to the equilibrium data among all the models tested for XeF_6. However, the fit becomes progressively poorer with increasing symmetry number, being poorest when low-lying electronic states are included. One can only infer from this that our data favor a symmetry lower than O_h for XeF_6. Our analysis may be useful when S° for XeF_6 is derived from calorimetric data because significantly different values of S° are obtained for the different models upon extrapolation from the range of our measurements to room temperature.

To derive ΔH°_0 for eq 17 from the k_6 data we have used a model with a symmetry number of 1 and obtain 17,930 ± 20 cal mole^{-1}. From the change of ΔH°_0 with model we estimate the absolute uncertainty to be ± 300 cal mole^{-1}. It is interesting to note that the bending frequencies derived in C_1 symmetry for XeF_6 are very similar in magnitude to those of TeF_6.

The recent electron-diffraction studies reported by Bartell, *et al.*,[34] and by Hedberg, *et al.*,[35] with XeF_6 appear to rule out O_h symmetry. Presently the structures suggested by Gillespie,[29] which have a symmetry number of 2 or 3, are the most reasonable possibilities. Blinc, *et al.*,[43] report a diamagnetic susceptibility for XeF_6 of -45×10^{-6} cm^3 mole^{-1}, which is what would be expected from the diamagnetism of the electrons alone. If there were low-lying electronic states one would expect XeF_6 to exhibit at least a small temperature-independent paramagnetism. For example, the same authors report that PtF_6, which has a nondegenerate ground state but low-lying electronic states,[44] has a temperature-independent paramagnetism of $+812 \times 10^{-6}$ cm^3 mole^{-1}. These recent observations thus appear to agree with the related inferences that can be drawn from our data.

While evidence is mounting in favor of Gillespie's prediction of an unsymmetrical structure for XeF_6, a fundamental question remains to be answered. Molecular orbital theory appears to favor O_h symmetry for XeF_6, but only for the particular models tested.[27,28] These tests have neglected the possible influence of the s electrons in determining the structure of XeF_6, because of the success of this approximation in explaining the structures of XeF_2 and XeF_4.[42,45] It remains to be demonstrated whether or not molecular orbital theory will still favor O_h symmetry if the energy of the s electrons is taken to be closer to that of the p electrons.

Acknowledgment.—We are indebted to Jack S. Ninomiya for assistance with the experimental work.

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[43] R. Blinc, E. Pirkmajer, J. Shirnik, and I. Zupančič, *J. Chem. Phys.*, to be published.

[44] W. Moffitt, G. L. Goodman, M. Fred, and B. Weinstock, *Mol. Phys.*, **2**, 109 (1959).

[45] R. E. Rundle, *J. Am. Chem. Soc.*, **85**, 112 (1963).

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The π System of Binuclear Copper(II) and Chromium(II) Acetates

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Previous work on the electronic structure of copper acetate is briefly reviewed. Evidence is presented for the charge-transfer character of the anomalous band at 3700 A in copper acetate. Although a definite assignment is difficult, even with very detailed calculations, chemical evidence suggests that the transition may be a local symmetry-forbidden $np_\pi \rightarrow \sigma^*(x^2 - y^2)$ excitation. The electronic spectrum of binuclear chromium(II) acetate is discussed qualitatively.

Introduction

The origin of band II ($\sim$28,000 cm^{-1}) in binuclear copper(II) acetate (*cf.* Figure 1) has been a topic of considerable interest, judging by the number of papers published and the many differing and conflicting assignments put forward. Originally, Tsuchida and Yamada,[1,2] from single-crystal spectral studies, sug-

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[1] R. Tsuchida and S. Yamada, *Nature*, **176**, 1171 (1955).

[2] R. Tsuchida, H. Nakamura, and S. Yamada, *ibid.*, **178**, 1192 (1956).

gested that the band was a diagnostic property of the copper–copper linkage. The intimate relationship of the band with the binuclear structure was confirmed by cryoscopic[3] and magnetic measurements.[3,4] A recent review[5] has emphasized this correspondence.

The original proposition was quite novel and Forster and Ballhausen[6] and Boudreaux,[7] using simple molecular orbital methods, assigned band II as an electron transition between Cu–Cu molecular orbitals. Ross, *et al.*,[8] on the other hand, favored a valence bond approach and, though they failed to arrive at any specific assignment, a metal–metal type of a transition appeared feasible within the framework of their model. Recently, Hansen and Ballhausen[9] assumed a weakly coupled chromophore model and assigned band II as a double electron excitation of $3d_{z^2} \rightarrow 3d_{x^2-y^2}$. In sharp contrast, Kokoszka, *et al.*,[10] have favored the single excitation $3d_{z^2} \rightarrow 3d_{x^2-y^2}$ within the monomer components of the binuclear structure.

In this paper we present some experimental observations which indicate the involvement of an unusual bridging π system of the dimer in the electronic spectrum of copper acetate. In fact, band II is proposed to be characteristic of the bridging π system rather than of the Cu–Cu linkage. This assignment appears to be consistent with the results of a simple Hückel molecular orbital calculation. The very weak metal–metal bonding in copper acetate is rather dramatically revealed in a molecular orbital description which includes configurational interaction. The "weakly interacting pair" model provides a reasonable interpretation of both the visible and the ultraviolet spectra of copper and chromium(II) acetates.

