Inorganica Chimica Acta, *191* (1992) 213–219

Polynuclear complexes of copper(II). Synthesis, characterization, crystal and molecular structure of the cations bis[oxamidate-*N,N*'-dipropylamine-2,2'-dimethyl-*N,N*',N_1,N_1'-copper(II)]copper(II) ($[CuN_4CuO_4CuN_4]^{2+}$) and bis[oxamidate-*N,N*'-dipropylamine-2,2'-dimethyl-*N,N*',N_1,N_1'-copper(II)]dicopper(II)-*O*,O_1,O_2,N_1,N_2-μ-(oxamidate-*N,N*'-dipropylamine-2,2'-dimethyl-*N,N*',*O*,N_1,N_1',O_1) ($[CuN_4(CuN_2O_3)_2CuN_4]^{2+}$) packed in the same crystal as their tetranitrate dihydrate salts

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(Received July 15, 1991; revised September 24, 1991)

Abstract

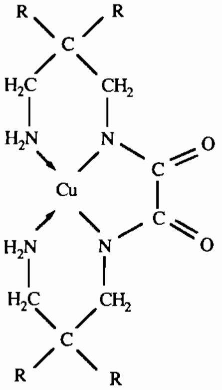
The product of the reaction between copper(II) nitrate and oxamidate-*N,N*'-dipropylamine-2-2'-dimethyl-*N,N*',N_1,N_1'-copper(II) was isolated and characterized by crystallographic and spectroscopic measurements. The title compound crystallizes in the triclinic space group $P\bar{1}$ with cell dimensions $a=12.426(1)$, $b=13.405(1)$, $c=15.605(2)$ Å, $\alpha=102.35(1)$, $\beta=105.34(1)$, $\gamma=113.74(1)°$, $Z=1$. The crystal consists of tricopper and tetracopper dications packed together in a 1:1 ratio and placed around inversion centres. The tricopper cation contains a central CuO_4 and two outer CuN_4 square units; the copper in the CuN_4 units exhibits a fifth interaction with a nitrate oxygen. The tetracopper cation contains two inner square pyramidal CuN_2O_3 units and two outer CuN_4 square units weakly bound to a fifth nitrate oxygen. The oxamidate ligands exhibit two different conformations and act as hexadentate ligands, with four N donor atoms and two O donor atoms.

Introduction

Oxamidate–copper(II) derivatives have been investigated in the last few years as versatile ligands which can yield dinuclear and polynuclear complexes [1–3]. The neutral planar 1:1 complex between Cu^{2+} and oxamidate dianions [CuN_4] was used as a dioxygen donor to build up polynuclear complexes.

In previous papers [4, 5] we reported the correlation between the stereochemistry and the magnetic and spectral properties of binuclear copper–copper and trinuclear copper–nickel–copper complexes with the oxamidate-*N,N*'-dipropylamine-2,2'-dimethyl dianion.

As a continuation of these studies we have investigated the formation of the complex between [CuN_4] and copper nitrate. A trimeric complex was expected in which a third copper(II) cation was captured between two [CuN_4] molecules. We obtained beautiful blue crystals, but their elemental analysis did not match with the expected formula. In order to obtain a clear insight into the molecular nature of the crystals we undertook



($R=H$, CH_3)

[CuN_4]

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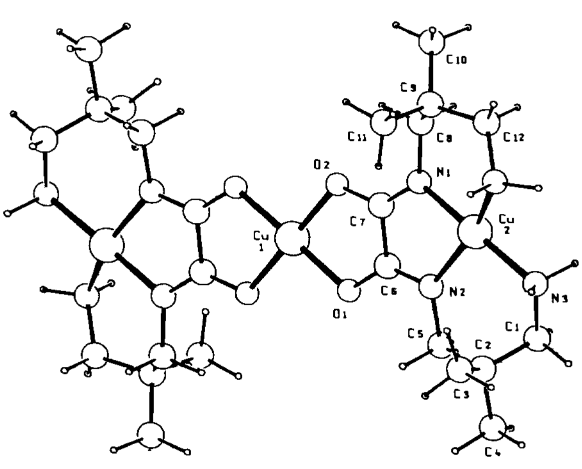


