

bromide and noncoordinating perchlorate anions was somewhat erratic, indicating again that lattice forces may be rather important in determining the final product isolated in the solid state.

The variation in stoichiometry among the complexes prepared in the presence of bromide and chloride ions was not totally unexpected. Although Tyree, *et al.*,⁷ report the preparation of $\text{VOL}_5(\text{ClO}_4)_2$ ($\text{L} = \text{C}_5\text{H}_5\text{NO}$), the compound VOL_2Cl_2 [$\text{L} = \text{dimethyl sulfoxide (DMSO)}$] was also noted. Selbin, *et al.*,¹⁰ record preparation of $\text{VOL}_5(\text{ClO}_4)_2$, VOL_5Br_2 , VOL_3Cl_2 , and VOL_3SO_4 ($\text{L} = \text{DMSO}$), for which conductometric data indicate 3, 2, 0, and 0 ions, respectively. As DMSO exhibits a ligational strength similar to that of pyridine N-oxide,²³ the complex stoichiometry for the various pyridine N-oxide compounds should, and apparently does, follow. Chloride ions and at times bromide and nitrate ions have also been shown to compete successfully with various amine N-oxides for coordination sites about a wide variety of central metal atoms of diverse oxidation states.^{10,24}

(23) Unpublished results.

(24) C. M. Harris, I. Kokot, S. L. Lenzer, and T. N. Lockyer, *Chem. Ind. (London)*, 651 (1962); J. T. Summers and J. V. Quagliano, *Inorg. Chem.*, **3**, 1767 (1964); L. R. Melby, N. J. Rose, E. Abramson, and J. C. Caris, *J. Am. Chem. Soc.*, **86**, 5117 (1964), are recent examples.

The coordination stereochemistry is quite obvious for compounds of the type VOL_5X_2 ($\text{L} = \text{substituted pyridine N-oxide}$). Four ligands occupy the equatorial positions while the fifth ligand coordinates *trans* to the vanadyl oxygen. From the previous discussion one would predict for $\text{VOL}_4\text{X}_2 \cdot \text{H}_2\text{O}$ that the *trans* axial ligand would be a water molecule (the remaining N-oxide ligands again being arranged in the equatorial plane), although the presence of X at this site cannot as yet be completely ruled out. The general absence of a pyridine N-oxide molecule in the *trans* axial position follows from a consideration of the spectral data for band I (Table III). This band is greatly displaced to longer wave lengths for such N-oxide coordination as is illustrated in the case of the perchlorate complexes. Here the shift in band position is 500 to 600 Å. in going from *trans* axial water coordination to coordination of $\text{C}_5\text{H}_5\text{NO}$ and $\text{C}_5\text{H}_5\text{NO}$, respectively. The main band (I) for the tetrakis compounds is evidently that expected for *trans* axial aquo (or possible anion) coordination. Yet a longer wave length shoulder for several of the tetrakis(substituted pyridine N-oxide)-oxovanadium(IV) chloride complexes suggests that perhaps some of the metal ions may be penta N-oxide coordinated.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FACULTY OF TECHNOLOGY, UNIVERSITY OF MANCHESTER, MANCHESTER 1, ENGLAND

Copper(II) Complexes of Unsaturated Acids

By B. J. EDMONDSON AND A. B. P. LEVER

Received June 7, 1965

Copper(II) salts of acrylic, vinylacetic, and allylacetic acids, and some adducts with nitrogen or phosphorus donor ligands, of formula $\text{Cu}(\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{CO}_2)_x\text{L}_x$ ($n = 0, 1, \text{ and } 2$; $x = 1 \text{ and } 2$) are reported. Magnetic, spectrophotometric, molecular weight, and conductivity data indicate that the simple salts, and the adducts with one donor ligand per copper atom, are binuclear both in the solid state and in solution. The complexes with two donor ligands per copper atom are polynuclear in the solid but tend to form dimers with loss of donor ligand, in solution. On the basis of infrared spectra it is tentatively suggested that the double bond coordinates to the copper(II) atom in the simple salts. The electronic spectra support the δ model for the metal-metal bond.