Molecular Orbital δ-Bond Model

Ross[8] has pointed out that the magnetic splitting parameters g_x, g_y, and g_z observed for copper acetate are closely similar to those found for $CuSO_4 \cdot 5H_2O$ and that both sets of g values are consistent with a ground state based on a half-filled $d_{x^2-y^2}$ orbital. More recently, Kokoszka,[10] *et al.*, from esr measurements on zinc-doped copper acetate monohydrate, have shown that g_x and g_y lie nearly along the oxygen–copper–oxygen bond axes, confirming that the single unpaired electron, centered on each copper atom, occupies a $d_{x^2-y^2}$ orbital. Accordingly, the present discussion is restricted to the "δ-bond model."

The limitations inherent in a simple molecular orbital treatment of copper acetate have been outlined by Jørgensen.[11] As he did not quote any numerical values, we shall reconsider the problem semiquantitatively. For the "δ-bond model," the bonding and antibonding molecular orbitals are

$$\psi_b = \frac{1}{\sqrt{2(1+S)}}(d_1 + d_2)$$

$$\psi_a = \frac{1}{\sqrt{2(1-S)}}(d_1 - d_2)$$

where d_1 and d_2 are the $3d_{x^2-y^2}$ atomic orbitals of the two copper atoms. Assuming a Hamiltonian of the form $\mathcal{H}(1,2) = H_{(1)}^{C} + H_{(2)}^{C} + e^2/r_{12}$, the configurations ψ_b^2, $\psi_b^1\psi_a^1$, ψ_a^2 give rise to four states, $^1\Phi_1$, $^3\Phi_2$ and $^1\Phi_3$, $^1\Phi_4$, respectively. The matrix elements of this two-electron problem have been evaluated by Jørgensen[11] and I'Haya.[12] Defining $(d_1|H^C|d_2) = \alpha S + \beta$ and neglecting Moffitt's "atoms-in-molecules" correction, the equation for the singlet–triplet separation becomes[12]

$$(^3\Phi_2|\mathcal{H}|^3\Phi_2) - (^1\Phi_1'|\mathcal{H}|^1\Phi_1') = \frac{1}{(1-S^2)}\{\sqrt{4\beta^2 + K_{ba}^2} - K_{ba}\} \quad (1)$$

where $^1\Phi_1'$ is $^1\Phi_1$ corrected for configurational interaction (CI) with $^1\Phi_4$. Provided S is small, $K_{ba}^2 \gg 4\beta^2$, then the above relation is approximated by Jørgensen's expression[11] $(E_a - E_b)^2/K_{ba}$. Numerical estimates of the matrix elements may be obtained by assuming $Z^* = 6$[13] (Slater overlap, $S_{\delta\delta} = 0.011$) and utilizing the data given by Hansen and Ballhausen.[9] The Coulombic integral $\alpha = (d_1|H^C|d_1)$ is taken to be some $-100{,}000$ cm^{-1} and β is estimated by the rather crude approximation $\beta_{ij} \simeq -2S_{ij}\sqrt{H_{ii}H_{jj}} \simeq -2200$ cm^{-1}. Although this value may well be in error by a factor of 2, the main conclusions of this calculation will not be significantly altered. Assuming the Mulliken approximation $(11|12) \simeq {}^1/_2S\{(11|11) + (11|22)\}$, the molecular repulsion integrals, reduced to integrals over atomic orbitals, are

$$J_{bb} = \frac{1}{2(1+S)^2}[(1+2S)\{(11|11) + (11|22)\} + 2(12|12)] \simeq 93{,}000 \text{ cm}^{-1}$$

$$J_{ba} = \frac{1}{2(1-S^2)}[(11|11) + (11|22) - 2(12|12)] \simeq 93{,}000 \text{ cm}^{-1}$$

$$J_{aa} = \frac{1}{2(1-S)^2}[(1-2S)\{(11|11) + (11|22)\} + 2(12|12)] \simeq 93{,}000 \text{ cm}^{-1}$$

$$K_{ba} = \frac{1}{2(1-S^2)}[(11|11) - (11|22)] \simeq 52{,}000 \text{ cm}^{-1}$$

where $(ij|kl) = \iint d_i^*(1)d_j(1)(e^2/r_{12})d_k^*(2)d_l(2)dV(1)dV(2)$. The state wave functions and values of matrix elements, expressed to three significant figures, are given in Table I. Equation 1 leads to a singlet–

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(3) R. L. Martin and A. Whitley, *J. Chem. Soc.*, 1394 (1958).

(4) M. Kondo and M. Kubo, *J. Phys. Chem.*, **62**, 468 (1958).

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

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

(7) E. A. Boudreaux, *Inorg. Chem.*, **3**, 506 (1964).

(8) M. L. Tonnet, S. Yamada, and I. G. Ross, *Trans. Faraday Soc.*, **60**, 840 (1964).

(9) A. E. Hansen and C. J. Ballhausen, *ibid.*, **61**, 631 (1965).

(10) G. F. Kokoszka, H. C. Allen, Jr., and G. Gordon, *J. Chem. Phys.*, **42**, 3693 (1965).

