X-Ray Crystal Structures of Some Adducts of Dimeric Copper(II) Acetate.† Nature of the Copper–Copper Interaction

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The crystal structures of the adducts of $Cu_2(OCOCH_3)_4$ with methanol (1), acetic acid (2), dimethylformamide (3), and 1,4-diazabicyclo[2.2.2]octane (4) have been determined using single-crystal *X*-ray diffraction methods. The compounds are isostructural with that of $Cu_2(OCOCH_3)_4{\cdot}2H_2O$ with the water molecules in the axial positions being replaced by the respective ligands. The ligand 1,4-diazabicyclo[2.2.2]octane bridges two dimer units producing a chain structure, in which this ligand is disordered around the N–N axis. Crystal data: (1), monoclinic, space group $P2_1/n$, a = 8.129(2), b = 7.447(1), c = 13.332(1) Å, β = 92.21(1)°, and Z = 2; (2), space group, $P2_1/n$, a = 15.153(2), b = 7.772(1), c = 8.229(1) Å, β = 103.08(1)°, and Z = 2; (3), triclinic, space group $P\bar{1}$, a = 8.002(1), b = 8.140(1), c = 9.394(2) Å, α = 105.85(2), β = 92.31(2), γ = 113.84(1)°, and Z = 1; (4), monoclinic, space group $A2/m$, a = 7.709(7), b = 15.490(8), c = 8.172(3) Å, β = 105.51(5)°, and Z = 2. The structures have been solved by the heavy-atom method and refined to R values of 0.041 (1), 0.029 (2), 0.032 (3), and 0.065 (4) using, respectively, 1 787, 1 892, 1 600, and 594 diffractometer-measured intensities. The *X*-ray crystallographic results together with literature data have been utilised to examine a general relationship between the donor ability of the axial ligands and the length of the Cu–Cu bond and draw some conclusions regarding the nature of this bond.

Over the past 25 years extensive work on dimeric copper(II) carboxylates employing spectroscopic, magnetic, and *X*-ray crystallographic techniques has been reported.[1-4] Copper(II) acetate monohydrate, $Cu_2(OCOCH_3)_4{\cdot}2H_2O$, is typical of this class of compounds. *X*-Ray and neutron diffraction analysis [5,6] have revealed that the compound has a dimeric structure in which the copper ions bridged by the acetate groups are separated by a distance [7] of 2.616 Å, the axial positions being occupied by the water molecules. This rather short copper–copper distance has provoked considerable controversy concerning the nature of the bonding, weak σ and δ bonds having been proposed.[8-10]

In this paper we report the *X*-ray crystallographic analyses of four adducts of dimeric copper(II) acetate, $Cu_2(OCOCH_3)_4{\cdot}2L$. The ligands (L) chosen are methanol (1), acetic acid (2), *N*,*N*-dimethylformamide (dmf) (3), and 1,4-diazabicyclo[2.2.2]octane (dabco) (4). Since the structures of several other copper(II) acetate adducts had been determined,[11-17] a study of the effect of varying the base strength of the axial ligands upon the copper–copper bond was undertaken. The same bridging ligand is retained in order to avoid changes introduced by the varying inductive effects of this group. The variation of the Cu–Cu bond distance with changes in the strength of the axial ligands, as reflected in the Cu–L distance should be a sensitive measure of the metal–metal interaction and provide a description of the copper–copper bond. Such a relation may best hold for ligands of similar types and for the same donor atoms. It is relevant that the mutual interactions of the metal–metal and metal–ligand bonds are an important aspect of the chemistry of metal cluster systems.[18] Very recently attempts have been made to examine the relationships between the donor ability of the axial ligands and the length of the metal–metal bond for dirhodium [19-22] and dichromium carboxylates [23] as well as for some binuclear platinum complexes.[24] No such effort has, however, been made for dimeric copper(II) carboxylates. Preliminary communications on this work have been published.[25,26]

Experimental

Preparation.—Adduct (1) was prepared by initially dehydrating powdered $Cu_2(OCOCH_3)_4{\cdot}2H_2O$ (BDH AnalaR sample) to a stoicheiometric weight loss and then dissolving it in dry methanol containing a few cm³ of 2,2-dimethoxypropane. The concentrate was sealed in a conical flask and cooled to −10 °C. Blue-green crystals of the adduct formed after 2 d. The acetic acid adduct (2) was prepared similarly, the solvent being acetic acid–acetic anhydride (3 : 1). The crystals of both the compounds are unstable in air and on removal from the solvent they revert to the polycrystalline acetate hydrate.

The preparation of the dmf adduct (3) was reported earlier.[27] There was no mention, however, about any precautions taken in handling the compound. We found the adduct to be highly unstable in air and hence the crystallisation was carried out in sealed capillary tubes. These were filled with the hot concentrate, sealed, and cooled gradually in vertical alignment. A lone crystal formed at the bottom of the solution in each tube. The adduct (4) was prepared according to the reported procedure.[27] Crystals were obtained by evaporation from methanol.

