

Structure of Zn(cyclam)(ClO₄)₂

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Abstract. Diperchlorato(1,4,8,11-tetraazacyclotetradecane)zinc(II), [Zn(ClO₄)₂(C₁₀H₂₄N₄)], $M_r = 464.67$, triclinic, $P\bar{1}$, $a = 8.279$ (4), $b = 8.419$ (4), $c = 8.076$ (4) Å, $\alpha = 116.70$ (5), $\beta = 95.80$ (4), $\gamma = 112.25$ (5)°, $V = 439.7$ (4) Å³, $Z = 1$, $D_m = 1.82$, $D_x = 1.75$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu(\text{Mo } K\alpha) = 16.77$ cm⁻¹, $F(000) = 240$, $T = 290$ K, $R(F) = 0.050$ for 2197 ($I > 3\sigma$) reflections. The complex is monomeric. The zinc atom occupies a crystallographic centre of symmetry and is in a tetragonally elongated octahedral coordination array comprising the four nitrogen atoms of the macrocycle and two oxygen atoms, one from each of the perchlorate groups. The overall geometry is thus similar to an analogous cobalt(II) complex, but the Zn—N bonds of 2.086 (2) and 2.090 (2) Å are approximately 0.1 Å longer than the Co—N bonds. The axial Zn—O(ClO₄) 'semi-coordinated' bonds are 2.380 (2) Å.

Introduction. Crystals of the title compound were produced adventitiously during attempts to synthesize [Zn(cyclam)(SC₆F₅)₂].2C₆F₅SH (Addison & Sinn, 1983). Since there is considerable current interest in metal complexes of N₄ macrocyclic ligands in general, and cyclam in particular, we determined the crystal structure for comparison with the analogous cobalt(II), nickel(II), copper(II), palladium(II) and silver(II) complexes. This series of complexes is unusual in that each metal atom exhibits a somewhat different mode of perchlorate bonding. The Co complex exists as isolated octahedra, with Co—O axial bonds of 2.409 (3) Å (Endicott, Lilie, Kuszaj, Ramaswamy, Schmonsees, Simic, Glick & Rillema, 1977); the Ni complex has the perchlorates shared between octahedra in a disordered structure (Prasad, Nyburg & McAuley, 1987); the Cu complex exists as isolated octahedra, but with a very strong Jahn–Teller elongation of the axial Cu—O bonds to 2.57 Å (Tasker &

Sklar, 1975); the Pd complex is four coordinate to the macrocycle, with ionic perchlorates (Toriumi, Yamashita, Ito & Ito, 1986); the Ag complex exists as two forms, one of which is disordered with no axial interactions whereas the other contains very weak axial Ag—O interactions of 2.788 (2) Å (Ito, Ito & Toriumi, 1981). In the Zn complex there is no possibility of Jahn–Teller distortion of the axial ligands.

Experimental. Crystals were obtained by adding a 1:1 molar ratio of Zn(ClO₄)₂.6H₂O (0.37 g) and cyclam (0.20 g) to a solution (24 ml) of 10% 2-methoxyethanol and 90% methanol (by volume) at 333 K. C₆F₅SH (0.067 ml) was added to a separate solution (10 ml) of the above solvent plus 5.0 M NaOH (0.10 ml), giving a 1:1 molar ratio of OH⁻ to C₆F₅SH. Both solutions were mixed in a beaker, which was then placed in a 3500 ml water bath at 333 K and allowed to cool to room temperature. The 1:2 ratio of C₆F₅SH to cyclam prevented the premature precipitation of the solid. Opaque crystals of irregular habit were obtained by slow evaporation, of the solution placed in petri dishes, at room temperature. The density was measured by flotation in CHBr₃/CHCl₃. A fragment measuring approximately 0.4 × 0.5 × 0.2 mm³ was employed to collect X-ray intensity data on a Nicolet P2₁ diffractometer, using graphite-monochromated Mo K α radiation. Unit-cell dimensions were from 15 reflections, $3.0 < \theta < 10.2^\circ$; no systematic absences, space group $P\bar{1}$ by intensity statistics and satisfactory structure solution and refinement; 2545 unique reflections, $1.5 < \theta < 30^\circ$, θ - 2θ scan, scan speed ranging from 2.0 to 29.3° min⁻¹, $[(\sin\theta)/\lambda]_{\text{max}} = 0.7035$ Å⁻¹; 2197 with $I > 3\sigma(I)$, $-11 \leq h \leq 11$, $-11 \leq k \leq 11$, $-11 \leq l \leq 11$; three intensity standards checked every 50 reflections showed no non-statistical variation during data

