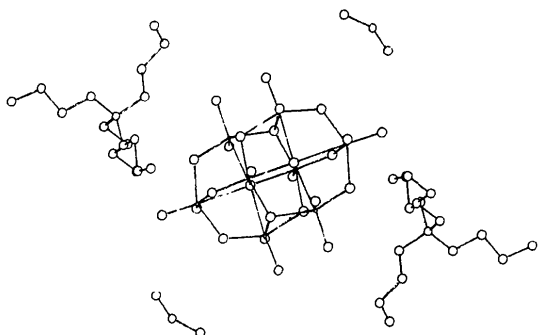


Table 3. Degree of distortion within the MoO₆ octahedron

Compound	Distortion Δl ($\times 10^4$)	Mo(1)	Mo(2)	Mo(3)	Mo(4)
[NH ₂ (CH ₃) ₂] ₂ [NBu ₄] ₂ salt	Δl ($\times 10^4$)	201	163	160	140
[HNEt ₃][NBu ₄] salt	Δl ($\times 10^4$)	218	175	160	145
[NH ₂ (CH ₃) ₂] ₄ salt	Δl ($\times 10^4$)	190	133	169	134


 Fig. 2. The crystal packing of [NH₂(CH₃)₂]₂[NBu₄]₂(Mo₈O₂₆).

atoms of the anions, which indicates the presence of hydrogen bonding to the [Mo₈O₂₆]⁴⁻ anion. Some of these hydrogen bonds may be responsible for the photochromic properties in the solid state. Crystal packing is shown in Fig. 2.

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Structure of Tetrakis(μ -acetato)-bis(4-pyridylmethanol)dicopper(II)

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Abstract. [Cu₂(C₂H₃O₂)₄(C₆H₇NO)₂], $M_r = 581.53$, triclinic, $P\bar{1}$, $a = 7.301$ (4), $b = 8.216$ (4), $c = 10.709$ (5) Å, $\alpha = 91.407$ (1), $\beta = 98.247$ (1), $\gamma = 114.242$ (3)°, $V = 577.27$ Å³, $Z = 1$, $D_m = 1.63$, $D_x = 1.67$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu =$

1.90 mm⁻¹, $F(000) = 298$, $T = 293$ K. Final $R = 0.042$ for 1699 observed reflections. The crystal contains centrosymmetric binuclear molecules with four carboxylate bridges spanning a Cu...Cu separation of 2.647 (1) Å, mean Cu—O 1.982 (2) Å and Cu—N(apical) 2.160 (3) Å. The Cu atoms are displaced by 0.211 (1) Å from the plane containing four oxygen atoms towards the ligand 4-pyridylmethanol.

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Introduction. Over the past 30 years extensive work on dimeric copper(II) carboxylate complexes employing spectroscopic, magnetic and X-ray methods has been reported (Kato, Jonassen & Fanning, 1964; Doedens, 1976; Melnik, 1981). Copper(II) acetate monohydrate, $\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{H}_2\text{O}$, is typical of this class of compounds. X-ray and neutron diffraction analysis (van Niekerk & Schoening, 1953; Brown & Chidambaram, 1983) have revealed that the compound has a dimeric structure in which the Cu^{II} atoms bridged by the four acetate groups are separated by a distance of 2.616 Å, the axial positions being occupied by the water molecules. The same bridging ligand is retained in order to avoid changes introduced by the varying inductive effects of this group. Recently (Melnik, 1982) attempts have been made to examine the relationships between the donor ability of the axial ligands and the lengths of the Cu—Cu bond as well as deviation of Cu^{II} atoms from the basal plane for dicopper carboxylates. In this work we have determined the crystal structures of $[\text{Cu}_2(\text{acet})_4(4\text{-pymet})_2]$ (acet = acetate, 4-pymet = 4-pyridylmethanol) to compare this structure with those found in other copper(II) acetates.