Many copper compounds have been observed to have subnormal magnetic moments¹ since Lifschitz and Rosenbohm² first observed in 1915 that the molar susceptibility of cupric acetate monohydrate was much less than the value of approximately 1600 c.g.s. usually observed with copper salts. Cupric acetate monohydrate exists as a binuclear molecule $\text{Cu}_2(\text{OAc})_4 \cdot 2\text{H}_2\text{O}$, in which the two copper atoms are bridged by the four acetate groups.³ The structure of the pyridine adduct is similar.⁴ These compounds exhibit anomalous paramagnetic behavior; their magnetic mo-

ments vary with temperature due to exchange interaction between the pairs of adjacent copper atoms. This leads to the formation of a lower diamagnetic singlet state and an excited paramagnetic triplet state.⁵⁻⁹ Many copper carboxylate derivatives show similar behavior. The magnetic interaction depends upon the nature of the attached ligands. There has been considerable interest in investigating the effect of varying the acid and of altering the donor ligand.

(5) R. L. Martin and H. Waterman, *ibid.*, 2545 (1957); 1359, 2960 (1959).

(6) R. L. Martin and A. Whitley, *ibid.*, 1394 (1958).

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

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

(9) M. Kishita, M. Inoue, and M. Kubo, *ibid.*, **3**, 237 (1964).

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

(2) J. Lifschitz and E. Rosenbohm, *Z. Elektrochem.*, **21**, 499 (1915).

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

(4) G. A. Barclay and C. H. L. Kennard, *J. Chem. Soc.*, 5245 (1961).

Although certain aromatic acids have been investigated,¹⁰⁻¹⁴ there appears to be no work dealing with unsaturated aliphatic acids. We have studied the copper complexes of acrylic, vinylacetic, and allylacetic acids and find that these too form binuclear complexes. There is infrared evidence that the double bond is coordinated to the copper(II) atom. No other complexes have been reported in which a double bond coordinates to a divalent copper atom, although of course such complexes with monovalent copper are very well known.¹⁵ The behavior of vinylacetic acid toward copper(II) ions in solution has been investigated previously.¹⁶

Experimental

Preparation of the Complexes.—In the preparations which follow, the C and H analyses were carried out in the Microanalytical laboratory under the direction of Mr. Manohin. The copper was estimated gravimetrically as the pyridine thiocyanate.

Bis(acrylate)copper(II).—Basic copper carbonate (1 g.) and acrylic acid (1.2 g.) were mixed and allowed to react at room temperature for 3 hr. The mixture was then dissolved in acetone (100 ml.) at reflux. After filtering hot, crystals of copper acrylate crystallized from the filtrate. The product was recrystallized from acetone. *Anal.* Calcd. for $C_{12}H_{12}Cu_2O_8$: C, 35.0; H, 2.9; Cu, 30.9. Found: C, 35.1; H, 3.0; Cu, 30.6.

Bis(acrylate)bis(pyridine)copper(II).—To an acetone solution of copper acrylate (0.5 g.) was added excess pyridine (2 ml.). The deep blue crystals were recrystallized from boiling benzene (150 ml.) and dried *in vacuo*. *Anal.* Calcd. for $C_{18}H_{18}Cu_2O_8N_4$: C, 52.8; H, 4.4; Cu, 17.5. Found: C, 52.6; H, 4.5; Cu, 17.6.

Bis(acrylate)pyridinecopper(II).—On shaking the above blue bis(pyridine) complex (1 g.) in sodium-dried ether (40 ml.) the solid dissolves, resulting in a green solution which almost immediately precipitates the desired green product. *Anal.* Calcd. for $C_{22}H_{22}Cu_2O_8N_2$: C, 46.4; H, 3.9; Cu, 22.3. Found: C, 46.3; H, 3.9; Cu, 22.2.

