

Fig. 1. The title compound viewed normal to the *bc* plane.

part in complex formation. The two oxathiane molecules are approximately eclipsed when viewed down the *c* axis. There are approximate local centres of inversion at the centres of the Cu_2Br_2 rings.

The dimensions of the Cu_2Br_2 rings are appreciably different. For the ring $Cu(1), Br(2), Cu(1'), Br(2')$ the average $CuBr$ distance is 2.537 Å and the average $Cu-S$ distance is 2.281 Å. The angles about the Cu atom range from 96.9 to 151.8°. $S(11)$ and $S(21)$ both use axial lone pairs for bonding to Cu^I . In the ring $Cu(2), Br(1), Cu(3), Br(1')$ the average $Cu-Br$ distance is 2.470 Å and the average $Cu-S$ distance 2.340 Å. The angles about the Cu atoms all lie between 107.3 and 110.9°. The S atoms use equatorial lone pairs for binding to $Cu(2)$ and $Cu(3)$. The $Cu-S$ distances in tetrahedral CuX_4^+ (Barnes *et al.*, 1982) range from 2.279 to 2.370 Å with no correlation between bond

length and the choice of axial or equatorial directions at the S atoms.

There does not appear to be a close analogue to the structure of (I). $CuBr(Et_2P.PEt_2)$ (Hartung, 1970) contains chains made up of Cu_2Br_2 and Cu_2P_4 rings but with only a single orientation for the Cu_2Br_2 rings.

$Cu-Cu$ bonds have been postulated in several structures containing Cu_2X_2 rings, typically $Cu-Cu$ 2.60 Å in $[CuI(AsEt_3)]_4$ (Mann, Purdie & Wells, 1936). However, the Cu_2Cl_2 ring in cyclooctadienyl $CuCl$ (Van der Hende & Baird, 1963) has $Cu \cdots Cu$ 2.944 Å and $CuBr(Et_2P.PEt_2)$ has $Cu \cdots Cu$ 3.49 Å with $Cu-Br$ 2.55 Å. In (I) the $Cu \cdots Cu$ distances 2.740 (3) and 2.865 (4) Å and the very acute $Cu-Br-Cu$ angles 65.4 and 70.9° suggest some $Cu \cdots Cu$ interaction.

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Aqua(3,7-diaza-2,7-nonadiene-2,8-dicarboxylato-*O,O',N,N'*)copper(II)

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Abstract. $C_9H_{14}CuN_2O_5$, monoclinic, $P2_1/n$, $a = 7.178$ (4), $b = 14.425$ (11), $c = 11.147$ (9) Å, $\beta = 106.25$ (5)°, $Z = 4$, $V = 1108.1$ (8) Å³, $D_m = 1.76$, $D_c = 1.76$ Mg m⁻³, $\mu(Mo K\alpha) = 2.06$ mm⁻¹. The structure was refined to $R = 0.035$ for 2114 observed reflections. The structure consists of discrete five-coordinate square-pyramidal neutral complexes. The tetradentate ligand is bonded in a square plane about Cu with $Cu-N = 1.984$ (3) and 1.972 (3) Å and $Cu-O = 1.958$ (3) and 1.953 (3) Å. The apical position is occupied by a water O atom at a distance of 2.310 (3) Å.

Introduction. The title compound was first prepared by Nakahara, Yamamoto & Matsumoto (1964) in connection with their studies on the stability of fused five- and six-membered rings in metal chelates. The blue needle-shaped crystals were prepared from 1,3-propanediamine, pyruvic acid and freshly precipitated $Cu(OH)_2$ and recrystallized from water (Nakahara *et al.*, 1964). Systematic absences of the type $h0l$, $h + l = 2n + 1$ and $0k0$, $k = 2n + 1$ indicated space group $P2_1/n$. The crystal chosen for data collection had dimensions 0.40 × 0.08 × 0.05 mm. Cell constants were calculated from angular settings of 16 reflections measured on a

Nicolet P3 diffractometer. An ω -scan method and graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$) were used to measure the 2850 independent reflections with $3^\circ < 2\theta < 55^\circ$. The intensities of two control reflections measured after every 50 data reflections showed no significant change. A total of 2114 reflections with intensities greater than $2\sigma(I)$ were treated as observed and used in the least-squares refinement. The intensities were corrected for Lorentz and polarization effects but not for absorption [$\mu(\text{Mo } K\alpha) = 2.06 \text{ mm}^{-1}$].

