Crystal structure of tetra(3-carboxyl-2,2,5,5-tetramethylpyrrolidin-1-oxyl) bis(dimethyl fumarate) bicopper(II) complex, $C_{21}H_{37}CuN_3O_7$

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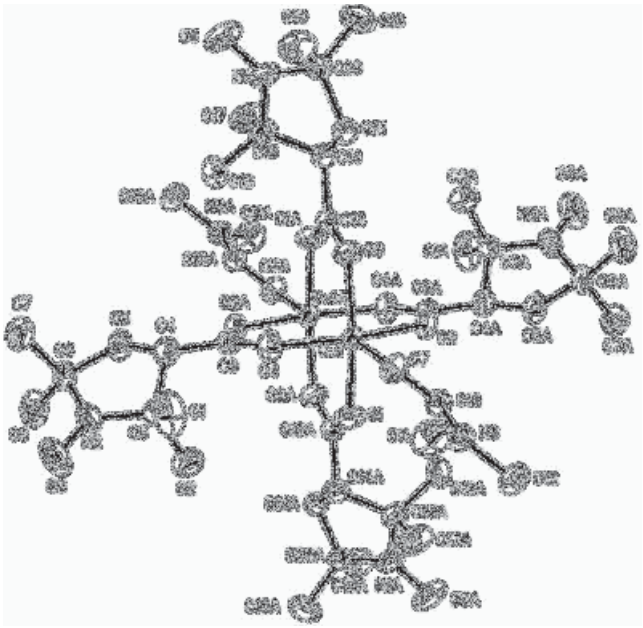

Abstract

$C_{21}H_{37}CuN_3O_7$, triclinic, $P\bar{1}$ (no. 2), a = 10.9210(9) Å, b = 11.626(1) Å, c = 12.038(1) Å, α = 85.588(2)°, β = 72.209(2)°, γ = 64.942(2)°, V = 1315.9 Å^3, Z = 2, $R_{gt}(F)$ = 0.0468, $wR_{ref}(F^2)$ = 0.1340, T = 296 K.

Table 1. Data collection and handling.

Crystal:	green prisms, size 0.20×0.30×0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	8.71 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	15419, 4591
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4168
$N(param)_{refined}$:	290
Programs:	SHELX [13]

Source of material

4-oxo-2,2,6,6-tetramethylpiperdin-1-oxyl **I** can be conveniently obtained by procedures given in the literature [1].The reaction of **I** with concentrated hydrochloric acid gave the isolable intermediate l-hydroxy-4-oxo-2,2,6,6-tetramethylpiperidine hydrochloride **II** which then was brominated to the 3-bromo-l-hydroxy-4-oxo-2,2,6,6-tetramethylpiperidine derivative which, in turn, was converted in situ to the corresponding radical **III** by oxidation using sodium nitrite. Compound **III** (25 g, 0.1 mmol) was added, portionwise, to a stirred solution of sodium hydroxide (8 g, 0.2mol) in water (150 mL). The reaction mixture was stirred for 3 h at about 20°C, acidified with 6 mol/L aqueous HC1 solution to pH 2, and quickly extracted with chloroform (3 × 80 mL). The organic layer was dried with anhydrous magnesium sulfate. After removal of the solvent in a rotating evaporator, the residue was recrystallized from a mixture of chloroform and hexane (3/1, *v*/*v*) to give 14.8 g (79.5%) of the yellow product **IV**.

A solution of HCTemPO (372 mg, 2 mmol) in water (10 mL) was dropped slowly into CuO (80 mg, 1 mmol) in water (5 mL). The mixed solution was stirred for 1 h at 70°C and was then cooled to room temperature to give green microcrystals.Crystals suitable for X-ray analysis were obtained by recrystallization DMF and water (1:1). m.p. 230-232, dec.; **Elemental analysis** found: C, 49.47 %; H, 7.56 %; N, 8.43 % ; calculated for $C_{42}H_{74}Cu_2N_6O_{14}$: C, 49.75 %; H, 7.35 %; N, 8.28 %.