(11) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Permagon Press Inc., New York, N. Y., 1964, pp 207, 146.

(12) Y. I'Haya, *Advan. Quantum Chem.*, **1**, 215 (1964).

(13) I. G. Ross and J. Yates, *Trans. Faraday Soc.*, **55**, 1064 (1959).

TABLE I

State wave function	Transformation in D_{4h}	Matrix elements × 10^{-3}, cm^{-1}	
		No configuration interaction	Including configuration interaction
$^1\Phi_1$	$^1A_{1g}$	$H_{11} = -111$	$H_{11}' = -159$
$^3\Phi_2$	$^3A_{2u}$	$H_{22} = -159$	
$^1\Phi_3$	$^1A_{2u}$	$H_{33} = -55$	
$^1\Phi_4$	$^1A_{1g}$	$H_{44} = -103$	$H_{44}' = -55$
		$H_{14} = -52$	

triplet separation of $\simeq$190 cm^{-1} (the experimental value[14] is $\simeq$300 cm^{-1}). In view of the approximate values of $S_{\delta\delta}$, α, and particularly β, the agreement is largely fortuitous. The wave functions for states 1 and 4 (including configuration interactions) are

$$^1\Phi_1' = 0.74\,^1\Phi_1 - 0.68\,^1\Phi_4$$

$$^1\Phi_4' = 0.74\,^1\Phi_4 + 0.68\,^1\Phi_1$$

where the degree of mixing is mainly determined by the value of K_{ba}.

As predicted by Jørgensen,[11] there is an extensive mixing of the antibonding configuration ψ_a^2 with the bonding configuration ψ_b^2. As a result the ground state of the dimer involves the two copper atoms in so weakly a bonding situation that it is virtually nonbonding. In fact, when the hypothesis of the "δ bond" was originally put forward, it was emphasized that "*the bond is so weak that the configuration of the binuclear molecule can only be maintained by the four bridging acetate groups.*"[14]

Visible Spectra of Copper and Chromium(II) Acetates

The weakly coupled chromophore model[9] provides a consistent interpretation of the d–d spectrum of copper acetate (*cf.* Figure 1). The energy states of the dimer correspond closely to the monomer states and the band I envelope is believed to contain all of the d–d type of transitions. The possibility that band II may be a $d_{z^2} \rightarrow d_{x^2-y^2}$ electron promotion[10] can be safely rejected (*cf.* later discussion on band II sensitivity to terminal and bridging ligands). In this model, however, configurational interaction (CI) must be invoked in order to obtain a singlet ground state.

The assumption of isotropic spin–spin coupling between pairs of copper atoms[15a] can lead to a similar interpretation of the spectrum. Taking the order of d levels in the monomer systems as $x^2 - y^2 > z^2 \sim xy > xz, yz$,[15b] the one-electron states in C_{4v} symmetry are $^2B_1 < {}^2A_1 \sim {}^2B_2 < {}^2E$. These interact, *via* $\mathcal{H}^{(1)} = -2J\mathbf{S}_1 \cdot \mathbf{S}_2$, with the ground state $^2B_1$ of the neighboring monomer and give rise to two series of singlet and triplet states for the dimer. The zero-order wave functions are identical for the two models.

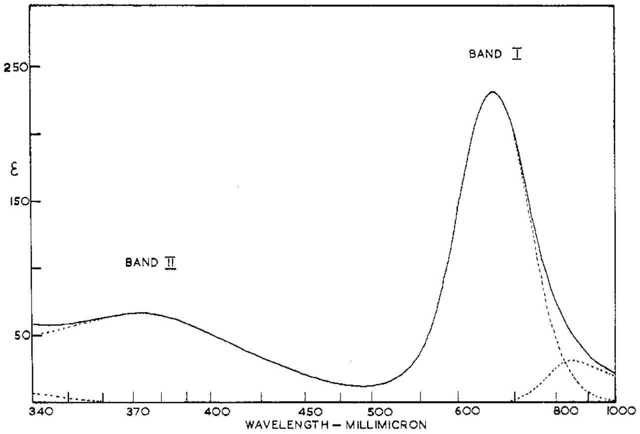

Figure 1.—Visible spectrum of anhydrous copper acetate in dioxane. Gaussian analysis is indicated by the dotted curve.

In the latter model, the singlet ground state for the dimer is immediately obtained if J is negative (*i.e.*, antiferromagnetic coupling), so that CI need not be considered. The remarkable success of this simple model in several of its more recent applications[15a,16–19] suggests that the nature of the metal–metal interaction may be essentially spin–spin exchange rather than "electrostatic," as assumed by Ballhausen.[9] Although it is likely that the interaction occurs directly between the metal atoms, the contribution from exchange *via* the bridging π system may be quite significant.[20] At present, nmr and esr experiments are being made to estimate the relative importance of these two pathways.