Fig. 1. Perspective drawing of the tricopper $[CuN_4CuO_4CuN_4]^{2+}$ dication. Bond distances around the copper atoms are as follows: Cu1–O1, 1.939(4); Cu1–O2, 1.911(3); Cu2–N1, 1.969(5); Cu2–N2, 1.985(4); Cu2–N3, 1.992(6); Cu2–N4, 1.993(4).

a complete X-ray diffraction study and found that the crystals consist of a 1:1 adduct of two dications: the expected $[CuN_4CuO_4CuN_4]^{2+}$ (Fig. 1) and an unexpected $[CuN_4(CuN_2O_3)_2CuN_4]^{2+}$ (Fig. 2).

The overall reaction stoichiometry can be schematized as follows:

$$5[CuN_4]+2Cu^{2+} \longrightarrow [CuN_4CuO_4CuN_4]^{2+}+[CuN_4(CuN_2O_3)_2CuN_4]^{2+}$$

Experimental

Synthesis

Copper(II) nitrate was used as the commercially available compound. The complex was obtained by a two-step reaction: (i) preparation of oxamidate-*N*,*N*′-dipropylamine-2,2′-dimethyl-*N*,*N*′,*N*$_1$,*N*$_1$′-copper(II) $[CuN_4]$ according to ref. 6, modified by ref. 7; (ii) reaction of $[CuN_4]$ with $Cu(NO_3)_2 \cdot 3H_2O$.

1 mol of diethyloxalate in 140 ml of absolute ethanol was reacted at 0 °C with 2 mol of 2,2-dimethyl-1,3-propanediamine in 240 ml of ethanol. The mixture was kept at 100 °C for 30 min. A solution of 1 mol $CuSO_4 \cdot 5H_2O$ in 5 ml of water was added to the previous solution and the mixture was treated with 2 mol of NaOH in 50 ml of water. A violet precipitate was formed, which was filtered and washed with water. A suspension of the compound in water was then dissolved in the minimum amount of CH_3COOH; a solution (0.1 M) of NaOH was added until the violet solution turned red; slowly a precipitate of $[CuN_4]$ was formed. *Anal.* Calc. for $C_{12}H_{24}N_4O_2Cu$: C, 45.06; H, 7.56; N, 17.51; Found: C, 45.76; H, 7.64; N, 17.41%.

1 mmol of the precipitate suspended in water (pH = 8.14) was treated under stirring with 0.5 mmol of $Cu(NO_3)_2 \cdot 3H_2O$ (pH = 4.45) dissolved in 15 ml of water. A filtration was done in order to eliminate the opacity of the solution. A very slow evaporation of the resultant blue solution (pH = 7.04) gave pale blue crystals suitable for X-ray experiments. *Anal.* Calc. for $C_{60}H_{124}Cu_7N_{24}O_{24}$: C, 35.84; H, 6.12; N, 16.72. Found: C, 35.75; H, 6.27; N, 16.62%. Carbon, hydrogen and nitrogen were determined with a Carlo Erba 1106 elemental analyzer.

Crystallography

Crystal data and experimental details are summarized in Table 1. The diffraction experiment was carried out on Enraf-Nonius diffractometer at room temperature using Mo Kα radiation.

The structure was solved by direct methods, which afforded the positions of the metal atoms; all the remaining non-hydrogen atoms were located by subsequent difference-Fourier syntheses. The refinement was carried out by full matrix least-squares calculations comprising the atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms. All the hydrogen atoms were placed in calculated positions (C–H = 1.05 Å) and allowed to ride with respect to their carrier atoms; their thermal factors were kept constant ($U = 0.1$ Å^2). The final difference Fourier map showed a maximum peak of residual electron density of about 0.4 e Å^{-3}. The SHELX package of crystallographic programs was used for the computations [8]. Absorption corrections were made according to Walker and Stuart [9]. Atomic coordinates of the non-hydrogen atoms are listed in Table 2. Relevant interatomic distances and bond angles are reported in Table 3. See also 'Supplementary material.'

Spectral measurements

The IR spectra were recorded in the solid state with a Bruker 113r FT-IR spectrophotometer. The spectra in the 4000–400 cm^{-1} range were measured in KBr discs; in the 400–50 cm^{-1} range they were measured in polyethylene discs. Atmospheric water was removed by flushing with dry nitrogen.