Discussion

The study of transition metal complexes with four carboxylate bridges (so-called "paddle-wheel") was stimulated by the antiferromagnetic properties of binuclear cupric acetate hydrate due to spin–spin interaction through the bridging carboxylate groups without Cu–Cu bonding (Cu–Cu 2.64 Å) [2, 3]. The analogous carboxylate complexes of other 3*d*-metals were prepared lately with using of steric effects of axial ligands: alpha-substituted pyridines (2-picoline, 2,6-lutidine, acridine or *N,N*-dimethylformamide) or cyclopentadienyl groups [4-7]. As part of studies of copper(II) carboxylates of this type, we report the crystal structure of $[Cu_2(CTemPO)_4(DMF)_2]$ complex. The title crystal structure consists of molecules with two Cu atoms linked by four CTemPO groups in a fashion similar to that of $[Cu_2(Indo)_4(DMF)_2]\cdot 1.6DMF$ [8] and of $Cu_2(C_3H_7NO)_2(C_7H_4ClO_2)_4$ [7]. The coordination of each Cu(II) ion is a distorted tetragonal pyramid. The Addison's criterion, which is 1 for an ideal trigonal bipyramid and 0 for an ideal tetragonal pyramid, respectively [9], has a value of 0.016 for the title moiety. The longer ($Cu1–O7_{DMF}$ = 2.125(2) Å) distance is viewed at the apical position. The Cu1 atom deviates by 0.2049 Å from the basal plane formed by the O1, O2, O3 and O4 atoms. A DMF molecule is bound trans to the Cu1–Cu1A vector on each of the Cu atoms, and a further two DMF molecules are loosely held in the lattice. These lattice DMF sites were highly mobile, and their sites were only partially occupied. During the data collection, some reductions in the intensities of the standard reflections were noted, and these are consistent with slow loss of these molecules of crystallization. The fused and conjugated five-membered rings are close to being planar (deviations less than 0.2339 Å), and the molecule makes no close contacts with other molecules in the structure. The two copper atoms in each dimeric unit are separated by a distance of

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2.6422(6) Å. This distance is similar to that found in $Cu_2(C_3H_7NO)_2(C_7H_4ClO_2)_4$ (2.6419(7) Å) and other Cu carboxylate dimers [9-10] and slightly longer than that found in $[Cu_2(\mu\text{-}OAc)_4(PhNHpy)_2]$ complex (2.45-2.50 Å) [11]. The distances of nitroxyl N1–O5 and N2–O6 are 1.273(4) Å and 1.266(4) Å, respectively. This distance is similar to that found in $Rh_2(O_2CCF_3)_4(Tempol)_2$ (Tempol = 2,2,6,6-tetramethyl-4-hydroxypiperidinyl- 1-oxy)(1.282(4) Å)[12].

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(21A)	2*i*	1.1151	0.8482	0.2623	0.067
H(21B)	2*i*	1.0301	0.8946	0.3944	0.067
H(10A)	2*i*	1.3953	0.3577	0.5222	0.058
H(5A)	2*i*	0.5627	0.6463	0.7944	0.076
H(5B)	2*i*	0.5169	0.7902	0.7651	0.076
H(14A)	2*i*	0.9548	0.7882	0.2379	0.070
H(4A)	2*i*	0.7088	0.7957	0.7841	0.071
H(7A)	2*i*	0.3584	0.9304	1.0468	0.118
H(7B)	2*i*	0.3358	0.9412	0.9232	0.118
H(7C)	2*i*	0.4703	0.9484	0.9377	0.118
H(8A)	2*i*	0.3417	0.7330	1.0790	0.139
H(8B)	2*i*	0.4399	0.6135	0.9918	0.139
H(8C)	2*i*	0.3161	0.7266	0.9588	0.139

