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(4-Nitrophenyl 1,3,5,8,12-pentaazacyclotetradec-3-yl ketone-N^1,N^5,N^8,N^{12})copper(II) Dinitrate

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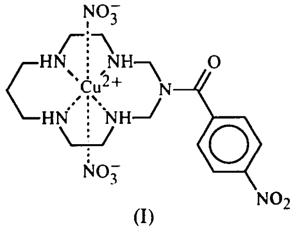
Abstract

In the crystal structure of $[Cu(C_{16}H_{26}N_6O_3)](NO_3)_2$, the metal ion lies in an elongated octahedral coordination. Only the four secondary amine N atoms of the macrocycle are bound to the Cu^{2+} centre which resides 0.080 (1) Å out of the N_4 donor plane. The coordination sphere is completed by two nitrate O atoms axially coordinated with different Cu—O distances.

Comment

Pentaaza macrocyclic systems, known as azacyclams, are obtained through one-pot template syntheses in which Cu^{2+} or Ni^{2+} ions behave as templating agents. These reactions involve the closure of an open-chain tetraamine, preoriented through coordination to the metal centre, by a primary amine, amide or sulfonamide group in the presence of excess formaldehyde and base, and offer the opportunity to append a variety of substituent groups onto the aza macrocyclic system (Fabbrizzi *et al.*, 1991; De Blas *et al.*, 1993; Abba *et al.*, 1994). The crystal structure determination of this class of compounds allows the influence of the substituent group on the spectral and electrochemical properties of the complexes to be defined (*e.g.* by comparing the distortions in the square-planar or octahedral geometries). Structures of azacyclam complexes of both Cu^{2+} and Ni^{2+} ions have been determined in recent years (Fabbrizzi *et al.*, 1991; De Blas *et al.*, 1993; Abba *et al.*, 1994), but no crystallographic characterization of a Cu^{2+}–azacyclam complex containing an amido group has been reported previously.

The crystal structure of the title complex, (I), shows copper(II) in an elongated octahedral coordination environment whose deviation from a regular geometry is only partially ascribable to the Jahn–Teller effect (Fig. 1). Only the four secondary amine N atoms of the macrocycle are bound to the metal centre giving a distorted square-planar geometry in which (i) two *trans*-N atoms (N2 and N4) lie up [δ(N2) = 0.036 (2) and δ(N4) = 0.037 (2) Å] and the other two (N3 and N5) lie down [δ(N3) = −0.037 (2) and δ(N5) = −0.037 (2) Å] with respect to the N_4 mean plane (tetrahedral distortion), and (ii) the Cu^{2+} ion resides 0.080 (1) Å out of the N_4 donor plane. The first coordination sphere of the metal ion is completed by two nitrate O atoms (O1 and O6) coordinated axially, with Cu—O distances that are quite different [Cu—O1 2.437 (2) and Cu—O6 2.673 (2) Å]. This is probably related to the Cu^{2+} displacement from the secondary amine plane towards the nitrate O1 atom. Although the O1—Cu—O6 angle [168.6 (1)°] does not deviate excessively from linearity, the O—Cu—N angle values, varying in the range 81.9 (1)–98.7 (1)°, are indicative of a significant distortion from a regular octahedron.



(I)

It is interesting to compare the copper geometry observed here with that found in the structure of (3-methanesulfonyl-1,3,5,8,12-pentaazacyclotetradecane)dinitratocopper(II) (De Blas *et al.*, 1994). Although the Cu—N bond distances and angles and the average Cu—O distance are very similar, De Blas and co-workers

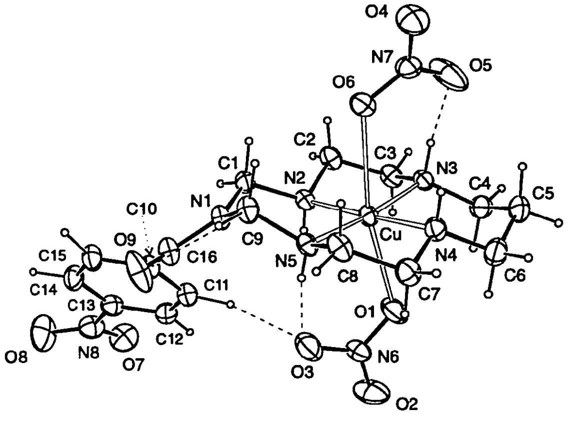


Fig. 1. A perspective view of the title complex shown with 30% probability ellipsoids.