Data Collection, Structure Solution, and Refinement.—Compounds (1)—(3) are extremely sensitive to atmospheric moisture and were therefore enclosed in thin-walled Lindemann glass capillaries in an inert-atmosphere glove-box. Preliminary crystal data were obtained from rotation and Weissenberg photographs and refined on the diffractometer, except for the dmf adduct (3). On prolonged exposure to *X*-rays, dissolution of adduct (3) in the surrounding mother-liquor was noted. The crystal data for this compound were obtained on the diffractometer.

Intensity data were collected on a Enraf-Nonius CAD-4 diffractometer using graphite-crystal monochromated Mo-K_α radiation (λ = 0.7017 Å) by the ω—2θ scan technique. The

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† *Supplementary data available* (No. SUP 23665, 47 pp.): thermal parameters, H-atom co-ordinates, least-squares planes, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Crystal and refinement data for adducts of copper(II) acetate

Compound	(1)	(2)	(3)	(4)
Formula	$Cu_2(OCOCH_3)_4\cdot 2CH_3OH$	$Cu_2(OCOCH_3)_4\cdot 2CH_3CO_2H$	$Cu_2(OCOCH_3)_4\cdot 2OCHN(CH_3)_2$	$Cu_2(OCOCH_3)_4\cdot C_6H_{12}N_2$
M	427.4	483.4	509.4	475.4
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$A2/m$
a/Å	8.129(2)	15.153(2)	8.002(1)	7.709(7)
b/Å	7.447(1)	7.772(1)	8.140(1)	15.490(8)
c/Å	13.332(1)	8.229(1)	9.394(2)	8.172(3)
α/°	90	90	105.85(2)	90
β/°	92.21(1)	103.08(1)	92.31(2)	105.51(5)
γ/°	90	90	113.84(1)	90
Z	2	2	1	2
D_c/g cm^{-3}	1.76	1.70	1.60	1.62
μ(Mo-K_α)/cm^{-1}	27.8	24.0	21.4	23.9
Crystal size/mm	0.2 × 0.2 × 0.3	0.2 × 0.2 × 0.35	0.2 × 0.3 × 0.4	0.2 × 0.25 × 0.3
No. of reflections ($I > 3\sigma_I$)	1 787	1 892	1 600	594
No. of variables	100	118	127	79
R	0.041	0.029	0.032	0.065
Weighting scheme (*w*)	$(14.0 + \lvert F\rvert + 0.02\lvert F\rvert^2)^{-1}$	$(14.0 + \lvert F\rvert + 0.04\lvert F\rvert^2)^{-1}$	$(5.0 + \lvert F\rvert + 0.01\lvert F\rvert^2)^{-1}$	$(\sigma_F^2 + 0.002\lvert F\rvert^2)^{-1}$
Largest peaks in final difference maps/e Å^{-3}	±0.5	±0.4	±0.4	±1.2

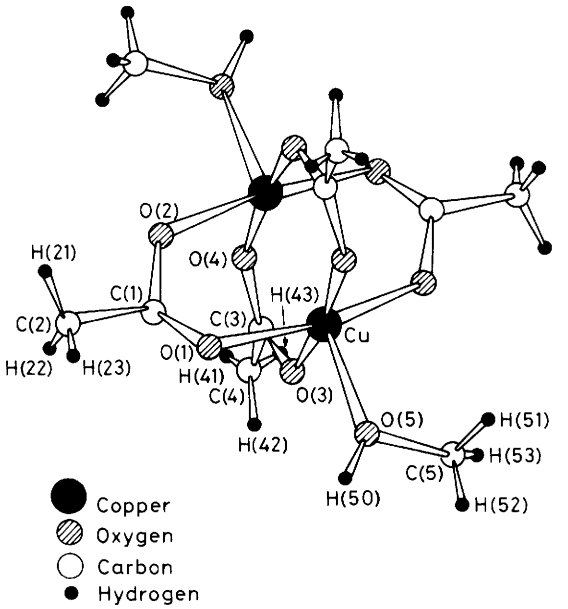

Figure 1. Copper(II) acetate–methanol adduct (1) viewed down *a*

total numbers of reflections collected in the range $1 < 2\theta < 60°$ for compounds (1)—(4) were 2 350, 3 110, 2 040, and 1 012 respectively. The data were corrected for Lorentz and polarisation effects but not for absorption.