The visible spectrum of chromium(II) acetate is given in Figure 2. It is characterized by an unusually broad band which undoubtedly is a composite of several bands. A plausible interpretation may be obtained by assuming that the 3d electrons are mainly localized on the chromium atoms and are subjected to a weak ligand field and a relatively weaker spin–spin perturbation by the electrons of the neighboring chromium atom. The monomer states will consist of a ground quintet and excited quintets, triplets, and singlets. Assuming an antiferromagnetic coupling[21] between the two ground quintets, the ground state of the dimer will be a singlet, separated from the next excited state, a triplet, by $-2J$, where $2J \simeq -700$ cm^{-1}.[22] At room temperature, most of the molecules will be in the singlet states and the observed spectrum will consist of singlet → singlet transitions which correspond to the spin-allowed quintet → quintet and spin-forbidden quintet → singlet transitions in the

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(14) B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 3837 (1956).

(15) (a) D. S. McClure, *J. Chem. Phys.*, **39**, 2850 (1963). (b) As mentioned above, it appears very likely that all of the d–d bands are contained within the band I envelope. Resolution of band I (*cf.* Figure 1) yields a high-intensity component which is assigned as the $^2B_1 \rightarrow {}^2E$ excitation. This is allowed in xy polarization under local C_{4v} symmetry. Excitations from the z^2 and xy orbitals are forbidden and the weaker, lower lying component may be assigned as one of these transitions. The relative positions of the z^2 and xy orbitals are therefore not known precisely but it is reasonable to assume xz, yz orbitals to be the most stable with the z^2 and xy orbitals lying somewhere between $x^2 - y^2$ and xz, yz orbitals.

(16) J. Ferguson, H. J. Guggenheim, and Y. Tanabe, *J. Appl. Phys. Suppl.*, **36**, 1046 (1965).

(17) K. Kambe, *J. Phys. Soc. Japan*, **5**, 48 (1950).

(18) J. S. Smart, "Magnetism," Vol. III, G. T. Rado and H. Suhl, Ed., Academic Press Inc., New York, N. Y., 1965.

(19) R. W. Adams, C. G. Barraclough, R. L. Martin, and G. Winter, *Inorg. Chem.*, **5**, 346 (1966).

(20) R. L. Martin and H. Waterman, *J. Chem. Soc.*, 1359 (1959), and references therein. Mixing of the $^2B_2$ (hole in xy) with $^2B_1$ (hole in $x^2 - y^2$) through spin–orbit coupling will make the π pathway available.

(21) Interaction between ground quintet and excited quintets and triplets may not necessarily be antiferromagnetic (*cf.* ref 15a).

(22) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 241.

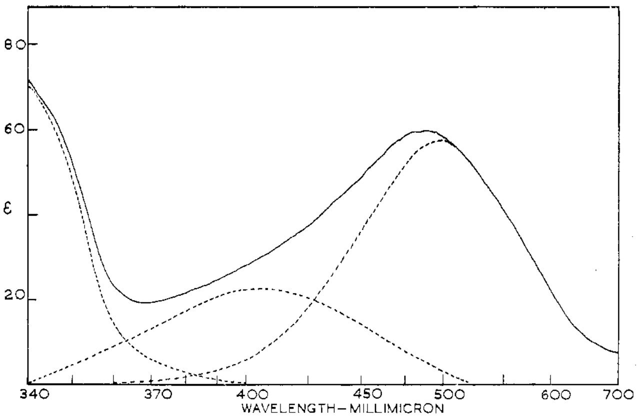

Figure 2.—Visible spectrum of chromium(II) acetate monohydrate in 95% ethanol.

monomer systems. The spin-selection rule is formally relaxed on assumption of spin exchange between pairs of chromium atoms and it is expected that these transitions will make some contribution to the band width and intensity[14] of the "chromium(II) d–d band."

A characteristic feature of the "d–d" spectra of the binuclear acetates is their remarkably high intensity.[23] In dioxane where the binuclear structure of copper acetate is particularly stable, $(\epsilon_{max})_I$ is $\simeq 220$. In water, however, $(\epsilon_{max})_I$ is $\simeq 20$. The latter value is of the order commonly observed for vibronically induced, parity-forbidden transitions and is consistent with a monomeric species whose average environment is $\simeq D_{4h}$. In the binuclear species, each metal atom is effectively in a field of symmetry $\leq C_{4v}$. The model calculations on tetrahedral molecules by Ballhausen and Liehr[24] have shown that the mixing of 3d and 4p wave functions by the crystal field yields contributions to intensity of the same order as those by the vibronic mechanism. It seems improbable that the present case will prove to be an exception and the dominant mechanism is suggested to be the same as in the case of tetrahedral molecules, namely, mixing of 3d and ligand functions by the C_{4v} ligand field. Actual calculations are deferred until the necessary description of the hybrid orbitals on the oxygen atoms is known (*cf.* discussion on the ultraviolet spectra).

Influence of Terminal Ligands on Band II.—The sensitivity of bands I and II to different terminal ligands has been mentioned in a previous publication.[25] A new set of data for a more closely related series of complexes is reported in Table II. The errors quoted in Table II are the errors involved in estimating the peaks of the broad spectral bands and susceptibility curves. The differences in the band maxima are small and negligible for the first three complexes in Table II. The band maxima for the cyano derivative, however, are significantly different. As these are reproducible (identical spectra for two different samples), a discussion on terminal effects seems justified.

