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Structure of a Binuclear Copper(II) Complex with both μ-Alkoxo and μ-Formato Bridges, [Cu$_2$(C$_{17}$H$_{15}$N$_2$O$_3$)(HCOO)]

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Abstract

The crystal structure of a binuclear copper(II) complex, μ-formato-1κO:2$\kappa O'$-μ-2,2'-[1,3-(2-hydroxypropanediyl-1:2κ^2O)bis(nitrilomethylidyne)]di-phenolato(3−)-1κ^2N,O:2κ^2N',O'-dicopper(II), [Cu$_2$(L-sal)(HCOO)], H$_3$(L-sal) = N,N'-bis(salicylidene)-1,3-diamino-2-propanol, was determined by X-ray diffraction. The title compound is ferromagnetic as a result of the roof-shaped structure of the Cu$_2$O(OCO) core ($-2J = -94$ cm^{-1}). The Cu···Cu distance is 3.260 (1) Å and the Cu—O—Cu bond angle is 115.2 (2)°.

Comment

The structures and magnetism of binuclear Cu^{II} complexes with both μ-alkoxo and μ-carboxylato bridges have been studied to reveal the orbital counter–complementary effect (Nishida & Kida, 1986; Kawata *et al.*, 1992). These Cu^{II} complexes are usually antiferromagnetic with the Cu—O—Cu angle greater than 130°. However, the antiferromagnetic interaction is depressed by the so-called roof-shaped distortion, which is measured by the dihedral angle between the two Cu coordination planes, τ (Charlot *et al.*, 1979; Charlot, Kahn, Jeannin & Jeannin, 1980). The $-2J$ value of the title complex is -94 cm^{-1} with $\tau = 51.4$ (2)°. The roof-shaped distortion is determined by the conformation of the five-membered chelate rings sharing an alkoxo group. When the combination of the enantiomeric conformation of the rings is $\delta\lambda$, the binuclear complex takes a flat form with a small τ angle (δ stands for a right-handed helical relation between the C—C bond axis and the line which connects the alkoxo O and secondary amine N atoms, λ for a left-handed helix). In Fig. 1 the combination is $\lambda\lambda$. It seems that the roof-shaped distortion is the result of the crystal packing force. Planar and roof-shaped structures of [Cu$_2$(L-ac)(CH$_3$COO)] (the ligand H$_3$L-ac is a 1:2 Schiff base derived from 1,3-diaminopropan-2-ol and acetylacetone) are observed in hydrated (Nishida & Kida, 1986) and anhydrous crystals (Fallon, Murray, Mazurek & O'Connor, 1985), respectively, and the magnetic and structural features have been compared (Mazurek *et al.*, 1985). Crystal structure analysis of [Cu$_2$(L-ac)(HCOO)] was also attempted in this study, but failed owing to the poor quality of
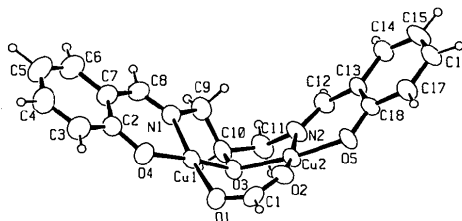

Fig. 1. *ORTEP*II drawing (Johnson, 1976) with the thermal ellipsoids scaled at the 50% probability level. The H atoms are represented by circles of radius 0.08 Å.

the crystals [simple cubic, $a = 22.388$ (4) Å, $V = 11221$ (5) Å^3, $Z = 24$, $D_m = 1.47$ (2), $D_x = 1.54$ Mg m^{-3}].