The structures were solved by the heavy-atom technique and refined by full-matrix least-squares treatment with anisotropic thermal parameters for non-hydrogen atoms. The hydrogen atoms were located from difference-Fourier syntheses at the end of the refinement with unit weights. These were included in subsequent calculations with a thermal parameter of 5.0 Å^2 but not refined. For adduct (4), the methyl hydrogens could not be precisely located although some electron density in the expected region was observed. In the final stages of refinement, weights were applied according to the scheme [28] $w = (a + b|F| + c|F|^2)^{-1}$ with constants *a* and *c* adjusted to give a fairly uniform agreement over the entire *F* range and $b = 1$. For adduct (4) the weighting scheme was $w = [\sigma(F)^2 + 0.002|F|^2]^{-1}$. Scattering factors were from ref. 29 for hydrogen and from ref. 30 for all other atoms.

In the structure analysis of compound (4) the choice of centrosymmetric space group *A*2/*m* in preference to *A*2 or *Am* was dictated by good refinement convergence with no abnormal features in the structure. It is to be noted that all dimeric copper(II) acetate adducts which have been investigated so far crystallise in centrosymmetric space groups. A consequence of this choice is that dabco with its inherent three-fold symmetry has to occupy a centre of inversion, which would imply disorder. Evidence for disorder is derived from the streaking of spots observed for low-angle reflections in Weissenberg photographs. Refinement of the occupancy parameters for carbon atoms C(3), C(4), and C(5) (Figure 4) did not reveal any significant departure from the value of 0.5.

Computations were carried out on our Institute's IBM 360/44 and DEC 1090 computers with the SHELX system of programs [31] for compound (4) and refinement programs due to Gantzel *et al.*[32] for the other compounds. Crystal and refinement data for the compounds are summarised in Table 1, final atomic co-ordinates for non-hydrogen atoms in Table 2.

Results and Discussion

Crystal Structures.—Figures 1—3 show perspective views of the adducts (1)—(3) while Figure 4 displays a packing diagram of adduct (4). Bond lengths and angles are given in Table 3. In all the four compounds the copper atoms are bridged in pairs by four acetate groups to form binuclear molecules similar to that found in $Cu_2(OCOCH_3)_4\cdot 2H_2O$. The distorted octahedral co-ordination around copper is completed by the donor atom of the axial ligand and the copper–copper contact.

A notable feature of the structure of adduct (1) is the intermolecular hydrogen bond (O···O 2.80 Å) between the methanol oxygen O(5) and the acetate oxygen O(3). The larger Cu–O(3) distance is possibly a consequence of this hydrogen bond. The orientation of the methyl group of the axial ligand is such that O(5)–C(5) is nearly parallel to Cu–

Table 2. Atomic co-ordinates ($\times 10^5$ for copper, $\times 10^4$ for the rest) with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Methanol adduct (1)			
Cu	5 989(4)	15 137(4)	3 300(2)
O(1)	1 235(3)	1 918(3)	−1 053(2)
O(2)	227(3)	−698(3)	−1 617(2)
O(3)	−1 604(3)	2 511(3)	−28(2)
O(4)	−2 619(3)	−108(3)	−588(2)
O(5)	1 593(4)	4 044(3)	863(2)
C(1)	941(4)	777(5)	−1 736(2)
C(2)	1 471(6)	1 214(6)	−2 778(3)
C(3)	−2 760(4)	1 529(4)	−381(2)
C(4)	−4 416(4)	2 381(5)	−583(3)
C(5)	1 547(6)	4 539(5)	1 887(3)
Acetic acid adduct (2)			
Cu	−6 894(2)	8 112(4)	2 993(4)
O(1)	1 459(1)	1 058(3)	834(3)
O(2)	281(1)	2 468(3)	1 353(2)
O(3)	744(1)	−1 925(3)	1 852(2)
O(4)	−449(1)	−521(3)	2 363(2)
O(5)	−1 705(1)	2 536(3)	951(3)
O(6)	−872(2)	4 871(3)	1 733(4)
C(1)	1 125(2)	2 298(3)	1 445(3)
C(2)	1 744(2)	3 639(5)	2 386(5)
C(3)	198(2)	−1 573(3)	2 736(3)
C(4)	325(3)	−2 462(4)	4 397(3)
C(5)	−1 636(2)	4 023(4)	1 400(4)
C(6)	−2 429(4)	5 072(6)	1 592(9)
dmf adduct (3)			
Cu	7 557(5)	13 711(5)	12 732(4)
O(1)	1 226(4)	−2 060(4)	−749(3)
O(2)	2 497(4)	265(4)	1 412(3)
O(3)	962(4)	474(4)	−2 117(3)
O(4)	2 243(4)	2 816(4)	37(3)
O(5)	1 911(4)	3 746(4)	3 323(3)
N	2 342(5)	6 717(4)	4 561(4)
C(1)	2 388(4)	−1 184(5)	443(4)
C(2)	3 740(6)	−1 962(6)	732(5)
C(3)	2 046(5)	2 135(5)	−1 354(4)
C(4)	3 186(6)	3 432(6)	−2 180(5)
C(5)	1 642(5)	5 143(5)	3 418(4)
C(6)	3 506(9)	6 913(7)	5 856(5)
C(7)	1 879(8)	8 290(7)	4 585(5)
dabco adduct (4)			
Cu	−13 319(16)	0	−13 981(15)
O(1)	69(8)	−902(4)	−2 191(7)
O(2)	2 281(7)	−910(4)	187(7)
N	−3 625(11)	0	−3 667(10)
C(1)	1 507(10)	−1 183(4)	−1 267(9)
C(2)	2 314(12)	−1 977(6)	−1 916(12)
C(3)	−3 219(23)	440(14)	−5 155(20)
C(4)	−4 204(28)	874(10)	−4 264(26)
C(5)	−5 188(23)	466(15)	−3 331(22)