Table 2. continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(19A)	2*i*	0.9196	1.1194	0.4245	0.120
H(19B)	2*i*	0.8780	1.2091	0.3253	0.120
H(19C)	2*i*	1.0381	1.1257	0.3142	0.120
H(18A)	2*i*	0.9262	1.1172	0.1295	0.140
H(18B)	2*i*	0.9605	0.9733	0.1122	0.140
H(18C)	2*i*	1.0797	1.0127	0.1168	0.140
H(16A)	2*i*	0.6207	0.9846	0.5165	0.139
H(16B)	2*i*	0.7717	0.9493	0.5278	0.139
H(16C)	2*i*	0.7227	0.8418	0.5214	0.139
H(12A)	2*i*	1.6014	0.2338	0.5550	0.120
H(12B)	2*i*	1.5964	0.2526	0.6841	0.120
H(12C)	2*i*	1.6787	0.3100	0.5826	0.120
H(17A)	2*i*	0.7225	0.8853	0.2204	0.149
H(17B)	2*i*	0.5915	0.9632	0.3263	0.149
H(17C)	2*i*	0.6730	0.8155	0.3299	0.149
H(11A)	2*i*	1.3577	0.5782	0.7086	0.131
H(11B)	2*i*	1.5219	0.5306	0.6815	0.131
H(11C)	2*i*	1.4386	0.4739	0.7829	0.131
H(2A)	2*i*	0.8317	0.4942	0.9812	0.166
H(2B)	2*i*	0.8978	0.4827	0.8450	0.166
H(2C)	2*i*	0.7458	0.4873	0.9008	0.166
H(1A)	2*i*	0.8619	0.6826	1.0034	0.154
H(1B)	2*i*	0.7936	0.8060	0.9405	0.154
H(1C)	2*i*	0.9284	0.6894	0.8691	0.154