Experimental

Crystal data

[Cu$_2$(C$_{17}$H$_{15}$N$_2$O$_3$)(CHO$_2$)]	Mo $K\alpha$ radiation
$M_r = 467.4$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 34
$P2_1/c$	reflections
$a = 12.756$ (2) Å	$\theta = 10$–$15°$
$b = 14.451$ (2) Å	$\mu = 2.483$ mm^{-1}
$c = 9.805$ (1) Å	$T = 297$ (2) K
$\beta = 105.69$ (1)°	Prism
$V = 1740.1$ (4) Å^3	$0.40 \times 0.40 \times 0.25$ mm
$Z = 4$	Dark green
$D_x = 1.784$ Mg m^{-3}	
$D_m = 1.78$ (2) Mg m^{-3}	

Data collection

Rigaku AFC-5 four-circle diffractometer	2497 observed reflections $[F > 3\sigma(F)]$
ω scans	$R_{int} = 0.018$
Absorption correction: by integration from crystal shape	$\theta_{max} = 27.5°$
	$h = 0 \rightarrow 16$
	$k = -18 \rightarrow 0$
$T_{min} = 0.369$, $T_{max} = 0.573$	$l = -12 \rightarrow 12$
4163 measured reflections	5 standard reflections monitored every 100 reflections
3991 independent reflections	intensity variation: 1%

Refinement

Refinement on F	$w = 1/\sigma^2$
$R = 0.047$	$(\Delta/\sigma)_{max} = 0.133$
$wR = 0.046$	$\Delta\rho_{max} = 1.06$ e Å^{-3}
$S = 4.65$	$\Delta\rho_{min} = -1.17$ e Å^{-3}
2497 reflections	Atomic scattering factors
309 parameters	from International Tables
All H-atom parameters refined	for X-ray Crystallography (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cu(1)	0.73340 (7)	0.59995 (6)	0.10086 (8)	0.0322 (3)
Cu(2)	0.88058 (7)	0.52676 (6)	0.40742 (8)	0.0295 (3)
O(1)	0.8631 (3)	0.5523 (3)	0.0575 (4)	0.042 (2)
O(2)	0.9178 (3)	0.4638 (3)	0.2491 (4)	0.035 (2)
O(3)	0.8077 (3)	0.6305 (3)	0.2910 (4)	0.031 (2)
O(4)	0.6597 (3)	0.5892 (3)	-0.0928 (4)	0.041 (2)
O(5)	0.9364 (3)	0.4211 (3)	0.5233 (4)	0.032 (2)
N(1)	0.6030 (4)	0.6354 (4)	0.1531 (6)	0.038 (2)
N(2)	0.8207 (4)	0.5801 (4)	0.5509 (5)	0.033 (2)
C(1)	0.9197 (5)	0.4924 (5)	0.1306 (7)	0.037 (3)
C(2)	0.5560 (5)	0.6006 (5)	-0.1522 (7)	0.037 (3)
C(3)	0.5167 (6)	0.5909 (6)	-0.3008 (8)	0.049 (3)
C(4)	0.4084 (6)	0.6019 (6)	-0.3709 (8)	0.057 (3)
C(5)	0.3321 (6)	0.6232 (6)	-0.2977 (9)	0.061 (4)
C(6)	0.3689 (6)	0.6328 (6)	-0.1533 (8)	0.055 (3)
C(7)	0.4774 (5)	0.6241 (5)	-0.0785 (8)	0.042 (3)
C(8)	0.5077 (5)	0.6382 (5)	0.0736 (7)	0.041 (3)
C(9)	0.6276 (6)	0.6510 (5)	0.3082 (7)	0.041 (3)
C(10)	0.7427 (6)	0.6842 (5)	0.3580 (7)	0.035 (3)
C(11)	0.7880 (6)	0.6768 (5)	0.5185 (7)	0.042 (3)
C(12)	0.8044 (5)	0.5384 (5)	0.6586 (6)	0.034 (3)
C(13)	0.8328 (5)	0.4438 (5)	0.6938 (6)	0.029 (2)
C(14)	0.7992 (5)	0.4055 (5)	0.8090 (7)	0.038 (3)
C(15)	0.8303 (6)	0.3192 (5)	0.8584 (7)	0.047 (3)
C(16)	0.8989 (6)	0.2676 (5)	0.7983 (7)	0.041 (3)
C(17)	0.9329 (6)	0.3025 (5)	0.6860 (7)	0.036 (3)
C(18)	0.9013 (5)	0.3905 (4)	0.6307 (6)	0.029 (2)

