

References

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Structure of the Blue Copper(II) Complex $\{[7R(S),14R(S)]-5,5,7,12,12,14$ -Hexamethyl-1,4,8,11-tetraazacyclotetradecane $\}$ nitratocopper(II) Perchlorate, $[\text{Cu}(\text{NO}_3)(\text{C}_{16}\text{H}_{36}\text{N}_4)](\text{ClO}_4)$

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Abstract. $M_r = 508.49$ (5), monoclinic, $P2_1/c$, $a = 8.769$ (5), $b = 17.809$ (5), $c = 14.344$ (5) Å, $V = 2240$ (3) Å³, $Z = 4$, $D_m = 1.48$ (5) (by flotation in CCl_4 -hexane), $D_x = 1.51$ Mg m⁻³, $\text{Mo } K\alpha$, $\lambda = 0.71069$ Å, $\mu = 1.187$ mm⁻¹, $F(000) = 1077.6$, $T = 296$ (4) K. $R(F) = 0.070$ for 1754 reflections. The central copper atom exhibits trigonal bipyramidal coordination with the four N atoms of the macrocyclic ligand and an O atom of a nitrate ion, the latter being on the equatorial plane. Thus, the four ligating N atoms of the macrocyclic ligand are not coplanar. Intramolecular hydrogen bonds are formed between the coordinated O atom and the two apical N atoms. The two non-ligating O atoms of each nitrate ion are hydrogen bonded to the two equatorial N atoms of the adjacent complex ion. The perchlorate ions are linked to the macrocyclic ligand by hydrogen bonds.

Introduction. In the blue complex $[\{\text{Cu}(\text{tet b})\}_2\text{Cl}](\text{ClO}_4)_3$,* the chloride ion sits between the adjacent copper atoms and acts as a bridging atom. However, the corresponding binuclear complexes with bromide and iodide are not formed because the ionic radius of Br^- or I^- is so large that the amine groups are too far away to form hydrogen bonds with perchlorate ions (Bauer, Robinson & Margerum, 1973). In order to investigate the stabilizing effect of the hydrogen bonds and the coordination bonds around the copper atom,

various atoms or ions are used to replace the chloride ion. In this work NO_3^- is used in place of Cl^- and the results are compared with our previous work on the crystal structure of $[\text{Cu}(\text{tet b})(\text{H}_2\text{O})](\text{ClO}_4)_2$ (Sheu, Lee, Lu, Liang & Chung, 1983). Detailed structures of the two isomorphous crystals are compared.

Experimental. 2 g of $[\{\text{Cu}(\text{tet b})\}_2\text{Cl}](\text{ClO}_4)_3$, prepared as described by Bauer *et al.* (1973), was dissolved in hot dilute nitric acid. Silver nitrate was then added to the solution until AgCl was completely precipitated. The precipitate of AgCl was filtered off. Blue needle crystals of $[\text{Cu}(\text{NO}_3)(\text{tet b})](\text{ClO}_4)$ were formed after evaporation of the solution. The crystals were dried in air at room temperature and used for X-ray work.

Experimental data and structure solution parameters are summarized in Table 1. After correction for background, Lorentz-polarization, absorption and time-decay effects, 1754 independent reflections were found with $F_o > 3\sigma(F)$.

Structure solved by heavy-atom method; full-matrix least-squares refinements (*ORFLS*; Busing, Martin & Levy, 1962) for coordinates and anisotropic temperature factors of non-hydrogen atoms; $\sum w(|F_o| - |F_c|)^2$ minimized, $w = [\sigma_F^2(I) + q|F_o|^2]^{-1}$, $\sigma_F(I) = [k/2(\text{Lp})^{1/2}]\{[\sigma^2(I)_{\text{counting}} + (0.02I)^2]/I\}^{1/2}$, Lp , I , k are the Lorentz-polarization factors, reflection intensity and scale factors, respectively; the factor 0.02 is the additional error estimated for our present instrumental instability (q set to 0.001 finally). To locate the H atoms in the methyl groups, one of the highest peaks around the C atom in the methyl groups was picked up from the difference Fourier map; the

* Abbreviation: The macrocyclic ligand, tet b, is the racemic form of $[7R(S),14R(S)]-5,5,7,12,12,14$ -hexamethyl-1,4,8,11-tetraazacyclotetradecane, in which the two hydrogen atoms attached to the asymmetric carbon chiral centers are on the same side of the macrocyclic plane (Whimp, Bailey & Curtis, 1970).

