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Spectroscopic, Magnetic and Structural Characterization of Tetrakis-μ-acetato-bis(3-pyridylcarbinol)dicopper(II) Monomethylenedichloride

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Abstract

The complex tetrakis-μ-acetato-bis(3-pyridylcarbinol)dicopper(II) monoethylenedichloride, Cu_2-$CH_3COO)_4(3\text{-pycar})_2 \cdot CH_2Cl_2$ was synthesized, and spectral and magnetic data obtained.

The crystal and molecular structures were determined from three-dimensional counter X-ray data. The complex crystallizes in the monoclinic space group $P2_1/c$ with four formula units (Z = 4) in a cell of dimensions a = 16.778(13) Å, b = 19.853(14) Å, c = 8.384(4) Å, and β = 97.38(5)°. The observed and calculated densities are 1.60 and 1.598 g cm^{-3}. The structure was refined by blocked-cascade full-matrix least-squares methods to an R factor of 0.043 using 2509 independent intensities. The structure consists of two independent centrosymmetric tetracarboxylato-bridged dimers with the 3-pyridylcarbinol molecules (ronicol) in the axial positions. The Cu–Cu, Cu–O_{eq} (mean) and Cu–N_{ax} distances in the two independent dimers are: 2.654(1), 1.963(4) and 2.197(5) Å; 2.634(1), 1.969(4) and 2.152(5) Å, respectively. The EPR spectrum of a polycrystalline sample of the complex revealed triplet state (S = 1) transitions. Variable temperature (93–293 K) magnetic measurements indicate an antiferromagnetic interaction of $-2J$ = 330(8) cm^{-1}.

The magnetic data and the X-ray crystallographic results, together with literature data, were used to determine the relationship between the donor ability of the axial ligands, the displacement of the copper(II) atoms from the basal plane towards the apical ligands, and the length of the Cu–Cu bond.

Introduction

It is well known that steroids are effective in relieving the pain and controlling the inflammation in rheumatoid arthritis, and the adverse effects of such drugs are also known [1]. An excellent review of studies on the treatment of rheumatoid and other degenerative diseases with non-steroid drugs [2] and copper compounds has been written [3]. One non-steroid anti-inflammatory agent in current use is ronicol (3-pyridylcarbinol). In this manuscript we describe the synthesis, spectral and magnetic properties, as well as X-ray structural analysis, of a copper(II) acetate adduct with ronicol.

Experimental

Preparation of the Complex

The green $Cu_2(CH_3COO)_4(3\text{-picar})_2 \cdot CH_2Cl_2$ was prepared by combining a warm methanol solution of copper(II) acetate monohydrate (together with a small amount of the corresponding free acid) and 3-pyridylcarbinol in a molar ratio of 1:1. The reaction was left to stand at room temperature. The fine crystals of green product which precipitated after two days were collected, washed with cold methanol, and dried at room temperature. The compound was purified by recrystallisation from CH_2Cl_2. *Anal.* Calc. for $Cu(CH_3COO)_2(3\text{-}HOCH_2C_5H_4N) \cdot 0.5CH_2Cl_2$: Cu, 19.06; C, 37.85;

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H, 4.23; N, 4.20; Cl, 10.64. Found: Cu, 19.1; C, 37.91; H, 4.27; N, 4.17; Cl, 10.55.

Spectral Measurements

An electronic spectrum (Nujol mull) in the region 1.0–2.8 μm^{-1} was recorded with a Cary 14 spectrophotometer. EPR spectra of polycrystalline samples were recorded on a Varian model E 9 spectrometer at room and liquid nitrogen temperature.

Magnetic Measurements

Magnetic susceptibilities were obtained over the temperature range 93–293 K by the Gouy method, using $HgCo(SCN)_4$ as a calibrant [4]. The sample was finely ground powder. Diamagnetic corrections were calculated from Pascal's constants [5] and the effective magnetic moments were calculated using the expression

$$\mu_{eff} = 2.83(\chi_M^{corr} \cdot T)^{1/2}$$

Data Collection

The crystal and refinement data are given in Table I. The unit cell parameters and the orientation matrix were determined by a least-squares refinement based on 17 centered reflections measured at 20 °C on a Nicolet R3m diffractomter. The intensity of one check reflection, recorded after every 99 measurements, remained essentially constant throughout the data collection. The intensities were corrected for Lorentz and polarization effects but not for absorption.