Experimental. The blue crystals of $[\text{Cu}_2(\text{acet})_4(4\text{-pymet})_2]$ were prepared by treating 4-pyridylmethanol (2.18 g, 0.02 mol) with copper(II) acetate (1.82 g, 0.01 mol) in hot methanol solution. The solution was left to stand at room temperature. The fine blue microcrystals that precipitated were filtered off, washed with cold methanol and dried at room temperature. The crude product was recrystallized from methanol. Prismatic crystal with dimensions $0.25 \times 0.72 \times 0.81$ mm; D_m by flotation in $\text{CH}_3\text{Br}/\text{CH}_3\text{OH}$; Syntex $P2_1$ diffractometer, graphite monochromator, $\theta/2\theta$ scan, $2\theta_{\text{max}} = 55^\circ$, time per reflection ca 60 s, two standard reflections, variation 0.5%; 15 reflections with $3.8 \leq 2\theta \leq 19.7^\circ$ were used for refinement of lattice parameters; maximum and minimum transmission factors, 0.557 and 0.346; index range $0 \leq h \leq 9$, $-10 \leq k \leq 9$, $-13 \leq l \leq 13$; 2943 reflections measured, 1699 observed reflections for $F \geq 3\sigma(F)$. Data reduction was performed by program *XP21* (Pavelčík, 1987). Non-H atoms were located by direct methods using program *SHELXS86* (Sheldrick, 1990). Refinement by full-matrix least squares based on F values (154 parameters) using program *SHELX76* (Sheldrick, 1976). Scattering factors and f' , f'' from *International Tables for X-ray Crystallography* (1974, Vol IV). An absorption correction was applied after isotropic refinement by program *DIFABS* (Walker, 1983). After anisotropic refinement all H atoms were located from difference map. These atoms were assigned fixed isotropic thermal parameters. H-atom coordinates were not refined. Maximum positive and negative electron

Table 1. Coordinates and equivalent isotropic displacement parameters (\AA^2) for non-H atoms with e.s.d.'s in parentheses

$$B_{\text{eq}} = (4/3)\sum_i\sum_j\beta_{ij}a_i a_j$$

	x	y	z	B_{eq}
Cu	0.13287 (8)	0.53911 (7)	0.60644 (5)	1.73 (2)
N	0.3673 (5)	0.6161 (5)	0.7722 (3)	2.8 (1)
O(1)	0.0338 (5)	0.7211 (4)	0.6425 (3)	4.0 (1)
O(2)	0.1872 (5)	0.3413 (4)	0.5375 (3)	3.7 (1)
O(3)	-0.0928 (5)	0.3609 (4)	0.6817 (3)	3.8 (1)
O(4)	0.3144 (5)	0.7052 (4)	0.4981 (3)	3.8 (1)
O(5)	1.0173 (6)	0.7600 (6)	1.0782 (4)	5.4 (2)
C(1)	0.3638 (8)	0.7152 (7)	0.8732 (4)	4.1 (2)
C(2)	0.5211 (8)	0.7787 (7)	0.9740 (4)	4.4 (2)
C(3)	0.6890 (8)	0.7396 (6)	0.9782 (4)	3.8 (2)
C(4)	0.6885 (7)	0.6322 (7)	0.8764 (4)	4.1 (2)
C(5)	0.5275 (7)	0.5749 (6)	0.7755 (4)	3.6 (2)
C(6)	0.8603 (9)	0.8114 (8)	1.0885 (5)	5.8 (2)
C(7)	0.2694 (6)	0.7246 (5)	0.3844 (4)	3.0 (1)
C(8)	0.4350 (7)	0.8569 (7)	0.3214 (5)	4.1 (2)
C(9)	-0.0998 (6)	0.7456 (6)	0.5689 (4)	2.9 (1)
C(10)	-0.1602 (8)	0.8906 (6)	0.6091 (5)	4.3 (2)

