Molecular Structure of Gaseous Copper(I) Acetate as determined by Electron Diffraction†

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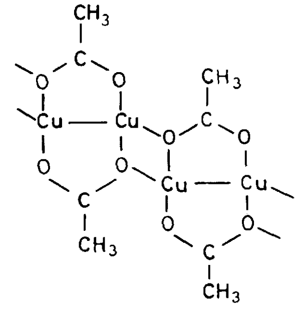
The molecular structure of gaseous copper(I) acetate has been determined by electron diffraction. The molecule is dimeric and its skeleton is planar. The molecular parameters and their uncertainties are r_g(Cu–Cu′) = 2.491 ± 0.003 Å, r_g(Cu–O) = 1.868 ± 0.002 Å, r_g(C–O) = 1.270 ± 0.002 Å, r_g(C–C) = 1.506 ± 0.003 Å, and the angle OCuO′ = 172.5 ± 0.1°. The Cu–Cu separation of 2.491 Å in gaseous copper(I) acetate is the shortest for a copper acetate compound reported so far.

Copper(I) acetate is polymeric in the solid phase,[1–3] and the copper atoms are bridged by acetate groups as shown below. The environment of the monovalent copper atom is square planar. The Cu–Cu separation in the monovalent copper acetate, 2.556 Å,[3] is significantly shorter than in the dimer of divalent copper acetate hydrate $Cu_2(O_2CCH_3)_4 \cdot 2H_2O$, 2.616 Å.[4]



On the other hand, mass spectroscopic studies on copper(I) acetate have shown that the main component in the vapour is the dimer.[5,6] We were interested in the configuration around the monovalent copper atom of gaseous copper(I) acetate and the Cu–Cu separation in the dimer, and thus undertook the molecular structure analysis of gaseous copper(I) acetate by electron diffraction.

Experimental

Data Collection.—Copper(I) acetate was prepared by reducing copper(II) acetate with copper metal in a mixed solution of anhydrous acetonitrile, acetic acid, and acetic anhydride under nitrogen.[6] A white residue was obtained by evaporation of the solvents and it was purified by sublimation under vacuum.

Electron diffraction photographs were taken by the use of an r^3-sector on Kodak electron-image plates at camera distances of 293.78 and 144.18 mm. The sample was sublimed at 493 K using a high-temperature nozzle. The accelerating voltage was 40 kV and the wavelength was determined from the diffraction patterns of thallium(I) chloride.[7] The exposure times were *ca.* 75 and 140 s for the long- and the short-camera-distance photographs, respectively, with an electron-beam current of 0.7 μA. The pressure in the diffraction chamber was 9 × 10^{-6} Torr during the experiment. Four plates were selected for photographs at each camera distance, and their optical densities were measured at 0.4-mm intervals by the use of a digital microphotometer. The electron diffraction unit and the digital microphotometer used in the present study have been described elsewhere.[8]