Structure Determination

The structure was solved by direct methods [6] and Fourier techniques and refined by blocked-cascade full-matrix least-squares with anisotropic temperature factors for all non-hydrogen atoms. The hydrogen atoms bonded to carbon were included at calculated positions with fixed bond lengths (C–H = 0.96 Å) and constrained angles. The isotropic thermal parameters for the hydrogen atoms were set 1.2 times the equivalent isotropic thermal parameters for the corresponding carbon atom. The positional parameters of hydrogen atoms were refined.

The hydrogen atoms of the hydroxyl groups could not be clearly found from a regular difference Fourier map. Consequently, a second and a third difference map was calculated using approximately one-third and one-fourth of the data respectively. These maps showed peaks appearing near the hydroxyl oxygen atoms. The hydrogen atoms were fixed at these positions.

The calculations were performed on a Nicolet R3m diffractometer system with SHELXTL [6] software for minicomputer (Nova 3). The neutral atom scattering factors have been taken from ref. 7. The anomalous dispersion corrections were made for all non-hydrogen atoms [6]. The figures were drawn with SHELXTL [6] programs on a Zeta-plotter.

The final atomic coordinates and the thermal parameters with their e.s.d.s for non-hydrogen atoms are given in Table II.

Results and Discussion

Spectral and Magnetic Results

The electron absorption spectrum of the compound shows a band with a maximum at ~1.40 μm^{-1} (band I) and a shoulder at ~2.70 μm^{-1} (band II). Band I can be assigned to d–d transitions and band II should be the characteristic of the bridging system with antiferromagnetic interaction [8].

The EPR spectrum at room temperature, as well as at liquid nitrogen temperature, shows the three typical well-resolved absorption bands due to the triplet state transitions observable when $D > h\nu$. The spectra can be adequately described by the spin Hamiltonian:

TABLE I. Crystal and Refinement Data of $Cu_2(CH_3COO)_4(3\text{-}HOCH_2C_5H_4N)_2 \cdot CH_2Cl_2$.

Crystal system	monoclinic	Collection	ω
Space group	$P2_1/c$	Radiation	MoKα
a (Å)	16.778(13)	2θ range	3° to 45°
b (Å)	19.853(14)	Scan speed (° min^{-1})	2.5° to 29.3°
c (Å)	8.384(4)	Scan range (°)	1
β (°)	97.38(5)	Refl. meas.	3970
V ($Å^3$)	2769.5	Obs. ($I > 2.5\sigma(I)$)	2509
Z	4	Residual electron	
μ (cm^{-1})	17.86	density (e $Å^{-3}$)	0.69
$F.W.$	666.40	Crystal size (mm^3)	0.15 × 0.20 × 0.28
$F(000)$	1360	R $(=\Sigma\Delta/\Sigma\lvert F_o\rvert)^a$	0.043
D_o (g cm^{-3})	1.60	R_w $(=\Sigma\Delta\sqrt{w}/\Sigma\lvert F_o\rvert\sqrt{w})^b$	0.043
D_c (g cm^{-3})	1.598		

[a] $\Delta = \lVert F_o\rvert - \lvert F_c\rVert$. [b] $\omega^{-1} = \sigma^2(F_o) + 0.0005\,F_o^2$.

TABLE II. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\times 10^3$) for Non-hydrogen Atoms with E.S.D.s in Parentheses.

