

Fig. 1. Molecular structure of the title compound along with the atom-numbering scheme. H atoms are omitted. Thermal ellipsoids (ORTEPII; Johnson, 1976) are drawn at 50% probability level.

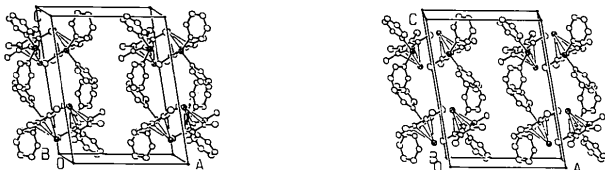


Fig. 2. Stereoscopic view of the molecular packing of the title compound.

C₅(CH₃)₅] (Beachley *et al.*, 1989) or in the 'quasi-dimer' (C₆H₅CH₂)₅C₅In (Schumann, Janiak, Görlitz, Loebel & Dietrich, 1989) is not observed. The shortest In...In distance is as long as 5.929 (1) Å which is

substantially longer than 3.986 (1), 3.986 (1), 5.428, 3.963 (1) and 3.631 (2) Å in the related structures of CpIn, MeCpIn, Me₃SiCpIn, (Cp*In)₆ and (C₆H₅CH₂)₅C₅In, respectively. Furthermore the shortest In...P ($-x, 0.5 + y, -0.5 - z$) distance of 3.703 (1) Å is not significantly shorter than the van der Waals distance of In and P of 3.73 Å (Bondi, 1964). The averaged In—C bond and the In—Cp (centroid) distances of 2.694 (3) and 2.4073 (15) Å are in good agreement with 2.671 and 2.382 (2) Å in the structurally closely related (C₆H₅CH₂)₅C₅In complex. Internal bond parameters of the ligand exhibit no unusual magnitudes.

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Structure of Perchlorato[(2*S*,6*R*,9*S*,13*R*)-2,6,9,13-tetraazatetradecane]copper(II) Perchlorate

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Abstract. [Cu(ClO₄)(C₁₀H₂₆N₄)]ClO₄, *M*_r = 464.79, monoclinic, *P*2₁/*n*, *a* = 7.440 (1), *b* = 14.678 (3), *c* = 16.903 (3) Å, β = 90.845 (1)°, *V* = 1845.7 Å³, *Z* = 4, *D*_x = 1.670 Mg m⁻³, λ(Mo *K*α) = 0.7093 Å, μ = 1.52 mm⁻¹, *F*(000) = 963.80, *T* = 298 (4) K, *R* =

0.049, *wR* = 0.074 for 2275 significant reflections. The coordination about Cu^{II} is distorted square pyramidal with the tetraamine equatorial and the O atom of a perchlorate ion axial. The Cu atom is slightly (0.014 Å) out of the square coordination

plane towards the O atom of the axial coordinated perchlorate ion. The configurations of the four chiral N centres are (2*S*,6*R*,9*S*,13*R*) and/or (2*R*,6*S*,9*R*,13*S*). In the quadridentate ligand the terminal six-membered chelate rings are in a stable chair form and the central five-membered chelate ring is in an unstable skew form.

Introduction. The Cu^{II} complexes of aliphatic tetraamines have been extensively studied. The Cu^{II} ion exhibits diverse stereochemistry in these complexes: trigonal bipyramidal (Sheu, Lee, Lu, Liang & Chung, 1983), square pyramidal (Lu, Wu & Chung, 1986), elongated tetragonal octahedral (Clay, Murray-Rust & Murray-Rust, 1979), or a distorted stereochemistry involving out-of-the-plane ligands positioned both along and off the *z* axis (Davey & Stephens, 1971). As part of our continuing studies on the structures of copper(II)-tetraamine complexes (Lu, Wu & Chung, 1986; Lee, Lee, Hong, Hsieh, Wu & Chung, 1986; Lee, Lee, Hong, Wu & Chung, 1986), the structure of the title compound, [Cu(α,ω -*N*-Me₂-3,2,3-tet)(OClO₃)]ClO₄, has been determined.

Experimental. The ligand 2,6,9,13-tetraazatetradecane was prepared according to the procedure of Clay, Corr, Micheloni & Paoletti (1985). It was isolated as the tetrahydrochloride salt and was recrystallized twice from aqueous ethanol solution. The tetrahydrochloride salt (1.50 g) was dissolved in distilled water (20 ml), and the solution was passed through an anion-exchange column (Amberlite IR400, OH⁻ form) directly into a solution of Cu(ClO₄)₂·6H₂O (1.62 g) in ethanol (20 ml). The resulting deep blue solution was evaporated to dryness. The blue powder was recrystallized from aqueous methanol solution. Single crystals of the title complex were obtained by slow evaporation and were used for the X-ray structure determination.