Table 2. *Geometric parameters* (Å, °)

Cu(1)—Cu(2)	3.260 (1)	N(2)—C(12)	1.280 (9)
Cu(1)—O(1)	1.942 (5)	C(2)—C(3)	1.414 (9)
Cu(1)—O(3)	1.901 (4)	C(2)—C(7)	1.43 (1)
Cu(1)—O(4)	1.884 (4)	C(3)—C(4)	1.37 (1)
Cu(1)—N(1)	1.937 (6)	C(4)—C(5)	1.39 (1)
Cu(2)—O(2)	1.965 (5)	C(5)—C(6)	1.37 (1)
Cu(2)—O(3)	1.959 (4)	C(6)—C(7)	1.385 (9)
Cu(2)—O(5)	1.921 (4)	C(7)—C(8)	1.45 (1)
Cu(2)—N(2)	1.934 (6)	C(9)—C(10)	1.49 (1)
O(1)—C(1)	1.227 (8)	C(10)—C(11)	1.527 (9)
O(2)—C(1)	1.240 (8)	C(12)—C(13)	1.432 (9)
O(3)—C(10)	1.420 (9)	C(13)—C(14)	1.42 (1)
O(4)—C(2)	1.304 (7)	C(13)—C(18)	1.43 (1)
O(5)—C(18)	1.326 (8)	C(14)—C(15)	1.36 (1)
N(1)—C(8)	1.255 (8)	C(15)—C(16)	1.40 (1)
N(1)—C(9)	1.485 (9)	C(16)—C(17)	1.38 (1)
N(2)—C(11)	1.468 (9)	C(17)—C(18)	1.398 (9)
O(1)—Cu(1)—O(3)	93.9 (2)	O(3)—Cu(2)—N(2)	84.3 (2)
O(1)—Cu(1)—O(4)	88.4 (2)	O(5)—Cu(2)—N(2)	92.4 (2)
O(1)—Cu(1)—N(1)	174.2 (2)	Cu(1)—O(1)—C(1)	121.6 (5)
O(3)—Cu(1)—O(4)	171.3 (2)	Cu(2)—O(2)—C(1)	131.0 (5)
O(3)—Cu(1)—N(1)	85.1 (2)	Cu(1)—O(3)—Cu(2)	115.2 (2)
O(4)—Cu(1)—N(1)	93.3 (2)	Cu(1)—O(3)—C(10)	112.4 (3)
O(2)—Cu(2)—O(3)	94.1 (2)	Cu(2)—O(3)—C(10)	113.2 (4)
O(2)—Cu(2)—O(5)	88.3 (2)	Cu(2)—O(5)—C(18)	125.7 (4)
O(2)—Cu(2)—N(2)	170.7 (2)	O(1)—C(1)—O(2)	128.7 (7)
O(3)—Cu(2)—O(5)	173.6 (2)		

The compound was prepared by reacting Cu^{II} formate and H$_3$(L-sal) (Nishida & Kida, 1986). The magnetic susceptibilities over the temperature range 80–300 K were determined by the Faraday method. The X-ray structure analysis was carried out on a MIPS 3230 workstation with the *Xtal*3.0 program system (Hall & Stewart, 1990).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71323 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: OH1028]

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Structure of the Monohydrido Bridged Dinuclear Platinum(II) Dihydride [(PEt₃)₂PhPt(μ-H)PtH(PEt₃)₂][BPh₄]

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Abstract

The structure of the cationic complex μ-hydrido-1:2κ^2H-hydrido-2κH-phenyl-1κC-tetrakis(triethyl-phosphine)-1κ^2P,2κ^2P-diplatinum(II) consists of two platinum-containing units, which lie on reciprocally perpendicular planes. In each unit, the Pt atom is coordinated in a distorted square-planar arrangement. One hydride ligand is in a bridging position, while the other hydride is terminal on Pt(2). The Pt···Pt distance is 3.093 (1) Å.