Table II

Reflectance Spectra and Experimental J Values for *para*-Substituted Pyridine Complexes of Copper Acetate

Compound	Band I, ±3 mμ	Band II, ±3 mμ	$-2J$, ±5 cm^{-1} [a]
$Cu(CH_3CO_2)_2$-4-CH_3py	682	370	325
$Cu(CH_3CO_2)_2$py	680	370	325
$Cu(CH_3CO_2)_2$-4-CH_3COpy	677	370	311
$Cu(CH_3 \cdot CO_2)_2$-4-CNpy	669	380	300

[a] Calculated from experimental $\chi_M(T)$ data.

The blue shift of band I on increasing electron-withdrawal character of the terminal ligand is indicative of increasing tetragonal distortion. The apparent red shift of band II favors a charge-transfer assignment. An increase in electron withdrawal effects by the terminal ligand stabilizes the 3d manifold but at the same time increases the splitting of the 3d orbitals. These opposing effects appear to be of comparable magnitude so that the direction of the charge transfer is not immediately predictable.

Influence of Bridging Ligands on Band II.—Successive chlorination of the bridging acetates provides convincing evidence for the assignment of band II as being charge transfer in origin. Figure 3 illustrates a systematic red shift in band I on increasing chlorine substitution of the acetate bridges. This is an accord with the expected reduction in ligand field. The marked deviation of copper trichloroacetate from the frequency maximum–pK_a plot may be attributed to extensive dissociation of the complex in most solvents.

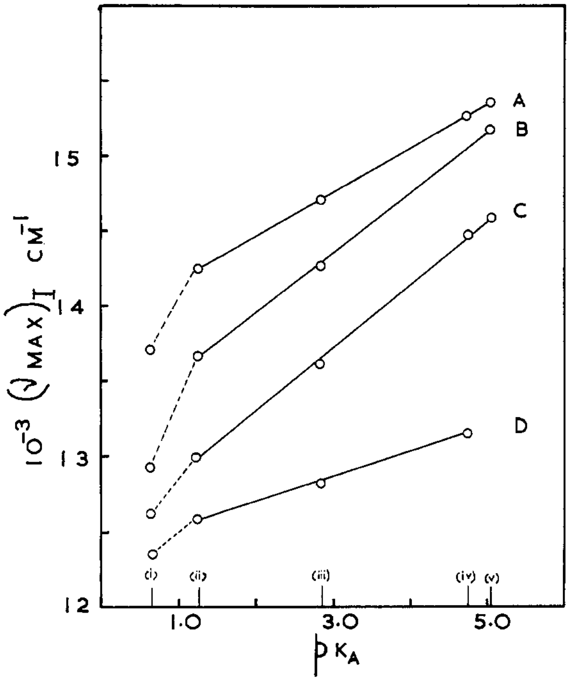

Figure 3.—Variation of copper band I (maximum) of anhydrous copper alkanoates with pK_a of the corresponding carboxylic acids: (i) trichloroacetic, (ii) dichloroacetic, (iii) monochloroacetic, (iv) acetic, and (v) trimethylacetic. Copper acetate and copper trimethylacetate are insoluble in ethyl ether and water, respectively. Solvents: A, dioxane; B, ethyl ether; C, ethanol; D, water.

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(23) E. Kokot and R. L. Martin, *Inorg. Chem.*, **3**, 1306 (1964).

(24) C. J. Ballhausen and A. D. Liehr, *J. Mol. Spectry.*, **2**, 342 (1958).

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

In water where all of the copper chloroacetates are certainly dissociated, this deviation is noticeably small. Unlike band I, band II (*cf.* Figure 4) exhibits a perceptible shift to higher energies, favoring a charge-transfer assignment. Again, the direction of the charge transfer is not clear for the stabilization of ligand orbitals is associated with a concomitant reduction in 3d-orbital splitting. However the observed blue shift is convincing evidence against the assignment of band II as an internal d–d transition whether it be a single[10] or a double[9] electron excitation.

Ultraviolet Spectra of Copper and Chromium(II) Acetates

The acetate anion is stabilized by a strongly delocalized π system. The orbitals on the oxygen atoms are usually considered as being partially sp hybridized. Bridging coordination to a metal is expected to modify the hybridization scheme in such a way as to maintain a $2p_\pi$ orbital on the oxygen atoms. The observed MOC angles in copper[26] and chromium(II)[27] acetates are about 131° and suggest a hybridization scheme intermediate between sp and sp^2. Although a quantitative study of the composition and orientation of the hybrid orbitals would require self-consistent field molecular orbital calculations, it is reasonable to assume for the present that there are two types of oxygen lone-pair orbitals, namely a p_π and a p hybrid containing a significant amount of s character n(s,p).

The p_π orbitals are able to π bond with the metal d_{xy} orbitals and so give rise to a bridging π system, characteristic of all binuclear molecules of the copper acetate type. The π system is represented schematically in Figures 5 and 6. The latter figure tends to overemphasize the delocalization which is rather weak at the metal atoms.[28,29] A simple Hückel molecular orbital calculation with the following choice of parameters:[30,31] $\alpha_{\mathrm{Cu}} = -100{,}000$, $\alpha_{\mathrm{C}} = -86{,}000$, $\alpha_{\mathrm{O}} = -128{,}000$, $\beta_{\mathrm{CO}} = -33{,}000$, and β_{MO} left as a variable parameter, leads to the orbital pattern given in Figure 7.