Bis(vinylacetato)copper(II).—Basic copper carbonate (1 g.) and vinylacetic acid (1.4 g.) were heated at 40° for 1 hr., and the product was dissolved in sodium-dried ether. *n*-Hexane was added to the filtered solution until precipitation was complete. The blue product was recrystallized from acetone and dried *in vacuo*. *Anal.* Calcd. for $C_{16}H_{20}Cu_2O_8$: C, 41.1; H, 4.3; Cu, 27.2. Found: C, 41.1; H, 4.1; Cu, 26.7.

Bis(vinylacetato)bis(pyridine)copper(II).—Basic copper carbonate (1 g.) and vinylacetic acid (1.5 g.) were heated at 40° for 2 hr. in pyridine (5 ml.). The blue product was refluxed several times with *n*-hexane to remove excess pyridine. *Anal.* Calcd. for $C_{18}H_{20}Cu_2O_8N_4$: C, 55.2; H, 5.1; Cu, 16.2. Found: C, 54.9; H, 4.9; Cu, 16.1.

Bis(vinylacetato)pyridinecopper(II).—The above bis(pyridine) complex was recrystallized from a *n*-hexane-benzene mixture giving the new product. *Anal.* Calcd. for $C_{28}H_{30}Cu_2O_8N_2$: C, 49.9; H, 4.8; Cu, 20.3. Found: C, 50.1; H, 4.6; Cu, 20.3.

Bis(vinylacetato)pyrazinecopper(II).—Acetone solutions of copper vinylacetate (1.9 g.) and pyrazine (1.3 g.) were mixed, and the green solid which formed after several hours was filtered and then refluxed for 8 hr. with sodium-dried ether. The crude product was recrystallized from chloroform and finally dried *in vacuo*. *Anal.* Calcd. for $C_{24}H_{28}Cu_2O_8N_4$: C, 45.9; H, 4.47; Cu, 20.3. Found: C, 45.9; H, 4.7; Cu, 20.6.

Bis(vinylacetato)triphenylphosphinecopper(II).—Sodium-dried

ether solutions of copper vinylacetate (1 g.) and triphenylphosphine (2.3 g.) were mixed and the solution left 24 hr. The green product was filtered, washed with sodium-dried ether, and finally recrystallized from benzene. *Anal.* Calcd. for $C_{52}H_{60}Cu_2O_8P_2$: C, 63.0; H, 5.0; Cu, 12.8. Found: C, 63.1; H, 5.3; Cu, 12.4.

Bis(allylaceto)copper(II).—Basic copper carbonate (1 g.) and allylacetic acid (1.8 ml.) were mixed and allowed to react for 3 hr. at room temperature; 15 ml. of *n*-hexane was added and the mixture was shaken for several hours. The blue crystals were washed with *n*-hexane and finally recrystallized from sodium-dried ether. *Anal.* Calcd. for $C_{20}H_{28}Cu_2O_8$: C, 45.9; H, 5.4; Cu, 24.3. Found: C, 45.9; H, 5.6; Cu, 23.8.

Bis(allylaceto)bis(pyridine)copper(II).—Two equivalents of pyridine was added to a *n*-hexane solution of copper allylaceto (1 g.). On standing at 0° for several hours light blue crystals formed which were filtered, dried, and finally recrystallized from a pyridine-*n*-hexane mixture. *Anal.* Calcd. for $C_{30}H_{34}Cu_2O_8N_4$: C, 57.2; H, 5.7; Cu, 15.1. Found: C, 57.1; H, 5.7; Cu, 14.7.

Bis(allylaceto)pyridinecopper(II).—The above light blue bis(pyridine) complex (1 g.) was left for several days in a vacuum desiccator over concentrated sulfuric acid, during which time the complex lost one molecule of pyridine to form the corresponding green copper allylaceto monopyridine derivative. The crude product was recrystallized from petroleum ether (30-40°). *Anal.* Calcd. for $C_{30}H_{38}Cu_2O_8N_2$: C, 52.9; H, 5.6; Cu, 18.7. Found: C, 53.1; H, 5.7; Cu, 18.4.