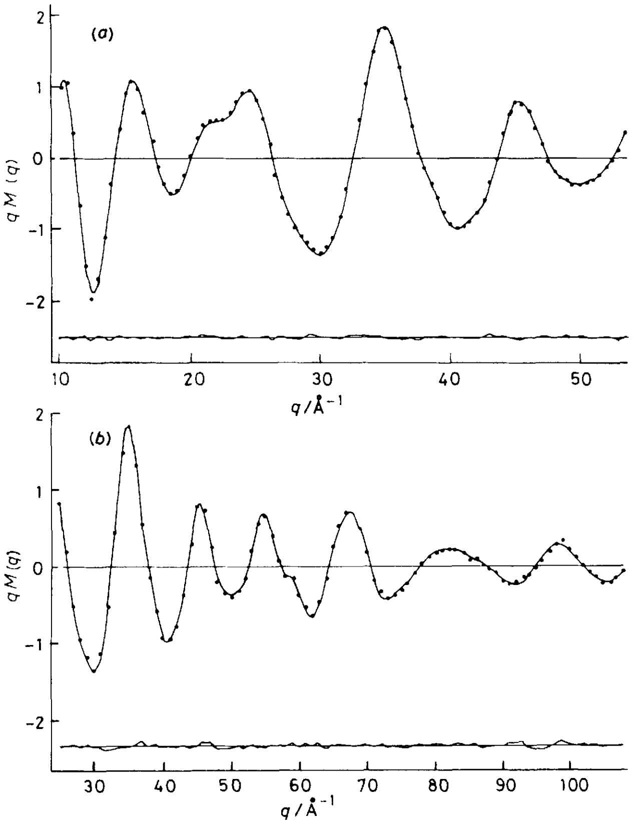


Figure 1. Molecular intensities for gaseous copper(I) acetate: (*a*) long- and (*b*) short-camera-distance data. Observed (·) and calculated data (—). The curves at the bottom show the residuals

Scattering intensities in the range of q = 10.0—53.5 $Å^{-1}$ were obtained from the long-camera-distance plates and in the range of q = 25.0—108.0 $Å^{-1}$ from the short-camera-distance plates. Here q represents $(40/\lambda)\sin(\theta/2)$, where λ = wavelength and θ = scattering angle. They were levelled using theoretical backgrounds, and the intensities for each camera distance were averaged. The elastic and inelastic scattering factors were taken from the tables prepared by Schäfer *et al.*[9] and by Cromer and Mann,[10] respectively. The inelastic scattering factor for hydrogen atom was taken from the table of Tavard *et al.*[11] The experimental background curve was drawn smoothly, and the experimental molecular intensities obtained are shown in

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† *Non-S.I. units employed*: Torr = 133 Pa, cal = 4.184 J.

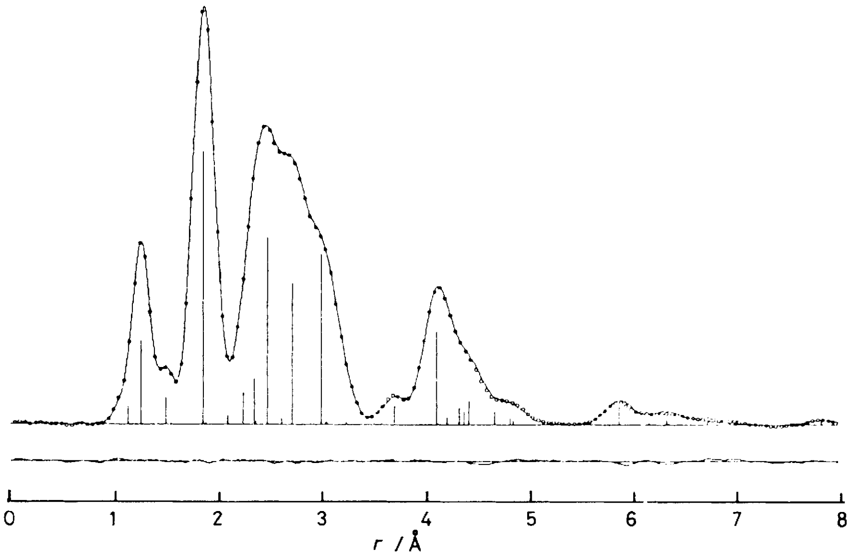

Figure 2. Radial distribution curve for gaseous copper(I) acetate: experimental (•) and theoretical data (—). The curve at the bottom shows the difference; vertical bars represent bond distances and their scattering powers

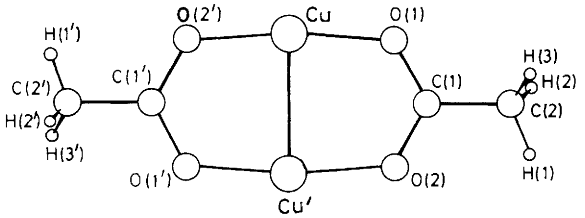

Figure 3. Numbering of atoms in dimeric copper(I) acetate

Figure 1. Figure 2 shows the experimental radial distribution function calculated from the molecular intensities. The molecular model of copper(I) acetate and the numbering of the atoms are shown in Figure 3.