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	2*i*	1.09833(3)	0.51683(3)	0.52985(3)	0.0329(2)	0.0419(2)	0.0451(2)	–0.0136(2)	–0.0140(2)	0.0029(1)
O(1)	2*i*	1.1074(3)	0.3617(2)	0.6119(2)	0.063(1)	0.059(1)	0.081(2)	–0.032(1)	–0.039(1)	0.029(1)
O(3)	2*i*	1.0579(2)	0.6688(2)	0.4385(2)	0.053(1)	0.051(1)	0.069(1)	–0.023(1)	–0.027(1)	0.015(1)
O(4)	2*i*	0.9423(2)	0.6189(2)	0.6638(2)	0.044(1)	0.077(2)	0.056(1)	–0.020(1)	–0.011(1)	–0.015(1)
O(2)	2*i*	1.2239(2)	0.4127(2)	0.3836(2)	0.040(1)	0.064(1)	0.054(1)	–0.014(1)	–0.0095(9)	–0.012(1)
O(7)	2*i*	1.2655(2)	0.5211(2)	0.5828(2)	0.047(1)	0.055(1)	0.072(2)	–0.019(1)	–0.029(1)	0.002(1)
N(3)	2*i*	1.4683(3)	0.4090(3)	0.6262(2)	0.046(1)	0.060(2)	0.060(2)	–0.022(1)	–0.025(1)	0.008(1)
C(13)	2*i*	0.9644(3)	0.6988(3)	0.3890(3)	0.042(2)	0.046(2)	0.055(2)	–0.016(1)	–0.011(1)	0.008(1)
N(2)	2*i*	0.6045(3)	0.7197(3)	0.9918(2)	0.057(2)	0.094(2)	0.044(2)	–0.025(2)	–0.008(1)	0.004(1)
C(9)	2*i*	0.8186(3)	0.6301(3)	0.6825(3)	0.044(2)	0.054(2)	0.046(2)	–0.013(1)	–0.015(1)	0.001(1)
C(3)	2*i*	0.7475(3)	0.6620(3)	0.9062(3)	0.046(2)	0.062(2)	0.047(2)	–0.019(1)	–0.013(1)	0.005(1)
C(20)	2*i*	0.9404(4)	1.0220(3)	0.2803(3)	0.058(2)	0.052(2)	0.053(2)	–0.026(2)	–0.021(1)	0.013(1)
N(1)	2*i*	0.7940(3)	1.0307(3)	0.3199(3)	0.057(2)	0.044(1)	0.090(2)	–0.014(1)	–0.036(2)	0.018(1)
C(21)	2*i*	1.0210(3)	0.8894(3)	0.3174(3)	0.046(2)	0.057(2)	0.062(2)	–0.022(1)	–0.015(1)	0.013(2)
O(5)	2*i*	0.6855(3)	1.1349(3)	0.3247(4)	0.077(2)	0.062(2)	0.161(3)	–0.018(2)	–0.061(2)	0.033(2)
C(10)	2*i*	1.3763(3)	0.4244(3)	0.5722(3)	0.047(2)	0.053(2)	0.052(2)	–0.024(1)	–0.018(1)	0.002(1)
C(6)	2*i*	0.4855(3)	0.7660(3)	0.9424(3)	0.042(2)	0.062(2)	0.059(2)	–0.019(1)	–0.006(1)	–0.006(2)
C(15)	2*i*	0.7797(4)	0.9120(3)	0.3591(3)	0.049(2)	0.054(2)	0.079(2)	–0.021(2)	–0.027(2)	0.016(2)
O(6)	2*i*	0.5860(4)	0.7292(5)	1.1004(3)	0.087(2)	0.206(4)	0.045(2)	–0.042(3)	–0.011(2)	0.006(2)
C(5)	2*i*	0.5628(3)	0.7259(4)	0.8133(3)	0.043(2)	0.075(2)	0.063(2)	–0.015(2)	–0.015(2)	–0.012(2)
C(14)	2*i*	0.9338(4)	0.8162(3)	0.3190(3)	0.053(2)	0.055(2)	0.064(2)	–0.021(2)	–0.017(2)	0.014(2)
C(4)	2*i*	0.7107(4)	0.7104(3)	0.7924(3)	0.050(2)	0.065(2)	0.055(2)	–0.016(2)	–0.014(2)	–0.004(2)
C(7)	2*i*	0.4051(5)	0.9098(4)	0.9646(4)	0.072(2)	0.066(2)	0.084(3)	–0.021(2)	–0.012(2)	–0.011(2)
C(8)	2*i*	0.3868(5)	0.7042(5)	0.9980(5)	0.064(2)	0.085(3)	0.116(4)	–0.038(2)	0.004(2)	–0.007(3)
C(19)	2*i*	0.9444(5)	1.1289(4)	0.3417(4)	0.097(3)	0.068(2)	0.096(3)	–0.042(2)	–0.047(3)	0.011(2)
C(18)	2*i*	0.9804(6)	1.0323(5)	0.1472(4)	0.120(4)	0.093(3)	0.062(3)	–0.047(3)	–0.022(2)	0.023(2)
C(16)	2*i*	0.7178(5)	0.9230(4)	0.4940(4)	0.077(3)	0.078(3)	0.081(3)	–0.018(2)	0.011(2)	0.006(2)
C(12)	2*i*	1.5973(4)	0.2912(4)	0.6107(4)	0.053(2)	0.080(3)	0.099(3)	–0.016(2)	–0.032(2)	0.017(2)
C(17)	2*i*	0.6829(5)	0.8922(5)	0.3039(5)	0.085(3)	0.088(3)	0.159(5)	–0.048(3)	–0.075(3)	0.051(3)
C(11)	2*i*	1.4447(5)	0.5058(4)	0.7063(4)	0.099(3)	0.092(3)	0.091(3)	–0.039(3)	–0.054(3)	–0.004(2)
C(2)	2*i*	0.8116(5)	0.5184(5)	0.9085(5)	0.082(3)	0.081(3)	0.125(4)	–0.014(2)	–0.011(3)	0.046(3)
C(1)	2*i*	0.8414(5)	0.7148(6)	0.9322(5)	0.072(3)	0.150(5)	0.091(3)	–0.049(3)	–0.017(2)	–0.037(3)

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