Bis(allylaceto)pyrazinecopper(II).—Copper allylaceto (1 g.) was refluxed in *n*-hexane (20 ml.) for 3 hr. and the solution was then filtered into a *n*-hexane solution of pyrazine (0.6 g.). The green precipitate was filtered, refluxed several times with sodium-dried ether, and finally recrystallized from acetone. *Anal.* Calcd. for $C_{28}H_{36}Cu_2O_8N_4$: C, 49.2; H, 5.3; Cu, 18.6. Found: C, 49.3; H, 5.5; Cu, 18.8.

Bis(allylaceto)triphenylphosphinecopper(II).—This was prepared in a similar manner to the vinylacetate adduct. Ether was found to be a suitable solvent for recrystallization. *Anal.* Calcd. for $C_{66}H_{68}Cu_2O_8P_2$: C, 64.2; H, 5.5; Cu, 12.1. Found: C, 64.3; H, 5.6; Cu, 12.0.

Spectrophotometric Data.—Infrared spectra were obtained with a Perkin-Elmer Model 21 spectrophotometer and electronic spectra with an Optika CF4 double beam grating spectrophotometer.

Magnetic Measurements.—The magnetic susceptibility data were obtained with a Newport Magnetic (gouy) balance with 1.5-in. pole pieces. Mercury tetrathiocyanatocobaltate(II) and nickel chloride solution were used as calibrants.

Molecular Weight Data.—These were obtained with a Mechrolab Series 300 osmometer (using concentrations of about 0.1 *M*) or with a Gallenkamp Model 7665K semimicro ebulliometer. In the latter case, some five measurements were made on each sample, at different concentrations from 0.01 to 0.1 *M*, and the molecular weight was estimated graphically. The value quoted in Table I is therefore a mean value over this concentration range. The deviation from the mean was not more than $\pm 5\%$.

Results and Discussion

Most of the complexes are soluble to some extent in organic solvents, including ether. Copper vinylacetate and allylaceto are dimeric in acetone (Table I). The acrylate is insufficiently soluble for a molecular weight measurement but is probably dimeric. Where solubility allowed, complexes with one donor ligand per copper atom have also been shown to be dimeric. The conductivity of these complexes in acetone was too low to be measured. Complexes with two donor ligands per copper atom are too unstable for a molecular weight determination.

The magnetic moments of the salts $Cu(CH_2=CH-(CH_2)_nCO_2)_2$ ($n = 0, 1, \text{ and } 2$) and their monoadducts

(10) J. Ploquin, *Bull. soc. chim. France*, **18**, 757 (1951).

(11) M. Kondo and M. Kubo, *J. Phys. Chem.*, **62**, 1558 (1958).

(12) J. Lewis and R. C. Thompson, *Nature*, **200**, 468 (1963).

(13) M. Inoue, M. Kishita, and M. Kubo, *ibid.*, **3**, 239 (1964).

(14) R. D. Gillard, D. M. Harris, and G. Wilkinson, *J. Chem. Soc.*, 2838 (1964).

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

(16) R. K. Resnik and B. E. Douglas, *Inorg. Chem.*, **2**, 1246 (1963).

TABLE I
 MOLECULAR WEIGHTS AND MAGNETIC MOMENTS IN SOLUTION

Complex	Solvent ^a	Magnetic moment, B.M. ^b	Mol. wt. ^c	
			Calcd.	Found
Cu ₂ (vinylacetate) ₄	Acetone (0.55)	1.43 (296°)	466	469
	Ethanol (0.37)	1.50 (295°)		^d
	Methanol (0.49)	1.58 (295°)		^d
Cu ₂ (vinylacetate) ₄ py ₂	Benzene (0.21)	1.42 (298°)	625	667 (495) ^e
Cu ₂ (allylacetate) ₄	Acetone (0.47)	1.42 (293°)	523	542
Cu ₂ (vinylacetate) ₄ (P(C ₆ H ₅) ₃) ₂	Benzene		991	1024
Cu ₂ (allylacetate) ₄ py ₂	Acetone		681	514

^a Solvent for both molecular weight and magnetic moment; molar concentration for magnetic moment determination in parentheses. ^b Temperature of measurement in parentheses—also see Table II. ^c Measurements in benzene were done with the osmometer, in acetone ebullioscopically. ^d Tendency to decompose in the boiling solvent, precludes ebullioscopic measurements. ^e Molecular weight in acetone; py = pyridine.