collection; Lorentz and polarization corrections were applied; no absorption corrections; the transmission factor was estimated to vary by a factor of two at most. In $P\bar{1}$ the zinc atom is constrained to lie at the crystallographic centre of symmetry. All other atoms (including hydrogens) were located from difference Fourier maps. The program used for F_{obs} refinement was *SHELX76* (Sheldrick, 1976). All hydrogen atoms were refined isotropically, with the exception of H(4) which was fixed in a calculated position. Final refinement values are $w = 1.0/[\sigma^2(F) + 4.095 \times 10^{-3}F^2]$, $R = 0.050$, $wR = 0.054$, $S = 0.987$, $(\Delta/\sigma)_{\text{max}} = 0.15$ for non-hydrogen atoms, no extinction correction was made; max. $\Delta\rho$ excursion in final difference map $1.45 \text{ e } \text{\AA}^{-3}$ (near Zn); calculations performed on a MicroVAX 3600 computer. Diagrams were produced using *ORTEP* (Johnson, 1976). Atomic scattering factors used were from Cromer & Mann (1968) (Cl, O, N, C) and *International Tables*

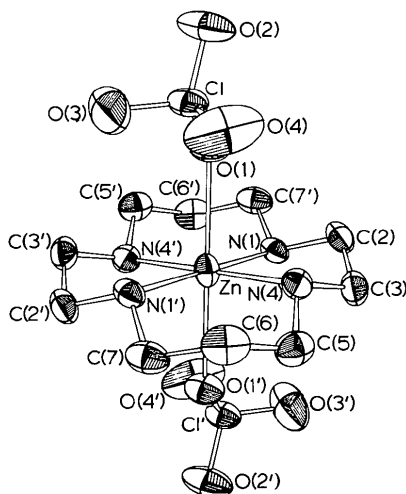


Fig. 1. ORTEP diagram of the structure.

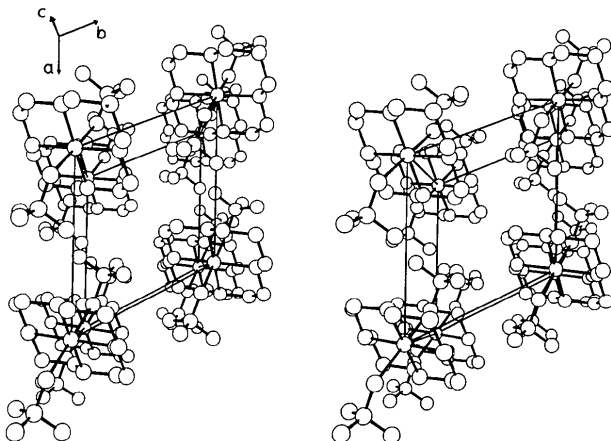


Fig. 2. Stereoplot showing crystal packing.

Table 1. Atomic positions and equivalent isotropic displacement factors U_{eq} (\AA^2)

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j, \quad \Delta U_{\text{eq}} = (\sum_i \sum_j \Delta U_{ij}^2)^{1/2}.$$

	x	y	z	U_{eq} (ΔU_{eq})
Zn	0.0000	0.0000	0.0000	0.0324 (6)
Cl	-0.2613 (1)	0.1918 (1)	-0.1240 (1)	0.040 (1)
O(1)	-0.1269 (3)	0.1215 (4)	-0.1644 (3)	0.045 (3)
O(2)	-0.2843 (5)	0.2743 (5)	-0.2361 (5)	0.071 (6)
O(3)	-0.4305 (4)	0.0237 (6)	-0.1727 (8)	0.093 (8)
O(4)	-0.2038 (7)	0.3326 (7)	0.0778 (5)	0.106 (9)
N(1)	0.2181 (3)	0.0732 (3)	-0.1076 (3)	0.032 (3)
N(4)	0.1553 (3)	0.2965 (3)	0.2407 (3)	0.034 (3)
C(2)	0.3276 (4)	0.2961 (4)	0.0118 (5)	0.041 (4)
C(3)	0.3418 (4)	0.3678 (4)	0.2239 (5)	0.042 (4)
C(5)	0.1503 (4)	0.3185 (5)	0.4323 (4)	0.044 (7)
C(6)	-0.0433 (5)	0.2382 (5)	0.4402 (5)	0.048 (5)
C(7)	-0.1618 (5)	0.0092 (5)	0.3205 (5)	0.044 (4)

