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Structure of Diperchlorato[(2*SR*,5*RS*,8*RS*,11*SR*)-2,5,8,11-tetraazadodecane]-nickel(II)

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Abstract. $[Ni(ClO_4)_2(C_8H_{22}N_4)]$, $M_r = 431{\cdot}90$, orthorhombic, $C222_1$, $a = 7{\cdot}661\,(3)$, $b = 15{\cdot}344\,(3)$, $c = 14{\cdot}323\,(3)$ Å, $V = 1683{\cdot}7\,(8)$ Å^3, $Z = 4$, $D_x = 1{\cdot}704$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7093$ Å, $\mu = 1{\cdot}52$ mm^{-1}, $F(000) = 895{\cdot}82$, $T = 295\,(3)$ K, $R = 0{\cdot}054$, $wR = 0{\cdot}074$ for 746 observed reflections. The central Ni^{II} atom and the two Cl atoms of the perchlorate groups are located on twofold axes. The coordination about Ni^{II} is a distorted square bipyramid with the tetraamine ligand equatorial and two O atoms of the perchlorate ions axial. The important bond distance is Ni—O(1) = 2·840 (11) Å. The bond angle of N(2)—Ni—N(2^{i}) is 93·4 (4)° and the *trans* N—Ni—N angles are 173·3 (5)°. The hydrogen bonds among the tetraamine and perchlorate groups stabilize the crystal structure.

Introduction. The crystal structures of transition metal complexes of $H_2N(CH_2)_lNH(CH_2)_mNH(CH_2)_nNH_2$ (*l,m,n*-tet) have been extensively studied (Marongiu, Lingafelter & Paoletti, 1969; Fawcett, Rudich, Toby, Lalancette, Potenza & Schugar, 1980; Lee, Lee, Hong, Hsieh, Wu & Chung, 1986; Boggs & Donohue, 1975). However, the crystal structures of transition metal complexes of $CH_3NH(CH_2)_lNH(CH_2)_mNH(CH_2)_nNHCH_3$ (Me$_2$-*l,m,n*-tet) have received little attention. An earlier report from this laboratory described the structure of the copper(II) complex of Me$_2$-2,2,2-tet (Wu, Wang, Liou & Chung, 1989). In this study, the structure of the nickel(II) complex has been determined.

Experimental. 2,5,8,11-Tetraazadodecane tetrahydrochloride was synthesized according to the method of Clay, Corr, Micheloni & Paoletti (1985). It (2·0 g) was dissolved in 10 cm^3 of water and the solution was passed through an anion exchange column (Amberlite IR400, OH$^-$form) directly into a hot aqueous solution of $Ni(ClO_4)_2.6H_2O$ (2·67 g). The solution was refluxed for two hours and was slowly evaporated to give reddish-orange crystals. The single crystals used in the X-ray analysis were obtained by recrystallization from methanol at room temperature.

A crystal of size 0·50 × 0·52 × 0·30 mm, cut from orange parallelepiped shape, was used for the X-ray structure determination; Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$. Unit-cell parameters from 25 reflections with $20 < 2\theta < 27°$, data collected by ω–2θ scans with scan width of $2(0{\cdot}60 + 0{\cdot}25\tan\theta)°$ and scan speed of 2·0 to 8·0° min^{-1}. Empirical absorption correction based on azimuthal rotation from three reflections (402, $5\bar{1}3$, 404) (North, Phillips & Mathews, 1968); the minimum, maximum and average correction factors are 0·9128, 0·9986 and 0·9590, respectively. Max.

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Table 1. *Atomic positional parameters and B_{eq}; e.s.d.'s refer to the last significant figure*

	x	y	z	B_{eq}*(Å^2)
Ni	0	0·18981 (8)	$\frac{1}{4}$	3·30 (5)
Cl(1)	$\frac{1}{2}$	0·2375 (3)	$\frac{1}{4}$	6·34 (17)
Cl(2)	0·8365 (5)	$\frac{1}{2}$	1	5·29 (15)
O(1)	0·3648 (12)	0·1861 (8)	0·2149 (11)	11·8 (8)
O(2)	0·4358 (14)	0·2897 (9)	0·3233 (8)	10·2 (6)
O(3)†	1·0045 (22)	0·4773 (12)	0·9764 (14)	8·7 (12)
O(4)†	0·812 (3)	0·4330 (16)	0·958 (3)	17·9 (26)
O(5)	0·750 (3)	0·4471 (14)	1·0552 (20)	26·1 (20)
N(1)	−0·0380 (13)	0·2783 (5)	0·1600 (6)	5·4 (4)
N(2)	−0·0124 (19)	0·1045 (5)	0·1533 (7)	7·0 (5)
C(1)	0·033 (3)	0·3588 (7)	0·1973 (12)	11·4 (11)
C(2)	0·009 (3)	0·2450 (9)	0·0638 (8)	8·9 (8)
C(3)	−0·085 (3)	0·1520 (10)	0·0627 (10)	9·3 (9)
C(4)	−0·122 (3)	0·0320 (10)	0·1728 (15)	11·6 (12)

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

† The occupanices of O(3) and O(4) are 0·5.