 TABLE II
 MAGNETIC MOMENTS AND INFRARED SPECTRA OF THE SOLID COMPLEXES

Complex ^a	10 ⁶ X _G ^b c.g.s.	10 ⁶ X _m ^c c.g.s.	μ _{eff} ^d	Infrared spectrum, ^f cm. ⁻¹		
				CO ₂ ⁻ asym.	CO ₂ ⁻ sym.	C=C
Cu ₂ (acrylate) ₄	3.643	808	1.38	1575	1430	1650, 1497
Cu ₂ (acrylate) ₂ py ₂	3.323	1367	1.80	1568 1585	1423	1640
Cu ₂ (acrylate) ₄ py ₂	2.880	914	1.47	1587	1429	1640
Cu ₂ (vinylacetate) ₄	2.931	763	1.35	1588	1411	1638, 1501
Cu(vinylacetate) ₂ py ₂	3.049	1374	1.81	1592	1410	1653
Cu ₂ (vinylacetate) ₄ py ₂	2.293	845	1.42	1595	1413	1660
Cu ₂ (vinylacetate) ₄ pyz ₂	2.695	980	1.53	1603	1413	1660
Cu ₂ (vinylacetate) ₄ (P(C ₆ H ₅) ₃) ₂	0.632	521	1.12	1567	1415	1638
Cu ₂ (allylacetate) ₄	2.902	863	1.43	1600	1421	1640, 1510
Cu(allylacetate) ₂ py ₂	^e	1595	1425	1638
Cu ₂ (allylacetate) ₄ py ₂	2.082	863	1.43	1595	1420	1638
Cu ₂ (allylacetate) ₄ pyz ₂	2.372	967	1.52	1600	1429	1640
Cu ₂ (allylacetate) ₄ (P(C ₆ H ₅) ₃) ₂	0.617	554	1.15	1558	1419	1638

^a py = pyridine; pyz = pyrazine. ^b Gram susceptibility. ^c Corrected molar susceptibility. ^d Magnetic moment from μ_{eff} = 2.84√X_mT measured at 293–296°K. ^e Loses pyridine too readily for an accurate measurement. ^f Sodium acrylate 1550, 1562, 1438, and 1640 cm.⁻¹; sodium vinylacetate 1564, 1414, and 1659 cm.⁻¹; sodium allylacetate 1560, 1420, and 1640 cm.⁻¹.

with pyridine, pyrazine, or triphenylphosphine are found to be lower, at room temperature, than the spin-only moment (1.73 B.M.) (Tables I and II). For a given acid, the magnetic moments lie in the sequence pyrazine > pyridine >> triphenylphosphine, implying that the magnetic interaction increases in that sequence. Comparison should strictly be made between the exchange energies (*J*), but until temperature range magnetic studies can be undertaken such data are not available. The trend in the magnetic moments probably, but not necessarily, reflects the trend in *J* values. The sequence is understandable in that the phosphorus ligand being more polarizable than a nitrogen ligand will push more charge onto the metal atom, thus increasing the metal overlap. Pyrazine is a much weaker base than pyridine and a much better π acceptor^{17,18}; it will therefore tend to drain charge off the copper atom and decrease the overlap. The magnetic moment is almost independent of the number of methylene groups in the acid.