Table 1. Fractional atomic coordinates ($\times 10^4$) and U_{eq} ($\times 10^2$) for the non-H atoms

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq} (\AA^2)
Cu	2556.6 (6)	5591.7 (2)	2737.6 (1)	2.43 (2)
O(1)	1933 (4)	4536 (2)	3660 (2)	3.3 (1)
O(2)	1737 (4)	4162 (2)	5559 (3)	4.0 (1)
O(3)	2222 (4)	4915 (2)	1174 (2)	3.3 (1)
O(4)	2701 (4)	5101 (2)	-712 (2)	4.0 (1)
O(5)	-538 (4)	6205 (2)	2244 (3)	3.6 (1)
N(1)	3382 (4)	6157 (2)	4427 (2)	2.5 (1)
N(2)	3747 (4)	6527 (2)	1893 (3)	2.6 (1)
C(1)	2133 (5)	4703 (2)	4812 (3)	2.9 (2)
C(2)	2990 (4)	5662 (2)	5274 (3)	2.7 (2)
C(3)	4276 (5)	7082 (2)	4682 (3)	3.0 (2)
C(4)	3737 (6)	7690 (2)	3524 (3)	3.5 (2)
C(5)	4586 (6)	7400 (2)	2476 (3)	3.5 (2)
C(6)	3775 (4)	6295 (2)	796 (3)	2.6 (1)
C(7)	2827 (4)	5356 (2)	361 (3)	2.7 (1)
C(8)	3279 (7)	5912 (3)	6604 (3)	4.2 (2)
C(9)	4628 (7)	6831 (3)	-53 (4)	4.0 (2)

Table 2. Bond lengths (\AA) and angles ($^\circ$)

Cu-N(1)	1.984 (3)	Cu-N(2)	1.972 (3)
Cu-O(1)	1.958 (3)	Cu-O(3)	1.953 (3)
Cu-O(5)	2.310 (3)		
C(1)-O(1)	1.275 (4)	C(7)-O(3)	1.279 (5)
C(1)-O(2)	1.231 (5)	C(7)-O(4)	1.230 (4)
C(1)-C(2)	1.543 (4)	C(6)-C(7)	1.532 (4)
C(2)-N(1)	1.276 (4)	C(6)-N(2)	1.273 (5)
N(1)-C(3)	1.473 (4)	N(2)-C(5)	1.467 (4)
C(3)-C(4)	1.518 (5)	C(4)-C(5)	1.520 (6)
N(1)-Cu-N(2)	96.8 (1)	O(1)-Cu-O(3)	95.2 (1)
N(1)-Cu-O(1)	82.7 (1)	N(2)-Cu-O(3)	83.0 (1)
N(1)-Cu-O(3)	169.1 (1)	N(2)-Cu-O(1)	167.5 (1)
O(5)-Cu-N(1)	94.6 (1)	O(5)-Cu-N(2)	98.1 (1)
O(5)-Cu-O(1)	94.4 (1)	O(5)-Cu-O(3)	96.3 (1)
Cu-N(1)-C(2)	113.8 (2)	Cu-N(2)-C(6)	113.8 (2)
Cu-N(1)-C(3)	123.6 (2)	Cu-N(2)-C(5)	123.7 (3)
O(1)-C(1)-O(2)	125.4 (3)	O(3)-C(7)-O(4)	126.4 (3)
O(1)-C(1)-C(2)	115.3 (3)	O(3)-C(7)-C(6)	115.1 (3)
O(2)-C(1)-C(2)	119.2 (3)	C(4)-C(7)-C(6)	118.5 (3)
C(1)-C(2)-C(8)	118.9 (3)	C(7)-C(6)-C(9)	119.1 (3)
C(1)-C(2)-N(1)	113.9 (3)	C(7)-C(6)-N(2)	114.3 (3)
C(8)-C(2)-N(1)	127.3 (3)	C(9)-C(6)-N(2)	126.7 (3)
C(2)-N(1)-C(3)	122.6 (3)	C(6)-N(2)-C(5)	122.4 (3)
N(1)-C(3)-C(4)	111.4 (2)	N(2)-C(5)-C(4)	111.9 (3)
C(3)-C(4)-C(5)	115.7 (3)		

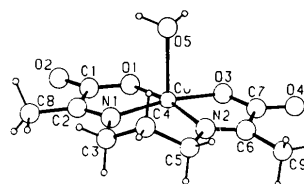


Fig. 1. Perspective view of the complex with the numbering scheme.

The structure was solved by the heavy-atom and Fourier methods and refined by full-matrix least squares. Positions of H atoms were found in a difference Fourier synthesis and included in the refinement with their isotropic thermal parameters fixed at 0.06 \AA^2 . The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = (20.0 + |F_o| + 0.013|F_o|^2 + 0.0002|F_o|^3)^{-1}$. The scattering factors and corrections for anomalous dispersion for Cu were taken from *International Tables for X-ray Crystallography* (1974). The final R value was 0.035 and R_w was 0.052, where $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. A final difference map revealed no electron density greater than 0.13 e \AA^{-3} . The weight analysis showed no dependence on $\sin \theta$ or on $|F_o|$, which suggests that the weighting scheme is appropriate. The computer programs used were the XRAY 76 system (Stewart, 1976) for solution and refinement of the structure and *PLUTO* (Motherwell, 1976) for drawing. The final atomic coordinates and thermal parameters of the non-H atoms are given in Table 1.* Bond lengths and angles are listed in Table 2.