Table 1. Experimental data and structure refinement parameters

Crystal size (mm)	0.1 × 0.2 × 0.3
Diffractometer and data collection technique	ω-2θ scan, four-circle diffractometer (Syntex P1) with Nb filter
Scan width (°)	2.0 + 0.7 tanθ; starting 1° below K _{α1} and 1° above K _{α2}
Number and θ range used for measuring lattice parameters	15 reflections with 12 < 2θ < 25°
Absorption correction applied	Experimental absorption correction based on ψ scan (North, Phillips & Mathews, 1968)
Transmission factors	0.700 to 0.888
Maximum value of (sinθ)/λ reached in intensity measurement	0.538 Å ⁻¹
Range of hkl	0, 0, 15 to 9, 19, -15
Intensity variation of standard reflections	~ 5%
Number of reflections measured	6223
Number of observed unique reflections	1754
Criterion for recognizing unobserved reflections	F _o < 3σ(F)
Method used to solve the structure	Patterson and Fourier methods
Maximum height in final difference Fourier synthesis	0.27 e Å ⁻³
Parameters refined, non-hydrogen atoms	(Coordinates and anisotropic temperature factors) 270
hydrogen atoms	(Coordinates and isotropic temperature factors) 132
Atomic scattering factors f' and f''	International Tables for X-ray Crystallography (1967, 1968)
Number of reflections per parameter	4
S = [Σw(F _o - F _c) ² / (m - n)] ^{1/2}	1.67
R _{int} (F) = Σ(F _o - <F _o >) / ΣF _o	0.039

other two H-atom positions were calculated on a tetrahedral basis with the following constraints: C—C—H and H—C—H set at 109.5°, C—H 0.95 Å. When all the hydrogen atoms had been geometrically positioned, least-squares refinement of all coordinates (isotropic temperature factors for H atoms) gave $R = 0.070$ ($R_w = 0.074$) for 1754 observed reflections; $\Delta_{av} = 0.2 \sigma$, $\Delta_{max} = 0.4 \sigma$.

Discussion. The final atomic coordinates and thermal factors are listed in Table 2.* The interatomic distances and bond angles are tabulated in Table 3. The atoms in the molecule are labelled in Fig. 1 and the displacements of the atoms from the least-squares plane [Cu, N(1), N(2) and N(3)] are also indicated. The stereoview and packing of molecules are shown in Fig. 2.

In addition to ionic interaction, the nitrate and perchlorate ions are linked to the macrocyclic ligand by a net of intra- and intermolecular hydrogen bonds (as illustrated in Fig. 3a). The perchlorate ions and a coordinated nitrate ion of an adjacent complex ion are located abreast. This is different from the complex [Cu(tet b)(H₂O)](ClO₄)₂ (Sheu, Lee, Lu, Liang & Chung, 1983). The neutral ligand H₂O is coordinated to the Cu atom with Cu—O distance of 2.23 (2) Å. The

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and the displacements from the best plane of [Cu, N(1), N(2) and N(3)] or [Cu, N(1), N(3) and N(4)] have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39110 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Atomic positional and thermal parameters of non-hydrogen atoms with e.s.d.'s in parentheses

The equivalent isotropic temperature factor is calculated using the expression $B_{eq} = \frac{1}{3} \sum_i \sum_j a_i a_j B_{ij}$, where the a_i 's are the unit-cell edges in direct space.

