

Fig. 1. Kristallstruktur der Titelverbindung.

(PPh₃)₂] findet man die größte Abweichung von dieser Ebene für Pd mit 0,079 Å. Die Pd-P(1)-P(2)-Ebene bildet mit der S-C(1)-Pd-Ebene einen Winkel von 7,5°, eine im Sinne beider obengenannten Modelle akzeptable Abweichung von der quadratisch-planaren Struktur.

Die Bindungswinkel um C(1) und die Pd-C(1)-Bindungslänge lassen für C(1) einen Hybridisierungszustand zwischen *sp*² und *sp*³ vermuten. Legt man das Dewar-Chat-Duncanson-Modell (Dewar, 1951; Chatt & Duncanson, 1953) zugrunde, so ist für den Bindungstyp (a) eine schwache σ -Bindung und eine starke π -Bindung zu erwarten. Durch die Erhöhung der Elektronendichte des antibindenden Liganden- π -Orbitals läßt sich wahrscheinlich die Verkürzung der C(1)-C-Bindungen (1,498 Å im Mittel) und die Verlängerung der C(1)-S-Bindung erklären; letztere weist

mit 1,762 Å auf einen partiellen Doppelbindungscharakter hin.

Der beobachtete geringe Transeinfluß [Pd-P(2), *trans* zu C(1): 2,342 (1) Å; Pd-P(1), *trans* zu S: 2,318 (1) Å] spricht jedoch für eine Pd-C(1)- σ -Bindung [Fall (b)]. Die Pd-S-Bindungslänge und die Bindungswinkel um das Pd-Atom sind nicht ungewöhnlich (Jones *et al.*, 1986; Kashiwagi, Yasuoka, Kehi, Kasai & Kakudo, 1968).

Man kann also die 'wahre' Struktur am besten als Resonanzhybrid der obengenannten Extremfälle beschreiben. Die Titelverbindung zeigt keine signifikanten Unterschiede zur nicht isotypen Pt-analogen Verbindung.

Wir danken dem Fonds der Chemischen Industrie für finanzielle Unterstützung.

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Acta Cryst. (1987). C43, 34-37

{Aqua[N,N'-bis(β -carbamoyl)ethyl]trimethylenediamine}perchlorato}copper(II) Perchlorate Monohydrate*

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(Received 15 April 1986; accepted 4 August 1986)

Abstract. [Cu(ClO₄)(C₉H₂₀N₄O₂)(H₂O)]ClO₄·H₂O, *M_r* = 514.76, triclinic, *P* $\bar{1}$, *a* = 8.103 (2), *b* =

10.853 (2), *c* = 12.198 (2) Å, α = 110.93 (2), β = 100.74 (2), γ = 94.88 (2)°, *U* = 970.78 (7) Å³, *Z* = 2, *D_x* = 1.761 Mg m⁻³, *Mo K α* , λ = 0.71069 Å, μ = 1.513 mm⁻¹. *F*(000) = 530, *T* = 296 (4) K, *R*(*F*) = 0.062 for 3704 observed reflections [*I* > 2.5 σ (*I*)]. The coordination geometry about Cu^{II} is a tetragonally

* Aqua(4,8-diazaundecanediamide)perchloratocopper(II) perchlorate monohydrate.

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distorted octahedron with the quadridentate ligand $C_9H_{20}N_4O_2$ (bctn) equatorial and the two monodentate ligands axial. This complex has the *RS* configuration for the two chiral N centers. The three six-membered rings are in a chair form. Hydrogen bonds are formed between perchlorates, the two water molecules and bctn.

Introduction. We have recently initiated a systematic structural study of copper(II) complexes of diamino-diamides. In previous papers we have reported the structures of copper(II) complexes with *N,N'*-bis(β -carbamoyl)ethylenediamine, bctn (Lee, Lu, Liu, Chung & Lee, 1984), and with *N,N'*-bis(β -carbamoyl)ethyl-2-hydroxytrimethylenediamine, bchtn (Lee, Hong, Liu, Chung & Lee, 1984). In this study, the title compound, $[Cu(bctn)(H_2O)(ClO_4)]ClO_4 \cdot H_2O$, has been synthesized and the three-dimensional structure determination by X-ray diffraction methods has been completed.