Structure Analysis.—The molecular parameters were obtained from least-squares analysis of the intensities. The assumption was that the molecular skeleton has D_{2h} symmetry and each methyl group has local C_{3v} symmetry. The geometrical molecular parameters, r_α, refined by least-squares analysis, were r(Cu–Cu′), r[Cu–O(1)], r[C(1)–C(2)], r[C(2)–H(1)], angles O(1)CuO(2′) and C(1)C(2)H(1), and the refined root-mean-square amplitudes were l(Cu–Cu′), l[Cu–O(1)], l[Cu $\cdots$ O(2)], l[Cu $\cdots$ C(1)], l[Cu $\cdots$ C(2)], l[C(1)–O(1)], l[C(1)–C(2)], l[O(1) $\cdots$ O(2)], and l[C(2)–H(1)]. The asymmetry parameter, κ, for the C–H bond was assumed to be 12 × 10^{-6} Å^3,[12] and those for other atomic pairs were ignored.

The vibrational mean amplitudes and the shrinkage corrections, $r_a - r_\alpha$,[13] were calculated from the Urey–Bradley force field. Since a normal vibration analysis has not been made for this molecule, the initial force constants were taken from those of bis(acetylacetonato)copper(II)[14] and acetate ion.[15] The force constants of K(Cu–Cu′), H[CuCu′O(2)], F[Cu $\cdots$ O(2)], and Y(Cu–Cu′) were set to tentative values, because they were not available from related molecules. These initial force constants were adjusted so that the mean amplitudes calculated using them agreed with the observed mean amplitudes. The final force constants are listed in Table 1. The calculated mean amplitudes and shrinkage corrections are listed in Table 2, and they were used in the least-squares analysis. The potential barrier for the internal rotation of the methyl group was assumed to be 0.48 kcal mol^{-1}, which was estimated for acetic acid in the microwave spectroscopic study.[16] Since the potential barrier was very small, the low barrier approximation[17] was applied in the present study; the molecular intensities were calculated at 5° intervals of the torsional angle of the methyl group and summed with the weights of the Boltzmann distribution.

Table 1. Urey–Bradley force field[a] for copper(I) acetate

K(Cu–Cu′)	0.4	H[O(1)C(1)O(2)]	0.10
K[Cu–O(1)]	1.5	H[O(1)C(1)C(2)]	0.31
K[C(1)–O(1)]	6.2	H[C(1)C(2)H(1)]	0.34
K[C(1)–C(2)]	3.3	H[H(1)C(2)H(2)]	0.45
K[C(2)–H(1)]	4.56	F[Cu $\cdots$ O(2)]	0.01
π(C)	0.62	F[Cu $\cdots$ C(1)]	0.10
Y(Cu–Cu′)	0.08	F[O(1) $\cdots$ O(2)]	0.50
Y[Cu–O(1)]	0.08	F[O(1) $\cdots$ C(2)]	0.50
Y[C(1)–O(1)]	0.14	F[C(1) $\cdots$ H(1)]	0.40
H[CuCu′O(2)]	0.05	F[H(1) $\cdots$ H(2)]	0.03
H[CuO(1)C(1)]	0.10		

[a] Units of the torsional force constant, Y, and the out-of-plane bending force constant, π, are 10^{-18} N m, while others are 10^2 N m^{-1}. The linear constant, F', was assumed to be $-0.1F$.

The r_g parameters were calculated from the r_α parameters obtained in the least-squares calculations,[13] and they are listed in Table 3 together with their limits of error. The observed mean amplitudes are listed in Table 4. The random errors were 2.6 times the errors estimated in the least-squares calculations. The systematic errors were estimated from the errors in both the measurements of camera distance (0.03%) and wavelength (0.06%). The correlation matrix is listed in Table 5. The best-fit molecular intensities and the theoretical radial distribution function are shown in Figures 1 and 2, respectively. The least-squares calculations were carried out on a HITAC M-280H computer in the Computer Center of the University of Tokyo.