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observed no displacement of the metal centre from the N_4 plane, symmetric Cu—O distances and less distortion in the coordination geometry. The orientation of the two coordinating nitrate ions is quite different; the N6, O1, O2, O3 and N7, O4, O5, O6 planes form a dihedral angle of 18.5 (3)° and are inclined by 81.9 (1) and 65.8 (1)°, respectively, with respect to the N_4 plane. They each interact with the acidic H atoms of the macrocycle by means of two hydrogen bonds [H3N···O5 1.96 (3), N3···O5 2.873 (4) Å and N3—H3N···O5 163 (3)°; H5N···O3 2.35 (3), N5···O3 3.056 (3) Å and N5—H5N···O3 151 (3)°].

The overall geometry of the azacyclam ring is similar to the geometries observed in analogous complexes (De Blas *et al.*, 1994, and references therein). The six- and five-membered chelate rings adopt a flattened chair and a twist conformation, respectively; the centrosymmetric space group allows the coexistence of both *RSRS* and *SRSR* cation configurations with two N—H bonds up and two down with respect to the CuN_4 coordination plane. The bis(ethylenediamine)copper(II) moiety adopts a λ–δ configuration permitted by a pseudosymmetry plane bisecting the N2—Cu—N5 and N3—Cu—N4 angles. The difference observed in the apex–apex distance of the six-membered rings [Cu···C5 3.324 (4) and Cu···N1 3.257 (3) Å] is ascribable to the N1—C bond lengths being shorter than the C5—C distances; in the present case, this feature seems less pronounced than that observed in the structure studied by De Blas *et al.* (1994). The non-coordinating tertiary amine N1 atom shows a clear sp^2 character, as expected for an amide N atom. There is an intramolecular C—H···O interaction involving the C9 and carboxylic O9 atoms, resulting in a five-membered ring [H9*b*···O9 2.28 (3), C9···O9 2.717 (4) Å and C9—H9*b*···O9 106 (2)°].

A dihedral angle of 54.5 (1)° is formed between the secondary amine N_4 plane and the phenyl ring whose orientation allows a possible intramolecular C—H···O interaction involving the aromatic ring and the nitrate O3 atom [H11···O3 2.54 (3), C11···O3 3.467 (4) Å and C11—H11···O3 148 (3)°]. In the nitro group, the bond distances are in the expected range, while the torsion angles around the C—N bond [O7—N8—C13—C12 −18.7 (5) and O8—N8—C13—C12 160.1 (3)°] indicate non-coplanarity with the aromatic ring. The H atoms on the secondary amine N2 and N4 atoms take part in quite weak hydrogen bonds, which connect symmetry-related molecules contributing to the crystal-packing stabilization (see Fig. 2) [H2N···O2^{i} 2.45 (3), N2···O2^{i} 3.183 (3) Å and N2—H2N···O2^{i} 150 (3)°; H4N···O9^{ii} 2.47 (3), N4···O^{ii} 3.202 (4) Å and N4—H4N···O9^{ii} 137 (3)°; symmetry codes: (i) $1-x$, $2-y$, $2-z$; (ii) $\frac{1}{2}+x$, $\frac{3}{2}-y$, $z-\frac{1}{2}$]. Besides the van der Waals forces, the crystal structure could be further stabilized by C—H···O contacts. One nitrate ion interacts with aliphatic H atoms belonging to two different macrocyclic rings [H7*a*···O6^{iii} 2.453 (3), C7···O6^{iii} 3.419 (4) Å and C7—H7*a*···O6^{iii} 160 (3)°; H6*a*···O4^{iii} 2.45 (3), C6···O4^{iii} 3.352 (4) Å and C6—H6*a*···O4^{iii} 155 (3)°; symmetry code: (iii) $x-\frac{1}{2}$, $\frac{3}{2}-y$, $z-\frac{1}{2}$].

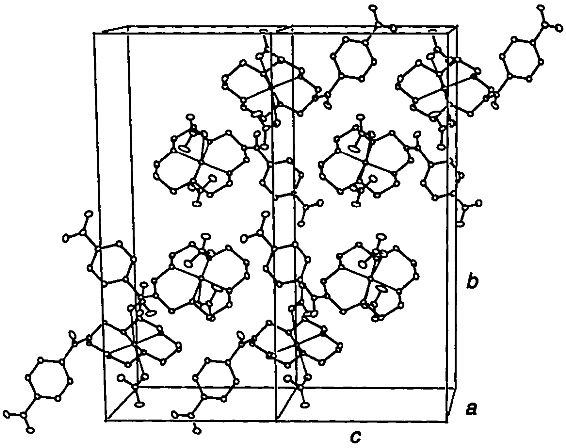

Fig. 2. A view of the crystal packing along the *a* axis. H atoms have been omitted.