Atom	x	y	z	U^a
Cu(1)	5359(1)	490(1)	−715(1)	30(1)
Cu(2)	238(1)	621(1)	5346(1)	30(1)
N(1)	5901(3)	1362(2)	−1777(6)	34(2)
C(1)	6660(4)	1360(3)	−2158(7)	34(2)
C(2)	6999(4)	1891(3)	−2902(7)	37(2)
C(3)	6534(4)	2458(4)	−3226(8)	53(3)
C(4)	5753(4)	2478(3)	−2825(9)	51(3)
C(5)	5469(4)	1916(3)	−2105(8)	44(2)
C(6)	7826(4)	1844(4)	−3362(9)	52(3)
O(1)	8331(3)	2377(2)	−2646(5)	57(2)
N(2)	620(3)	1636(2)	5931(6)	32(2)
C(7)	129(3)	2157(3)	5530(7)	34(2)
C(8)	305(3)	2813(3)	5958(7)	32(2)
C(9)	1041(4)	2933(3)	6871(9)	48(3)
C(10)	1551(4)	2410(4)	7285(10)	68(3)
C(11)	1326(4)	1771(3)	6792(10)	53(3)
C(12)	−277(4)	3374(3)	5477(9)	47(3)
O(2)	−1089(3)	3163(2)	5154(6)	43(2)
O(3)	5710(3)	786(2)	1491(5)	46(2)
O(4)	5113(3)	−34(3)	2687(5)	50(2)
C(13)	5538(4)	488(4)	2710(8)	37(2)
C(14)	5860(5)	774(4)	4318(8)	50(3)
O(5)	6277(3)	−124(2)	−603(6)	46(2)
O(6)	5687(3)	−939(2)	630(6)	54(2)
C(15)	6270(4)	−691(4)	46(8)	41(3)
C(16)	7016(4)	−1111(4)	119(11)	72(4)
O(7)	−789(3)	862(2)	4034(6)	43(2)
O(8)	−1183(3)	−186(2)	3442(5)	43(2)
C(17)	−1284(4)	435(3)	3386(7)	33(2)
C(18)	−2060(4)	703(4)	2540(9)	47(3)
O(9)	760(3)	523(2)	3393(5)	37(2)
O(10)	360(3)	−527(2)	2797(5)	48(2)
C(19)	743(4)	3(3)	2540(8)	34(2)
C(20)	1176(4)	4(4)	1088(8)	54(3)
Cl(1)	2738(2)	811(2)	4635(4)	118(1)
Cl(2)	3820(2)	1895(2)	4255(6)	170(2)
C(21)	3724(5)	1062(6)	4761(16)	109(5)
H(O1)	8401	2299	−1841	
H(O2)	−1345	2894	6059	

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

$$H = g\beta HS + D(S_z^2 - 1/3S(S+1))$$

where $S = 1$ and D the zero-field splitting parameter, and other symbols have their usual meanings. The experimental D value is related to the interaction between the two coupled electrons by both the direct magnetic dipole–dipole interaction inversely dependent on the separation distance, and by the pseudo-dipolar interaction occurring via the bridging ligand's molecular orbitals. The observed values at 293 K are: $g_\perp = 2.082$; $g_\parallel = 2.375$ and $|D| = 0.341$ cm^{-1}; and at 77 K are: $g_\perp = 2.078$; $g_\parallel = 2.370$ and $|D| = 0.340$ cm^{-1}. These values are comparable to those reported for other familiar copper(II) carboxylato complexes [9]. The $|D|$ value of about 0.3 cm^{-1} is large compared to magnetic quantities (~3000 G), but is small compared to vibrational frequencies. At room temperature nearly 50% of the dimers are in the thermally-populated triplet state. Therefore interdimer dipolar couplings may also be expected to be significant at room temperature.