Table 2. *Bond lengths* (Å) *and bond angles* (°)

Ni—N(1)	1·895 (7)	Ni—N(2)	1·908 (9)
N(2)—C(4)	1·421 (24)	Cl(1)—O(1)	1·396 (11)
C(1)—C(1^{i})	1·59 (4)	Cl(1)—O(2)	1·409 (11)
C(2)—C(3)	1·596 (25)	Cl(2)—O(3)	1·376 (15)
Cl(2)—O(4)	1·205 (19)	Cl(2)—O(5)	1·312 (15)
N(1)—C(1)	1·452 (15)	N(1)—C(2)	1·513 (15)
N(2)—C(3)	1·588 (19)	Ni—O(1)	2·840 (11)
N(1)—Ni—N(1^{i})	88·4 (4)	N(1)—Ni—N(2)	89·5 (4)
Ni—N(2)—C(3)	107·2 (7)	N(1)—Ni—N(2^{i})	173·3 (5)
Ni—N(2)—C(4)	115·1 (11)	C(3)—N(2)—C(4)	108·4 (14)
N(2)—Ni—N(2^{i})	93·4 (4)	O(1)—Cl(1)—O(1^{ii})	111·2 (8)
O(1)—Cl(1)—O(2)	109·3 (7)	N(1)—C(1)—C(1^{i})	103·1 (12)
O(1)—Cl(1)—O(2^{ii})	108·2 (8)	O(2)—Cl(1)—O(2^{ii})	110·7 (8)
O(3)—Cl(2)—O(3^{iii})	41·3 (11)	O(3)—Cl(2)—O(4)	78·7 (16)
N(1)—C(2)—C(3)	101·8 (11)	O(3)—Cl(2)—O(4^{iii})	118·8 (14)
O(3)—Cl(2)—O(5)	117·6 (12)	O(3)—Cl(2)—O(5^{iii})	118·6 (14)
N(2)—C(3)—C(2)	104·3 (10)	O(4)—Cl(2)—O(4^{iii})	162·4 (18)
O(4)—Cl(2)—O(5)	72 (3)	O(4)—Cl(2)—O(5^{iii})	98·6 (20)
O(5)—Cl(2)—O(5^{iii})	119·5 (12)	Ni—N(1)—C(1)	107·6 (7)
Ni—N(1)—C(2)	109·9 (6)	C(1)—N(1)—C(2)	122·2 (13)
Ni—O(1)—Cl(1)	130·9 (7)		

Symmetry-equivalent bond lengths and angles are excluded. Symmetry code: (i) $-x, y, 0{\cdot}5-z$; (ii) $1{\cdot}0-x, y, 0{\cdot}5-z$; (iii) $x, 1{\cdot}0-y, 2{\cdot}0-z$.

$(\sin\theta)/\lambda = 0{\cdot}59$ Å^{-1} ($0 \le h \le 9$, $0 \le k \le 18$, $0 \le l \le 17$); standard reflections $\bar{3}73$, $3\bar{7}3$ and $22\bar{7}$ checked every hour, varied within 1%; 853 reflections collected; 746 unique with $I > 2{\cdot}5\sigma(I)$. The heavy atom Ni was located by using Patterson synthesis and the additional Cl atoms were checked by direct methods. Other atom positions (including H atoms) were obtained by alternate difference Fourier synthesis and least-squares-fit methods. The function minimized in the full-matrix least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where w = Hughes weight: $|F_o| > 200$, $w = 1{\cdot}0$; $|F_o| \le 200$, $w = 200/|F_o|$. 127 parameters with anisotropic atomic parameters for non-H atoms and isotropic temperature factors for H atoms. $R = 0{\cdot}054$, $wR = 0{\cdot}074$, $S = 5{\cdot}32$; $(\Delta/\sigma)_{\max} = 0{\cdot}04$, $(\Delta/\sigma)_{\rm av} = 0{\cdot}02$ in the final cycle; $(\Delta\rho)_{\max} = 0{\cdot}51$ (8), $(\Delta\rho)_{\min} = -0{\cdot}37$ (8) e Å^{-3}. Secondary-extinction coefficient 5·7 (4) × 10^{-4} (length in cm). Atomic scattering factors 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 are listed in Table 1.* Table 2 lists bond lengths and bond angles. The structure refinement is heavily affected by the weighting scheme applied in the least-squares fit. The coordination around the nickel atom is square bipyramidal with two perchlorate anions at the fifth and sixth sites. One of the perchlorate groups, Cl(2)O$_4^-$, is in a disordered state. The maximum distance of the atoms from the best tetraamine plane is 0·14 Å. The conformation of the quadridentate ligand, Me$_2$-2,2,2-tet, is in the stable planar structure within 0·14 Å with all three five-membered chelate rings having a *gauche* form. The numbering scheme and the displacements of the atoms from the tetraamine plane are shown in Fig. 1. The four Ni—N distances span a narrow range, 1·895 (7) to 1·908 (9) Å, and are slightly shorter (but within the standard deviation) than the average Ni—N distance of nickel(II) tetraamine complexes (Lu, Chung & Ashida, 1991). The axial Ni—O(1) bond length is 2·840 (11) Å. The angle Ni—O(1)—Cl(1) is 130·9 (7)°. The configuration of the four chiral N centers is 2*SR*, 5*RS*, 8*RS* and 11*SR* (Bosnich, Poon & Tobe, 1965).