	x	y	z	B _{eq} (Å ²)
Cu	0.2702 (2)	0.2132 (1)	0.0707 (1)	2.06 (9)
N(1)	0.0768 (11)	0.1574 (5)	0.0921 (6)	1.9 (6)
N(2)	0.3857 (10)	0.1528 (5)	0.1781 (6)	2.2 (5)
N(3)	0.4635 (10)	0.2680 (5)	0.0554 (6)	2.9 (7)
N(4)	0.1528 (11)	0.3071 (5)	0.1178 (6)	1.9 (6)
N(11)	0.2950 (13)	0.1756 (6)	-0.1356 (7)	3.2 (8)
Cl(1)	-0.2104 (4)	0.1884 (2)	-0.1218 (2)	4.1 (3)
O(11)	0.2888 (10)	0.1520 (5)	-0.0543 (5)	4.0 (6)
O(12)	0.2942 (13)	0.1315 (6)	-0.2004 (6)	5.7 (9)
O(13)	0.3010 (13)	0.2437 (5)	-0.1512 (6)	5.1 (8)
O(1)	-0.0607 (24)	0.1689 (19)	-0.1101 (13)	29.5 (40)
O(2)	-0.2589 (21)	0.1753 (10)	-0.0323 (10)	11.5 (17)
O(3)	-0.2048 (33)	0.2595 (9)	-0.1473 (11)	22.1 (31)
O(4)	-0.2487 (21)	0.1427 (8)	-0.1927 (10)	11.2 (17)
C(1)	-0.0093 (13)	0.2029 (6)	0.1608 (9)	2.6 (8)
C(2)	0.0891 (13)	0.0749 (7)	0.1118 (9)	2.9 (8)
C(3)	-0.0684 (16)	0.0419 (9)	0.1227 (10)	3.9 (10)
C(4)	0.1915 (13)	0.0591 (6)	0.1967 (7)	1.8 (7)
C(5)	0.3625 (14)	0.0701 (6)	0.1877 (8)	3.5 (8)
C(6)	0.4356 (16)	0.0409 (7)	0.2767 (9)	3.4 (9)
C(7)	0.4256 (15)	0.0304 (7)	0.1031 (8)	2.5 (8)
C(8)	0.5495 (14)	0.1778 (7)	0.1718 (9)	2.9 (8)
C(9)	0.5519 (15)	0.2600 (7)	0.1425 (8)	3.0 (8)
C(10)	0.4570 (14)	0.3457 (6)	0.0176 (8)	2.8 (8)
C(11)	0.6139 (15)	0.3818 (8)	0.0100 (10)	4.6 (10)
C(12)	0.3513 (15)	0.3960 (6)	0.0728 (8)	3.1 (6)
C(13)	0.1786 (14)	0.3800 (6)	0.0696 (8)	3.3 (8)
C(14)	0.1161 (15)	0.3773 (8)	-0.0299 (8)	3.5 (9)
C(15)	0.0979 (16)	0.4441 (7)	0.1243 (10)	5.0 (11)
C(16)	-0.0055 (14)	0.2841 (8)	0.1283 (9)	4.4 (10)

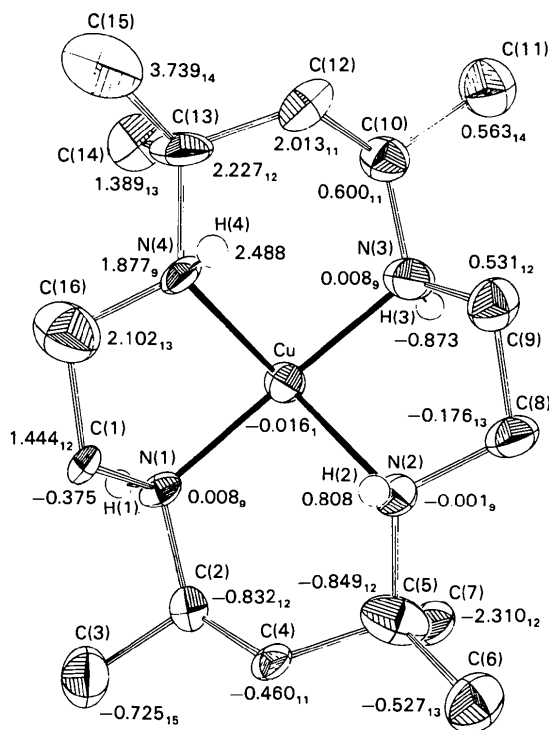


Fig. 1. Perspective view of the structure of Cu(C₁₆H₃₆N₄), showing the atom numbering scheme and displacements of atoms from least-squares plane of Cu, N(1), N(2) and N(3) (Å). E.s.d.'s are shown as subscripts. Thermal ellipsoids are depicted at the 50% probability level.

Table 3. Bond lengths (Å) and angles (°)

The prime and asterisk indicate 'screw related atoms' and 'atoms translated to the next cell', respectively.