The absorption spectra (Table III) and magnetic moments of these complexes are dependent upon the

solvent, and it is probable that the solvent occupies a coordination site. Where a donor ligand is already present, molecular weight studies imply that there may be some equilibrium displacement of the donor ligand by the solvent. In addition to the broad band at 680–740 mμ, a band is observed near 370 mμ. This is seen in other *n*-alkanoate complexes of copper(II) and has been ascribed¹⁹ to the presence of the metal interaction. It seems probable that all the complexes described here as having low magnetic moments have a structure (Figure 1) directly analogous to that of copper acetate.³

Their infrared spectra include two bands attributable to the asymmetric and symmetric vibrations of the carboxyl group (Table II). The frequencies observed are similar to those found in copper acetate²⁰ and may be ascribed to the presence of two equivalent oxygen atoms. One cannot determine from the infrared spectrum whether these two equivalent oxygen atoms are ionically or covalently bonded to the copper atom.²¹ It is of interest that the asymmetric frequency in the

(19) R. Tsuchida and S. Yamada, *Nature*, **176**, 1171 (1955).

(20) S. Yamada, H. Nakamura, and R. Tsuchida, *Bull. Chem. Soc. Japan*, **31**, 303 (1958).

(21) A. B. P. Lever, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 5262 (1962).

(17) A. B. P. Lever, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 4761 (1964).

(18) A. B. P. Lever, S. M. Nelson, and T. M. Shepherd, *Inorg. Chem.*, **4**, 810 (1965).

TABLE III
 ELECTRONIC SPECTRA DATA,^a CM.⁻¹ (ε)

Complex	Band		
	I	II	III
Cu ₂ (acrylate) ₄	14,660 ^b	26,530	
	14,060 ^c (118)		40,820 (3410)
	14,140 ^d (149)		39,840 (5370)
Cu(acrylate) ₂ py ₂	15,550 ^b		
	15,170 ^e (136)		
Cu ₂ (acrylate) ₄ py ₂	13,930 ^b	26,670	
	13,890 ^f (266)	26,810 sh	
Cu ₂ (vinylacetate) ₄	14,660 ^b	26,530 sh	
	14,080 ^c (92)		39,680 (3430)
	14,160 ^d (145)		38,610 (3790)
	14,490 ^f (149)	26,460 sh	
	14,600 ^g (295)	27,030 sh	
	14,730 ^h (328)	26,880 sh	38,760 (9050)
Cu(vinylacetate) ₂ py ₂	14,860 ⁱ (199)		38,310 (2520)
	15,500 ^b		
Cu ₂ (vinylacetate) ₄ py ₂	15,150 ^e (175)		
	13,440 ^b	26,810 sh	
Cu ₂ (vinylacetate) ₄ pyz ₂	13,660 ^f (248)	26,880 sh	
	14,180 ^b	25,970 sh	
Cu ₂ (vinylacetate) ₄ (P(C ₆ H ₅) ₃) ₂	14,250 ^f (229)	26,740 sh	
	13,150 ^b	26,810 sh	
Cu ₂ (allylacetate) ₄	14,120 ^f (71)		
	14,350 ^b	26,950	
	14,200 ^c (174)		40,160 (3140)
	14,270 ^d (143)		38,760 (5610)
	14,660 ^f (165)	26,670 sh	
Cu(allylacetate) ₂ py ₂	14,710 ^g (208)		
	15,380 ^b		
Cu ₂ (allylacetate) ₄ py ₂	15,170 ^e (96)		
	13,870 ^b		
Cu ₂ (allylacetate) ₄ pyz ₂	14,180 ^f (216)	26,320 (92)	
	13,720 ^b	25,450	
Cu ₂ (allylacetate) ₄ (P(C ₆ H ₅) ₃) ₂	14,410 ^f (243)	26,670 sh	
	13,720 ^b	26,530	
Cu ₂ (allylacetate) ₄ (P(C ₆ H ₅) ₃) ₂	14,680 ⁱ (68)		

^a The molar extinction coefficients are expressed in terms of the monomeric formula weight throughout. ^b Diffuse reflectance spectrum. ^c Methanol. ^d Ethanol. ^e Pyridine. ^f Benzene. ^g Acetone. ^h Ether. ⁱ Dichloromethane. ^j Chloroform.

