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Acta Cryst. (1993). C**49**, 674–677

Synthesis and Structure of (Acetato-*O*,*O*′)(perchlorato-*O*)(2,2′:6′2″-terpyridine-*N*,*N*′,*N*″)copper(II)

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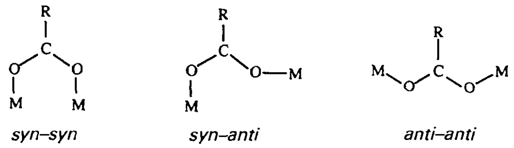
(*Received* 9 *December* 1991; *accepted* 29 *September* 1992)

Abstract. (Acetato-*O*,*O*′)(perchlorato-*O*)(2,2′:6′,2″-terpyridine-*N*,*N*′,*N*″)copper(II), [Cu(ClO$_4$)(CH$_3$CO$_2$)(C$_{15}$H$_{11}$N$_3$)], $M_r = 455.32$, triclinic, $P\bar{1}$, $a = 11.010\,(3)$, $b = 10.791\,(3)$, $c = 8.356\,(2)$ Å, $\alpha = 83.56\,(2)$, $\beta = 86.11\,(2)$, $\gamma = 64.67\,(2)°$, $V = 891.4\,(7)$ Å^3, $Z = 2$, $D_x = 1.696$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 14.66$ cm^{-1}, $F(000) = 462$, $T = 298$ K, final $R = 0.062$ and $wR = 0.066$ for 1011 reflections with $I \geq 2.5\sigma(I)$. The structure consists of discrete neutral [Cu(terpy)(CH$_3$COO)(ClO$_4$)] units (terpy = 2,2′:6′,2″-terpyridine). The coordination environment around Cu$^{\rm II}$ ions is distorted 4 + 2 octahedral. The equatorial plane is composed of the three N atoms of the terpyridine ligand and one O atom of the acetate group, whereas the apical positions are occupied by the other O atom of the acetate ligand and one O atom of the perchlorate anion.

Introduction. Since the determination of the crystal structure of copper(II) acetate monohydrate (van Niekerk & Schoening, 1953), carboxylate-containing Cu$^{\rm II}$ complexes have been exhaustively investigated from both structural and magnetic viewpoints (Wilkinson, Gillard & McCleverty, 1987; Kato & Muto, 1988). These studies have identified three structural types of carboxylate O-atom coordination, *i.e.* unidentate, chelating and bridging. We are interested in the last coordination mode because our current research work deals with the chemical and structural effects that govern exchange-coupling interactions in polynuclear species (Lloret, Julve, Faus, Solans, Journaux & Morgenstern-Badarau, 1990). In this respect, the ability of simple carboxylates to form bridging ligands is well established (Mehrotra & Bohra, 1983), the most important types being *syn–syn*, *syn–anti* and *anti–anti*.



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It was recently suggested (Folgado, Escrivá, Beltrán-Porter, Fuertes & Miravitlles, 1987) that the $[Cu(terpy)(CH_3COO)]^+$ complex as a perchlorate salt is a dimer, on the basis of analytical, IR and ESR data. However, the lack of structural data does not allow unambiguous assignment of a dimeric structure. We have been able to grow single crystals of this compound and its structure, which is reported herein, shows that it is a monomer.

Experimental. The starting products were pure reagents and used as received. 0.25 mmol of terpy dissolved in a minimum amount of methanol was added with stirring to a warm methanolic solution (50 ml) of 0.25 mmol of $Cu(CH_3COO)_2{\cdot}H_2O$. 0.25 mmol of $NaClO_4$ as a solid were added to the resulting blue–green solution and polyhedral blue crystals were obtained as product by slow evaporation at room temperature. Analytical data (C, H, N and Cl) support the formula $[Cu(C_{15}H_{11}N_3)(CH_3COO)(ClO_4)]$.