Cu—N(1)	1.992 (9)	C(2)—C(3)	1.510 (18)
Cu—N(2)	2.128 (9)	C(2)—C(4)	1.534 (16)
Cu—N(3)	1.971 (9)	C(4)—C(5)	1.519 (17)
Cu—N(4)	2.080 (9)	C(5)—C(6)	1.516 (17)
Cu—O(11)	2.106 (8)	C(5)—C(7)	1.513 (17)
N(1)—C(1)	1.486 (15)	C(8)—C(9)	1.524 (17)
N(1)—C(2)	1.500 (15)	C(10)—C(11)	1.523 (18)
N(2)—C(5)	1.493 (14)	C(10)—C(12)	1.517 (17)
N(2)—C(8)	1.507 (15)	C(12)—C(13)	1.542 (18)
N(3)—C(9)	1.472 (15)	C(13)—C(14)	1.526 (17)
N(3)—C(10)	1.487 (14)	C(13)—C(15)	1.559 (18)
N(4)—C(13)	1.489 (15)	C(16)—C(1)	1.520 (18)
N(4)—C(16)	1.456 (16)	Cl—O(1)	1.368 (22)
N(1)—O(1)*	3.138 (21)	Cl—O(2)	1.376 (15)
N(1)—O(11)	2.818 (12)	Cl—O(3)	1.319 (17)
N(2)—O(13)*	3.159 (13)	Cl—O(4)	1.344 (15)
N(3)—O(2)	3.207 (20)	N(11)—O(11)	1.241 (12)
N(3)—O(11)	3.009 (12)	N(11)—O(12)	1.217 (14)
N(4)—O(12)*	3.078 (13)	N(11)—O(13)	1.234 (14)
N(1)—Cu—N(4)	85.8 (4)	C(13)—N(4)—C(16)	116.2 (9)
N(4)—Cu—N(3)	93.8 (4)	N(4)—C(16)—C(1)	108.8 (10)
N(3)—Cu—N(2)	85.8 (4)	C(16)—C(1)—N(1)	107.6 (10)
N(2)—Cu—N(1)	92.1 (4)	N(1)—H(1)...O(1)*	156.4 (9)
C(1)—N(1)—C(2)	116.4 (9)	N(1)—H(1)...O(11)	83.6 (6)
N(1)—C(2)—C(3)	109.7 (10)	N(3)—H(3)...O(2)	138.9 (7)
N(1)—C(2)—C(4)	111.7 (9)	N(3)—H(3)...O(11)	112.3 (6)
C(3)—C(2)—C(4)	112.1 (10)	N(2)—H(2)...O(13)*	164.6 (7)
C(2)—C(4)—C(5)	118.7 (9)	N(4)—H(4)...O(12)*	173.4 (6)
C(4)—C(5)—C(6)	107.1 (10)	O(1)—Cl(1)—O(2)	98.4 (12)
C(6)—C(5)—C(7)	111.1 (10)	O(2)—Cl(1)—O(3)	115.8 (11)
C(7)—C(5)—N(2)	109.6 (9)	O(3)—Cl(1)—O(4)	112.4 (10)
C(5)—N(2)—C(8)	115.3 (9)	O(4)—Cl(1)—O(1)	99.9 (14)
N(2)—C(8)—C(9)	108.4 (10)	O(1)—Cl(1)—O(3)	103.9 (19)
C(8)—C(9)—N(3)	108.6 (10)	O(2)—Cl(1)—O(4)	121.8 (10)
C(9)—N(3)—C(10)	114.7 (9)	O(11)—N(11)—O(12)	120.0 (11)
N(3)—C(10)—C(11)	112.7 (10)	O(12)—N(11)—O(13)	119.7 (10)
C(11)—C(10)—C(12)	110.1 (10)	O(13)—N(11)—O(11)	120.3 (10)
N(3)—C(10)—C(12)	112.4 (9)	Cu—N(3)—O(11)	44.2 (2)
C(10)—C(12)—C(13)	118.6 (10)	Cu—N(1)—O(11)	48.2 (3)
C(12)—C(13)—C(14)	112.3 (10)	Cu—N(1)—O(1)*	98.4 (6)
C(14)—C(13)—N(4)	110.6 (9)	Cu—N(3)—O(2)	116.4 (5)
C(14)—C(13)—C(15)	109.4 (10)	Cu—N(2)—O(13)*	98.8 (4)
C(15)—C(13)—N(4)	109.5 (10)	Cu—N(4)—O(12)*	111.3 (4)

H₂O molecule is situated between perchlorate ions and links perchlorate ions together through hydrogen bonds. The distance between Cu and nitrate oxygen O(11) in [Cu(NO₃)(tet b)](ClO₄) is 2.106 (8) Å, which is significantly shorter than the Cu—OH₂ distance of 2.23 (2) Å; this is probably due to the ionic character of the Cu—O bond.