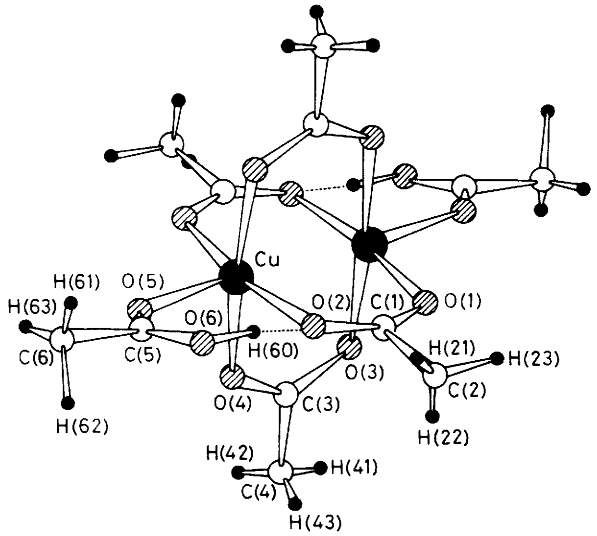

Figure 2. Copper(II) acetate–acetic acid adduct (2) viewed down *b*; key as in Figure 1

O(2′) [torsion angle O(2′)–Cu–O(5)–C(5) 2.6°]. The methyl carbon C(5) of the axial ligand makes a short intramolecular contact of 3.22 Å with oxygen O(2′) of the acetate group. The larger values of O(5)–Cu–O(2′) and Cu–O(2′)–C(1′) could possibly be attributed to the inward movement of O(2′) as a result of this short contact. The other bond lengths and angles are as expected.

The acetic acid ligand in compound (2) occupies the axial position and is bonded to copper through the carbonyl oxygen. The hydroxyl oxygen O(6) is involved in strong intramolecular hydrogen bonding (O · · · O 2.62 Å) with the acetate oxygen O(2). The elongation of Cu–O(2) and C(1)–O(2) and the orientation of the axial ligand are possibly consequences of this hydrogen bond. An identical situation exists in the structure[23] of $Cr_2(OCOCH_3)_4{\cdot}2CH_3CO_2H$ with which compound (2) is isomorphous. The axial ligand is tilted towards O(2) as is evident from the angles O(5)–Cu–O(1′) 101.2° and O(5)–Cu–O(2) 89.3°. Consequently atom O(2) experiences a slight inward movement which is reflected in the opening up of the angle Cu–O(2)–C(1).

The co-ordination of dmf in compound (3) is through the amide oxygen which is sterically favoured over nitrogen. The dmf molecule is planar, the maximum deviation of N from the plane of C(5),C(6),C(7) being 0.022 Å. Its dimensions agree with those reported in the literature.[33] The acetate framework does not suffer from any noticeable distortion of the type observed in the structures described earlier.

In the structure of compound (4), copper and nitrogen atoms are situated on mirror planes. In addition the asymmetric unit consists of one of the acetate groups and three disordered carbons of the ligand dabco, which exists in two orientations occurring with 50% occupancy. The ligand dabco bridges through its two nitrogens the copper atoms of adjacent dimers. This results in a novel chain structure, similar to that of the pyrazine adduct,[11] the chains running along [101]. The estimated standard deviations (e.s.d.s) in the atomic co-ordinates are in general higher than those in the other structures presumably due to disorder and the smaller number of reflections obtained. The dimensions of dabco agree well with those reported in the literature,[34,35] where its disorder was also reported. The orientation of the axial ligand is described by the torsional angles O(1)–Cu–N–C(3) −79.9(9), O(1)–Cu–N–C(4) −134.6(9), and O(1)–Cu–N–C(5) 165.8(9)°.