The diagram may be interpreted in the following way. At each copper atom, the interaction between the metal orbitals and the σ orbital of the terminal ligand and the σ, π, and lone-pair orbitals of the bridging ligands will yield a set of antibonding molecular orbitals (mainly metal in character). The order of these orbitals is generally considered to be $x^2 - y^2 > z^2 \sim xy > xz, yz$.[9] Since the metal–metal interaction is particularly weak, the binuclear species will be associated with an approximately degenerate pair of such orbital sets. In Figure 7 the even and odd combinations are labeled (as required by the full molecular symmetry). For the purposes of symmetry arguments the ground-state configuration may be described as $(\sigma^*_{x^2-y^2}, b_{1g})^2$ where the b_{1g} combination corresponds to the mildly bonding "molecular orbital." It should be emphasized, however, that because of the

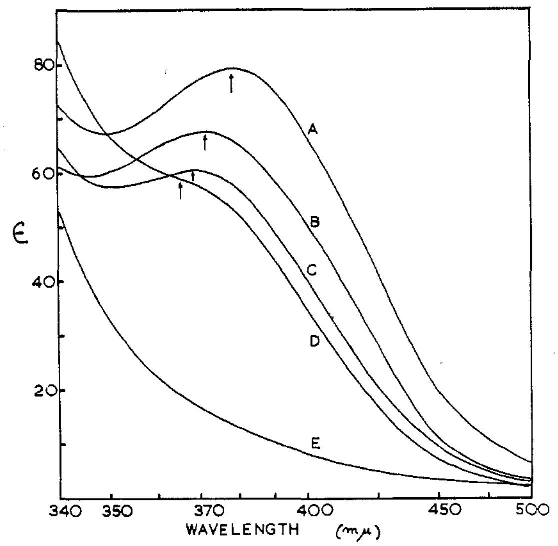

Figure 4.—Band II of anhydrous copper alkanoates in dioxane: A, trimethylacetate; B, acetate; C, monochloroacetate; D, dichloroacetate; E, trichloroacetate.

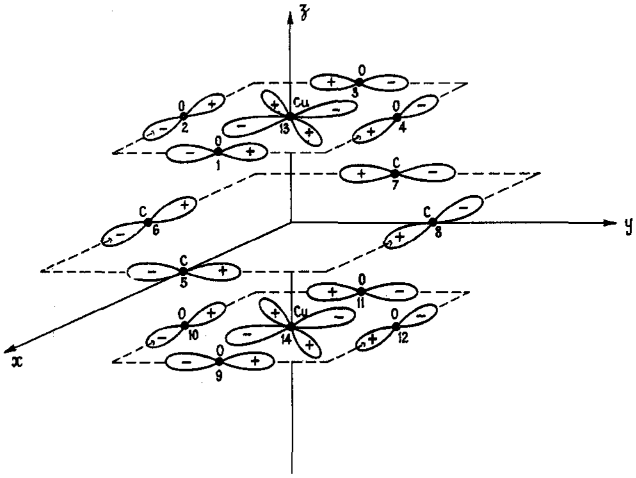

Figure 5.—π-Bonding scheme in binuclear copper and chromium(II) acetates. The metal atoms are actually displaced 0.22 A above the plane of the oxygen atoms.

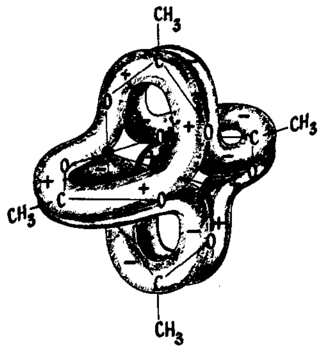

Figure 6.—"Multiple doughnut" representation of the acetate π system.

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

(27) J. N. Van Niekerk, F. R. L. Schoening, and J. F. de Wet, *ibid.*, **6**, 501 (1953).

(28) The overlap integral $S(3d\pi, 2p\pi(\mathrm{O}))$ is roughly 20% that of $S(2p\pi\text{-}2p\pi(\mathrm{C}))$—using Slater functions for $2p\pi(\mathrm{C})$ and $2p\pi(\mathrm{O})$ and the Cu radial function of Richardson,[29] *et al.*, for $3d\pi$.

(29) J. W. Richardson, W. C. Niewport, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962).

(30) J. P. Fackler, Jr., and F. A. Cotton, *Inorg. Chem.*, **2**, 105 (1963).

(31) C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory," W. A. Benjamin, Inc., New York, N. Y., 1964, p 122.