Experimental

The title compound was prepared by reacting 1,9-diamino-3,7-diazanonone (2.3.2-tet) with copper(II) nitrate trihydrate, 4-nitrobenzamide, excess formaldehyde and triethylamine in ethanol at 323 K for 24 h. The reaction mixture was cooled and treated with 70% perchloric acid giving the required crystalline product.

Crystal data

$[Cu(C_{16}H_{26}N_6O_3)](NO_3)_2$
$M_r = 537.98$
Monoclinic
$P2_1/n$
$a = 7.935$ (1) Å
$b = 25.116$ (3) Å
$c = 11.081$ (2) Å
$\beta = 96.40$ (1)°
$V = 2194.6$ (6) Å^3
$Z = 4$
$D_x = 1.6282$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 28$–$32°$
$\mu = 1.962$ mm^{-1}
$T = 293$ (3) K
Prism
0.36 × 0.14 × 0.13 mm
Violet

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.76$, $T_{max} = 0.79$
5038 measured reflections
3912 independent reflections
3612 observed reflections $[I > \sigma(I)]$

$R_{int} = 0.014$
$\theta_{max} = 70°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 30$
$l = -13 \rightarrow 13$
3 standard reflections monitored every 300 reflections
intensity decay: 1.0%

Refinement

Refinement on F
$R = 0.050$
$wR = 0.039$
$S = 1.744$
3612 reflections
386 parameters
H atoms: see below
$w = 1/[\sigma(F)^2]$
$(\Delta/\sigma)_{\max} = 0.03$
$\Delta\rho_{\max} = 0.407$ e Å^{-3}
$\Delta\rho_{\min} = -0.086$ e Å^{-3}

Extinction correction: Zachariasen (1963)
Extinction coefficient: 2.0885×10^{-7}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol IV, Tables 2.2A, 2.3.1 and 2.2C)

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

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

	x	y	z	$U_{\rm eq}$
Cu	0.72267 (5)	0.85729 (2)	0.96197 (4)	0.0345 (1)
O9	0.2754 (3)	0.7977 (1)	1.2427 (2)	0.0791 (9)
O1	0.5638 (3)	0.9336 (1)	0.8740 (2)	0.0725 (9)
O2	0.3629 (3)	0.9908 (1)	0.8707 (3)	0.0816 (10)
O3	0.3566 (3)	0.9187 (1)	0.9751 (3)	0.0780 (10)
O4	1.1242 (3)	0.72169 (9)	0.9698 (3)	0.0701 (9)
O5	1.1339 (4)	0.8033 (1)	0.9316 (3)	0.1239 (13)
O6	0.9231 (3)	0.77317 (9)	1.0164 (2)	0.0586 (8)
O7	0.2718 (4)	1.05255 (9)	1.5149 (2)	0.0751 (11)
O8	0.1458 (4)	0.9978 (1)	1.6234 (2)	0.0953 (12)
N1	0.5324 (3)	0.8252 (1)	1.1973 (2)	0.0388 (7)
N2	0.7399 (3)	0.88664 (9)	1.1353 (2)	0.0345 (8)
N3	0.9348 (3)	0.89809 (9)	0.9462 (2)	0.0356 (7)
N4	0.7106 (3)	0.8256 (1)	0.7951 (2)	0.0399 (8)
N5	0.5267 (3)	0.80933 (9)	0.9863 (2)	0.0347 (7)
N6	0.4258 (3)	0.9483 (1)	0.9055 (3)	0.0479 (9)
N7	1.0595 (3)	0.7657 (1)	0.9716 (3)	0.0511 (9)
N8	0.2312 (4)	1.0078 (1)	1.5423 (3)	0.0562 (10)
C16	0.3898 (4)	0.8303 (1)	1.2559 (3)	0.0464 (10)
C1	0.6898 (4)	0.8523 (1)	1.2332 (3)	0.0389 (9)
C2	0.9178 (4)	0.9054 (1)	1.1626 (3)	0.0438 (9)
C3	0.9629 (4)	0.9346 (1)	1.0509 (3)	0.0428 (10)
C4	0.9469 (4)	0.9252 (1)	0.8295 (3)	0.0482 (11)
C5	0.9263 (4)	0.8862 (2)	0.7240 (3)	0.0546 (12)
C6	0.7506 (5)	0.8624 (1)	0.6969 (3)	0.0540 (11)
C7	0.5413 (4)	0.8007 (1)	0.7709 (3)	0.0481 (11)
C8	0.5089 (4)	0.7706 (1)	0.8843 (3)	0.0447 (10)
C9	0.5357 (4)	0.7840 (1)	1.1058 (3)	0.0434 (10)
C10	0.3720 (4)	0.8781 (1)	1.3345 (3)	0.0404 (9)
C11	0.3789 (4)	0.9293 (1)	1.2885 (3)	0.0454 (10)
C12	0.3364 (4)	0.9725 (1)	1.3583 (3)	0.0455 (10)
C13	0.2867 (4)	0.9627 (1)	1.4707 (3)	0.0442 (10)
C14	0.2826 (4)	0.9122 (1)	1.5197 (3)	0.0500 (12)
C15	0.3251 (4)	0.8694 (1)	1.4508 (3)	0.0489 (10)