Table 2. Bond lengths (\AA) and bond angles ($^\circ$) with e.s.d.'s in parentheses

Coordination sphere of Cu^{II}			
Cu—N	2.160 (3)	N—Cu—O(1)	96.1 (1)
Cu—O(1)	1.962 (4)	N—Cu—O(2)	96.2 (2)
Cu—O(2)	1.975 (4)	N—Cu—O(3)	97.8 (2)
Cu—O(3)	1.992 (3)	N—Cu—O(4)	94.3 (1)
Cu—O(4)	1.999 (3)	O(1)—Cu—O(2)	167.7 (2)
Cu—Cu ^I	2.647 (1)	O(1)—Cu—O(3)	89.3 (2)
		O(1)—Cu—O(4)	89.1 (1)
		O(2)—Cu—O(3)	89.2 (1)
Average Cu—O	1.982 (2)	O(2)—Cu—O(4)	89.8 (1)
		O(3)—Cu—O(4)	167.9 (2)
First acetate ligand			
C(7)—O(3)	1.276 (5)	O(3)—C(7)—O(4)	123.8 (4)
C(7)—O(4)	1.246 (5)	O(3)—C(7)—C(8)	118.3 (4)
C(7)—C(8)	1.513 (6)	O(4)—C(7)—C(8)	117.8 (4)
Second acetate ligand			
C(9)—O(1)	1.250 (6)	O(1)—C(9)—O(2)	125.0 (5)
C(9)—O(2)	1.262 (5)	O(1)—C(9)—C(10)	117.8 (4)
C(9)—C(10)	1.503 (8)	O(2)—C(9)—C(10)	-117.3 (4)
4-Pyridylmethanol ligand			
N—C(1)	1.347 (7)	Cu—N—C(1)	121.4 (4)
N—C(5)	1.341 (7)	Cu—N—C(5)	121.0 (3)
C(1)—C(2)	1.372 (6)	C(1)—N—C(5)	117.5 (4)
C(2)—C(3)	1.384 (9)	N—C(5)—C(4)	123.0 (5)
C(3)—C(4)	1.384 (7)	C(5)—C(4)—C(3)	119.6 (5)
C(3)—C(6)	1.498 (7)	C(4)—C(3)—C(2)	116.6 (5)
C(4)—C(5)	1.388 (6)	C(4)—C(3)—C(6)	122.7 (5)
C(6)—O(5)	1.391 (9)	C(2)—C(3)—C(6)	120.7 (5)
		C(3)—C(2)—C(1)	121.4 (5)
		C(2)—C(1)—N	121.8 (5)
Average C—N	1.344 (5)	Average N—C—C	122.4 (4)
C—C	1.405 (3)	C—C—C	120.2 (2)

Symmetry code: (i) $-x, -y+1, -z+1$.

density in final difference map 0.4 and -0.4 e \AA^{-3} ; final $R = 0.042$, $wR = 0.044$, $w = 0.1141/[\sigma^2(F_o) + 0.0010 F_o^2]$; $S = 0.049$, $(\Delta/\sigma)_{\text{max}} = 0.03$ in final refinement cycle. Calculations were performed on a PC-386 computer.

Discussion. Coordinates and displacement parameters of non-H atoms are given in Table 1.* Interatomic bond distances and angles are listed in Table 2. The structure consists of centrosymmetric binuclear units $[\text{Cu}_2(\text{acet})_4(4\text{-pyrmet})_2]$ held together by hydrogen bonds. The molecular structure of the compound is shown in Fig. 1. An intermolecular hydrogen bond $\text{O}(5)\cdots\text{O}(3)$ ($-x+1, -y+1, -z+2$) [2.841 (6) Å] stabilizes the position of the 4-pyridylmethanol.