A prismatic blue crystal of dimensions 0.1 × 0.1 × 0.2 mm was selected and mounted on a Philips PW1100 four-circle diffractometer equipped with a graphite monochromator. Accurate cell dimensions were obtained by least-squares refinement of 25 well centred reflections ($8 \le \theta \le 12°$) using Mo $K\alpha$ radiation. Space group $P\bar{1}$ was assumed throughout the structure analysis and was confirmed by successful refinement of the structure. Examination of three standard reflections, monitored every 2 h, showed no systematic loss of intensity during data collection. 1231 reflections were measured in the range $2 \le \theta \le 25°$ ($-16 \le h \le 6$, $-15 \le k \le 15$, $0 \le l \le 12$), using the ω-scan technique, with scan width 0.8° and scan speed 0.03° s^{-1}; 1011 reflections were considered observed [with $I \ge 2.5\sigma(I)$] and used in the determination of the structure. Lorentz and polarization corrections were applied to the intensity data, absorption and extinction corrections being ignored. The structure was solved by direct methods with *MULTAN*11/84 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1984) and refined by full-matrix least-squares methods using *SHELX*76 (Sheldrick, 1976). The function minimized was $\sum w(|F_o| - |F_c|)^2$, where the weighting scheme applied to each observation was $w = [\sigma^2(F_o) + 0.0087|F_c|^2]^{-1}$. All non-H atoms were refined anisotropically. All H atoms were placed in calculated positions and refined with an overall isotropic temperature factor [$U = 0.09$ (1) Å^2] using a riding model for computed atoms. Final $R = 0.062$ and $wR = 0.066$ (257 parameters refined). The largest Δ/σ was 0.1. In the final difference map the maximum and minimum heights were 0.3 and -0.3 e Å^{-3}, respectively. The effect of anomalous dispersion was included for non-H atoms. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99–100, 149). Geometrical calculations were performed with *XANADU* (Roberts & Sheldrick, 1975) and molecular illustrations were drawn with *SCHAKAL* (Keller, 1987). The final atomic coordinates and equivalent isotropic temperature factors for non-H atoms are given in Table 1, and the selected interatomic distances and angles in Table 2.*

Table 1. *Fractional atomic coordinates* (× 10^4; Cu × 10^5) *and equivalent isotropic temperature factors* (Å^2)

$$B_{eq} = (8\pi^2/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cu	25743 (11)	42858 (11)	24288 (12)	2.86 (8)
Cl	1859 (3)	1494 (3)	1902 (4)	3.32 (16)
O(1)	943 (8)	5878 (9)	2878 (10)	3.87 (46)
O(2)	2585 (10)	6487 (10)	3171 (12)	4.87 (54)
O(3)	1323 (10)	2992 (10)	1852 (14)	6.71 (65)
O(4)	1026 (10)	1171 (9)	975 (12)	6.25 (59)
O(5)	1855 (14)	947 (15)	3538 (13)	6.50 (85)
O(6)	3209 (12)	941 (14)	1260 (15)	6.66 (77)
N(1)	2777 (10)	4812 (9)	63 (12)	3.97 (52)
N(2)	4432 (8)	3031 (8)	2020 (10)	2.54 (45)
N(3)	3032 (9)	3195 (9)	4617 (11)	3.06 (50)
C(1)	1319 (12)	6828 (12)	3119 (14)	2.39 (55)
C(2)	307 (14)	8233 (14)	3210 (20)	5.62 (85)
C(3)	1791 (12)	5810 (13)	− 881 (16)	4.42 (67)
C(4)	2058 (14)	6142 (14)	− 2451 (15)	4.38 (74)
C(5)	3374 (12)	5494 (12)	− 3120 (12)	2.89 (56)
C(6)	4357 (9)	4507 (11)	− 2153 (12)	2.28 (50)
C(7)	4023 (9)	4169 (10)	− 581 (12)	2.62 (53)
C(8)	4999 (11)	3094 (10)	561 (12)	2.77 (52)
C(9)	6315 (11)	2222 (11)	242 (16)	3.40 (61)
C(10)	7048 (11)	1317 (12)	1465 (16)	3.34 (66)
C(11)	6468 (12)	1272 (12)	3000 (18)	3.54 (67)
C(12)	5124 (10)	2147 (10)	3283 (13)	2.30 (48)
C(13)	4313 (11)	2252 (10)	4733 (14)	2.98 (56)
C(14)	4753 (13)	1444 (13)	6196 (14)	3.19 (61)
C(15)	3880 (12)	1613 (12)	7455 (13)	3.05 (61)
C(16)	2568 (12)	2567 (11)	7313 (16)	3.92 (66)
C(17)	2138 (11)	3378 (11)	5865 (12)	1.96 (53)

Table 2. *Selected bond distances* (Å) *and angles* (°)