In the crystal (Figure 4), chains of binuclear copper acetate units are packed along [010] in such a manner that the bulky acetate groups are in close proximity to each other. Owing to its smaller size and symmetric nature, the ligand dabco finds

Table 3. Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

Methanol adduct (1)

Cu-O(1)	1.958(2)	C(1)-O(1)	1.261(4)
Cu-O(2′)	1.963(2)	C(1)-O(2)	1.255(4)
Cu-O(3)	1.980(2)	C(1)-C(2)	1.506(5)
Cu-O(4′)	1.967(2)	C(3)-O(3)	1.266(4)
Cu-O(5)	2.160(3)	C(3)-O(4)	1.256(4)
Cu-Cu′	2.596(1)	C(3)-C(4)	1.503(5)
		C(5)-O(5)	1.416(5)
O(1)-Cu-O(3)	89.1(1)	Cu-O(1′)-C(1′)	123.8(2)
O(3)-Cu-O(2′)	89.4(1)	Cu-O(3)-C(3)	121.6(2)
O(2′)-Cu-O(4′)	89.6(1)	Cu-O(4′)-C(3′)	124.1(2)
O(4′)-Cu-O(1)	89.9(1)	Cu-O(5)-C(5)	121.4(2)
O(5)-Cu-O(1)	93.8(1)	O(1)-C(1)-O(2)	125.1(3)
O(5)-Cu-O(2′)	96.8(1)	O(1)-C(1)-C(2)	117.8(3)
O(5)-Cu-O(3)	94.3(1)	O(2)-C(1)-C(2)	117.1(3)
O(5)-Cu-O(4′)	96.2(1)	O(3)-C(3)-O(4)	124.7(3)
Cu-O(1)-C(1)	121.8(2)	O(3)-C(3)-C(4)	118.0(3)
		O(4)-C(3)-C(4)	117.3(3)

Acetic acid adduct (2)

Cu-O(1′)	1.962(2)	C(1)-C(2)	1.495(4)
Cu-O(2)	1.998(2)	C(3)-O(3)	1.250(3)
Cu-O(3′)	1.955(2)	C(3)-O(4)	1.261(4)
Cu-O(4)	1.952(2)	C(3)-C(4)	1.504(4)
Cu-O(5)	2.197(2)	C(5)-O(5)	1.210(4)
Cu-Cu′	2.581(1)	C(5)-O(6)	1.306(4)
C(1)-O(1)	1.247(3)	C(5)-C(6)	1.490(6)
C(1)-O(2)	1.271(3)		
O(1′)-Cu-O(3′)	89.92(9)	Cu-O(4)-C(3)	122.6(2)
O(3′)-Cu-O(2)	89.08(8)	Cu-O(5)-C(5)	129.8(2)
O(2)-Cu-O(4)	89.43(8)	O(1)-C(1)-O(2)	123.5(2)
O(4)-Cu-O(1′)	89.70(9)	O(1)-C(1)-C(2)	118.9(2)
O(5)-Cu-O(1′)	101.18(8)	O(2)-C(1)-C(2)	117.6(2)
O(5)-Cu-O(2)	89.31(8)	O(3)-C(3)-O(4)	125.5(3)
O(5)-Cu-O(3′)	93.57(8)	O(3)-C(3)-C(4)	117.7(3)
O(5)-Cu-O(4)	96.57(8)	O(4)-C(3)-C(4)	116.8(3)
Cu-O(1′)-C(1′)	120.8(2)	O(5)-C(5)-C(6)	122.6(3)
Cu-O(2)-C(1)	126.2(2)	O(5)-C(5)-C(6)	123.9(3)
Cu-O(3′)-C(3′)	122.2(2)	O(6)-C(5)-C(6)	113.5(3)

dmf adduct (3)

Cu-O(1′)	1.970(3)	C(1)-C(2)	1.506(6)
Cu-O(2)	1.957(3)	C(3)-O(3)	1.251(5)
Cu-O(3′)	1.961(3)	C(3)-O(4)	1.248(5)
Cu-O(4)	1.969(3)	C(3)-C(4)	1.508(6)
Cu-O(5)	2.163(3)	C(5)-O(5)	1.222(5)
Cu-Cu′	2.614(1)	C(5)-N	1.315(5)
C(1)-O(1)	1.253(5)	C(6)-N	1.434(7)
C(1)-O(2)	1.246(5)	C(7)-N	1.465(7)
O(1′)-Cu-O(3′)	90.1(1)	Cu-O(5)-C(5)	119.0(3)
O(3′)-Cu-O(2)	88.6(1)	O(1)-C(1)-O(2)	125.0(4)
O(2)-Cu-O(4)	90.7(1)	O(1)-C(1)-C(2)	117.3(4)
O(4)-Cu-O(1′)	88.3(1)	O(2)-C(1)-C(2)	117.6(4)
O(5)-Cu-O(1′)	92.6(1)	O(3)-C(3)-O(4)	125.3(4)
O(5)-Cu-O(2)	99.0(1)	O(3)-C(3)-C(4)	117.6(4)
O(5)-Cu-O(3′)	97.6(1)	O(4)-C(3)-C(4)	117.1(4)
O(5)-Cu-O(4)	93.9(1)	O(5)-C(5)-N	125.3(4)
Cu-O(1′)-C(1′)	123.6(3)	C(5)-N-C(6)	121.1(4)
Cu-O(2)-C(1)	122.9(3)	C(5)-N-C(7)	121.0(4)
Cu-O(3′)-C(3′)	123.8(3)	C(6)-N-C(7)	117.8(4)
Cu-O(4)-C(3)	122.5(3)		

dabco adduct (4)