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

Cu—O1	2.437 (3)	N2—C2	1.487 (4)
Cu—O6	2.673 (2)	N3—C3	1.477 (4)
Cu—N2	2.048 (2)	N3—C4	1.474 (4)
Cu—N3	1.995 (2)	N4—C6	1.488 (4)
Cu—N4	2.006 (2)	N4—C7	1.479 (4)
Cu—N5	2.009 (2)	N5—C8	1.487 (4)
O9—C16	1.219 (4)	N5—C9	1.463 (4)
O1—N6	1.242 (4)	N8—C13	1.477 (4)
O2—N6	1.223 (4)	C16—C10	1.499 (4)
O3—N6	1.242 (4)	C2—C3	1.515 (5)
O4—N7	1.220 (4)	C4—C5	1.520 (5)
O5—N7	1.222 (4)	C5—C6	1.516 (5)
O6—N7	1.254 (4)	C7—C8	1.514 (5)
O7—N8	1.218 (4)	C10—C11	1.389 (4)
O8—N8	1.210 (4)	C10—C15	1.397 (4)
N1—C16	1.371 (4)	C11—C12	1.395 (5)
N1—C1	1.439 (4)	C12—C13	1.369 (5)
N1—C9	1.450 (4)	C13—C14	1.383 (4)
N2—C1	1.475 (4)	C14—C15	1.380 (5)
N4—Cu—N5	85.9 (1)	O1—N6—O3	117.5 (3)
N3—Cu—N5	173.3 (1)	O1—N6—O2	120.8 (3)
N3—Cu—N4	94.4 (1)	O5—N7—O6	120.1 (3)
N2—Cu—N5	93.5 (1)	O4—N7—O6	121.7 (3)
N2—Cu—N4	177.5 (1)	O4—N7—O5	118.2 (3)
N2—Cu—N3	85.9 (1)	O7—N8—O8	124.1 (3)
O1—Cu—N5	98.7 (1)	O8—N8—C13	117.8 (3)
O1—Cu—N4	88.5 (1)	O7—N8—C13	118.1 (3)
O1—Cu—N3	88.0 (1)	O9—C16—N1	121.6 (3)
O1—Cu—N2	94.0 (1)	N1—C16—C10	119.0 (3)
O6—Cu—N5	86.9 (1)	O9—C16—C10	119.3 (3)
O6—Cu—N4	81.9 (1)	N1—C1—N2	111.7 (2)
O6—Cu—N3	86.5 (1)	N2—C2—C3	107.0 (2)
O6—Cu—N2	95.6 (1)	N3—C3—C2	108.3 (2)
O1—Cu—O6	168.6 (1)	N3—C4—C5	111.4 (3)
C1—N1—C9	116.6 (2)	C4—C5—C6	115.1 (3)
C16—N1—C9	118.5 (3)	N4—C6—C5	111.5 (3)
C16—N1—C1	124.2 (3)	N4—C7—C8	107.2 (3)
Cu—N2—C2	105.5 (2)	N5—C8—C7	107.1 (2)
Cu—N2—C1	119.0 (2)	N1—C9—N5	108.7 (2)
C1—N2—C2	111.3 (2)	C16—C10—C15	117.7 (3)
Cu—N3—C4	116.9 (2)	C16—C10—C11	121.2 (3)
Cu—N3—C3	107.8 (2)	C11—C10—C15	120.5 (3)
C3—N3—C4	112.6 (2)	C10—C11—C12	119.6 (3)
Cu—N4—C7	106.5 (2)	C11—C12—C13	118.6 (3)
Cu—N4—C6	115.8 (2)	N8—C13—C12	119.0 (3)
C6—N4—C7	113.2 (2)	C12—C13—C14	122.9 (3)
Cu—N5—C9	114.9 (2)	N8—C13—C14	118.1 (3)
Cu—N5—C8	107.4 (2)	C13—C14—C15	118.6 (3)
C8—N5—C9	113.3 (2)	C10—C15—C14	119.7 (3)
O2—N6—O3	121.7 (3)		

All H atoms were positioned experimentally and inserted with an overall atomic displacement parameter equal to 5.0 Å^2, with only their *xyz* parameters being refined.