The electronic spectrum of the solid compound was recorded as a mull transmission spectrum with a Cary 2300 Varian spectrometer.

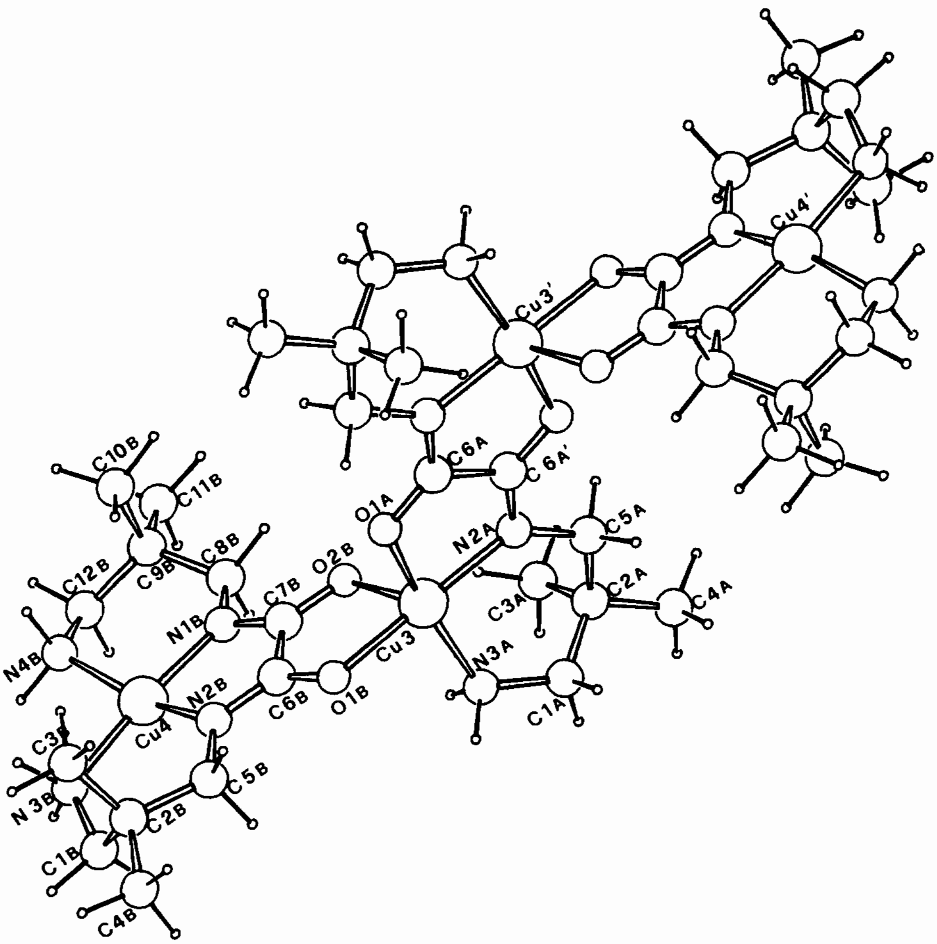


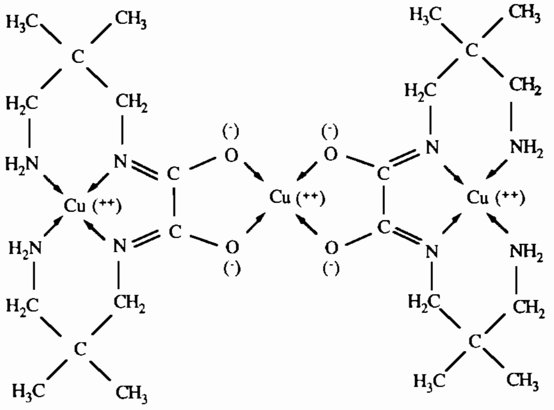
Fig. 2. Perspective drawing of the tetracopper $[CuN_4(CuN_2O_3)_2CuN_4]^{2+}$ dication. Bond distances around the copper atoms are as follows: Cu3–O1A, 1.982(5); Cu3–N2A, 1.977(5); Cu3–N3A, 1.986(7); Cu3–O1B, 2.005(4); Cu3–O2B, 2.244(5); Cu4–N1B, 1.941(5); Cu4–N2B, 1.962(6); Cu4–N3B, 1.992(5); Cu4–N4B, 2.023(7).

