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Nitrato(1,4,7,10-tetraazacyclododecane)copper(II) Nitrate

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Abstract. [Cu(C₈H₂₀N₄)(NO₃)⁺.NO₃⁻, C₈H₂₀CuN₅O₃.NO₃⁻, *M_r* = 359.8, monoclinic, *P*2₁/*n*, *a* = 12.00 (1), *b* = 13.76 (1), *c* = 8.86 (2) Å, β = 90.10 (3)° from diffractometer measurements (Mo *K*α radiation), *V* = 1463.8 Å³, *Z* = 4, *D_m* = 1.60, *D_c* = 1.63 Mg m⁻³, *F*(000) = 748, μ = 1.409 mm⁻¹. The complex contains five-coordinate Cu^{II} in a square-pyramidal environment, the Cu being 0.5 Å above the plane containing the four N atoms of the macrocycle.

Introduction. Systematic absences from precession photographs *h*0*l*: *h* + *l* odd, 0*k*0: *k* odd indicated space group *P*2₁/*n*. Data were collected for *hk*0–8 with θ_{max} = 25° on a Stoe STADI-2 two-circle diffractometer (graphite-monochromated Mo *K*α radiation). This gave 2803 data of which 1862 unique reflexions with *I* > 3σ(*I*) were used in subsequent calculations. Lorentz and polarization corrections (but none for extinction or absorption) were applied, and the data scaled by a Wilson plot. The structure was solved by direct phasing methods with *SHELX* 76 (Sheldrick, 1976), which was used for all calculations. Complex neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Weighted full-matrix least-squares refinement (including isotropic H atoms) converged at *R* = 0.052 for 1862 observed reflexions (*R* = ∑||*F_o*| – |*F_c*||/∑|*F_o*|); *R_w* = 0.059 {*R_w* = ∑(|*F_o*| – |*F_c*|| *w*^{1/2})/∑(|*F_o*| *w*^{1/2}), *w* = 3.43/[σ²(*F_o*) + 0.000656*F_o*²]}.

In the final cycle all shifts in parameters were less than their e.s.d.'s. Positional parameters are given in Table 1, bond distances and angles in Table 2.*

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34416 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

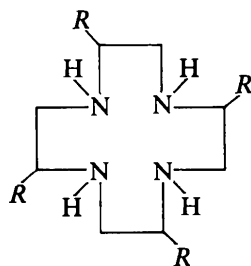
Table 1. Fractional atomic coordinates (×10⁴) with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
Cu(1)	3468 (0)	5711 (0)	2922 (1)
C(2)	1678 (6)	6187 (5)	4787 (9)
C(3)	2642 (7)	6374 (5)	5797 (8)
C(5)	3941 (5)	7447 (4)	4385 (8)
C(6)	4875 (5)	7375 (5)	3237 (9)
C(8)	3906 (7)	7127 (5)	794 (9)
C(9)	3398 (7)	6340 (5)	–162 (7)
C(11)	1611 (6)	5872 (7)	1161 (10)
C(12)	1196 (5)	5251 (6)	2482 (12)
O(14)	4529 (3)	4426 (3)	3080 (5)
O(15)	3094 (4)	3579 (3)	2458 (7)
O(16)	4685 (4)	2900 (3)	2620 (6)
O(18)	3112 (4)	3940 (4)	8666 (6)
O(19)	2580 (5)	3758 (5)	6382 (7)
O(20)	1569 (4)	4524 (4)	7940 (8)
N(1)	1973 (4)	5371 (4)	3827 (7)
N(4)	3712 (4)	6460 (3)	4859 (6)
N(7)	4539 (4)	6671 (4)	1994 (7)
N(10)	2749 (5)	5619 (4)	889 (6)
N(13)	4102 (3)	3637 (3)	2683 (5)
N(17)	2423 (4)	4069 (4)	7652 (7)
H(1A)	1957	4727	4516
H(2A)	1518	6817	4093
H(2B)	944	6024	5447
H(3A)	2505	7041	6409
H(3B)	2721	5778	6581
H(4A)	4256	6119	5675
H(5A)	3208	7764	3878
H(5B)	4202	7885	5333
H(6A)	5622	7115	3787
H(6B)	5029	8083	2758
H(7A)	5279	6277	1662
H(8A)	3260	7588	1254
H(8B)	4460	7560	109
H(9A)	2832	6660	–969
H(9B)	4044	5949	–751
H(10A)	2770	5014	100
H(11A)	1550	6637	1449
H(11B)	1128	5736	154
H(12A)	363	5469	2787
H(12B)	1192	4498	2133

