

Dinitrato(*N,N,N',N'*-tetramethylethylenediamine)copper(II)

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Abstract. $C_6H_{16}N_4O_6Cu$, $M_r = 303.76$, monoclinic, $C2/c$, $a = 13.8971$ (11), $b = 7.4956$ (6), $c = 12.2960$ (10) Å, $\beta = 103.62$ (1)°, $Z = 4$, $D_c = 1.62$, $D_m = 1.62$ (2) g cm⁻³; $R = 0.023$ for 1064 observed reflections. The Cu atom displays [4 + 2] coordination with four normal contacts of 2.005 (2) Å to two diamine N and two O atoms (dihedral angle 22.5°), and two longer contacts of 2.440 (2) Å to a second set of O atoms. The chelated O atoms subtend an angle of 56.9 (1)° at the Cu.

Introduction. Dark blue crystals of the title compound were prepared, analyzed and found to have lattice constants as reported earlier for Cu(tmen)(NO₃)₂, where tmen = *N,N,N',N'*-tetramethylethylenediamine (Lemmetti, Karhu & Ehder, 1972). The data crystal was a monoclinic parallelepiped approximately 0.02 cm on each edge. An initial mount afforded precession and cone-axes photographs which indicated a monoclinic, centered cell with systematic absences ($h + k$ odd for hkl and l odd for $h0l$ reflections) consistent with space groups Cc or $C2/c$; structure analysis was attempted in both groups and showed the latter to be correct. The crystal was remounted, transferred to a Picker FACS-I fully automated diffractometer (b^* axis coincident with φ axis), and lattice constants were determined from 21 intense reflections by a least-squares fit of carefully measured $\pm 2\theta$ values ($63^\circ < 2\theta < 76^\circ$) for the Cu $K\alpha_1$ - $K\alpha_2$ doublet [$\lambda(Cu K\alpha_1)$ 1.54050 Å, $\lambda(Cu K\alpha_2)$ 1.54434 Å].

Intensity data were collected to a $2\theta_{max}$ of 50° with Zr-filtered Mo $K\alpha$ radiation, using a fixed $\theta/2\theta$ rate of 1° min⁻¹. A variable scan width, $1.6^\circ + 0.48^\circ \tan \theta$, and 10 s background measurements at both extremities of the scan were used to measure 1243 independent reflections. Periodically measured reference reflections showed a random variation of approximately $\pm 2\%$ and no systematic decay. Intensities were corrected for absorption as a function of φ (maximum deviation of 10% in a φ scan at $\chi = 90^\circ$; $\mu = 17$ cm⁻¹ for Mo $K\alpha$), for Lorentz and polarization effects in the usual manner, and were then converted to structure amplitudes.

The structure was solved by a combination of heavy-atom and Fourier synthesis methods, and was refined by full-matrix least-squares calculations which minimized $\sum w(|F_o| - |F_c|)^2$ and used weights of $1/\sigma^2(F_o) = 1/(|F_o|/2I_n)^2 [I_s + (t_s/t_b)^2 I_b + (0.02I_n)^2]$; I_s , I_b and I_n are scan, background and net intensities, and t_s and t_b are scan and background times. There were 173 reflections having $|F_o| < 3\sigma(F_o)$ which were considered unobserved and not used in the refinement. Scattering factors for nonhydrogen atoms were taken from tabulations of Cromer & Waber (1965) and for H from Stewart, Davidson & Simpson (1965); Cu values were corrected for both real and imaginary anomalous-dispersion effects (Cromer & Liberman, 1970). All non-hydrogen atoms were readily located and anisotropic refinement on these atomic positions converged with $R = 0.043$. Data were then checked for effects of secondary extinction, and six intense reflections (114, 113, 111, 204, 402, and 310) with $(\sin \theta/\lambda < 0.2)$ had $|F_c| > |F_o|$ and $|\Delta F| > R|F_o|$ and were deleted from the data set. A difference Fourier map clearly showed the positions of the eight H atoms. Three cycles of