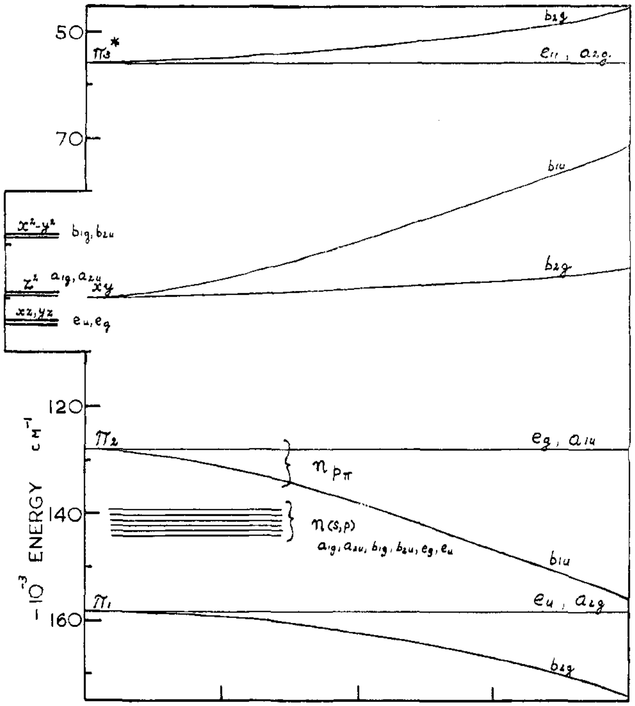

Figure 7.—π molecular orbitals in copper acetate; $\Delta E = [xz, yz - (x^2 - y^2)] \simeq 15{,}000\ cm^{-1}$.

extensive mixing with the configuration $(\sigma^*_{x^2-y^2}, b_{2u})^2$ the electrons are essentially localized on their parent metal atoms. The low-lying triplet would correspond to the configuration $[\sigma^*_{x^2-y^2}, (b_{1g})^1(b_{2u})^1]$. In the present calculation it is observed that π bonding for the whole molecule splits the two xy combinations. As β_{MO} is small ($\sim$3000 cm^{-1}), this splitting does not lead to any significant consequences.[30] The parameter values are only rough estimates and the orbital diagram should be interpreted qualitatively.

The hybrid lone-pair orbitals n(s,p) transform in D_{4h} as a_{1g}, b_{1g}, e_g, a_{2u}, b_{2u}, e_u. The b_{1g} and b_{2u} combinations are of particular importance for they overlap with the $d_{x^2-y^2}$ combinations b_{1g} and b_{2u}. Estimates of the energies of these hybrids require a specification of the degree of mixing of the oxygen 2s and $2p_\sigma$ orbitals. This is not known, but above considerations indicate considerable p character so that the n(s,p) set should not be far removed in energy from the np_π orbitals. In Figure 7 the n(s,p) set is tentatively represented as a cluster lying some 15,000 cm^{-1} below the np_π combinations. The mutual lone-pair overlap and also the lone-pair–metal d orbital overlap is neglected in the present discussion.

The ultraviolet spectrum of copper acetate (*cf.* Figure 8) consists of one very broad and asymmetric band which may be resolved into at least two Gaussian bands. The effect of bridging substituents on band III is complicated by an irregular variation in band width and ϵ_{max}. Although our data at present are incomplete, the general characteristics of band III resemble those of band II. Both bands are sensitive to the polarity of solvents. Band II is clearly resolved only in dioxane and remains as a poorly defined shoulder of varying contour in most other solvents. It appears to exhibit a blue shift on increasing solvent polarity.[32] A clearly defined blue shift is observed for band III in the favorable case of copper trimethylacetate. ν_{max} of band III is 38,200 cm^{-1} in hexane, 39,100 cm^{-1} in ethanol, and 40,700 cm^{-1} in methanol.

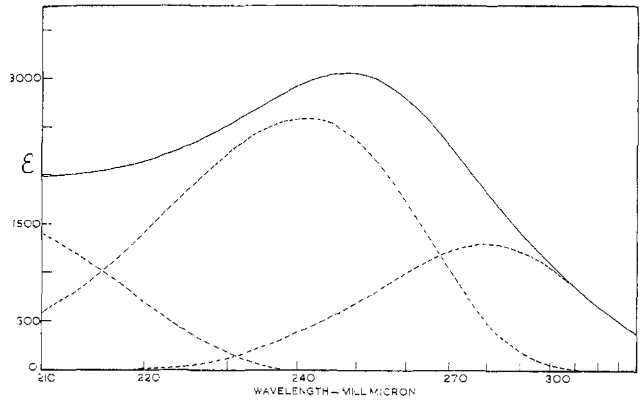

Figure 8.—Band III of copper acetate monohydrate in 95% ethanol.

A consistent assignment of band III would be the electron promotion $n(s,p) \rightarrow \sigma^*_{x^2-y^2}$. Some excitations from the b_{1g}, b_{2u}, e_u, and e_g combinations of hybrid lone pairs to the b_{1g} and b_{2u} combinations of $\sigma^*_{x^2-y^2}$ molecular orbitals are allowed by the over-all molecular symmetry and also by local symmetry. These charge-transfer transitions are therefore of the $^1A \rightarrow {}^1W$ type (Platt notation).[33,34] The low-lying band II, on the other hand, is postulated to be an $np_\pi \rightarrow \sigma^*_{x^2-y^2}$ excitation. This transition is strongly forbidden by local symmetry since overlap between $d_{x^2-y^2}$ and p_π orbitals is formally zero, and accordingly band II may be classified as a $^1A \rightarrow {}^1U$ charge transfer.