Results and discussion

The triclinic unit cell contains a trinuclear dication $[CuN_4CuO_4CuN_4]^{2+}$ and a tetranuclear dication $[CuN_4(CuN_2O_3)_2CuN_4]^{2+}$ both located around inversion centres, four nitrate anions and two lattice water molecules. The water molecules are engaged in hydrogen bonds to the aminic hydrogens, and the nitrate anions play a role as weakly bonded ligands (see later).

The oxamidate ligands, N-functionalized by the aminic residues $-CH_2C(CH_3)_2CH_2NH_2$, can adopt, by rotation around the central C–C bond, two different conformations described hereafter as *cis* and *trans* (see structural diagrams). The former is found in $[CuN_4]$ and is present in both cations; the latter has been observed in the tetranuclear dication (see later).

The trinuclear cation $[CuN_4CuO_4CuN_4]^{2+}$ consists of two $[CuN_4]$ units coordinated to a third Cu(II) cation through two negatively charged oxygen atoms from each oxamidate ligand.



Structural diagram of $[CuN_4CuO_4CuN_4]^{2+}$, ligand in the *cis* conformation.

The central copper in this cation, Cu(1) (see Fig. 1), sits on an inversion centre. The atoms in the oxamidate skeleton and the copper ions are coplanar (maximum

TABLE 1. Crystal data and experimental details for $[Cu_3(C_{12}H_{24}N_4O_2)_2][Cu_4C_{12}H_{24}N_4O_2)_3](NO_3)_4 \cdot 2H_2O$

Formula	$C_{60}H_{124}N_{24}O_{24}Cu_7$
M_r (amu)	2010.6
Crystal system	triclinic
Space group	$P\bar{1}$ (No. 2)
a (Å)	12.426(1)
b (Å)	13.405(1)
c (Å)	15.605(2)
α (°)	102.35(1)
β (°)	105.34(1)
γ (°)	113.74(1)
V (Å^3)	2138.1(5)
Z	1
D_{calc} (g cm^{-3})	1.56
μ(Mo Kα) (cm^{-1})	17.9
$F(000)$	1047
Crystal dimensions (mm)	0.2×0.3×0.2
Crystal colour	blue
Scan mode	ω–2θ
θ-range (°)	2–26
Octants of reciprocal space explored	$\pm h$, $\pm k$, l
Scan width (°)	$0.8+0.35\text{tg}\theta$
Prescan speed (° min^{-1})	5.49
Prescan acceptance, $\sigma(I)/I$	0.333
Maximum scan time (s)	60
Requested, $\sigma(I)/I$	0.03
Data collected	8724
Observed unique reflections ($I>2\sigma(I)$)	3226
Parameters refined	190
R,R_w (%)	3.5, 3.6
k, g[a]	1.26, 4×10^{-4}
Residual electron density (e Å^{-3})	0.4
Transmission factor range	68–100

[a] The weighting scheme employed was $w=k/[\sigma^2(F)+|g|F^2]$, where both k and g were independently determined.

deviation from the average plane 0.01 Å). The Cu···Cu contact is 5.190(1) Å. The Cu(2) atoms show tetrahedral-like deviations from planarity (N(1)–Cu(2)–N(3) 173.1(2)°, N(2)–Cu(2)–N(4) 157.1(2)°) generated by steric interferences among the hydrogen atoms belonging to the outer NH_2 groups (N(3) and N(4)). The same kind of effect was observed in the recently reported structure of $[CuN_4NiO_6CuN_4]^{2+}$ [7]. The two six-membered rings incorporating the Cu(2) atoms have similar half chair conformations and the axial CH_3 groups (C(3) and C(11)) stick out from the same side of the coordination plane. Neglecting the just cited deviations from planarity of the CuN_4 units, an idealized mirror plane, containing the copper atoms and perpendicular to the plane of the donor atoms, bisects the cation so that the overall molecular symmetry can be approximated as C_{2h}. The coordination around Cu(2) and Cu(2)′ is completed by the interaction with a nitrate oxygen (O(2N)···Cu(2) 2.47(1) Å) approaching the metal atoms from the side not hindered by the methyl groups. Some average bond distances are: Cu(1)–O,