Cu-O(1)	1.977(6)	C(1)-C(2)	1.54(1)
Cu-O(2′)	1.972(6)	N-C(3)	1.50(2)
Cu-N	2.193(8)	N-C(4)	1.47(2)
Cu-Cu′	2.632(2)	N-C(5)	1.49(2)
C(1)-O(1)	1.241(9)	C(3)-C(5″)	1.49(2)
C(1)-O(2)	1.252(9)	C(4)-C(4″)	1.47(3)
O(1)-Cu-O(1‴)	89.9(2)	Cu-O(1)-C(1)	121.7(5)
O(1)-Cu-O(2″)	88.2(2)	Cu-O(2′)-C(1′)	124.8(5)
O(2″)-Cu-O(2′)	91.2(2)	O(1)-C(1)-O(2)	125.4(7)
N-Cu-O(1)	96.3(2)	O(1)-C(1)-C(2)	116.7(7)
N-Cu-O(2′)	95.8(2)	O(2)-C(1)-C(2)	117.6(7)
Cu-N-C(3)	113.0(8)	N-C(3)-C(5″)	112(1)
Cu-N-C(4)	112.7(8)	N-C(4)-C(4″)	113(2)
Cu-N-C(5)	110.7(8)	N-C(5)-C(3″)	111(1)

Primed atoms are related by a centre of symmetry, doubly primed by a two-fold rotation, and triply primed by mirror symmetry.

sufficient space in the structure to take up alternative orientations about the N-N axis. Since each nitrogen atom has sp^3 hybridisation, it is not possible for the N-C bonds to align with the four Cu-O bonds. The ligand adopts two of four possible positions for optimum avoidance of adjacent Cu-O bonds. The other alternative where each dabco ligand conforms to the space-group mirror plane is not observed in the actual structure.

Copper-Copper Bonding.—A survey of the structural data of several carboxylate-bridged transition-metal dimers suggests that it is the metal-metal interactions alone which determine the metal-metal internuclear separation.[19] Cotton and Rice [23] examined a series of dichromium carboxylates $Cr_2(O_2CR)_4\cdot 2L$ and found a general qualitative correlation of the quadruply bonded Cr-Cr distance and the Cr-L (axial) distance, all ligands L possessing either oxygen or nitrogen donors. The need to distinguish the oxygen donors from the nitrogen donors was recognised from the fact that chromium can attain a better overlap with nitrogen lone pairs at a longer distance than with oxygen donors. In a similar fashion, Christoph and co-workers [19-21] have investigated the *trans*-influence effects of the axial ligands in $Rh_2(O_2CR)_4\cdot 2L$ compounds which contain a formal Rh-Rh single bond. During the correlation, the need to separate the σ donors from π acceptors was noted.

The results [23] have demonstrated that the variation of the metal-metal distance is to a certain extent affected by the donor strength of the bridging ligand. The structures of thiocyanate adducts [15] of $Cu_2(O_2CR)_4\cdot 2L$ show that for R = H and CH_3 the Cu-Cu distance changes from 2.716 to 2.643 Å respectively. In the present work, therefore, the axial ligands alone are varied, keeping the bridging ligand the same.

The parameters of primary interest in adducts of dimeric copper(II) acetate are the Cu-Cu and the Cu-L(axial) distances. These vary in the present work from 2.581 to 2.632 Å and 2.197 to 2.160 Å respectively. A larger Cu-Cu distance is usually associated with a greater displacement of the copper atoms from the plane of the equatorial co-ordination towards the axial ligand. Except for the thiocyanate adduct, the bridge length (Cu-O-C-O-Cu) is remarkably constant (Table 4). The angular dimensions of the acetate framework, *viz.* Cu-O-C and O-C-O angles, readjust themselves to accommodate the varying Cu-Cu distances. This is in agreement with the observations of Koh and Christoph.[19]

The relevant data on copper(II) acetate adducts are compiled in Table 4 and plotted in Figure 5. The numbers in Figure 5 refer to the compound numbers used in Table 4.