O(1)—Cu	1.932 (8)	O(2)—Cu	2.526 (8)
O(3)—Cu	2.441 (6)	N(1)—Cu	2.019 (11)
N(2)—Cu	1.942 (9)	N(3)—Cu	2.029 (9)
O(2)—Cu—O(1)	57.5 (3)	O(3)—Cu—O(1)	92.1 (3)
O(3)—Cu—O(2)	149.6 (3)	N(1)—Cu—O(1)	98.1 (4)
N(1)—Cu—O(2)	91.4 (3)	N(1)—Cu—O(3)	91.9 (3)
N(2)—Cu—O(1)	164.3 (3)	N(2)—Cu—O(2)	106.9 (3)
N(2)—Cu—O(3)	103.4 (3)	N(2)—Cu—N(1)	79.3 (4)
N(3)—Cu—O(1)	102.9 (4)	N(3)—Cu—O(2)	98.1 (3)
N(3)—Cu—O(3)	89.5 (3)	N(3)—Cu—N(1)	158.9 (4)
N(3)—Cu—N(2)	80.0 (4)		

Discussion. A perspective view of the molecule with the atomic numbering scheme, and a view of the crystal packing in the solid are depicted in Figs. 1 and 2, respectively.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55716 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0532]

The environment of the Cu atom is best described as an elongated and strongly distorted octahedron [O(2)—Cu—O(1) = 57.5 (3)°]. The equatorial plane is composed of the three N atoms of the terpyridine ligand and the O(1) atom of the acetate. The apical positions are occupied by the O(2) atom of the acetate ligand and the O(3) atom from the perchlorate anion. The two N atoms N(1) and N(3) of the terminal pair of pyridine rings in the terpy ligand form bonds of equal length to the Cu^{II} ion [2.019 (11) and 2.029 (9) Å for Cu—N(1) and Cu—N(3), respectively], whereas the N atom N(2) of the central pyridine ring is linked to the metal ion at a significantly shorter distance [1.942 (9) Å for Cu—N(2)]. These structural features result from the geometric constraints of the terpyridine ligand, as previously reported (Anderson, Packard & Wicholas, 1976). The bond distance of the remaining equatorial bond [1.932 (8) Å for Cu—O(1)] is very close to that reported for the parent $[Cu(terpy)(HCOO)(H_2O)]ClO_4$ complex (Folgado, Escrivá, Beltrán-Porter, Fuertes & Miravitlles, 1987). The axial distances are very long [2.526 (8) and 2.441 (6) Å for Cu—O(2) and Cu—O(3), respectively], as expected for apical bond lengths in six-coordinate Cu^{II} complexes. The angles subtended at the ligating atoms are markedly far from the ideal 90 and 180° [158.9 (4), 79.3 (4) and 57.5 (3)° for N(1)—Cu—N(3), N(1)—Cu—N(2) and O(1)—Cu—O(2), respectively]. The constraints of both tridentate terpyridine and chelating acetate ligands are responsible for these structural features. The basal atoms exhibit significant deviations from the mean basal plane and the Cu atom is displaced by 0.13 Å from this plane in the direction of the O(3) atom of the semi-coordinated perchlorate.

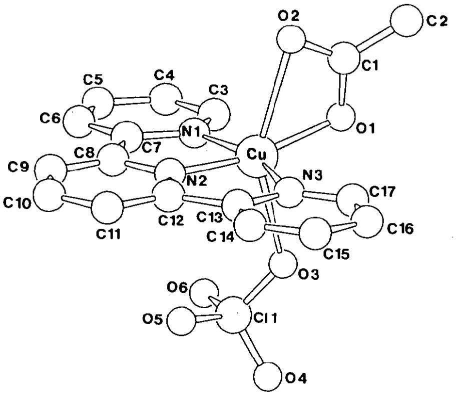

Fig. 1. Molecular structure of the $[Cu(terpy)(CH_3COO)(ClO_4)]$ complex showing the atom numbering.

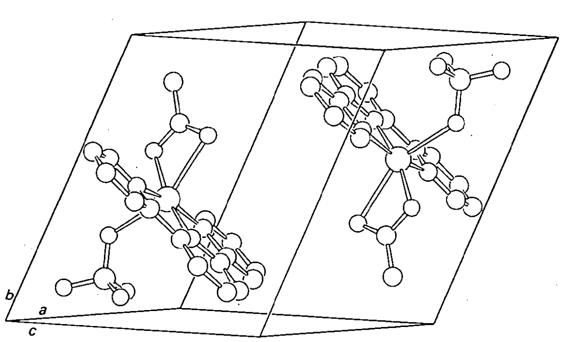

Fig. 2. Packing of the $[Cu(terpy)(CH_3COO)(ClO_4)]$ molecules in the unit cell.