Data collection: *CAD*-4 *Manual* (Enraf–Nonius, 1988). Cell refinement: *DATCIN* (Enraf–Nonius, 1988). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MULTAN*80 (Main *et al.*, 1980). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1257). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Ammonium, Potassium and Lithium Salts of D,L-Glyceric Acid

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Abstract

The crystal structures of the ammonium, potassium and lithium salts of racemic glyceric acid (ammonium glycerate, $NH_4^+.C_3H_5O_4^-$, potassium glycerate, $K^+.C_3H_5O_4^-$, and lithium glycerate, $Li^+.C_3H_5O_4^-$) have been determined by X-ray analysis. The crystals of the potassium and ammonium salts are isomorphous. The α-hydroxy O atom lies almost in the plane of the carboxylate group in all three structures. There are networks of hydrogen bonds in all three crystals in which all the H atoms of the hydroxyl groups and the N-bonded H atoms in the ammonium salt are involved.

Comment

Glycerates are known to be intermediate compounds in many metabolic pathways. They are also the precursors of the 2-phospho-D-glycerates (Heinz & Lamprecht, 1967). Only two structures (of the Ca salts of glyceric acid) have been characterized to date, di(D,L-glycerate) dihydrate (Taga, Ohashi & Osaki, 1978) and di(L-glycerate) dihydrate (Lis & Popek, 1993). In this paper, the crystal structures of the ammonium (I), potassium (II), and lithium (III) salts of D,L-glyceric acid are presented. This work is a part of our systematic study of the structures of glycerate residues in different chemical environments (Lis & Jerzykiewicz, 1996).

$$CH_2(OH){-}CH(OH){-}COO^-.\ M^+$$

(I) $M = NH_4^+$
(II) $M = K^+$
(III) $M = Li^+$

The same numbering scheme has been used for the glycerate residues of all three compounds. The structures of the anions in (I) and (II) are essentially the same, so only the view of the glycerate anion in the potassium salt is included in this work. The D-isomers of the anions of the potassium and lithium salts are shown in Figs. 1 and 2.

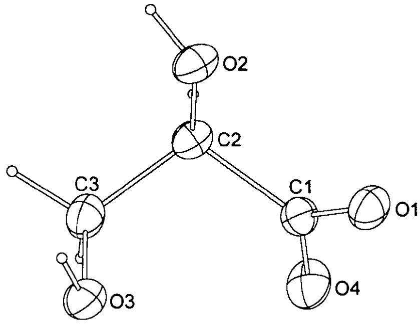

Fig. 1. The molecular structure and numbering scheme of the glycerate anion in the potassium D,L-glycerate crystal. Displacement ellipsoids are shown at the 50% probability level. The anion is shown as the D-isomer. The anion in the ammonium salt is essentially identical in structure and so is not shown as a separate figure.

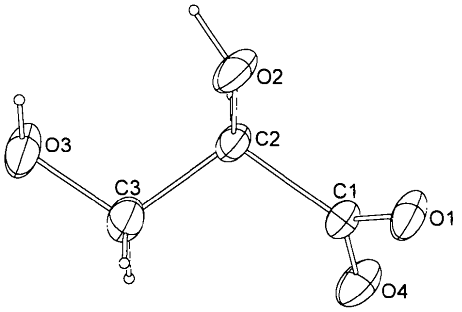

Fig. 2. The molecular structure and numbering scheme of the glycerate anion in the lithium D,L-glycerate crystal. Displacement ellipsoids are shown at the 50% probability level. The anion is shown as the D-isomer.

The crystals of (I) are composed of ammonium cations and the D- and L-glycerate anions. The structure of the crystal is stabilized by an extensive network of hydrogen bonds (Fig. 3). The NH_4^+ cation is bridged through O4, O2 and three O1 atoms to the four symmetry-related glycerate anions (Table 3). The O1 atom appears to be involved, as an acceptor, in the hydrogen-bond interaction with three different ammonium cations. The N-bonded atom H4 is involved in the bifurcated interaction with the O1 and O2 atoms of the same glycerate ion.

The crystal of (II) is isomorphous with the crystal of (I). Fig. 4 shows the crystal packing of (II). One glycerate ion chelates the K^+ ion through O1, O2 and

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