The spectrum of chromium(II) acetate (*cf.* Figure 9) supports the assumption of partially filled 3d orbitals on the chromium atoms. The spectrum exhibits an apparent "electronic progression" which may be interpreted as one-electron excitations from n(s,p) and np_π lone pairs to the partially filled 3d manifold. Successive excitations from n(s,p) and np_π combinations will give rise to $^1A \rightarrow {}^1W$ and $^1A \rightarrow {}^1U$ progressions, respectively (exceptions to this generalization are the $n(s,p) \rightarrow (xy)$ and $np_\pi \rightarrow (xy)$ transitions which are of the types $^1A \rightarrow {}^1U$ and $^1A \rightarrow {}^1W$, respectively). The assignment of the spectrum is complicated by the splitting of the various n(s,p) and np_π combinations which overlap differently with the metal 3d, 4s, and 4p orbitals, and a more detailed examination of the spectrum will be presented in a future publication. For the present it should be noted that the counterparts of the copper bands III and II should exist and lie at higher energies (the lower electronegativity of chromium would displace the 3d mani-

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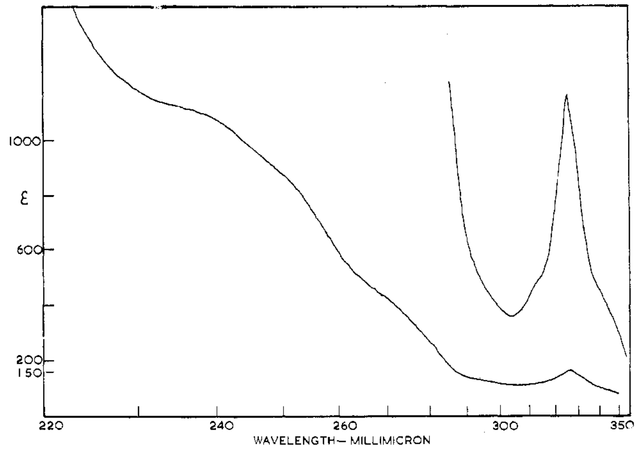

Figure 9.—Ultraviolet spectrum of chromium(II) acetate monohydrate in 95% ethanol. The band system at 326 mμ is also recorded at a higher concentration.

fold to higher energies). The counterpart of band II would certainly be obscured by the more intense $^1A \rightarrow {}^1W$ transitions while the corresponding band III of chromous acetate is believed to be the strong absorption wing which extends through the ultraviolet region. An interesting feature of the chromium(II) acetate spectrum is the presence of a relatively sharp peak at ~30,700 cm^{-1} which appears to sit on a broader band. This may be an n(s,p) excitation to the "nonbonding $d_{xz,yz}$[11] orbitals" or possibly one of the components of $np_\pi \rightarrow (xy)$. Alternatively it may be a d–d type of intraconfigurational transition corresponding to a quintet → singlet excitation in the monomer. Several states arising from the free ion term ^1I have essentially the same configuration as the ground quintet of the monomer. The observed intensity appears to be too large for this assignment.

Experimental Section

Methods of preparing amine- and chloro-substituted derivatives of copper acetate have been described in the literature.[35,36] The electronic spectra were recorded on a Beckman DK-2 diffuse-reflectance and a Shimadzu Seisakusho spectrophotometer. Extinction coefficients were always based on monomeric formula weights. Magnetic measurements on the pyridine derivatives were made by the Gouy-tube method, in the temperature range 90–340°K. The observed $\chi_M(T)$ curves closely resembled those of copper butyrate and copper dicarboxylate pyridine derivatives.[23,25]

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Mixed Complexes of Copper(I) Cyanides[1]

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The mixed ligand complexes Cu(phen)CN, Cu(bipy)CN, $Cu(P(C_6H_5)_3)_2CN$, and $Cu(As(C_6H_5)_3)_2CN$ have been prepared. Unlike the compounds $CuCN \cdot NR_1R_2R_3$, these compounds are stable toward oxidation and loss of the other ligands. The compounds appear to have a polymeric structure possibly involving N–Cu bridging of the cyanide ligand and apparently owe their stability to both this structure and some π bonding.

Mixed ligand complexes are currently of interest because of the possibility of observing mutual modifications of the bonding of the individual ligands. Although mixed cyanide–halide complexes of both gold(III)[2] and platinum(II)[3] have been reported, an investigation of complex copper(I) cyanide ions in aqueous solution has shown that mixed ligand complexes are not formed with halide ions as potential ligands.[4] The reaction of solid cuprous cyanide with aqueous halide ions also produced the tricyanocuprate(I) ion, $Cu(CN)_3^{2-}$, and not the mixed ligand complex.[4] The reaction of copper(I) cyanide with amines and with methyl iodide has been reported in the early literature[5,6] to produce addition compounds of the type $CuCN \cdot RNH_2$ or $CuCN \cdot CH_3I$, which readily lose the addend at reduced pressure or on heating and which are readily oxidized in air. Although structures of most of these compounds are not known, the compound $CuCN \cdot NH_3$ has recently been studied by X-ray analysis.[7] This compound was found to consist of layers of bridged copper cyanide molecules with ammonia molecules between the layers; the ammonia was however lost on standing for 3 days.

As the ions $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$ are known to

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