Experimental. The ligand, *N,N'*-bis(β -carbamoyl)ethyl-trimethylenediamine, was prepared from trimethylenediamine (0.2 mol) and acrylamide (0.4 mol) in acetonitrile (100 cm³) by heating under reflux for 2 h. The solution was cooled and the product was recrystallized from chloroform (Chao & Chung, 1981). The single crystal used in X-ray analysis was obtained by recrystallization from an aqueous solution at room temperature [293 (5) K], and was sealed in a capillary tube with some mother liquor. The crystals thus grown are plate like and blue in color and deteriorate gradually on exposure to air.

Experimental data and structure solution parameters together with the refinement procedure are listed in Table 1. The H atoms of the amines, amide and water molecules were located on the difference maps. Positions of other H atoms were calculated theoretically. The temperature factors of H atoms were assigned initially according to that of the average value of $[Cu(bchtn)](ClO_4)_2$ (Lee, Hong, Liu, Chung & Lee, 1984). In the last cycle of least-squares calculation, $R(F)$ reduced to 0.062.

Discussion. The atomic coordinates and temperature factors are listed in Table 2.* In Fig. 1, the structure of this complex and the deviations of the atoms from the least-squares plane through the donor atoms O(1), O(2), N(2), N(3) are shown, where N(3) and O(1) are 0.10 (1) and 0.11 (1) Å below the least-squares plane and N(2) and O(2) 0.10 (1) and 0.09 (1) Å above it, so

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and perchlorate bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43345 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Experimental data and structure refinement parameters*

Crystal size (mm)	0.2 × 0.3 × 0.55
Diffractometer and data collection technique used	ω -2 θ scan, four-circle diffractometer (Nonius CAD-4) with graphite monochromator
Scan width (2 θ) (°)	2 (0.7 + 0.35 tan θ)
Number and θ range used for measuring lattice parameters	25 reflections with 11 < 2 θ < 20°
Absorption correction applied	Experimental absorption correction based on ψ scan (North, Phillips & Mathews, 1968)
Max. and min. transmission factors	0.793 and 0.635
Max. and min. (sin θ)/ λ in intensity measurement (Å ⁻¹)	0.7028 and 0.0451
Range of <i>hkl</i>	0, -15, -16 to 11, 15, 16
Standard reflections and intensity variation	211; 311; 412 < 4%
Number of reflections measured	4710
Number of unique observed reflections	3704 [$I > 2.5\sigma(I)$]
Method used to solve the structure	Patterson and Fourier methods
Max. and min. heights in difference Fourier synthesis (e Å ⁻³)	1.18 [around Cl(2)] and 0.303
Parameters refined, nonhydrogen atoms	Coordinates, anisotropic and temperature factors (254 parameters)
Quantity minimized	$\sum w(\Delta F)^2$; $w = 1/\sigma_F^2$
Number of reflections per parameter	14
$R(F)$ and wR	0.062 and 0.062
S	1.812
Av., max. Δ/σ	0.009, 0.015
Programs used	XTAL83; Stewart, Hall, Alden Olthof-Hazekamp, Doherty, Pogoaga & Norden (1983)
Computer	CDC Cyber-840
Atomic scattering factors	International Tables for X-ray Crystallography (1974)

Table 2. *Atomic positional and thermal parameters of non-hydrogen atoms*

$B_{eq} = (4/3) \sum_i \sum_j a_i \cdot a_j B_{ij}$, where a_i 's are the length vectors in direct space.