Discussion. The crystal structure consists of discrete square-pyramidal Cu^{II} complexes (Fig. 1). The square pyramid about Cu consists of two N atoms and two O atoms of the tetradentate ligand and an O atom of the water molecule. The complex has nearly C_s symmetry with the approximate mirror plane passing through Cu, C(4) and O(5). The square pyramid about Cu is significantly distorted. The Cu atom is displaced $0.201(1) \text{ \AA}$ out of the best plane through the four basal atoms towards the apical water molecule. The Cu-O(5) bond is not quite perpendicular to the basal plane as evidenced by the O(5)-Cu-N(1) [$94.6(1)^\circ$] and O(5)-Cu-N(2) [$98.1(1)^\circ$] angles and by the O(5)-N(1) [$3.164(4) \text{ \AA}$] and O(5)-N(2) [$3.241(5) \text{ \AA}$] distances. The dihedral angle between the Cu, N(1), O(1) and Cu, N(2), O(3) planes is $15.7(3)^\circ$.

The least-squares plane through the basal atoms of the pyramid reveals the puckering of the ligand (Table 3). These four atoms are almost planar. Interestingly all

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38060 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Equation of least-squares plane through N(1), N(2), O(1) and O(3) and deviations (Å) of atoms from the plane

$$\text{Equation: } 0.8802X - 0.4016Y + 0.2528Z = -1.4348.$$

Cu	-0.201 (1)	C(2)	0.022 (4)
O(1)	0.013 (3)	C(3)	0.015 (5)
O(2)	0.099 (5)	C(4)	-0.674 (5)
O(3)	-0.013 (3)	C(5)	0.035 (5)
O(4)	0.189 (5)	C(6)	0.170 (4)
N(1)	-0.013 (3)	C(7)	0.117 (4)
N(2)	0.013 (3)	C(8)	0.055 (6)
C(1)	0.038 (4)	C(9)	0.401 (6)

of the non-H atoms are on the same side of the plane except the ring atom C(4). All of the intraligand distances are in reasonable agreement with those previously observed. There is considerable distortion in bond angles from the expected tetrahedral and trigonal values, presumably required in order to achieve the tetradentate bonding.

Both water H atoms participate in hydrogen bonding. The hydrogen bonds O(5)—H(O5)···O(2) ($-x, 1-y, 1-z$) and O(5)—H'(O5)···O(4) ($-x, 1-y, -z$) are 2.863 (5) and 2.719 (4) Å with acceptor distances of 2.03 (6) and 1.99 (5) Å and hydrogen-bond angles 166 (5) and 174 (7)°. These bonds link molecules related by a translation along the *c* axis with formation of chains in the *c* direction.

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Structure of Barium 2,4,6-Trinitroresorcinolate Monohydrate

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Abstract. C₆H₃N₃O₈²⁻·Ba²⁺·H₂O (BaTNR), monoclinic, *P2/c*, *a* = 7.546 (8), *b* = 8.082 (5), *c* = 8.756 (3) Å, β = 106.52 (5)°, *V* = 513.16 Å³, *D_c* = 2.58 Mg m⁻³, *Z* = 2. The structure was solved by the Patterson method and refined by the least-squares method to a final *R* factor of 0.051 for 963 observed reflections. The Ba atom is surrounded by nine O atoms, the Ba—O distances ranging from 2.694 (14) to 2.899 (16) Å.

Introduction. Lead, barium and silver salts of nitrophenol and polynitrophenol have good detonating properties and are sensitive to flames; therefore, they can be used as initiating agents, and as igniter powder or delay powder. Seldom, however, has their structure been reported. In order to study the structural features of BaTNR and to compare them with the structure of the related lead compound (normal salt, N-LTNR) reported earlier by Reed (1959), we have determined the crystal structure of BaTNR.

Experimental. Crystals of BaTNR appear in the forms of yellow chips and elongated prisms. They belong to

point group *C_{2h}*. A single crystal approximately 0.3 × 0.3 × 0.1 mm was selected for the experiment. Preliminary cell parameters were obtained by means of rotation and Weissenberg photography. The possible space groups are *P2/c* and *Pc* from the systematic absences (*h0l* absent when *l* odd). Accurate cell parameters were obtained with a four-circle diffractometer.

Intensities of 963 observed reflections within the range 3° ≤ θ ≤ 26° were collected on a Philips PW 1100 automatic four-circle diffractometer with graphite-monochromated Mo *K*α radiation employing the θ–2θ scan technique. All the reflection data were corrected for Lorentz and polarization factors, but not for absorption. The scale and temperature factors were obtained by Wilson's statistical method.

The space group *P2/c* was assumed and this was confirmed at a later stage by intensity calculations. The calculated density indicates that there are two BaTNR molecules in a unit cell. This requires that the Ba atoms must be on a set of special positions. The Patterson synthesis showed that the Ba atom was on a twofold axis. Accordingly, Ba atoms can be located on either of