In each structural unit the two copper centres are bridged by the four carboxylate groups of the acetates. The distorted square-based pyramidal coordination about each Cu atom is completed in the axial positions by a 4-pyridylmethanol N atom. The displacement of the Cu^{II} atom from the basal plane toward the apical ligand is 0.211 (1) Å. Interatomic bond distance $\text{Cu}-\text{N}(\text{apical})$ [2.160 (3) Å], mean value of $\text{C}-\text{O}(\text{acetate})$ distances [1.258 (3) Å], the sum of all interatomic distances in CuO_4N (the half value of the $\text{Cu}-\text{Cu}$ distance was also included in the sum) [11.41 (8) Å] as well as the bridging $\text{Cu}-\text{O}-\text{C}-\text{O}-\text{Cu}$ distance [6.48 (3) Å] found in the structure of the complex are very close to the values calculated for 31 other binuclear copper(II) acetate compounds (Table 3). Small differences in the values of $\text{Cu}-\text{Cu}$, $\text{Cu}-\text{O}$, $\text{Cu}-\text{basal plane}$ and $\text{basal plane}-\text{basal plane}$ distances may be explained by the influence of the axial ligand (Melník, 1981). The dihedral angle between the planes of two acetates is $89.8 (2)^\circ$ and the angle between the 4-pyridylmethanol ring and the acetate ligand (Table 2) is $21.8 (1)^\circ$. The C(6) and O(5) atoms are displaced from the

Table 3. *Structural characteristics for binuclear copper(II) acetates*

Mean values with standard deviations in parentheses are tabulated. Lists of structural data and references for the 32 compounds used in the evaluation have been deposited for brevity.

	Mean value (Å, °)	This structure (Å, °)
Cu—Cu	2.621 (8)	2.647 (1)
Cu—O	1.976 (5)	1.982 (2)
Cu—apical (N,O)	2.16 (2)	2.160 (3)
C—O	1.250 (2)	1.258 (5)
Cu—basal plane	0.221 (9)	0.211 (1)
Basal plane—basal plane	2.17 (2)	2.226 (2)
Bonds sum around Cu	11.36 (2)	11.41 (8)
Cu—O—C—O—Cu	6.43 (1)	6.48 (3)
Cu—O—C	123.0 (2)	125.6 (7)
O—C—O	125.2 (6)	124.4 (5)
Cu—O—C—O—Cu	372.0 (2)	375.6 (5)

plane of the 4-pyridylmethanol ring by 0.043 (6) and 0.049 (5) Å, respectively. Details of least-squares planes have been deposited. Mean values of bond lengths C—C, N—C, and bond angles N—C—C, C—C—C of 4-pyridylmethanols (Table 3) are in good agreement with those found in $\text{Cu}(\text{salicylate})_2(2\text{-pyridylmethanol})_2$, which are 1.348 (1) and 1.375 (1) Å, and $119.9 (5)$ and $119.7 (3)^\circ$, respectively (Hoang, Valach, Dunaj-Jurčo & Melník, 1992). Mean values of C—O bond lengths and O—C—O angles are also very close to those found in other acetates (Table 3).

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* Lists of structural data and references used in Table 3, least-squares-planes data, anisotropic displacement parameters, H-atom parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55349 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0509]

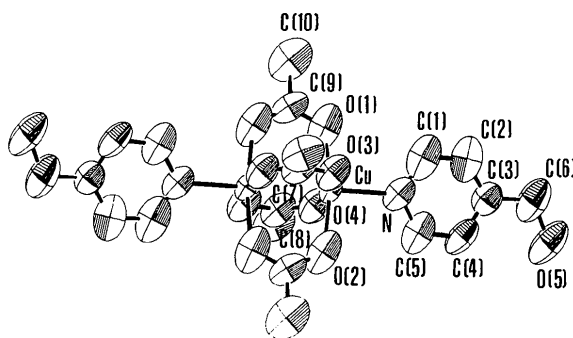


Fig. 1. Molecular structure with thermal ellipsoids [ORTEP, Johnson (1965)]. H atoms are omitted.

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