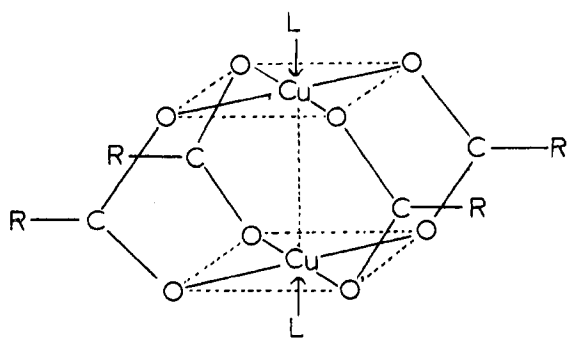


Figure 1.—Binuclear copper alkenoate: L is a donor ligand and R is an unsaturated residue.

Cu₂(acid)₄L₂ compounds follows the same trend as the magnetic moments, being highest for the pyrazine derivatives and lowest for the triphenylphosphine derivatives. It is difficult to get any bonding information from the infrared frequencies, but it is probably fair to say that the asymmetric frequency increases with increasing copper-oxygen bond strength. The weakly basic and π accepting pyrazine renders the copper atom fairly positive and thus increases the interaction between the copper atom and the negative oxygen atoms;

the more polarizable triphenylphosphine, by increasing the electron density on the copper atom, decreases the metal-oxygen bond strength.

Complexes with two donor ligands per copper atom have normal magnetic moments (Table II), and their main visible absorption band is at appreciably higher energies than is the absorption of the dimeric complexes. No band is observed near 370 mμ. They tend to lose ligand on standing, forming the corresponding dimeric complex. The allylacetate complex is the least stable in this respect, and the acrylate complex the most stable. Their infrared spectra do not differ noticeably from those of the dimeric complex, implying that there are still two equivalent oxygen atoms present. Since the magnetic moments are normal we assume that the complexes are polynuclear six-coordinate derivatives with bridging carboxyl groups. The bridge, being in an *anti-anti* configuration, rather than in a *syn-syn* configuration,⁵ holds the copper atoms too far apart for any interaction to occur.

There is yet the question of whether the simple salts have a structure as in Figure 1 but with no ligand coordinated above and below the planes of oxygen atoms or whether a double bond coordinates to the

copper atoms in the axial positions. It seems likely, for steric reasons, that the double bond would have to come from neighboring dimer units.

All the complexes exhibit absorption near 1640 cm.^{-1} (Table III) due to the uncoordinated double bonds. The simple salts exhibit additional absorption near 1500 cm.^{-1} , exactly where we might expect a coordinated double bond to occur.¹⁵ These additional bands are clearly absent in the pyridine, pyrazine, and triphenylphosphine derivatives. However, these ligands do absorb in this general region, and we cannot be sure that the absorption band has not shifted and been obscured. Nevertheless the evidence does seem to indicate that the axial positions are occupied by double bonds coordinating to the cupric atoms. We are unable to prove this point by selective bromination or iodination or by locating variations in the proton magnetic resonances (paramagnetism broadened the lines). If the solids do in fact contain polymer units, in which the dimers are linked by double bond coordination, absolute proof could only be derived from an X-ray analysis. It is pertinent that the nickel and cobalt complexes of these acids are insoluble polymers²² which exhibit a band near 1640 cm.^{-1} but do not show a band near 1500 cm.^{-1} . Polymerization presumably occurs *via* bridging carboxyl groups in these cases. The absorption spectra (Table III) of these complexes merit further comment. Three absorption bands are observed near $14,500$ (band I), $27,000$ (band II), and $39,000\text{ cm.}^{-1}$ (band III), closely analogous to the spectrum of copper acetate.²³ The shoulder on the low energy side of band I, observed by Graddon,²³ was not observed in these complexes.

Band I is sensitive to the nature of the ligand in the axial position; its energy increases in the sequence pyridine < methanol \simeq triphenylphosphine \simeq ethanol < pyrazine < benzene < acetone < ether < dichloromethane.