Table 4. Structural parameters for $Cu_2(OCOCH_3)_4 \cdot 2L$

No.	L [a]	Cu–Cu/Å	Cu–L/Å [b]	Bridge length/Å	ΔCu [c]	Ref.
1	Acetic acid	2.581(1)	2.197(2)	6.44	0.18	This work
2	Methanol	2.596(1)	2.160(3)	6.46	0.18	This work
3	dmf	2.614(1)	2.163(3)	6.42	0.20	This work
4	Water	2.616(1)	2.156(4)	6.46	0.19	7
5	Urea	2.625	2.130	—	—	12
6	Pyrazine (100 K)	2.576(1)	2.162(4)	6.44	0.26	11
7	Pyrazine (300 K)	2.583(1)	2.171(6)	6.43	0.28	11
8	Pyridine [d]	2.630(3)	2.126(10)	6.44	0.22	13
9	dabco	2.632(2)	2.193(8)	6.44	0.21	This work
10	Thiocyanate	2.643(3)	2.08	6.54	—	15
11	Pyridine [e]	2.645(3)	2.186(8)	6.41	0.22	14
12	Quinoline	2.652(2)	2.224(6)	6.41	—	16
13	2-Methylpyridine	2.671(4)	2.240(12)	6.45	0.23	17

[a] Ligands 1—5 are oxygen donors and the rest are nitrogen donors. [b] The mean value is tabulated when more than one chemically equivalent distance is present. [c] Deviation of copper from the plane of four co-ordinating atoms. [d] Monoclinic form. [e] Orthorhombic form.

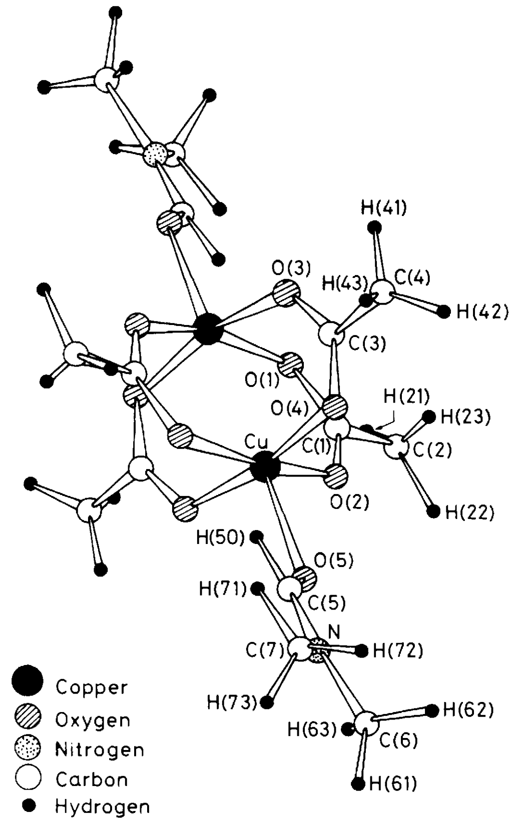

Figure 3. Copper(II) acetate–dmf adduct (3) viewed down *b*

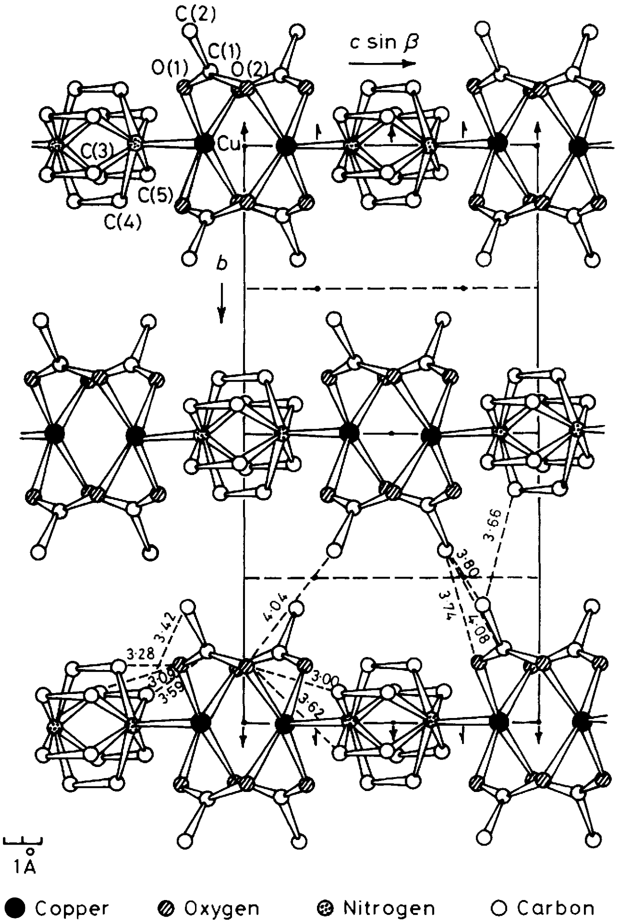

Figure 4. Packing diagram of copper(II) acetate–dabco adduct (4) viewed down *a*. Broken lines indicate short contact distances