Results and Discussion

Since the polymeric chain of copper(I) acetate lies on a mirror plane in the solid phase,[1–3] the monovalent copper atoms and

Table 2. Root-mean-square amplitudes (l) and shrinkage corrections[a] for copper(I) acetate

Atomic pair	$10^4\ l$/Å	$10^4(r_a - r_\alpha)$/Å
Cu–Cu′	1 142	−40
Cu–O(1)	697	58
Cu ··· O(2)	1 294	−18
Cu ··· C(1)	930	12
Cu ··· C(2)	936	80
Cu ··· H(1)	1 405	94
Cu ··· H(2)	1 639	90
Cu ··· H(1′)	1 656	78
Cu ··· H(2′)	1 512	97
O(1) ··· O(2)	647	82
O(1) ··· C(1)	441	71
O(1) ··· C(2)	720	169
O(1) ··· O(1′)	1 330	−14
O(1) ··· O(2′)	967	58
O(1) ··· C(1′)	1 075	9
O(1) ··· C(2′)	1 103	36
O(1) ··· H(1)	1 049	193
O(1) ··· H(2)	1 413	198
O(1) ··· H(1′)	1 765	31
O(1) ··· H(2′)	1 784	36
O(2) ··· H(1)	1 521	172
O(2) ··· H(2)	1 181	205
O(2) ··· H(1′)	1 615	41
O(2) ··· O(2′)	1 861	31
C(1)–C(2)	512	152
C(1) ··· C(1′)	992	−5
C(1) ··· C(2′)	1 039	13
C(1) ··· H(1)	1 074	176
C(1) ··· H(1′)	1 663	11
C(2) ··· C(2′)	1 084	2
C(1)–H(1)	784	94
C(2) ··· H(1′)	1 713	−4
H(1) ··· H(2)	1 253	101
H(1) ··· H(1′)	2 036	−2
H(1) ··· H(2′)	2 426	−25

[a] The parameter r_a represents the centre of gravity of the radial distribution function (K. Kuchitsu, *Bull. Chem. Soc. Jpn.*, 1967, **40**, 505). The parameter $r_\alpha = r_e + \langle \Delta Z \rangle$, where r_e is an equilibrium internuclear distance and $\langle \Delta Z \rangle$ the linear average displacement (see ref. 13).

Table 3. Molecular parameters[a] obtained from least-squares analysis for copper(I) acetate

	r_α	r_g	Error
Cu–Cu′	2.490	2.491	0.003
Cu–O(1)	1.860	1.868	0.002
C(1)–O(1)	1.261	1.270	0.002
C(1)–C(2)	1.489	1.506	0.003
C(2)–H(1)	1.129	1.145	0.010
Angle O(1)CuO(2′)	172.5		0.1
Angle C(1)C(2)H(1)	105.2		1.9
Angle O(1)C(1)O(2)[b]	125.9		0.2

[a] Bond distances in Å, bond angles in degrees. The parameter r_g represents the thermal average internuclear distance and is equal to $r_\alpha + K + \delta r + \cdots$, where K is the perpendicular amplitude of internuclear distance and δr is the centrifugal distortion due to molecular rotation (see ref. 13). In the present study δr was assumed to be zero. [b] Dependent parameter.

Table 4. Root-mean-square amplitudes for copper(I) acetate

	l_{obs}[a]/Å	l_{calc}[b]/Å
Cu–Cu′	0.112(3)	0.114
Cu–O(1)	0.068(2)	0.070
Cu ··· O(2)	0.138(3)	0.129
Cu ··· C(1)	0.085(4)	0.093
Cu ··· C(2)	0.092(3)	0.094
C(1)–O(1)	0.046(3)	0.044
C(1)–C(2)	0.047(5)	0.051
O(1) ··· O(2)	0.069(7)	0.065
C(2)–H(1)	0.085(15)	0.078

[a] Results obtained by the least-squares analysis. [b] Values calculated from the force constants in Table 1.

the ligands are strictly in the same plane. In the present study on gaseous copper(I) acetate the angle between the Cu_2O_4 and the acetate planes was varied as a parameter in the least-squares calculations in order to elucidate the planarity of the molecule, but it converged to 2.8 ± 5.7°, though other molecular parameters remained unchanged in complete agreement with those listed in Table 3 and 4. Thus the above assumption of the planarity of the molecule is quite reasonable.