Table 1. *Final positional parameters*

Estimated standard deviations are in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>
Cu	0.0	0.06671 (5)	0.25
O(1)	-0.0993 (1)	0.2573 (2)	0.1881 (1)
O(2)	-0.0167 (1)	0.1978 (2)	0.0648 (1)
O(3)	-0.1280 (2)	0.4060 (3)	0.0338 (2)
N(1)	-0.1027 (1)	-0.1255 (2)	0.2316 (1)
N(2)	-0.0814 (2)	0.2900 (3)	0.0923 (2)
C(1)	-0.1718 (2)	-0.0838 (4)	0.3031 (3)
C(2)	-0.1589 (2)	-0.1450 (5)	0.1136 (2)
C(3)	-0.0470 (2)	-0.2917 (3)	0.2702 (2)
H(C1)	-0.209 (2)	0.025 (3)	0.271 (2)
H'(C1)	-0.135 (2)	-0.071 (3)	0.376 (2)
H''(C1)	-0.217 (2)	-0.160 (4)	0.294 (2)
H(C2)	-0.112 (2)	-0.170 (4)	0.065 (2)
H'(C2)	-0.192 (2)	-0.042 (4)	0.094 (2)
H''(C2)	-0.204 (2)	0.238 (4)	0.108 (2)
H(C3)	-0.088 (2)	-0.390 (3)	0.242 (2)
H'(C3)	-0.029 (2)	-0.286 (3)	0.350 (2)

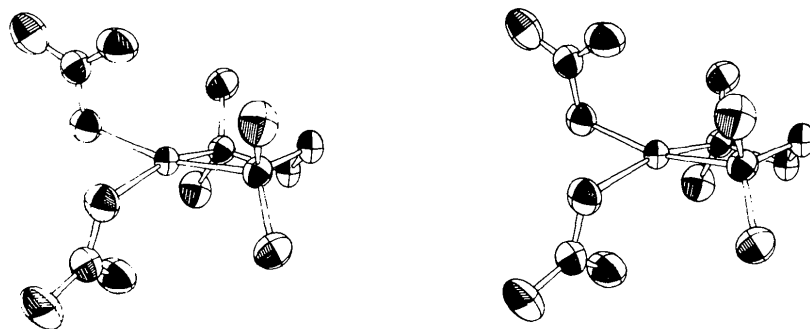


Fig. 1. A stereoview of the $\text{Cu}(\text{tmen})(\text{NO}_3)_2$ molecule (Johnson, 1965).

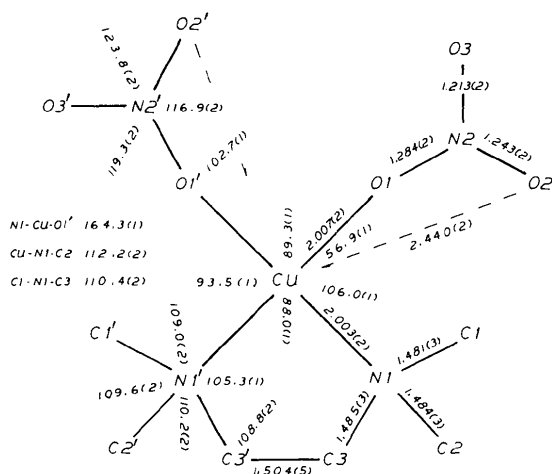


Fig. 2. A schematic representation of the $\text{Cu}(\text{tmen})(\text{NO}_3)_2$ molecule with bond distances (Å) and angles (°) indicated.

refinement on all atomic positions and temperature factors (using isotropic thermal parameters for H atoms) converged with $R = 0.023$ and $R_w = 0.034$, where $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$. The final difference map was featureless and contained a maximum peak of $0.3 \text{ e } \text{Å}^{-3}$. Final atomic positional coordinates for all atoms are listed in Table 1. The molecular structure is shown in Fig. 1 and intramolecular bond lengths and angles are shown in Fig. 2.*

Discussion. Established structures of copper(II) complexes with the fully *N*-substituted ligand tmen display a wide variety of structural types that include monomers or dimers and span coordination numbers of four through six. The diverse manner in which solvent

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32665 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

molecules and/or counterbalancing anions complete the coordination sphere indicates that the Cu–tmen system is extremely sensitive to preparative conditions and chemical environment. We are investigating this feature and have previously reported our findings for $[\text{Cu}(\text{tmen})(\text{OH})_2](\text{ClO}_4)_2$ as a four-coordinate dimer (Arcus, Fivizzani & Pavkovic, 1977), and also for $[\text{Cu}(\text{tmen})\text{SO}_4(\text{H}_2\text{O})_2]\text{H}_2\text{O}$ as a hydrated five-coordinate monomer (Balvich, Fivizzani, Pavkovic & Brown, 1976). The conformation of the diamine ligand in these two complexes is significantly less twisted about the ethylene C atoms than found in other tmen complexes of known structure (Mitchell, Bernard & Wasson, 1970; Estes, Estes, Hatfield & Hodgson, 1975; Luukkonen & Pajunen, 1973). In the search for additional examples containing this reduced-twist conformation, the structure determination of the anhydrous complex $\text{Cu}(\text{tmen})(\text{NO}_3)_2$ was undertaken.