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}(\text{Å}^2)$
Cu	0.25721 (8)	0.15642 (5)	0.22670 (5)	2.41 (4)
Cl(1)	-0.1667 (2)	0.4773 (1)	0.1623 (1)	3.4 (1)
Cl(2)	0.6712 (2)	0.1571 (2)	0.4023 (2)	4.8 (1)
O(11)	-0.2894 (6)	0.4285 (5)	0.0505 (4)	6.1 (4)
O(12)	0.0002 (5)	0.4791 (5)	0.1401 (5)	6.3 (5)
O(13)	-0.1885 (7)	0.3981 (7)	0.2275 (6)	8.8 (7)
O(14)	-0.1830 (7)	0.6081 (5)	0.2270 (5)	8.1 (5)
O(21)	0.6244 (11)	0.0291 (7)	0.3840 (8)	13.2 (9)
O(22)	0.7749 (15)	0.2261 (8)	0.5031 (7)	20.9 (11)
O(23)	0.5427 (5)	0.2235 (5)	0.3705 (5)	6.5 (4)
O(24)	0.7662 (11)	0.1415 (14)	0.3070 (14)	24.5 (21)
O(W1)	-0.0655 (6)	0.1264 (5)	0.1009 (4)	6.0 (4)
O(W2)	0.5341 (7)	-0.2540 (6)	0.2403 (5)	7.0 (5)
O(1)	0.2320 (5)	-0.0398 (3)	0.1743 (4)	3.8 (3)
O(2)	0.3702 (5)	0.1126 (3)	0.0894 (3)	3.4 (3)
N(1)	0.1425 (6)	-0.2461 (5)	0.1544 (5)	4.3 (4)
N(2)	0.1489 (5)	0.1765 (4)	0.3659 (4)	2.7 (3)
N(3)	0.2578 (5)	0.3476 (4)	0.2438 (4)	2.6 (2)
N(4)	0.4497 (7)	0.1247 (5)	-0.0712 (4)	4.1 (4)
C(1)	0.1513 (7)	-0.1177 (5)	0.2083 (5)	3.0 (3)
C(2)	0.0605 (7)	-0.0669 (6)	0.3068 (6)	4.2 (4)
C(3)	0.1550 (8)	0.0611 (6)	0.4040 (5)	3.8 (4)
C(4)	0.2123 (7)	0.3027 (6)	0.4739 (4)	3.6 (4)
C(5)	0.1940 (7)	0.4243 (6)	0.4467 (5)	3.9 (4)
C(6)	0.3054 (7)	0.4497 (5)	0.3687 (5)	3.7 (4)
C(7)	0.3597 (7)	0.3911 (5)	0.1720 (5)	3.3 (4)
C(8)	0.3122 (7)	0.3007 (5)	0.0394 (5)	3.4 (4)
C(9)	0.3807 (6)	0.1719 (5)	0.0203 (5)	2.8 (3)

that the square-planar coordination geometry of Cu^{II} undergoes a very slight tetrahedral distortion. The Cu—N(amino) and Cu—O(amide) bond lengths range from 2.006 (5) to 2.009 (4) Å and from 1.972 (4) to 1.987 (4) Å respectively. A perchlorate O atom and a water O atom are coordinated axially. These axial Cu^{II} bond lengths are significantly longer than the equatorial Cu^{II}—O and Cu^{II}—N bond distances, so that the coordination geometry of copper(II) undergoes tetragonal distortion, and is of the 4 + 2 type (Pavcovic & Brown, 1982; Lee, Lu, Liu, Chung & Lee, 1984) as would be predicted on the basis of the Jahn–Teller effect.

This complex has the *RS* configuration at the two chiral centers N(2) and N(3), and the three six-membered chelate rings adopt the stable chair conformation. The hydrogen-bonding network listed in Table 3 (see also Fig. 2) stabilizes the crystal lattice. Hence the crystal state collapses through dehydration when the crystal has been exposed to air for several weeks.

The temperature factors of three perchlorate O atoms are larger than usual. This may be due to the disordered orientation of the perchlorate ion. It is manifested in the residual peaks around the perchlorate ions in the difference Fourier map. Atoms in each amide group lie in a plane as usual.

Comparison of results. For this crystal and [Cu(bcen)(H₂O)(NO₃)]NO₃·H₂O, we found the following significant results: (1) Both crystals are triclinic. (2) The structures of the two crystals consist of Cu^{II} monomers with tetragonal N₂O₄ ligand donor sets. (3) [Cu(bctn)(H₂O)(ClO₄)]ClO₄·H₂O has the *RS* configuration at the two chiral amine N centers. (4) The coordination bonds Cu—N and Cu—O of [Cu(bctn)(H₂O)(ClO₄)]ClO₄·H₂O are slightly longer than those of [Cu(bcen)(H₂O)(NO₃)]NO₃·H₂O. (5) The dihedral

angles between the planes O(1), N(2), N(3) and N(2), N(3), O(2) for Cu(bctn)²⁺ and Cu(bcen)²⁺ are 7.6 (1) and 14.5 (3)^o respectively.

We thank the National Science Council of Taiwan for financial support.