The molecular parameters of gaseous copper(I) acetate and related molecules are listed in Table 6. The Cu–Cu′ and Cu–O bond distances of the compound with a d^{10} electronic configuration are evidently shorter than the corresponding ones of the compound having a d^9 electronic configuration.

The configuration around the copper atom of polymeric copper(I) acetate in the solid phase is distorted square planar with two short Cu–O bonds, one long bridging Cu–O bond, and a metal–metal bond.[1–3] When this polymer is heated, the interchelate bonds are broken and the polymer decomposes to dimers, the structure of which is similar to that of $[\{\mathrm{Cu^I(PhN{=}NNPh)}\}_2]$.[18] The Cu–Cu′ distance, 2.491 ± 0.003 Å, and the Cu–O distance, 1.868 ± 0.002 Å, of the gaseous dimer are shorter than the corresponding ones of the crystalline polymer, 2.556 and 1.915 Å respectively.[3] These may be attributed to the fact that the metal in the dimer has less ligand atoms. The force constant for the metal–metal bond in gaseous copper(I) acetate was estimated to be 0.4×10^2 N m^{-1}, corresponding to a wavenumber of 166 cm^{-1}. The observed root mean-square amplitude of 0.112 Å is significantly larger than those of normal single bonds.[13] The small force constant and the large mean amplitude indicate that the metal–metal bonding in the complex is weak. Although the Cu–Cu′ distance of dimeric copper(I) acetate is shorter than that in metallic copper (2.556 Å), it is a little larger than twice the radius of copper atom (1.21 Å) which is obtained by subtraction of the covalent single-bond radius of oxygen (0.66 Å)[19] from the Cu–O distance of dimeric copper(I) acetate. The Cu–Cu bond of dimeric copper(I) acetate cannot be effectively stabilized because the twenty d electrons of the copper atoms fill up all the bonding and antibonding molecular orbitals relating to d atomic orbitals, while the metal–metal bonds in $Cr_2(O_2CR)_4$[20] and $Mo_2(O_2CR)_4$[21] behave as quadruple bonds.[22]

The OCuO′ angle appears to correlate with the Cu–Cu′ distance. The drastic change of the Cu–Cu′ distance does not directly give a change of the OCuO′ angle, but the latter appears to be reduced by the simultaneous change of the Cu–O distance. The structure of the bridging acetate group is essentially the same in the gas and the solid phases, as well as in the monovalent- and divalent-copper compounds. The C–C distance of the complex is the same as that of acetic acid,[23] but the C–O distance in the complex is a mean of the values in acetic acid because of conjugation.

Table 5. Correlation matrix for $Cu_2(O_2CCH_3)_2$[a]