The individual pyridine rings of the terpyridine ligand are planar within ±0.013 Å. However, the ligand as a whole is not planar: the dihedral angles between the middle and outer pyridyl rings are 3.5 and 3.1°. The interatomic distances and angles in the terpy ligand are in agreement with those found in previously described structures of monoterpyridine-containing Cu^{II} complexes (Anderson, Packard & Wicholas, 1976; Rojo, Vlasse & Beltrán-Porter, 1983; Henke, Kremer & Reinen, 1983; Allmann, Kremer & Kucharzcyk, 1984; Rojo, García, Mesa, Vía & Arriortúa, 1988; Folgado, Ibáñez, Coronado, Beltrán, Savariault & Galy, 1988; Solans, Aguiló, Gleizes, Faus, Julve & Verdaguer, 1990; Castro, Faus, Julve & Gleizes, 1991; Aguiló, Solans, Castro, Faus & Julve, 1992). The dihedral angle between the mean basal plane N(1)N(2)N(3)O(1) and the acetate plane O(1)C(1)O(2) is 84.7°.

The acetate group coordinates to the metal ion in an asymmetrical chelating fashion [1.932 (8) and 2.526 (8) Å for Cu—O(1) and Cu—O(2), respectively]. The semi-coordination of the perchlorate anion through O(3) precludes the formation of the corresponding chain of Cu^{II} ions bridged by *syn–anti* acetato groups as observed in $[Cu(dien)(CH_3COO)]ClO_4$ (Towle, Hoffman, Hatfield, Singh & Chaudhuri, 1988) with dien = diethylenetriamine. A similar situation has been reported for related formate-containing Cu^{II} complexes: the axial coordination of a water molecule in $[Cu(terpy)(HCOO)(H_2O)]ClO_4$ (Folgado, Escrivá, Beltrán-Porter, Fuertes & Miravitlles, 1987) precludes the formation of the Cu^{II} chain through the formato bridge in a *syn–anti* fashion as found in [Cu(dien)(HCOO)]HCOO (Davey & Stephens, 1971).

IR data for $[Cu(terpy)(CH_3COO)(ClO_4)]$ support the unidentate coordination of perchlorate and the chelating coordination mode of acetate. The semi-coordination of perchlorate is manifested by the split of ν_3 (1120, 1110 and 1090 cm^{-1}) and ν_4 (615 and 625 cm^{-1}) perchlorate bands (Hathaway, 1987). The ν_{as} (COO) and ν_s (COO) stretching frequencies are located at 1580 and 1400 cm^{-1}, respectively, leading to a $\Delta\nu$ value of 180 cm^{-1} which is consistent with the chelating acetate (Deacon & Phillips, 1980).

This work was partially supported by the CICYT (Spain) (Project PB88-0490). RR acknowledges the Conselleria de Cultura, Educació i Ciència de la Generalitat Valenciana, for a doctoral grant.

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Acta Cryst. (1993). C**49**, 677–680

Structure of $[W_2(\mu\text{-}C_2)\{OC(CH_3)_3\}_6]$: a Dimetallabutadiyne

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(*Received* 21 *January* 1992; *accepted* 13 *October* 1992)

Abstract. (μ-Dicarbido)-hexa(1,1-dimethylethoxy)-ditungsten, $[W_2(C_2)(C_4H_9O)_6]$, $M_r = 830.41$, rhombohedral, $R\bar{3}$, $a = 11.301\,(4)$ Å, $\alpha = 52.93\,(3)°$, $V = 851.40\,(5)$ Å^3, $Z = 1$, $D_x = 1.62$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 71.7$ cm^{-1}, $F(000) = 406$, $T = 223$ K, $R = 0.039$, $wR = 0.055$ for 948 observed $[F_o > 5\sigma(F_o)]$ reflections. The structure of the title compound was determined as part of investigations concerning the presence or absence of π conjugation in metal–carbon multiply bonded complexes. The compound undergoes a destructive phase transition at low temperature, but data collected at 223 K were sufficient for refinement. The molecule exhibits a diyne-like structure, with the W$\equiv$C bond length [1.79 (1) Å] within the range observed for high-oxidation-state alkylidyne complexes. The internal C—C bond is unusually short [1.38 (2) Å] for a single bond, but such shortening has been observed previously in organic diynes. These data are critically compared to those reported for the toluene solvate of the title compound.

Introduction. Molecules and polymers containing conjugated π systems are of current interest in organic chemistry owing to their potential uses in photonics (Prasad & Williams, 1991). A developing facet of this work is the incorporation of transition metals into such molecules, either as pendant groups (Marder, Perry, Tiemann & Schaefer, 1991) or as integral parts of the chain framework (Cayton & Chisholm, 1989; Gilbert & Rogers, 1991). Our interest lies in the latter, and we became interested in those metals for which metal–carbon multiple bonds exist, anticipating that such moieties could be used as templates for conjugated metal–carbon π chains. In an effort to ascertain what types of molecules might

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