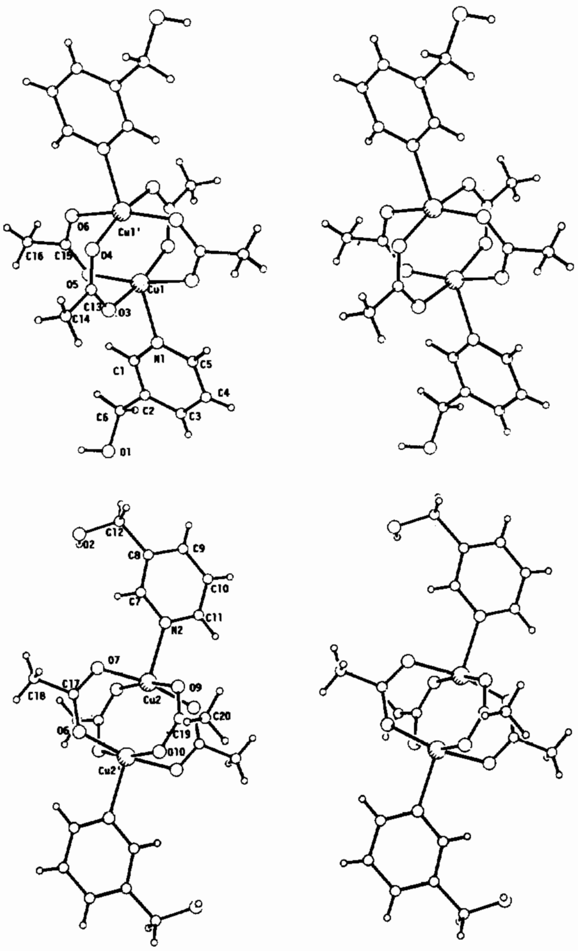

Fig. 1. Stereoview of the dimeric units of $Cu_2(CH_3COO)_4(3\text{-}pic) \cdot CH_2Cl_2$.

The molar susceptibilities corrected for diamagnetism, and magnetic moments for the compound are reported at various temperatures in Table III. The temperature–susceptibility data can be described by the equation:

$$\chi_M^{corr} = \frac{Ng^2\beta^2}{3kT}\left[1 + \frac{1}{3}\exp\left(\frac{-2J}{kT}\right)\right]^{-1} + N\alpha$$

where $-2J$ is the energy separation between a singlet and a triplet level, and $N\alpha$ was taken as 60×10^{-6}

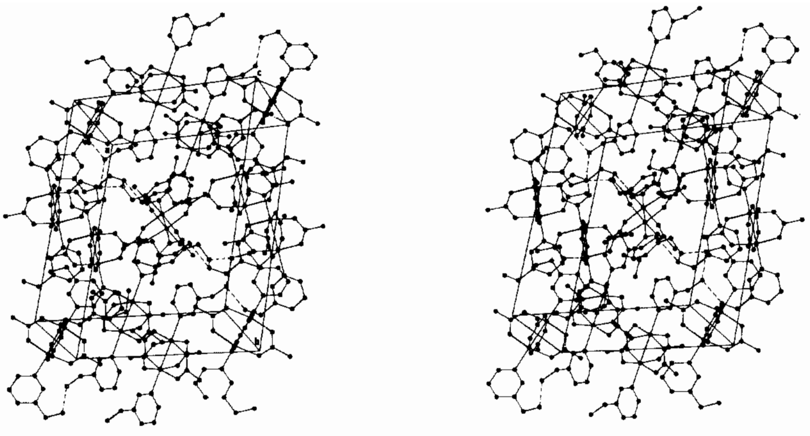

Fig. 2. Stereoview of the packing.

cm^3 mol^{-1}. The energy separation between the two spin states of the compound, $-2J$ = 330(8) cm^{-1}, is about the same as that of the pyridine adducts, 325 cm^{-1} [10] and 333 cm^{-1} [11].

Description and Discussion of the Structure

The crystal structure of tetrakis-μ-acetato-bis(3-pyridylcarbinol)dicopper(II) monomethylenedichloride, $Cu_2(CH_3COO)_4(3\text{-pycar})_2 \cdot CH_2Cl_2$ consists of two independent centrosymmetric tetracarboxylato-bridged dimers. A view of the binuclears is shown in Fig. 1, and the packing with hydrogen bonds is given in Fig. 2. Interatomic bond distances and angles are listed in Table IV and hydrogen bonds in Table VII. Least-squares planes of the molecules are given in Table VI.

This kind of binuclear structure is very often found in copper(II) carboxylato complexes, where the copper atoms are bridged by four carboxylato groups. In these complexes the Cu–Cu separations are in the range 2.56–2.88 Å [12, 13]. The Cu–Cu separation is usually longer when the axial ligand is a nitrogen instead of an oxygen atom. The Cu–Cu distances vary from 2.576 Å to 2.886 Å for CuO_4N chromophores, and from 2.563 Å to 2.666 Å for CuO_5 chromophores [12].