The crystal dimensions were 0.33 × 0.37 × 0.30 mm. The intensity data were collected on a Nonius diffractometer, using the θ -2 θ -scan mode. Cell dimensions were obtained from 25 reflections with 2 θ angles in the range 20–30°. The *hkl* ranges were $-8 \leq h \leq 8$, $0 \leq k \leq 17$, $0 \leq l \leq 20$. Maximum $\sin\theta/\lambda = 0.59 \text{ \AA}^{-1}$, 3498 reflections measured, 3233 unique reflections, 2275 significant reflections with $I \geq 2.5\sigma(I)$. Three strong standard reflections, checked every hour, varied within 1%. Empirical absorption correction based on azimuthal rotation from three reflections (135, 155, 159) (North, Phillips & Mathews, 1968); the maximum and minimum transmission factors were 0.8537 and 0.9889, respectively. Patterson synthesis, difference Fourier synthesis and least-squares fit were used to locate the heavy Cu atom and other atoms. The function minimized in

full-matrix least-squares fit was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$, $\sigma(F_o)$ from counting statistics. 253 parameters with anisotropic temperature factors for non-H atoms and isotropic for H atoms excluding the refinement of H atomic coordinates which were located by difference Fourier synthesis and theoretical calculations (Lu, Lee, Liang & Chung, 1981). $R = 0.049$, $wR = 0.074$, $S = 2.62$, $(\Delta/\sigma)_{\max} = 0.045$, $(\Delta\rho)_{\max} = 0.84$, $(\Delta\rho)_{\min} = -0.60 \text{ e \AA}^{-3}$. Secondary-extinction coefficient = $4.3(5) \times 10^{-5}$ (length in cm). Atomic scattering factors were from *International Tables for X-ray Crystallography* (1974, Vol. IV). *NRCVAX* programs (Gabe, Le Page, White & Lee, 1987) for the VAX compiler were used to solve the structure.

Discussion. The atomic coordinates and isotropic temperature factors for non-H atoms are listed in Table 1.* The bond lengths and bond angles between non-H atoms are listed in Table 2. A view of the quadridentate ligand with the numbering scheme showing displacements above and below the best plane formed by the four N atoms is shown in Fig. 1. Fig. 2 shows a stereoview of one molecule excluding the H atoms on the C atoms.

As shown in Fig. 2, the two bulky axial *N*-methyl groups lie above the metal ion and hinder the axial position opposite to the coordinated perchlorate group. Thus, this complex is five coordinated; the geometry about the Cu^{II} ion is slightly distorted square pyramidal with the tetraamine equatorial and a perchlorate O atom axial. The tetraamine is coordinated in a square plane with very slight tetrahedral distortion. The displacement of the Cu atom from the best plane formed by the tetraamine N atoms is 0.014 Å towards the O atom of the axial coordinated perchlorate ion (Fig. 1). The equatorial Cu—N distances span a rather narrow range of 2.035 (6)–2.057 (6) Å, which are slightly longer than the typical Cu—N distances for copper(II)-tetraamine complexes (Marongiu, Lingafelter & Paoletti, 1969; Fawcett, Rudich, Toby, Lalancette, Potenza & Schugar, 1980; Lee, Lee, Hong, Hsieh, Wu & Chung, 1986; Wu, Wang, Liou & Chung, 1989). The Cu—O (apical) distance, 2.530 (5) Å, is within the range 2.520 (2)–2.883 (2) Å reported for axial Cu—O bonds (Tasker & Sklar, 1975).

The conformation of the coordinated quadridentate ligand, α,ω -*N*-Me₂-3,2,3-tet, is not in its most stable planar form, as both six-membered chelate rings are in a stable chair form but the five-

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54609 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates and isotropic temperature factors for non-H atoms

B_{eq} is the mean of the principal axes of the thermal ellipsoid.