Table 2. Bond distances (Å) and bond angles (°) with e.s.d.'s in parentheses

Cu(1)—O(14)	2.183 (4)	C(8)—N(7)	1.449 (10)
Cu(1)—N(1)	2.022 (5)	C(9)—N(10)	1.570 (9)
Cu(1)—N(4)	2.023 (5)	C(11)—C(12)	1.533 (13)
Cu(1)—N(7)	2.019 (5)	C(11)—N(10)	1.430 (10)
Cu(1)—N(10)	2.001 (6)	C(12)—N(1)	1.522 (11)
C(2)—C(3)	1.484 (11)	O(14)—N(13)	1.251 (5)
C(2)—N(1)	1.453 (9)	O(15)—N(13)	1.228 (6)
C(3)—N(4)	1.536 (9)	O(16)—N(13)	1.234 (6)
C(5)—C(6)	1.518 (10)	O(18)—N(17)	1.234 (8)
C(5)—N(4)	1.448 (8)	O(19)—N(17)	1.219 (9)
C(6)—N(7)	1.521 (9)	O(20)—N(17)	1.228 (7)
C(8)—C(9)	1.503 (11)		
N(1)—Cu(1)—O(14)	107.8 (2)	N(13)—O(14)—Cu(1)	116.5 (3)
N(4)—Cu(1)—O(14)	105.9 (2)	C(2)—N(1)—Cu(1)	105.7 (4)
N(4)—Cu(1)—N(1)	84.7 (2)	C(12)—N(1)—Cu(1)	104.9 (4)
N(7)—Cu(1)—O(14)	100.6 (2)	C(12)—N(1)—C(2)	113.1 (5)
N(7)—Cu(1)—N(1)	151.6 (2)	C(3)—N(4)—Cu(1)	107.5 (4)
N(7)—Cu(1)—N(4)	85.5 (2)	C(5)—N(4)—Cu(1)	105.0 (4)
N(10)—Cu(1)—O(14)	104.9 (2)	C(5)—N(4)—C(3)	112.9 (5)
N(10)—Cu(1)—N(1)	87.8 (2)	C(6)—N(7)—Cu(1)	106.8 (4)
N(10)—Cu(1)—N(4)	149.1 (2)	C(8)—N(7)—Cu(1)	104.4 (4)
N(10)—Cu(1)—N(7)	87.1 (2)	C(8)—N(7)—C(6)	113.2 (5)
N(1)—C(2)—C(3)	107.2 (6)	C(9)—N(10)—Cu(1)	106.3 (4)
N(4)—C(3)—C(2)	109.8 (5)	C(11)—N(10)—Cu(1)	104.1 (5)
N(4)—C(5)—C(6)	106.0 (5)	C(11)—N(10)—C(9)	114.9 (6)
N(7)—C(6)—C(5)	109.3 (5)	O(15)—N(13)—O(14)	120.4 (4)
N(7)—C(8)—C(9)	108.3 (6)	O(16)—N(13)—O(14)	119.6 (4)
N(10)—C(9)—C(8)	108.8 (5)	O(16)—N(13)—O(15)	119.9 (4)
N(10)—C(11)—C(12)	107.8 (6)	O(19)—N(17)—O(18)	121.1 (6)
N(1)—C(12)—C(11)	109.8 (6)	O(20)—N(17)—O(18)	118.7 (6)
		O(20)—N(17)—O(19)	120.2 (6)

Discussion. The ability of 1,4,7,10-tetraazacyclododecane (*L*) (I) to form metal complexes is limited by its aperture, which is smaller than most transition-metal ions (Martin, DeHayes, Zompa & Busch, 1974). No *trans*-octahedral MLX_2 complexes are known, although there is evidence for square-planar Ni^{II} complexes in solutions containing large amounts of inert electrolyte at high temperature (Fabbrizzi, 1977). Folded *cis*-octahedral complexes are known for Co^{II} (Loehlin & Fleischer, 1976; Iitaka, Shina & Kimura, 1974) and suggested for Ni^{II} (Smierciak, Passariello & Blinn, 1977). For $CuLX_2$ ($X = Cl, NO_3$) spectral and other evidence suggest five-coordination (Styka, Smierciak, Blinn, DeSimone & Passariello, 1978) and the enthalpy of formation of $CuL^{2+}(aq.)$ is smaller than that of other Cu^{II} complexes containing larger macro-



(I) $R = H$
(II) $R = Et$

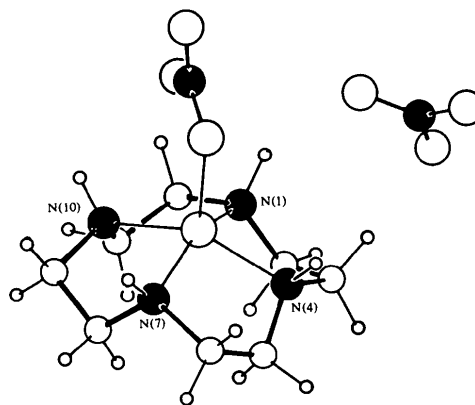


Fig. 1. General view of the structure.

cycles (Anichini, Fabbrizzi, Paoletti & Clay, 1978), but a Cu^{II} complex of the tetraoxa analogue of (I) is *cis*-octahedral (van Remoortere, Boer & Steiner, 1975).

The structure of the title compound consists of isolated NO_3^- anions and $CuLNO_3^+$ cations (Fig. 1) in which the CuL moiety has almost perfect C_{4v} symmetry. The Cu is displaced 0.51 Å from the N_4 plane. The five-membered rings have *gauche* conformations. Although the most stable arrangement of the free ligand is not known it is likely to be the same as in cyclododecane (Dunitz, 1968) and in (II) (Sakurai, Kobayashi, Tsuboyama & Tsuboyama, 1978), and the conformation in the complex is essentially identical to these.

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