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

Cu—O(1)	1.972 (4)	C(3)—N(2)	1.485 (9)
Cu—N(2)	2.006 (5)	N(2)—C(4)	1.488 (6)
Cu—N(3)	2.009 (4)	C(4)—C(5)	1.484 (9)
Cu—O(2)	1.987 (4)	C(5)—C(6)	1.503 (9)
Cu—O(W1)	2.702 (5)	C(6)—N(3)	1.484 (6)
Cu—O(23)	2.500 (4)	N(3)—C(7)	1.474 (8)
C(1)=O(1)	1.254 (8)	C(7)—C(8)	1.516 (7)
C(1)—N(1)	1.301 (7)	C(8)—C(9)	1.505 (8)
C(1)—C(2)	1.488 (9)	C(9)—N(4)	1.300 (8)
C(2)—C(3)	1.492 (7)	C(9)=O(2)	1.239 (8)
O(1)—Cu—N(2)	93.3 (2)	C(3)—N(2)—Cu	113.0 (3)
N(2)—Cu—N(3)	94.1 (2)	Cu—N(2)—C(4)	115.8 (4)
N(3)—Cu—O(2)	93.6 (2)	N(2)—C(4)—C(5)	113.0 (4)
O(1)—Cu—O(2)	79.5 (2)	C(4)—C(5)—C(6)	115.4 (5)
O(1)—Cu—N(3)	167.9 (2)	C(5)—C(6)—N(3)	112.4 (4)
O(2)—Cu—N(2)	172.2 (2)	C(6)—N(3)—Cu	116.3 (4)
O(W1)—Cu—O(23)	169.1 (2)	Cu—N(3)—C(7)	114.7 (3)
Cu—O(1)—C(1)	130.2 (4)	N(3)—C(7)—C(8)	113.0 (4)
O(1)—C(1)—N(1)	119.5 (5)	C(7)—C(8)—C(9)	110.4 (5)
O(1)—C(1)—C(2)	121.5 (5)	C(8)—C(9)—N(4)	117.9 (6)
N(1)—C(1)—C(2)	119.0 (6)	C(8)—C(9)—O(2)	120.7 (5)
C(1)—C(2)—C(3)	112.2 (5)	N(4)—C(9)—O(2)	121.4 (5)
C(2)—C(3)—N(2)	122.6 (5)	C(9)—O(2)—Cu	129.0 (3)
Hydrogen bonds			
D—H...O	D...O	∠D—H...O	
N(1)—H(2)...O(12)	3.037 (8)	144.7 (3)	
N(2)—H(7)...O(24)	3.009 (10)	159.7 (6)	
N(3)—H(14)...O(12)	2.967 (7)	140.7 (3)	
N(4)—H(19)...O(W2) ⁱⁱ *	2.895 (9)	154.1 (4)	
N(4)—H(20)...O(2 ⁱⁱ)*	3.027 (7)	130.9 (3)	
O(W1)—H(21)...O(1 ⁱⁱ)*	3.133 (6)	124.3 (5)	
O(W1)—H(22)...O(13)	3.146 (8)	121.7 (3)	
O(W2)—H(24)...O(21)	2.888 (8)	120.7 (5)	

* Center-related atoms [symmetry code: (ii) $-x, -y, -z$]; *International Tables for Crystallography* (1983).

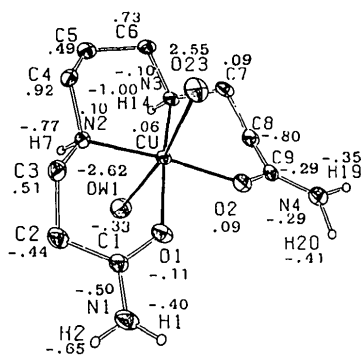


Fig. 1. Perspective view of [Cu(ClO₄)(C₉H₂₀N₄O₂)(H₂O)]⁺, showing the atom-numbering scheme and displacements of atoms from the least-squares plane of O(1), N(2), N(3) and O(2) (Å). E.s.d.'s are around 0.01 Å. Thermal ellipsoids are depicted at the 50% probability level. O(W1) and O(23) are the coordinated water and perchlorate O atoms, respectively.

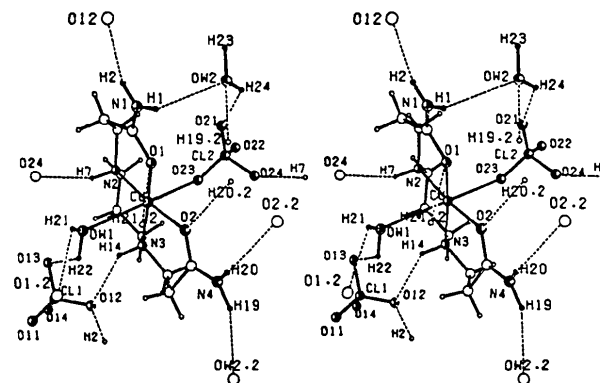


Fig. 2. Stereoview of the molecule, illustrating the shape of the ligand complex and the hydrogen-bonding network [ORTEPII; Johnson (1976)].