From Fig. 3(b), we can clearly see that four nitrogen atoms of tet b and the oxygen of the nitrate ion form a slightly distorted trigonal bipyramid around the Cu atom. N(2), N(4) and O(11) are on the equatorial plane and N(1) and N(3) occupy the apices. From the calculations with *BOUNDAL*,* we also found that two groups of atoms are nearly co-planar: plane 1 Cu, N(1), N(2) and N(3) and plane 2 Cu, N(1), N(3) and N(4). The dihedral angle between the two planes is 65.4 (1)°. †

* This program was designed by Professor T. Y. Lee. With it, we can calculate all the equivalent positions of all the atoms, all the atomic distances around an atom within some given distance, the bond angles between atoms, also torsional angles or dihedral angles, with atomic labelling given, by using the atomic coordinates as input file.

† See deposit footnote.

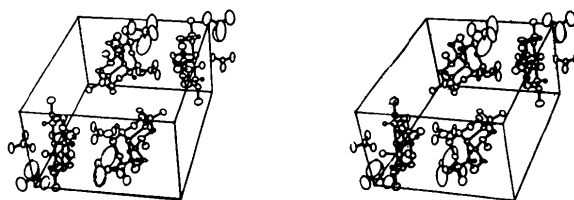
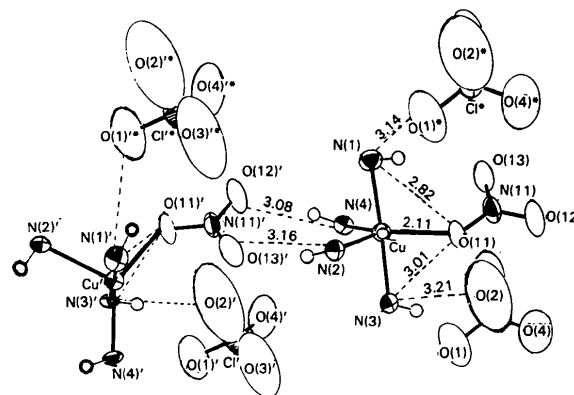
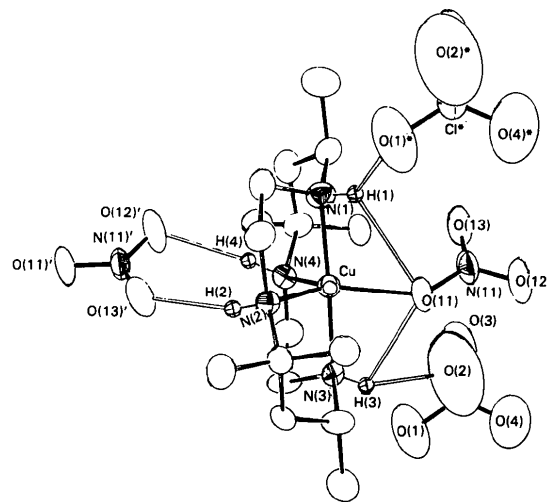


Fig. 2. Stereoview of the packing of the molecules in a unit cell. Origin lower right corner, *a* axis towards the reader, *c* axis to the left, *b* axis upwards.



(a)



(b)

Fig. 3.(a) ORTEP (Johnson, 1976) drawing for the coordination sphere and adjacent perchlorate ions of two neighboring molecules illustrating the intramolecular and intermolecular hydrogen bonds (dotted line). The prime represents screw related atoms, while the asterisk indicates an atom translated to the next cell. (b) Perspective view of the structure of [Cu(NO₃)(C₁₆H₃₆N₄)](ClO₄), showing part of the atom scheme. Hydrogen bonds are indicated by open lines. Thermal ellipsoids are plotted with 50% probability. (Distances in Å.)

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