TABLE 2. Fractional atomic coordinates

	x	y	z
Cu1	0.0	0.0	0.0
Cu2	0.13572(8)	−0.06452(6)	0.31896(5)
N1	0.1918(4)	0.0587(4)	0.2656(3)
C1	0.0065(7)	−0.3205(5)	0.2896(5)
C2	−0.1123(6)	−0.3382(5)	0.2151(4)
C3	−0.1822(7)	−0.2900(7)	0.2639(6)
C4	−0.2023(7)	−0.4699(5)	0.1588(5)
C5	−0.0842(6)	−0.2828(5)	0.1426(4)
N2	0.0117(4)	−0.1590(3)	0.1850(3)
C6	0.0178(5)	−0.0973(4)	0.1317(4)
O1	−0.0535(3)	−0.1296(3)	0.0442(2)
O2	0.1296(3)	0.0902(3)	0.1258(2)
C7	0.1220(5)	0.0280(5)	0.1790(4)
N3	0.0876(5)	−0.1984(4)	0.3640(3)
C8	0.3040(6)	0.1759(5)	0.3179(4)
C9	0.3045(6)	0.2350(5)	0.4137(4)
C10	0.4260(8)	0.3539(6)	0.4610(5)
C11	0.1911(8)	0.2543(7)	0.3967(6)
C12	0.3177(7)	0.1688(6)	0.4803(5)
N4	0.2086(5)	0.0512(4)	0.4507(3)
Cu3	−0.00788(8)	−0.35019(7)	0.91692(6)
O1A	0.1198(4)	−0.3621(3)	1.0155(3)
C6A	0.0696(6)	−0.4571(5)	1.0286(4)
N2A	−0.1243(5)	−0.5059(4)	0.9125(4)
C5A	−0.2632(6)	−0.5806(6)	0.8581(6)
C2A	−0.3208(6)	−0.5381(5)	0.7878(5)
C3A	−0.2832(8)	−0.5592(7)	0.7015(5)
C4A	−0.4662(7)	−0.6116(7)	0.7473(6)
C1A	−0.2826(6)	−0.4118(6)	0.8252(6)
N3A	−0.1504(5)	−0.3281(4)	0.8474(4)
Cu4	0.30499(8)	−0.08562(7)	0.77744(6)
N1B	0.1891(5)	−0.2509(4)	0.7415(4)
C1B	0.3823(8)	0.1645(6)	0.8753(5)
C2B	0.3970(6)	0.1469(5)	0.9703(5)
C3B	0.5236(7)	0.1491(6)	1.0141(5)
C4B	0.3984(7)	0.2510(6)	1.0376(6)
C5B	0.2842(6)	0.0368(5)	0.9612(5)
N2B	0.2529(4)	−0.0691(4)	0.8856(3)
C6B	0.1712(6)	−0.1683(5)	0.8838(5)
O1B	0.1181(4)	−0.1845(3)	0.9435(3)
O2B	0.0480(4)	−0.3725(3)	0.7916(3)
C7B	0.1308(6)	−0.2753(5)	0.7988(4)
N3B	0.4066(6)	0.0857(4)	0.8088(4)
C8B	0.1506(7)	−0.3457(6)	0.6537(5)
C9B	0.2571(7)	−0.3360(6)	0.6215(5)
C10B	0.3575(8)	−0.3473(7)	0.6959(6)
C11B	0.2012(9)	−0.4372(7)	0.5266(6)
C12B	0.3235(7)	−0.2229(6)	0.6057(5)
N4B	0.3951(5)	−0.1151(4)	0.6923(4)
N1N	−0.3967(7)	0.1076(5)	0.6268(4)
O1N	−0.3625(5)	0.1478(5)	0.5698(4)
O2N	−0.3322(5)	0.0729(5)	0.6762(4)
O3N	−0.4968(6)	0.0982(5)	0.6356(4)
N2N	0.1037(9)	0.9461(8)	0.6048(7)
O4N	0.0114(8)	0.8940(8)	0.5246(5)
O5N	0.2036(8)	0.9538(8)	0.6085(5)
O6N	0.0906(7)	0.9897(7)	0.6754(6)
O1W	0.6627(6)	0.0862(6)	0.8566(4)