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}(\text{\AA}^2)$
Cu	0.23930 (8)	0.74351 (4)	0.09251 (4)	2.46 (3)
Cl(1)	-0.26951 (20)	0.74417 (14)	0.03881 (11)	4.60 (8)
Cl(2)	0.88762 (21)	0.97410 (10)	0.25602 (10)	3.72 (6)
O(1)	-0.4044 (7)	0.7410 (4)	0.0977 (4)	5.9 (3)
O(2)	-0.0976 (7)	0.7490 (5)	0.0709 (4)	7.6 (4)
O(3)	-0.2962 (12)	0.8177 (9)	-0.0121 (6)	14.4 (7)
O(4)	-0.2834 (14)	0.6672 (8)	-0.0077 (8)	16.6 (8)
O(5)	0.8809 (8)	1.0675 (4)	0.2768 (4)	6.6 (3)
O(6)	0.9897 (10)	0.9256 (4)	0.3135 (4)	7.8 (4)
O(7)	0.9773 (14)	0.9652 (6)	0.1852 (5)	11.2 (5)
O(8)	0.7181 (9)	0.9391 (6)	0.2531 (7)	11.6 (6)
N(1)	0.1978 (7)	0.7776 (4)	0.2076 (3)	3.2 (2)
N(2)	0.2712 (6)	0.6107 (3)	0.1252 (3)	3.1 (2)
N(3)	0.2664 (7)	0.6947 (4)	-0.0192 (3)	3.8 (2)
N(4)	0.2215 (10)	0.8781 (4)	0.0595 (4)	5.3 (3)
C(1)	0.3637 (11)	0.7811 (6)	0.2567 (5)	4.9 (4)
C(2)	0.0593 (9)	0.7191 (5)	0.2466 (4)	4.2 (3)
C(3)	0.1053 (10)	0.6199 (5)	0.2502 (4)	4.3 (3)
C(4)	0.1173 (9)	0.5735 (5)	0.1702 (5)	4.3 (3)
C(5)	0.3117 (10)	0.5572 (4)	0.0532 (5)	4.4 (3)
C(6)	0.2170 (11)	0.5977 (5)	-0.0158 (4)	4.9 (3)
C(7)	0.1859 (11)	0.7443 (6)	-0.0854 (4)	5.1 (4)
C(8)	0.2354 (12)	0.8428 (6)	-0.0860 (4)	5.5 (4)
C(9)	0.1607 (13)	0.8990 (5)	-0.0222 (5)	5.9 (4)
C(10)	0.3629 (16)	0.9365 (6)	0.0856 (6)	6.9 (5)

Table 2. Selected bond lengths (Å) and angles (°)

Cu—N(1)	2.040 (5)	N(3)—C(6)	1.472 (10)
Cu—N(2)	2.039 (5)	N(3)—C(7)	1.457 (9)
Cu—N(3)	2.035 (6)	N(4)—C(9)	1.481 (11)
Cu—N(4)	2.057 (6)	N(4)—C(10)	1.422 (12)
Cu—O(2)	2.530 (5)	C(2)—C(3)	1.496 (10)
N(1)—C(1)	1.478 (9)	C(3)—C(4)	1.521 (11)
N(1)—C(2)	1.501 (9)	C(5)—C(6)	1.479 (11)
N(2)—C(4)	1.488 (8)	C(7)—C(8)	1.493 (13)
N(2)—C(5)	1.484 (8)	C(8)—C(9)	1.474 (13)
N(1)—Cu—N(2)	89.64 (20)	Cu—N(3)—C(6)	106.0 (4)
N(1)—Cu—N(3)	173.01 (23)	Cu—N(3)—C(7)	119.6 (5)
N(1)—Cu—N(4)	90.80 (24)	C(6)—N(3)—C(7)	114.4 (6)
N(2)—Cu—N(3)	84.43 (22)	Cu—N(4)—C(9)	118.0 (5)
N(2)—Cu—N(4)	177.0 (3)	Cu—N(4)—C(10)	116.8 (5)
N(3)—Cu—N(4)	95.3 (3)	C(9)—N(4)—C(10)	112.3 (7)
Cu—N(1)—C(1)	114.1 (4)	N(1)—C(2)—C(3)	114.6 (5)
Cu—N(1)—C(2)	113.2 (4)	C(2)—C(3)—C(4)	114.5 (6)
C(1)—N(1)—C(2)	110.3 (5)	N(2)—C(4)—C(3)	110.4 (5)
Cu—N(2)—C(4)	113.7 (4)	N(2)—C(5)—C(6)	109.6 (5)
Cu—N(2)—C(5)	107.9 (4)	N(3)—C(6)—C(5)	107.7 (6)
C(4)—N(2)—C(5)	113.1 (5)	N(3)—C(7)—C(8)	113.0 (6)
Cu—O(2)—Cl(1)	164.5 (9)	C(7)—C(8)—C(9)	116.2 (7)
		N(4)—C(9)—C(8)	117.1 (7)

membered ring is in an unstable skew form. Thus, it appears to be relatively unstable. These structural features are consistent with a relatively high heat of formation and a small stability constant for the Cu^{II} complex (Bianchini, Fabbrizzi, Paoletti & Lever, 1975).