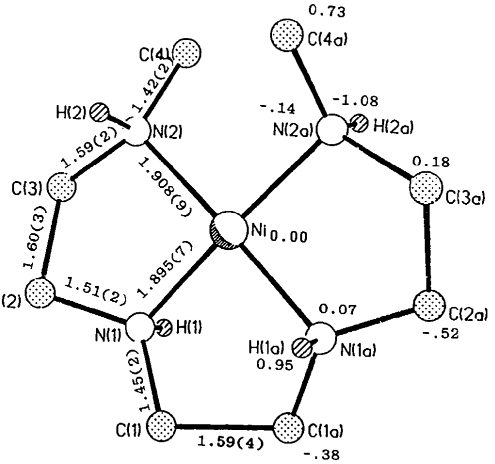

Fig. 1. Perspective view of the atom-numbering scheme of the molecule excluding the perchlorate ions and the H atoms except those attached to N(1) and N(2), and their symmetry-related atoms. Bond lengths (Å) and displacements from the best NiN$_4$ plane (Å) are indicated on the half molecule and its symmetry-related half, respectively.

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* 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 54107 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The hydrogen bonds among the tetraamine and perchlorate groups are N(1)—H(1)···O(2) and N(2)—H(2)···O(4) with corresponding lengths of 3·061 and 3·011 Å, respectively. These hydrogen bonds stabilize the crystal structure.

Comparing the structure of this crystal with that of perchlorato(Me$_2$-2,2,2-tet)copper(II) perchlorate monohydrate (Wu, Wang, Liou & Chung, 1989), we find that they are isomorphous. Both nickel(II) and copper(II) ions are six-coordinated, distorted square bipyramidal with the Me$_2$-2,2,2-tet ligand equatorial and the O atoms of the perchlorate ions axial. All of the five-membered rings for both complexes have the stable *gauche* conformation and the hydrogen bonds stabilize the crystal structures. The Ni—N$_4$ distances, 1·895 (7) to 1·908 (9) Å, are shorter than the Cu—N$_4$ distances, 1·990 (10) to 1·994 (14) Å; while the Ni—O distance, 2·840 (11) Å, is much longer than the Cu—O distance, 2·578 (8) Å. The N—*M*—N angles of the five-membered rings for the Ni^{II} complex are larger than those for the Cu^{II} complex.

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Structure of {Bis[(1-methylimidazol-2-yl)methyl]amine}(1-methylimidazole)copper(II) Diperchlorate

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Abstract. $[Cu(C_{14}H_{21}N_7)]^{2+}.2ClO_4^-$, $M_r = 549{\cdot}81$, monoclinic, $P2_1/n$, $a = 9{\cdot}171$ (1), $b = 8{\cdot}999$ (1), $c = 26{\cdot}677$ (3) Å, $\beta = 94{\cdot}08$ (1)°, $V = 2196{\cdot}1$ (5) Å^3, $Z = 4$, $D_x = 1{\cdot}66$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}70930$ Å, $\mu = 13{\cdot}0$ cm^{-1}, $F(000) = 1124$, $T = 295$ K, final $R = 0{\cdot}063$ for 2687 observed reflections. The geometry around the Cu^{II} ion is best described as a distorted octahedron with coordination to two imidazole N atoms and an amine N atom of the bis[(1-methylimidazol-2-yl)methyl]amine ligand (bmima), one imidazole N atom from a 1-methylimidazole ligand and two O atoms from the two disordered perchlorate anions. The N atoms occupy equatorial positions of the octahedron with Cu—N bond distances ranging from 1·954 (6)–2·056 (5) Å. The perchlorate O atoms are weakly coordinated and occupy axial positions with Cu—O bond distances ranging from 2·55 (1)–2·72 (1) Å. One of the coordinated perchlorates is also partially hydrogen bonded to the amine H atom of the bmima ligand.

Introduction. Imidazole complexes of copper are of interest as models of the histidine (imidazole) ligands known to be present at the active site of numerous copper proteins. For instance, imidazoles are found at the active sites of plastocyanin (Guss & Freeman, 1983), azurin from *Pseudomonas aeruginosa* (Norris, Anderson & Baker, 1988) and deoxyhemocyanin from *Panularis interruptus* (Linzen, Soeter, Riggs, Schneider, Schartau, Moore, Yokota, Behrens, Nakashima, Takagi, Nemoto, Vereifken, Bak, Beintema, Volbeda, Gaykema & Hol, 1985). Hemocyanin functions as an oxygen transport protein and is found in the hemolymph of several species of arthro-

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