TABLE III. Magnetic Data of $Cu_2(CH_3COO)_4(3\text{-}HOCH_2\text{-}C_5H_4N)_2 \cdot CH_2Cl_2$ ($-\Delta \times 10^6$ = 158.9 cm^3 mol^{-1}).

T (K)	$\chi_M^{corr} \times 10^6$ (cm^3 mol^{-1})	μ_{eff} (B.M.)
93	574	0.65
113	610	0.74
133	635	0.82
153	720	0.94
173	765	1.03
193	803	1.11
213	816	1.18
233	827	1.24
253	860	1.32
273	896	1.40
293	903	1.45

The Cu–Cu distances in the two independent dimers, 2.654(1) and 2.634(1) Å agree well the distances reported for CuO_4N chromophores [12, 13]. It must be noted that only in three cases have two crystallographically-independent binuclear units been found, namely $Cu_2(C_6H_5CH_2COO)_4(urea)_2$ [14], $Cu_2(C_2H_5COO)_4(py)_2$ [15], and $Cu_2(C_2H_5COO)_2(4\text{-pic})_2$ [16]. These compounds differ mostly in their Cu–Cu and Cu–L (axial) bond lengths on the long coordinates, which yield different distortion of the coordination polyhedra. The Cu–Cu distances are 2.623 and 2.630 Å for urea [14], 2.649 and 2.642 Å for pyridine [15] and 2.655 and 2.659 Å for the 4-picoline [16] adduct, respectively.

The Cu(1) and Cu(2) atoms are bonded at mean distances of 1.963 and 1.970 Å to four oxygen atoms of the bridging acetato ligands respectively. The arrangements of the four oxygen atoms around the copper(II) atoms are planar, but the copper(II) atoms are displayed by 0.217 and 0.205 Å from the mean planes toward the apical nitrogen atoms of the 3-pyridylcarbinol (Cu–N are 2.197(5) and 2.152(5) Å). The distorted octahedral coordination around the copper(II) atom is completed by a centrosymmetrically-related copper(II) atom. The Cu–Cu–N linkage is linear for Cu(2) but deviates a little for Cu(1), being 179.4(2) and 175.0(1) respectively.

The two binuclears are very similar except for the dihedral angles and apical distances. The dihedral angle between the least-squares planes of the basal plane and pyridine ring is 90.9 for Cu(1) and 84.1° for Cu(2), see Table VI. The same can also be seen from the dihedral angles between the least-

TABLE IV. Interatomic Distances (Å) and Angles (°) with Their Standard Deviations.

Environment of copper(II) ions

	n = 1 m = 0	n = 2 m = 4		n = 1 m = 0	n = 2 m = 4
Cu(n)–O(3 + m)	1.959(5)	1.980(4)	O(4^{i} + m)–Cu(n)–O(6^{i} + m)	88.5(2)	90.5(2)
O(5 + m)	1.955(4)	1.963(4)	N(n)–Cu(n)–O(3 + m)	93.2(2)	96.5(2)
O(4^{i} + m)	1.961(4)	1.969(4)	O(5 + m)	98.4(2)	97.6(2)
O(6^{i} + m)	1.979(4)	1.967(5)	O(4^{i} + m)	99.6(2)	95.5(2)
N(n)	2.197(5)	2.152(5)	O(6^{i} + m)	94.3(2)	94.4(2)
Cu(n^{i})	2.654(1)	2.634(1)	Cu(n^{i})	175.0(1)	179.4(2)
			Cu(n^{i})–Cu(n)–O(3 + m)	83.8(1)	83.5(1)
O(3 + m)–Cu(n)–O(5 + m)	90.2(2)	90.6(2)	O(5 + m)	85.6(1)	83.0(1)
O(4^{i} + m)	167.2(2)	168.0(2)	O(4^{i} + m)	83.4(1)	84.5(1)
O(6^{i} + m)	89.4(2)	88.1(2)	O(6^{i} + m)	81.8(1)	85.1(1)
O(5 + m)–Cu(n)–O(4^{i} + m)	89.1(2)	88.3(2)			
O(6^{i} + m)	167.3(2)	168.1(2)			