Comment

In a preliminary communication, the preparation, characterization and the partially refined X-ray structure of the title compound were reported (Bracher, Grove, Venanzi, Bachechi, Mura & Zambonelli, 1978). The dihydrido-bridged isomer [(PEt₃)₂PhPt(μ-H)₂Pt(PEt₃)₂]⁺ has been studied also and its structure reported (Bachechi, Bracher, Grove, Kellenberger, Pregosin, Venanzi & Zambonelli, 1983).

The crystal structure contains discrete tetraphenylborate anions and dinuclear dihydridoplatinum(II) cations with no short contacts between atoms of different ions. The complex cation is shown in Fig. 1.

The structure of the cationic complex (I) consists of two Pt-containing units, which lie on almost perpendicular planes forming a dihedral angle of 82°. The hydride ligands were not located by X-ray analysis, but the coordination geometry of the Pt atoms is consistent with the NMR data (Bracher *et*
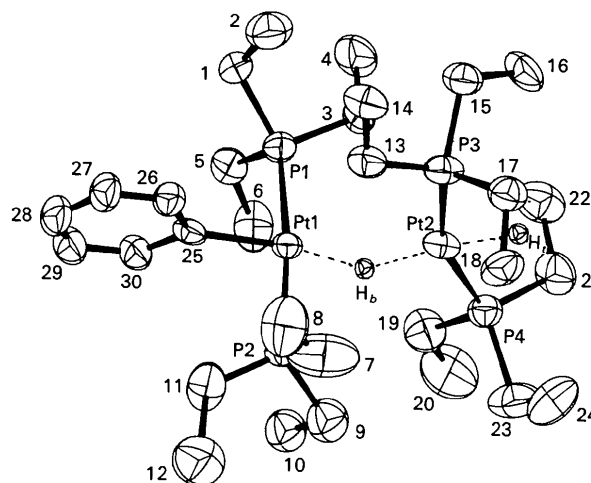

Fig. 1. Perspective view of the cationic complex with ellipsoids at the 30% probability level. In the core, the hydride ligands are placed at calculated sites.

al., 1978), which indicates the presence of one bridging and one terminal hydride ligand. In each unit, the Pt atom is coordinated in a distorted square-planar arrangement with apparent vacant sites. When these sites are considered occupied by the hydrides, one of them, *trans* to C(25), is bridging, while the other, bound to Pt(2), is terminal. The C(25)—Pt(1)···Pt(2) angle of 164.3 (4)° indicates that the bridging hydride is not collinear with the two metal centres.

$$\varphi(1) \wedge \varphi(2) = 82° \quad \varphi(1) \wedge \varphi(3) = 84° \quad \varphi(2) \wedge \varphi(3) = 14°$$

(I)
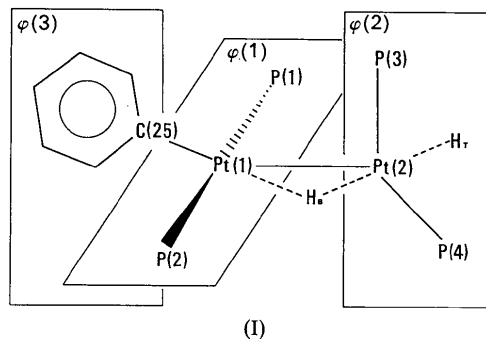
The probable positions of the hydride ligands were calculated using the program *HYDEX* (Orpen, 1980) at the potential energy minima and are represented in Fig. 1.

The Pt···Pt distance of 3.093 (1) Å is among the longest observed in Pt complexes with one hydrido bridge, together with those found in the trihydride [(PEt₃)₂HPt(μ-H)PtH(PEt₃)₂]⁺ [3.028 (1) Å (Bachechi, 1993)] and the monohydride [(PEt₃)₂PhPt(μ-H)PtPh(PEt₃)₂]⁺ [3.238 (1) Å (Carmona, Thouvenot, Venanzi, Bachechi & Zam-