Known copper–copper and copper–axial ligand distances span a range of 0.10 and 0.16 Å respectively. These variations are of comparable magnitude to those observed in the dirhodium tetracarboxylates [19] and binuclear platinum complexes.[24] The axial ligands studied here cover a wide range of strong to weak σ-donor ability. Although pyridine can function as a π acceptor in some circumstances, the long Cu–N distances and the lack of preferred orientation of the pyridine rings relative to the plane of the acetate groups [13,14] suggest that pyridine functions here almost entirely as a σ-donor base. A trend that emerges from the data in Figure 5 is that the Cu–Cu bond lengthens as the ligands in the axial positions become stronger; apparently these two parameters are approximately inversely related. A major factor affecting the metal–metal bond length is the extent of axial co-ordination. One would expect, therefore, that this affects the Cu–Cu bond primarily by introducing electron density into the d_{z^2}–d_{z^2} component of the bond, since the Cu–L(axial) bonding uses to some extent the same copper d_{z^2} orbitals. A stronger axial ligand co-ordination thus tends

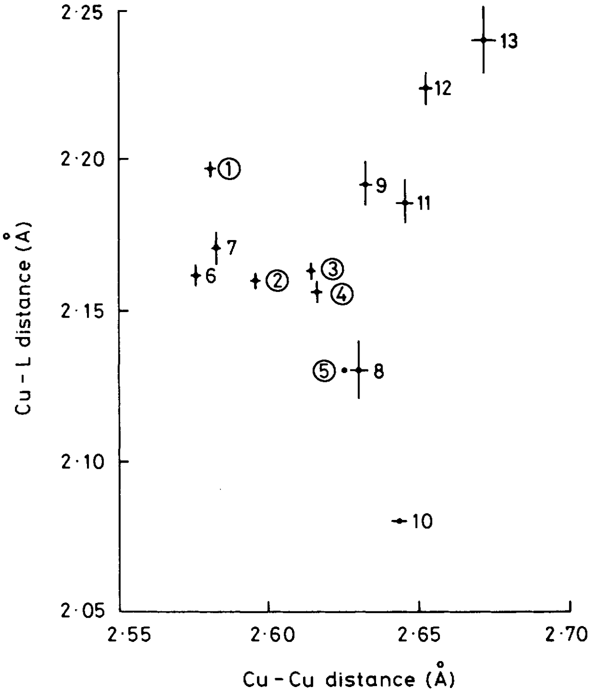

Figure 5. Plot of Cu–Cu *vs.* Cu–L distances in copper(II) acetate adducts. Encircled numbers indicate O-donor ligands and the rest are N-donor ligands

to weaken the Cu–Cu interaction. As seen from Table 4, the more basic are the axial ligands the more they would lengthen the Cu–Cu distance. If these results are interpreted on the basis of previously proposed σ and δ bonding models,[8–10] the former model would be favoured.

Secondary effects due to the increased electron density on the metal would only enhance the respective lengthening (or shortening) of the metal–metal bond. Alternatively, if we assume that the M–M bond possesses π-type characteristics (δ bond), then differing σ-donor strengths of the ligands L will yield the same qualitative conclusions as before. However, in this case the amount of weakening of the M–M interaction is very much less because this interaction is affected only by secondary inductive effects of the axial ligand.

The axial ligands considered here include both oxygen and nitrogen donors. There is much greater consistency in the results depicted in Figure 5 for O-bonded ligands. This is expected on the basis that the inherent co-ordination tendency of oxygen donors towards a metal differs from that of nitrogen donors. The oxygen donors presently considered are all relatively small molecules. A similar relationship is noted for nitrogen-donor ligands such as pyridine (monoclinic form), pyrazine, and thiocyanate. Considerable deviations are observed for adducts with dabco, pyridine (orthorhombic form), quinoline, and 2-methylpyridine (2Me-py), where the Cu–N distances are longer than expected on the basis of the present correlation. These deviations could be interpreted as arising from substantial steric effects associated with these bulky ligands. For example, the *X*-ray structure of the 2Me-py adduct has revealed that the elongation of the Cu–N distance may be due to a short contact (3.05 Å) between the methyl carbon and one of the acetate oxygens. Steric interference by the methyl groups of 2Me-py is manifested in other compounds too.[36] Similarly in compound (4) there are short contacts (four each) between the methylene carbons of dabco and the acetate oxygens, O(2)···C(5) 3.00 Å and O(1)···C(3) 3.09 Å (Figure 4), with a consequent increase in Cu–O(2′)–C(1′) (124.8°) and decrease in Cu–Cu–O(2′) (82.7°).

In terms of the above bonding models, the observed variation of the Cu–Cu bond distances in Table 4 as a function of the axial ligand seem consistent with a σ bond. Other parameters that would appear relevant in the present discussion have been considered for rhodium dicarboxylates.[19]

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