3-Pyridylcarbinol ligands

	n = 1 m = 0	n = 2 m = 6		n = 1 m = 0	n = 2 m = 6
N(n)–C(1 + m)	1.351(8)	1.338(7)	Cu(n)–N(n)–C(1 + m)	123.0(4)	120.7(4)
C(1 + m)–C(2 + m)	1.384(9)	1.371(8)	N(n)–C(1 + m)–C(2 + m)	124.0(5)	124.2(5)
C(2 + m)–C(3 + m)	1.377(9)	1.387(9)	C(1 + m)–C(2 + m)–C(3 + m)	117.1(6)	117.0(5)
C(3 + m)–C(4 + m)	1.394(11)	1.361(10)	C(2 + m)–C(3 + m)–C(4 + m)	120.1(6)	119.7(6)
C(4 + m)–C(5 + m)	1.381(10)	1.372(10)	C(3 + m)–C(4 + m)–C(5 + m)	118.1(6)	119.2(5)
C(5 + m)–N(n)	1.327(8)	1.332(8)	C(4 + m)–C(5 + m)–N(n)	123.4(6)	122.7(6)
C(2 + m)–C(6 + m)	1.489(10)	1.502(8)	C(5 + m)–N(n)–C(1 + m)	117.3(5)	117.1(6)
C(6 + m)–O(n)	1.440(8)	1.419(8)	C(5 + m)–N(n)–Cu(n)	119.6(4)	122.0(4)
			C(1 + m)–C(2 + m)–C(6 + m)	121.3(6)	121.5(5)
O(1)•••O(2)^{ii}	2.650		C(2 + m)–C(6 + m)–O(n)	111.3(6)	114.1(5)
O(2)•••O(1)^{iii}	2.691		C(3 + m)–C(2 + m)–C(6 + m)	121.6(6)	121.5(5)

Carboxylato ligands

	n = 1 m = 0	n = 1 m = 2	n = 2 m = 4	n = 2 m = 6
C(13 + m)–O(3 + m)	1.246(8)	1.252(9)	1.261(7)	1.254(8)
O(4 + m)	1.256(8)	1.250(8)	1.244(7)	1.265(8)
C(14 + m)	1.498(9)	1.498(10)	1.498(8)	1.495(10)
O(3 + m)–C(13 + m)–O(4 + m)	124.7(6)	125.1(6)	124.9(5)	124.2(6)
C(14 + m)	117.6(6)	117.7(6)	116.3(5)	119.0(6)
O(4 + m)–C(13 + m)–C(14 + m)	117.7(6)	117.2(6)	118.4(5)	116.8(6)
C(13 + m)–O(3 + m)–Cu(n)	124.0(4)	122.1(4)	123.7(4)	125.3(4)
C(13 + m)–O(4 + m)–Cu(n)^{i}	124.1(4)	125.5(4)	123.4(4)	122.4(4)

^{i}1 − *x*, −*y*, −*z* for Cu1 and −*x*, −*y*, 1 − *z* for Cu2. ^{ii}−1 + *x*, 0.5 − *y*, 0.5 + *z*. ^{iii}−1 + *x*, *y*, 1 + *z*.

TABLE V. Structural and Magnetic Data for $Cu_2(CH_3COO)_4L_2$, where L is N Donor Ligand.