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

Zn—O(1)	2.380 (2)	N(1)—C(2)	1.477 (3)
Zn—N(1)	2.086 (2)	N(4)—C(3)	1.475 (4)
Zn—N(4)	2.090 (2)	N(4)—C(5)	1.481 (4)
Cl—O(1)	1.447 (2)	C(2)—C(3)	1.512 (5)
Cl—O(2)	1.403 (2)	C(5)—C(6)	1.506 (5)
Cl—O(3)	1.417 (3)	C(6)—C(7)	1.522 (5)
Cl—O(4)	1.403 (3)	C(7)—N(1')	1.475 (4)
O(1)—Zn—N(1)	86.0 (1)	Zn—N(1)—C(7')	114.7 (2)
O(1)—Zn—N(4)	89.0 (1)	C(2)—N(1)—C(7')	113.2 (2)
N(1)—Zn—N(4)	85.3 (1)	Zn—N(4)—C(3)	105.2 (2)
O(1)—Cl—O(2)	110.3 (2)	Zn—N(4)—C(5)	114.3 (2)
O(1)—Cl—O(3)	107.7 (2)	C(3)—N(4)—C(5)	114.7 (2)
O(1)—Cl—O(4)	108.9 (2)	N(1)—C(2)—C(3)	109.0 (2)
O(2)—Cl—O(3)	110.1 (2)	N(4)—C(3)—C(2)	109.9 (2)
O(2)—Cl—O(4)	111.9 (2)	N(4)—C(5)—C(6)	112.6 (2)
O(3)—Cl—O(4)	107.8 (3)	C(5)—C(6)—C(7)	116.0 (2)
Zn—O(1)—Cl	127.5 (1)	N(1')—C(7)—C(6)	112.3 (2)
Zn—N(1)—C(2)	105.6 (2)		

for *X-ray Crystallography* (1974) (Zn, H); anomalous-dispersion factors were from Cromer & Liberman (1970).

Discussion. Atomic positions are given in Table 1.* The molecular geometry and atomic numbering are depicted in Fig. 1. The complex is monomeric, with the two perchlorates coordinated axially in a tetragonally distorted octahedral arrangement about the zinc atom. There is no disorder, save a slight rotational freedom about the Cl—O(1) bond. The Cl—O(coordinated) bond [1.447 (2) \AA] is significantly longer than the other three (av. 1.407 \AA). The molecule is constrained to lie about a crystallographic centre of symmetry, and the conformation of the cyclam heterocycle is the commonly observed *trans*-III arrangement (for a description of the possible arrangements see Thöm, Fox, Boeyens &

* Lists of structure factors, thermal parameters and hydrogen coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52868 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Hancock, 1984). Within the cyclam moiety the five-membered rings are *gauche* whereas the six-membered rings are in a slightly flattened chair conformation. This complex is thus essentially isostructural with the Co analogue. The Zn—O bond length of 2.380 (2) Å compares with Co—O of 2.409 (3) Å, but the Zn—N bonds of 2.086 and 2.090 (2) Å are considerably longer than the Co—N bonds of 1.982 and 1.978 (4) Å. The cyclam macrocycle accommodates this difference by alteration of the bond angles, principally those at the nitrogen atoms.

Bond distances and angles are given in Table 2 and a stereoplot in Fig. 2.

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Structure of Sodium (Trimethylenediaminetetraacetato)ferrate(III) Trihydrate

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Abstract. Na[Fe(C₁₁H₁₄N₂O₈)]·3H₂O, $M_r = 435.12$, orthorhombic, $P2_12_12_1$, $a = 11.486$ (4), $b = 16.664$ (7), $c = 8.867$ (3) Å, $V = 1697$ (1) Å³, $Z = 4$, $D_x = 1.703$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 9.05$ cm⁻¹, $F(000) = 900$, room temperature, $R = 0.0416$ for 2686 independent reflections [$|F_o| > 3\sigma(|F_o|)$]. The Fe atom is surrounded octahedrally by four O and two N atoms of the title ligand (tdta). This complex anion has been spontaneously resolved by crystallization to take the Δ configuration in the crystal used for the analysis.

Introduction. In the course of investigations into the Raman spectra of iron(III) complexes with trimethylenediaminetetraacetate (tdta), we have found that the lithium salt of the Fe^{III} complex with tdta has two different crystalline forms. One of them has been identified as Li[Fe(tdta)]·3H₂O, which has an octahedral six-coordinate structure (Yamamoto, Mikata,

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Miyoshi & Yoneda, 1988). In contrast to the Li salt, the sodium salt of the Fe^{III} complex with tdta has been obtained only as a stable yellow crystalline form. In order to establish the geometry adopted by the sodium salt and to find out the origin of the stability in the crystalline state, we have determined its structure and report it here.

Experimental. The title complex was prepared as follows: a solution containing 5.76 g of the barium salt of tdta, prepared by the method of Weyh & Hamm (1968), 4.72 g of iron(III) sulfate, and 1.42 g of sodium sulfate in 50 cm³ of water were stirred at room temperature for 2 h. After removing the precipitate, the filtrate was concentrated to 10–20 cm³. The crystals were obtained from the solution by evaporation at room temperature.

Yellow crystal, 0.50 × 0.50 × 0.40 mm; Enraf-Nonius CAD-4 diffractometer, 50 kV and 26 mA; unit-cell dimensions by least-squares refinement from 25 reflections with $20 < 2\theta < 24^\circ$; ω - 2θ scan, scan rate 4.12–16.48° min⁻¹, scan width (1.0 + 0.35tan θ)°;

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