Previously we have reported the crystal structure of [N,N'-bis(3-aminopyrpyl)-1,2-ethanediamine]-perchloratocopper(II) perchlorate hemihydrate, [Cu(3,2,3-tet)(OCIO₃)]ClO₄·½H₂O (Lee, Lee, Hong, Hsieh, Wu & Chung, 1986). The configurations of the two chiral N centres of this complex are of the

same *R* or *S* configuration, and are different from those of the title complex, two asymmetric N atoms which have the four chiral N centres of (2*S*,6*R*,9*S*,13*R*) or (2*R*,6*S*,9*R*,13*S*). The arrangement of the tetraamine in [Cu(3,2,3-tet)(OCIO₃)]ClO₄·½H₂O appears to be relatively strain free; the conformation of the coordinated tetraamine is in its most stable planar form, with both six-membered rings in a stable chair form and the five-membered ring in a stable *gauche* form. Thus, this complex is much more stable than the title complex (Clay, Corr, Mecheloni & Paoletti, 1985). Structural data of six Cu^{II} complexes of linear aliphatic tetraamines have been reported (Sarconi, Paoletti & Ciampolini, 1961; Weatherburn, Billo, Jones & Margerum, 1970; Barbucci, Fabbrizzi & Paoletti, 1972; Clay, Murray-Rust & Murray-Rust, 1979; Clay, Corr, Micheloni & Paoletti, 1985). For these six complexes, the title complex is the only complex which contains an unstable five-membered chelate ring. In addition, the Cu—N bond distances of the title complex are significantly longer than those of the other tetraamine

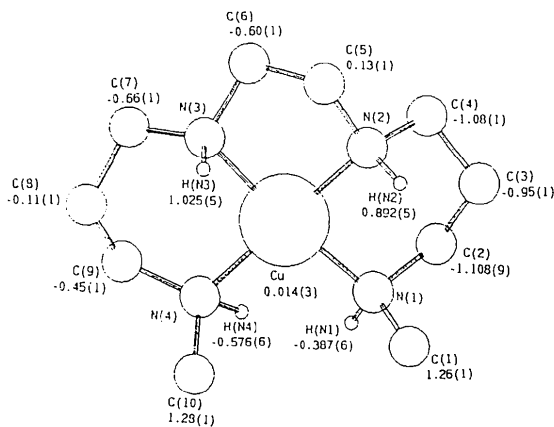


Fig. 1. Perspective view of the atom-numbering scheme of the molecule excluding the perchlorate groups and the H atoms attached to the C atoms. The displacements from the best plane formed by the four N atoms coordinated to the Cu^{II} atom are indicated.

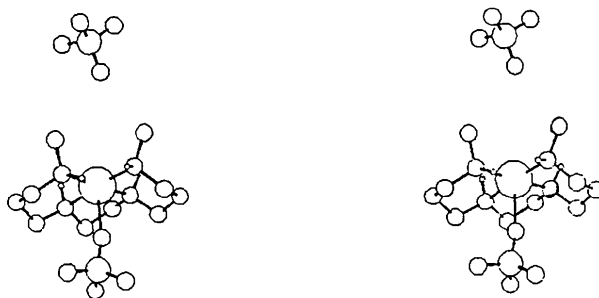


Fig. 2. A stereoview of the molecular packing excluding the H atoms on the C atoms.

complexes. It is interesting to note that $[\text{Cu}(\alpha,\omega\text{-N-Me}_2\text{-2,2,2-tet})]^{2+}$ is more stable than $[\text{Cu}(2,2,2\text{-tet})]^{2+}$; however, $[\text{Cu}(\alpha,\omega\text{-N-Me}_2\text{-3,2,3-tet})]^{2+}$ is less stable than $[\text{Cu}(3,2,3\text{-tet})]^{2+}$. The effects of the two *N*-methyl groups in $[\text{Cu}(\alpha,\omega\text{-N-Me}_2\text{-2,2,2-tet})]^{2+}$ and $[\text{Cu}(\alpha,\omega\text{-N-Me}_2\text{-3,2,3-tet})]^{2+}$ are completely different from each other.

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Structure of Potassium Hydrogen Diethylmalonate Monohydrate

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Abstract. $[\text{K}(\text{C}_7\text{H}_{11}\text{O}_4)]\cdot\text{H}_2\text{O}$, $M_r = 216.27$, tetragonal, $P4_3$, $a = 9.251(3)$, $c = 13.123(4)$ Å, $V = 1123(1)$ Å³, $Z = 4$, $D_x = 1.29$ Mg m⁻³, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 0.45$ mm⁻¹, $F(000) = 456$, $T = 293$ K, $R = 0.041$ for 1121 observed reflections. The asymmetric unit contains one formula unit of potassium hydrogen diethylmalonate linked by a hydrogen bond to the water molecule. Each molecule is intramolecularly hydrogen bonded and the carboxylic and

carboxylate groups lying in the same plane of symmetry are equivalent.

Introduction. As part of our studies on malonic acid derivatives (Delarbre, Maury & Bardet, 1985; Dubourg, Rambaud, Delarbre, Maury & Declercq, 1988), we describe herein the crystal structure of potassium hydrogen diethylmalonate. Raman and infrared studies on the KH malonate acid and KH