Complex[a]	Cu–Cu (Å)	Cu–O (basal) (Å)	Cu–N (apical) (Å)	Cu–basal plane (Å)	Cu–O–C (°)	O–C–O (°)	−2J (cm^{-1})	Ref.
$Cu_2X_4(pz)_2$	2.576(1)[b]	1.964(4)	2.167(5)	0.28	122.5(3)	124.8		17
	2.583(1)[c]	1.964(5)	2.171(4)	0.26	122.7(4)	125.3(6)	325	17, 18

(continued overleaf)

TABLE V. *(continued)*

Complex[a]	Cu–Cu (Å)	Cu–O (basal) (Å)	Cu–N (apical) (Å)	Cu–basal plane (Å)	Cu–O–C (°)	O–C–O (°)	–2J (cm^{-1})	Ref.
Cu_2X_4(hexa)$_2$	2.624(1)	1.975(2)	2.212(2)		122.9(1)	125.4(2)		31
Cu_2X_4(py)$_2$[d]	2.630(3)	1.981(10)	2.126(10)	0.22	123.4(7)	125.1(9)	325	10, 19
Cu_2X_4(diaza)$_2$	2.632(2)	1.975(6)	2.193(8)	0.21	123.3(5)	125.4(7)		20
Cu_2X_4(3-pycar)$_2$·CH_2Cl_2[e]	2.634(1)	1.970(4)	2.152(5)	0.205	124.5(4)	124.5(6)	330(8)	This work
	2.654(1)	1.963(4)	2.197(5)	0.217	123.0(4)	124.9(6)		
Cu_2X_4(NCS)$_2$	2.643(3)	2.03(1)	2.08(2)		123(1)	126(1)	305	21
Cu_2X_4(py)$_2$[f]	2.645(3)	1.955(8)	2.186(8)	0.22	123.4(9)	125.6(10)	333[g]	11, 22
Cu_2X_4(quin)$_2$	2.652(2)	1.977(5)	2.224(6)	0.227	123.7(7)	125.9(8)	320	23–25
Cu_2X_4(benz)$_2$	2.663(1)	1.979(4)	2.145(5)	0.215		125.3(6)	324	26, 27
Cu_2X_4(3-nic)$_2$	2.663(3)	1.973(6)	2.175(6)	0.184	123.9(6)	122.9(8)		28
Cu_2X_4(2-pic)$_2$	2.671	1.975(10)	2.240(12)	0.23	121.7(10)	125.9(14)	318	29

[a] X = CH_3COO^-; pz = pyrazine; py = pyridine; diaza = 1,4-diazabicyclo[2,2,2]octane; 3-pycar = 3-pyridylcarbino; quin = quinoline; bentz = bentzimidazole; 3-nic = nicotinamide-N,N-diethyl; 2-pic = 2-picoline; hexa = hexamethylen-tetramin-N,N′. [b] At 100 K. [c] At 300 K. [d] Monoclinic form. [e] Two crystallographically independent binuclears. [f] Orthorhombic form. [g] Form not known.

TABLE VI. Least-Squares Planes (*; unit weights) and Deviations from the Planes (Å).

(a) $8.109x + 14.882y - 4.281z = 5.168$		(b) $4.665x + 18.658y + 1.352z = 1.788$	
Cu(1)	0.217	Cu(2)	0.205
Cu(1)	–2.435	Cu(2)^{ii}	–2.428
N(1)	2.410	N(2)	2.358
O(3)*	–0.001	O(7)*	–0.002
O(5)*	0.001	O(9)*	0.002
O(4)^{i}*	–0.001	O(8)^{ii}*	–0.002
O(6)^{i}	0.001	O(10)^{ii}*	0.002
(c) $3.852x + 7.388y + 7.230z = 2.001$		**(d) $8.849x + 2.605y - 7.547z = -3.497$**	
Cu(1)	–0.092	Cu(2)	–0.165
Cu(1)^{i}	–0.058	Cu(2)^{ii}	–0.388
N(1)*	–0.006	N(2)*	–0.004
C(1)*	0.009	C(7)*	0.001
C(2)*	–0.006	C(8)*	0.005
C(3)*	0.000	C(9)*	–0.004
C(4)*	0.003	C(10)*	0.000
C(5)*	–0.000	C(11)*	0.004
C(6)	–0.056	C(12)	–0.001
O(1)	1.051	O(2)	–0.540
(e) $13.825x - 12.246y - 0.800z = 6.891$		**(f) $9.206x + 0.776y - 7.535z = -3.699$**	
Cu(1)	0.026	Cu(2)	–0.062
Cu(1)^{i}	0.018	Cu(2)^{ii}	–0.076
O(3)*	0.000	O(7)*	0.000
O(4)*	0.000	O(8)*	0.000
C(13)*	0.000	C(17)*	0.000
C(14)	–0.005	C(18)	–0.061
(g) $3.66x + 8.124y + 7.131z = 1.771$		**(h) $12.344x - 6.991y + 4.018z = 1.936$**	
Cu(1)	0.082	Cu(2)	0.072
Cu(1)^{i}	0.043	Cu(2)^{ii}	0.074
O(5)*	0.000	O(9)*	0.000