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Acta Cryst. (1987). C43, 37–39

Structure of N,N,N',N' -Tetramethylethylenediammonium Tetrachlorodioxosmate(VI)

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(Received 4 June 1986; accepted 28 July 1986)

Abstract. $C_6H_{18}N_4^{2+}.OsCl_4O_2^{2-}$, $M_r = 482.2$, monoclinic, $P2_1/n$, $a = 8.914(4)$, $b = 11.326(2)$, $c = 14.061(2)$ Å, $\beta = 94.74(2)^\circ$, $U = 1414.7$ Å³, $Z = 4$, $D_m = 2.21(3)$, $D_x = 2.263$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 96.98$ cm⁻¹, $F(000) = 912$, room temperature, final $R = 0.032$ for 2928 reflections [$F > 2\sigma(F)$]. The structure contains *trans*-[OsO₂Cl₂]²⁻ anions [Os–O = 1.718(4), 1.728(4), Os–Cl = 2.381(1)–2.397(1) Å] and [Me₂HNCH₂CH₂NHMe₂]²⁺ cations. The anion approximates to the D_{4h} point group and the cation has approximate C_i symmetry. There is hydrogen bonding between N and Cl atoms [minimum N(H)⋯Cl 3.221(6) Å]. There are no hydrogen bonds involving O atoms.

Introduction. The reaction of potassium osmate(VI), $K_2[OsO_2(OH)_4]$, with bidentate amine hydrohalides in water produces dioxosmium(VI) complexes, for example $[OsO_2X_2(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2)]$ ($X = \text{Cl}$ or Br) from $[\text{Me}_2\text{HNCH}_2\text{CH}_2\text{NHMe}_2]X_2$ (Harbron & Levason, 1987). Various attempts to produce single crystals of these materials by reaction over several days mostly produced orange-brown powders but one preparation afforded a few air-stable brown crystals, one of which was used for the present study.

Experimental. Density measured by flotation in carbon tetrachloride/1,2-dibromoethane. Preliminary data from photographic X-ray examination and accurate cell dimensions from 25 accurately centred reflections using an Enraf–Nonius CAD-4 diffractometer fitted with

graphite monochromator and Mo radiation. Intensities of 3796 reflections were recorded [$1 < \theta < 28^\circ$; h (0–11), k (0–14), l (–18 to 18)] using a crystal $0.4 \times 0.1 \times 0.1$ mm. The standard reflection showed decay (19%) during the experiment and this was allowed for in the data reduction. An empirical ψ -scan absorption correction was applied. (Transmission: max. 99.9, min. 85.9%). Systematic absences: $h0l$, $h + l \neq 2n$; $0k0$, $k \neq 2n$. After data reduction 3402 unique reflections remained, $R_{\text{int}} = 0.022$, of which 2933 with $F > 2\sigma(F)$ were used in the analysis. Two possible Os positions were identified from the Patterson synthesis and by repeated structure factor and electron density syntheses the correct Os position and the remaining non-H atoms were located. Evidence for some of the H atoms came from a difference electron density synthesis and H atoms bonded to C were introduced in geometrically calculated positions [$d(\text{C–H}) = 1.0$ Å] with a common refined temperature factor. Five reflections (020, $\bar{1}11$, 002, $\bar{1}13$, $\bar{2}02$) apparently affected by extinction were removed and full-matrix least-squares refinement minimizing $\sum w(\Delta F)^2$ converged to $R = 0.032$ {109 parameters, 2928 reflections, anisotropic (Os, Cl, O) and isotropic (N, C, H) atoms, $w = 1/[\sigma^2(F) + 0.0006F^2]$, max. shift/e.s.d. 0.4, $wR = 0.041$ }. The residual electron density was in the range 0.96 to -1.84 e Å⁻³. The H atoms bonded to N were not introduced into the model. Scattering factors for neutral atoms and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). All calculations were carried out using *SHELX76* (Sheldrick, 1976), *ORTEP* (Johnson, 1965), *PLUTO* (Motherwell & Clegg, 1978) and *GEOM* (Mallinson, 1984; Mallinson & Muir, 1985) on an ICL

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