TABLE 3. Relevant interatomic distances (Å) and bond angles (°)

Cu1–O1	1.939(4)
Cu1–O2	1.911(3)
Cu2–N1	1.969(5)
Cu2–N2	1.985(4)
Cu2–N3	1.992(6)
Cu2–N4	1.993(4)
N1–C7	1.266(7)
N1–C8	1.470(6)
C1–C2	1.51(1)
C1–N3	1.510(7)
C2–C3	1.53(1)
C2–C4	1.539(7)
C2–C5	1.52(1)
C5–N2	1.461(6)
N2–C6	1.288(9)
C6–O1	1.280(6)
C6–C7	1.502(6)
O2–C7	1.290(8)
C8–C9	1.53(1)
C9–C10	1.528(8)
C9–C11	1.50(1)
C9–C12	1.52(1)
C12–N4	1.475(8)
Cu3–O1A	1.982(5)
Cu3–N2A	1.977(5)
Cu3–N3A	1.986(7)
Cu3–O1B	2.005(4)
Cu3–O2B	2.244(5)
O1A–C6A	1.262(9)
N2A–C5A	1.474(8)
C5A–C2A	1.49(1)
C2A–C3A	1.54(1)
C2A–C4A	1.53(1)
C2A–C1A	1.49(1)
C1A–N3A	1.457(9)
Cu4–N1B	1.941(5)
Cu4–N2B	1.962(6)
Cu4–N3B	1.992(5)
Cu4–N4B	2.023(7)
N1B–C7B	1.31(1)
N1B–C8B	1.463(9)
C1B–C2B	1.53(1)
C1B–N3B	1.50(1)
C2B–C3B	1.53(1)
C2B–C4B	1.55(1)
C2B–C5B	1.518(9)
C5B–N2B	1.467(9)
N2B–C6B	1.297(8)
C6B–O1B	1.28(1)
C6B–C7B	1.524(9)
O2B–C7B	1.251(7)
C8B–C9B	1.50(1)
C9B–C10B	1.55(1)
C9B–C11B	1.53(1)
C9B–C12B	1.52(1)
C12B–N4B	1.483(8)
N1N–O1N	1.22(1)
N1N–O2N	1.26(1)
N1N–O3N	1.25(1)
N2N–O4N	1.26(1)
N2N–O5N	1.19(1)

(*continued*)

TABLE 3. (*continued*)

N2N–O6N	1.21(1)
O2N....Cu2	2.47(1)
O5N....Cu4	2.06(1)
O1W....H12B	2.06(1)
O1–Cu1–O2	86.4(1)
N3–Cu2–N4	92.0(2)
N2–Cu2–N4	157.1(2)
N2–Cu2–N3	95.0(2)
N1–Cu2–N4	92.7(2)
N1–Cu2–N3	173.1(2)
N1–Cu2–N2	82.5(2)
Cu2–N1–C8	125.2(4)
Cu2–N1–C7	113.5(4)
C7–N1–C8	121.3(5)
C2–C1–N3	114.0(6)
C1–C2–C5	112.8(6)
C1–C2–C4	109.2(6)
C1–C2–C3	109.6(6)
C4–C2–C5	106.5(5)
C3–C2–C5	110.4(6)
C3–C2–C4	108.2(6)
C2–C5–N2	113.9(5)
Cu2–N2–C5	129.3(3)
C5–N2–C6	118.3(5)
Cu2–N2–C6	112.4(4)
N2–C6–C7	115.4(5)
N2–C6–O1	128.1(5)
O1–C6–C7	116.5(5)
Cu1–O1–C6	110.3(3)
Cu1–O2–C7	111.1(3)
C6–C7–O2	115.8(5)
N1–C7–O2	128.4(5)
N1–C7–C6	115.8(5)
Cu2–N3–C1	117.9(4)
N1–C8–C9	111.6(6)
C8–C9–C12	111.2(6)
C8–C9–C11	109.5(6)
C8–C9–C10	106.4(6)
C11–C9–C12	115.0(7)
C10–C9–C12	105.6(6)
C10–C9–C11	108.6(6)
C9–C12–N4	115.7(5)
Cu2–N4–C12	120.8(4)
O1B–Cu3–O2B	78.9(1)
N3A–Cu3–O2B	92.0(2)
N3A–Cu3–O1B	90.5(2)
N2A–Cu3–O2B	109.1(2)
N2A–Cu3–O1B	171.0(2)
N2A–Cu3–N3A	93.3(2)
O1A–Cu3–O2B	103.7(2)
O1A–Cu3–O1B	91.1(2)
O1A–Cu3–N3A	164.2(2)
O1A–Cu3–N2A	83.0(2)
Cu3–O1A–C6A	111.0(4)
Cu3–N2A–C5A	129.7(5)
N2A–C5A–C2A	114.5(7)
C5A–C2A–C1A	115.0(6)
C5A–C2A–C4A	109.4(6)
C5A–C2A–C3A	109.6(7)
C4A–C2A–C1A	109.6(7)
C3A–C2A–C1A	107.4(6)