For a given ligand, the absorption energy is almost independent of the acid. The ligands lie in the same order as their effectiveness as donors toward copper, the strongest donors lying on the left and the weakest on the right. Band II usually occurs as a shoulder on the edge of the rising ultraviolet absorption, but is sometimes obscured. Its position varies slightly with solvent, but being only a shoulder, it is difficult to locate exactly. It does not appear in the spectra of the magnetically normal pyridine derivatives. Band III is very much more intense than the other bands and is presumably charge transfer in origin.^{8,23-25} It is almost independent of the solvent, except that in methanol there is a decided shift to the blue. There is also a dependence of band III on the acid, as observed earlier.²³ It is reasonable to assign this band as a π

to d transition, from the carboxyl π orbital to the hole in the copper d shell. Where the carboxyl group is conjugated to the double bond, as in the acrylate, the π electrons would be reduced in energy, thus increasing the energy of the transition as observed.

The assignments of the other bands are more difficult to tie down. There is a controversy about whether the copper-copper bond in binuclear copper carboxylates should be regarded as a σ bond (leaving a hole in a molecular orbital formed by the d_{z^2} atomic orbitals) or as a δ bond (leaving a hole in a molecular orbital formed from $d_{x^2-y^2}$ atomic orbitals^{5,8,23,26-30}; see Figure 2, ref. 8).

Band I has been shown to be polarized x, y and band II is z polarized.^{25,27} Electron spin resonance data^{2,31} are interpreted²⁷ to indicate the presence of a δ bond and lead to the assignment of band I to the $d_{xy} \rightarrow d_{x^2-y^2}$ transition. The energy of such a transition should be virtually independent of the solvent; this is not the case. However, recently³² a polarized single crystal study of copper acetate has confirmed the presence of a shoulder on band I. This shoulder is assigned tentatively as $d_{xy} \rightarrow d_{x^2-y^2}$. Band I is assigned^{8,32} as $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ and thus would be solvent dependent. Our data would be consistent with band I being d_{z^2} or $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$, whose energy would decrease with increasing donor strength. Little can be said about band II because its position is difficult to locate; however, it does not appear to be solvent dependent.

The σ bond model requires that all transitions terminate on the d_{z^2} orbital and therefore requires that all transitions should be solvent dependent, though perhaps to varying extents. This does not seem to be borne out in practice. It was suggested earlier²³ that band III was independent of the solvent. We have studied this band in a wider range of solvents and find that there is some slight dependence. Replacement of ethanol by methanol shifts the band some 1000 cm.^{-1} to higher energy. This could be interpreted to imply that the copper acceptor orbital was solvent-sensitive (*i.e.*, d_{z^2}) since we would not at first sight expect the oxygen donor orbital to be especially sensitive toward the solvent. However, the variation does not seem to be systematic, as with band I, and it is likely that the methanol is behaving in a special way.

Acknowledgment.—We are indebted to the Department of Scientific and Industrial Research for a maintenance grant (to B. J. E.) and for a special grant (to A. B. P. L.) to purchase the Optika spectrophotometer.

(26) I. G. Ross, *Trans. Faraday Soc.*, **55**, 1058 (1959); I. G. Ross and J. Yates, *ibid.*, **55**, 1064 (1959).

(27) M. L. Tonnet, S. Yamada, and I. G. Ross, *ibid.*, **60**, 840 (1964).

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

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

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

(31) H. Abe and J. Shimada, *Phys. Rev.*, **90**, 316 (1953).

(32) C. W. Reimann, G. F. Kokoszka, and G. Gordon, *Inorg. Chem.*, **4**, 1082 (1965).

(22) B. J. Edmondson and A. B. P. Lever, to be published.

(23) D. P. Graddon, *J. Inorg. Nucl. Chem.*, **17**, 222 (1961).

(24) E. A. Boudreaux, *Inorg. Chem.*, **4**, 506 (1964).

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