The crystal structure of $\text{Cu}(\text{tmen})(\text{NO}_3)_2$ is composed of discrete monomeric molecules with an irregular $[4 + 2]$ coordination polyhedron about Cu. This arrangement consists of two diamine N atoms and one O atom from each nitrate group forming a distorted square base, and a second O atom from each nitrate group [considerably more distant from Cu at $2.440(2) \text{ Å}$] positioned above and below the base. Bond distances from Cu to the four base atoms are all within 2σ of their average value of 2.005 Å , and bond angles about Cu are all near 90° . However, this group of atoms significantly departs from planarity, as is evident from the 22.5° dihedral angle at which the $\text{N}(1)-\text{Cu}-\text{N}(1')$ and $\text{O}(1)-\text{Cu}-\text{O}(1')$ planes cross, and from the $164.3(1)^\circ$ angle that *trans*- $\text{N}(1')$ and $\text{O}(1)$ donor atoms subtend at Cu. The distant apical atoms and Cu are in a plane $[\text{O}(2)-\text{Cu}-\text{O}(2')]$ almost perpendicular (91.3°) to that of the $\text{N}(1)-\text{Cu}-\text{N}(1')$ atoms, with the $\text{Cu}-\text{O}(2)$ vector tilted 23.8° away from a normal to the latter plane.

The nitrate group is essentially planar with $\text{N}(2)$ 0.003 Å (2.5σ) removed from the best least-squares plane. It is orientated at angles of 71.4 and 87.8° to the $\text{N}(1)-\text{Cu}-\text{N}(1')$ and $\text{O}(1)-\text{Cu}-\text{O}(1')$ planes contain-

ing major coordinated atoms. N—O bond lengths within the group of 1.284 (2), 1.243 (2), and 1.213 (2) Å for N(2)—O(1), N(2)—O(2), and N(2)—O(3) respectively, clearly indicate the degree of Cu—O coordination, with O(1) strongly bonded, O(2) weakly bonded, and O(3) nonbonded. Correspondingly, the bite across chelated atoms O(1) and O(2) at 2.153 (2) Å, and the angle they subtend at N(2) of 116.9 (2)°, is the smallest within the nitrate anion. Another indicator of the dissimilar bonding of chelated atoms O(1) and O(2) is the angle of 56.91 (6)° subtended at the Cu atom. In typical first-row transition-metal complexes this angle ranges from 50–65°, and the lower values are associated with more asymmetric chelation. This same type of nitrate anion chelation is also present in other *d*⁹ complexes such as [Cu(etsal)NO₃]₂, *trans*-[Cu(DEAEPH)₂(NO₃)₂]²⁺, *cis*-Cu(DMAEP)(NO₃)₂, and polymeric Cu(pyrazine)(NO₃)₂ (Sinn, 1976; Lewis & Hodgson, 1973*a,b*; Santoro, Mighell & Reimann, 1970). However, in comparable *d*⁸ complexes, such as Ni(tmen)(NO₃)₂ and Ni[2,6-(diacetyl)pybis(anil)]-(NO₃)₂, nitrate anion chelation is much more symmetric (Turpeinen, 1973; Alyea, Ferguson & Restivo, 1975).

In the diamine portion of the molecule, bonds from N(1) to all C atoms are alike to within 1σ of their average distance of 1.483 (3) Å, angles about N(1) range from 105 to 112°, and the diamine N atoms are separated by a bite distance of 2.783 Å and subtend an angle of 88.0 (1)° at the Cu atom. All of these ligand features (which are independent of conformation) are fully in accord with values reported for other tmen complexes. Remaining bonding parameters about ethylene C atoms show the ligand conformation to be *gauche* and of the same degree as found in most tmen and en complexes. The pertinent values are: C(3)—C(3') 1.504 (5) Å, N(1)—C(3)—C(3') 108.8 (2)°, α = 27.9° and β = 55.0°. A less twisted form of tmen is present in the copper sulfate and hydroxy-perchlorate complexes, where corresponding values for the sulfate compound are: 1.372 (14) Å, 114.5 (7) and 116.8 (7)°, α = 17.4° and β = 35.1°; α and β are as defined by Raymond, Corfield & Ibers (1968).

Individual molecules are well separated in this structure, as evidenced by minimal intermolecular contacts of 3.4 Å for C—O and 2.7 Å for O—H, and in particular there are no structurally significant contacts

to the non-coordinated atom O(3). It is noted that except for the lack of a third nonbonded O atom, the detailed bonding arrangement in the closely related nitrito complex, Cu(tmen)(NO₂)₂, exactly parallels that found here for Cu(tmen)(NO₃)₂ (Luukkonen, 1973). The same correspondence is also found for the related nickel nitrito and nitrate complexes of tmen (Drew & Rogers, 1965; Turpeinen, 1973).

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