(continued on facing page)

TABLE VI. *(continued)*

O(6)*	0.000	O(10)*	0.000
C(15)*	0.000	C(19)*	0.000
C(16)	−0.014	C(10)	−0.051

Angles between the planes (°):

a–c = 90.9; c–e = 90.7; c–g = 2.3; e–g = 91.7; b–d = 84.1; d–f = 5.4 and d–h = 98.3; f–h = 95.4

^{i}1 − *x*, −*y*, −*z*. ^{ii}−*x*, −*y*, 1 − *z*.

TABLE VII. Hydrogen Bonds.

A–H···B	A–H	H···B	A···B	∢A–H···B
O1–H(O1)···O2^{ii}	0.688	2.001	2.650	157.6
O2–H(O2)···O1^{iii}	1.063	1.636	2.691	171.1

^{ii}−1 + *x*; 0.5 − *y*, 0.5 + *z*. ^{iii}−1 + *x*, *y*, 1 + *z*.

squares planes of the bridged acetato groups and pyridine ring. The angles are 90.7, 98.3°, 2.3 and 5.4°, respectively. The oxygen atoms of the methoxy groups deviate most from the least-squares plane of the pyridine rings, by 1.05 and 0.54 Å. The packing and hydrogen bonds may cause these differences.

The acetato groups are planar and perpendicular to each other. The bond lengths and angles agree well in the acetato groups, as in the 3-pyridylcarbinol molecules, with the values reported for familiar complexes [12, 15, 16]. In the pyridine rings the C–N bond lengths are slightly shorter than the C–C bond lengths [15, 16]. The C–H bond lengths vary from 0.82(6) to 1.03(7) Å.

In general the Cu–Cu distances and the displacement of the copper(II) atoms from the basal plane towards the apical ligands increase when the pK_a value of the bridged ligands decreases. Also the Cu–Cu distances increase when the pK_a value of the axial ligand becomes higher. The antiferromagnetic interaction in binuclear copper(II) carboxylato complexes tends to increase as either the axial ligand or the carboxylate substituent becomes a stronger electron donor [9, 12].

Inspection of the data in Table V reveals that when the Cu–Cu distance increases, the Cu–N(axial) distance tends to increase as well as the displacement of the copper(II) atom from the basal plane towards the axial ligand. However, there exist a few exceptions to this observation when the axial ligand bridges the copper(II) atoms of adjacent dimers, as for instance in $Cu_2(CH_3COO)_4(pz)_2$ [17], $Cu_2(CH_3COO)_4(diaza)_2$ [20], and $Cu_2(CH_3COO)_4(hexa)_2$ [31]. The π-back bonding [32] may cause the shortening of the Cu–N(axial) distance in isothiocyanato compound [21] and the steric effects the elongation in 2-picoline [29] and quinoline [23] adducts. In spite of the differences in bond lengths the bridge length (Cu–O–C–O–Cu) remains nearly constant, from 6.41 to 6.49 Å for the compounds in Table V.

The insensitivity of the singlet–triplet separation (−2J) to the Cu–Cu distance has been previously noted [12], and we can see in Table V that the present data are following the same trend. In the same paper [12] detailed discussions of the crystal structural data and an exchange interaction of binuclear copper(II) carboxylato complexes have been presented, and will not therefore be considered here.

Medium-to-strong hydrogen bonds [30] connect the binuclears together by the hydroxyl groups of 3-pyridylcarbinol, Table VII. All other intermolecular contacts are longer than 3.260 Å for O(2)···C(6) (−1 + *x*, ½ − *y*, ½ + *z*).

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