	r(CuCu′)	*r*(CuO)	*r*(CO)	*r*(CC)	*r*(CH)	Angle OCuO′	Angle CCH	*l*(CuCu′)	*l*[CuO(2)]
r(CuCu′)	1.00								
r(CuO)	−0.01	1.00							
r(CO)	0.40	−0.29	1.00						
r(CC)	−0.25	0.14	−0.25	1.00					
r(CH)	−0.01	−0.21	0.01	0.21	1.00				
Angle OCuO′	−0.55	0.00	0.37	0.22	0.03	1.00			
Angle CCH	0.00	0.58	−0.25	−0.02	−0.35	−0.10	1.00		
l(CuCu′)	−0.01	0.03	0.09	0.31	−0.02	0.16	0.03	1.00	
l[CuO(2)]	−0.13	−0.07	−0.06	0.00	−0.07	−0.01	−0.16	0.29	1.00
l[CuO(1)]	−0.01	0.21	−0.10	−0.03	−0.23	−0.02	0.32	0.19	0.15
l[CuC(1)]	−0.01	0.06	−0.05	0.15	−0.05	0.00	0.03	0.72	0.63
l[CuC(2)]	0.03	−0.20	0.01	−0.07	0.02	−0.10	−0.23	0.04	0.18
l(CO)	−0.16	0.13	−0.42	0.29	0.30	−0.13	0.14	0.14	0.10
l(CC)	−0.02	0.17	−0.04	−0.07	−0.23	0.00	0.06	−0.06	−0.05
l(OO)	−0.09	0.03	−0.11	−0.08	−0.05	0.05	0.30	0.46	−0.01
l(CH)	−0.32	0.26	−0.72	0.34	0.05	−0.20	0.24	0.05	0.08
R(L)	−0.07	0.35	−0.33	0.11	−0.18	−0.11	0.48	0.25	0.19
R(S)	0.02	0.22	−0.18	−0.01	−0.20	−0.14	0.32	0.22	0.15

	l[CuO(1)]	*l*[CuC(1)]	*l*[CuC(2)]	*l*(CO)	*l*(CC)	*l*(OO)	*l*(CH)	*R*(L)	*R*(S)
l[CuO(1)]	1.00								
l[CuC(1)]	0.21	1.00							
l[CuC(2)]	0.13	0.11	1.00						
l(CO)	0.45	0.17	0.11	1.00					
l(CC)	−0.09	−0.07	−0.05	−0.19	1.00				
l(OO)	0.04	0.23	−0.06	0.09	−0.01	1.00			
l(CH)	0.28	0.11	0.02	0.62	−0.08	0.09	1.00		
R(L)	0.73	0.31	0.10	0.52	−0.13	0.14	0.46	1.00	
R(S)	0.76	0.24	0.16	0.52	−0.02	0.11	0.32	0.63	1.00

[a] *R*(L) and *R*(S) are the indices of resolution for the long- and short-camera-distance data respectively.

Table 6. Comparison of molecular parameters

	$Cu_2(O_2CCH_3)_2$[a]	$Cu_2(O_2CCH_3)_2$[b]	$Cu_2(O_2CCH_3)_4 \cdot 2H_2O$[b]	CH_3COOH[c]
	(gas)	(solid)	(solid)	(gas)
r(Cu–Cu)/Å	2.491(3)	2.556(6)	2.616(3)	
r(Cu–O)/Å	1.868(2)	1.915(28)	1.969(37)	
r(C–O)/Å	1.270(2)	1.25(3)	1.260(18)	1.213(9), 1.363(9)
r(C–C)/Å	1.506(3)	1.53(3)	1.501(18)	1.519(15)
Angle OCuO′/°	172.5(1)	169.6(8)	168.8(6)	
Angle OCO/°	125.9(2)	124.0(27)	124.8(18)	123.0(18)
Ref.	This work	3	4	23

[a] Distances are r_g parameters and angles are r_α parameters. [b] Digits in parentheses represent three times standard deviations in the references. [c] r_a parameter values in ref. 23 are reduced by 0.2% and they are transformed to r_g parameters by the expression $r_g = r_a + l^2/r_a$.

To obtain information about the potential barrier of the methyl group we assumed a six-fold potential barrier to gaseous copper(I) acetate and varied the height of the barrier in the range 0.0—2.0 kcal mol^{-1}. However, the agreement between the experimental and theoretical molecular intensities was not improved in any cases, the molecular parameters obtained from least-squares calculations remaining unchanged, probably because of the small contribution of the hydrogen atoms of this molecule to the electron diffraction intensities.

The present experimental electron diffraction data were completely explainable on the basis of the dimer model only, and did not reveal the trimer and the tetramer of gaseous copper(I) acetate, which have been detected in low abundance from mass spectroscopic studies.[5,6]

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