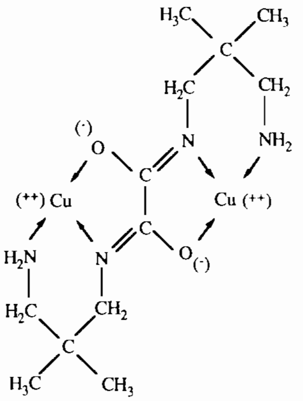
(*continued*)

TABLE 3. (*continued*)

C3A–C2A–C4A	105.3(6)
C2A–C1A–N3A	117.0(7)
Cu3–N3A–C1A	120.7(5)
N3B–Cu4–N4B	89.8(2)
N2B–Cu4–N4B	162.2(2)
N2B–Cu4–N3B	94.8(2)
N1B–Cu4–N4B	93.5(2)
N1B–Cu4–N3B	173.6(3)
N1B–Cu4–N2B	83.7(2)
Cu4–N1B–C8B	127.2(5)
Cu4–N1B–C7B	114.4(4)
C7B–N1B–C8B	118.0(6)
C2B–C1B–N3B	113.6(6)
C1B–C2B–C5B	112.2(6)
C1B–C2B–C4B	106.9(6)
C1B–C2B–C3B	110.6(7)
C4B–C2B–C5B	106.6(6)
C3B–C2B–C5B	111.9(6)
C3B–C2B–C4B	108.4(6)
C2B–C5B–N2B	114.1(6)
Cu4–N2B–C5B	129.9(4)
C5B–N2B–C6B	117.0(6)
Cu4–N2B–C6B	112.8(4)
N2B–C6B–C7B	115.6(6)
N2B–C6B–O1B	126.9(6)
O1B–C6B–C7B	117.4(6)
Cu3–O1B–C6B	116.2(4)
Cu3–O2B–C7B	109.3(4)
C6B–C7B–O2B	118.1(6)
N1B–C7B–O2B	128.6(6)
N1B–C7B–C6B	113.4(6)
Cu4–N3B–C1B	117.3(5)
N1B–C8B–C9B	114.5(6)
C8B–C9B–C12B	114.0(8)
C8B–C9B–C11B	108.5(8)
C8B–C9B–C10B	109.5(7)
C11B–C9B–C12B	107.6(6)
C10B–C9B–C12B	108.7(7)
C10B–C9B–C11B	108.4(7)
C9B–C12B–N4B	115.5(6)
Cu4–N4B–C12B	118.8(5)
O2N–N1N–O3N	119.2(7)
O1N–N1N–O3N	120.7(7)
O1N–N1N–O2N	120.1(8)
O5N–N2N–O6N	121.0(1)
O4N–N2N–O6N	120.0(1)
O4N–N2N–O5N	118.0(1)

1.925; Cu(2)–N(amidate), 1.977; Cu(2)–N(amine), 1.993 Å. This trend of bond lengths can be related to the size and donor abilities of the coordinated atoms.

Peculiar to the tetranuclear dication $[CuN_4(CuN_2O_3)_2CuN_4]^{2+}$ is the tetrameric assemblage of two outer four-coordinate and two inner five-coordinate Cu(II) cations. The structure can be described as follows: an oxamidate ligand adopting the *trans* conformation is coordinated to two inner copper ions (Cu(3) and Cu(3)′) by three donor atoms per metal atom, defining three in-plane coordination sites (atoms labelled A in Fig. 2).



Structural diagram of the central moiety of $[CuN_4(CuN_2O_3)_2CuN_4]^{2+}$ showing the ligand in the *trans* form.

A distorted square-pyramidal geometry is formed around each of these inner Cu atoms by the oxygen atoms of an outer $[CuN_4]$ molecule. The O atoms occupy the remaining basal and the apical coordination sites. The tetranuclear cation has precise C_i symmetry and the inversion centre is located in the middle of the C(6A)–C(6A)′ bond of the central oxamidate ligand. The square-pyramidal coordination geometry around Cu(3) and Cu(3)′ exhibits angular distorsions caused by the ring constraints. The copper atom lies 0.20 Å above the average basal plane, toward the apical oxygen atom. The bond distances are more regular than the angles and the four basal distances, two Cu–N and two Cu–O, range between 1.977(5) and 2.005(4) Å. Expectedly the apical Cu–O distance is significantly longer than the basal ones (Cu(3)–O(2B) 2.244(5) Å). The geometry of the square-planar CuN_4 moieties is substantially equivalent to that found in the cation $[CuN_4CuO_4CuN_4]^{2+}$ both in ring conformations and bond distances. The following values can be compared with those previously cited: N(1B)–Cu(4)–N(3B), 173.6(3)°; N(2B)–Cu(4)–N(4B), 162.2(2)°; Cu(4)–N(amidate), 1.95; Cu(4)–N(amine), 2.01 Å. Cu(4) and Cu(4)′ exhibit a fifth weak interaction with a nitrate oxygen (Cu(4)···O(5N) 2.86(1) Å), paralleling the analogous interaction of Cu(2) and Cu(2)′.

It should be noted that the copper cations in both complexes exhibit two kinds of coordination, i.e. purely square-planar in the CuO_4 fragment and more or less stretched square pyramids in the fragments CuN_4O and CuN_2O_3. The ability of coordinating a fifth ligand, even though weakly, can be related to the presence of formally neutral nitrogen donors in the coordination polyhedron that, in contrast with the negatively charged oxamidate oxygens, do not completely saturate the electron demand from the metal ion.

The presence of the oxamidate ligand in *trans* conformation deserves some comment. Very probably the weak acidity of the copper nitrate solution is enough to protonate a N-amidate nitrogen to which partial decomplexation can follow accompanied by greater conformational freedom of the ligand.

Spectroscopy

The electronic spectrum exhibits a broad absorption shoulder at about 556 nm. The frequently observed high-energy absorption for copper(II) polymers is present as a broad maximum at about 400 nm.

An IR broad band centred at 3445 cm^{-1} can be assigned to the OH stretching of the lattice water molecule. The bands $\nu(NH)$ are in the normal region between 3240 and 3334 cm^{-1}. The $\nu(CO)_{as}$ and the $\nu(CO)_{sym}$ stretching frequencies of the oxamidate group at 1625, 1605 and 1586 cm^{-1} (in this range H–O–H bending modes also fall), and 1355 and 1326 cm^{-1}, respectively, are diagnostic of the presence of the bis-bidentate behaviour of the oxamidate [5, 10]. In the IR region one new band due to Cu–O and one new band due to Cu–N stretching vibrations are clearly detected at 550 and 359 cm^{-1}, respectively [4]. The band at 317 cm^{-1} can be assigned to $\nu(Cu(O\text{–}NO_2)$ in which the Cu–O bond length is longer than in the previous one.

Supplementary material

Atomic coordinates of the hydrogen atoms (Table A, 3 pages); anisotropic thermal parameters of non-hydrogen atoms (Table B, 3 pages); and observed and calculated structurc factors (Table C, 19 pages) are available from the authors on request.

Acknowledgements

We thank the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST) of Italy for support this research, and the Centro Interdipartimentale Grandi Strumenti of Modena University for intensity data collection.

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