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. $Na[Fe(C_{11}H_{14}N_2O_8)].3H_2O$, $M_r = 435.12$, orthorhombic, $P2_12_12_1$, $a = 11.486 (4)$, $b = 16.664 (7)$, $c = 8.867 (3)$ Å, $V = 1697 (1)$ Å^3, $Z = 4$, $D_x = 1.703$ g cm^{-3}, λ(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 Λ 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)].3H$_2$O, which has an octahedral six-coordinate structure (Yamamoto, Mikata,

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 cm^3 of water were stirred at room temperature for 2 h. After removing the precipitate, the filtrate was concentrated to 10–20 cm^3. 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 $20 < 2\theta < 24°$; ω–2θ scan, scan rate 4·12–16·48° min^{-1}, scan width (1·0 + 0·35tanθ)°;

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Table 1. *Final atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for the non-H atoms*

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Fe	0·35994 (3)	0·24529 (2)	0·76461 (4)	1·44 (2)
O(1)	0·4009 (2)	0·1680 (1)	0·9243 (3)	2·27 (8)
O(2)	0·4681 (3)	0·1524 (2)	1·1584 (3)	2·88 (10)
O(3)	0·2456 (2)	0·3053 (1)	0·8835 (3)	2·10 (8)
O(4)	0·2118 (2)	0·4195 (2)	1·0059 (3)	2·68 (9)
O(5)	0·2702 (2)	0·1619 (1)	0·6560 (3)	2·31 (8)
O(6)	0·2829 (3)	0·0633 (2)	0·4926 (4)	4·96 (17)
O(7)	0·3486 (2)	0·3264 (1)	0·6019 (3)	2·24 (8)
O(8)	0·4065 (3)	0·3683 (2)	0·3758 (3)	3·10 (10)
N(1)	0·4761 (2)	0·3205 (1)	0·8966 (3)	1·55 (7)
N(2)	0·4999 (2)	0·2039 (2)	0·6183 (3)	1·81 (8)
C(1)	0·4984 (3)	0·2792 (2)	1·0408 (4)	2·04 (10)
C(2)	0·4531 (3)	0·1929 (2)	1·0455 (3)	1·90 (9)
C(3)	0·4067 (3)	0·3942 (2)	0·9211 (4)	1·95 (10)
C(4)	0·2785 (3)	0·3729 (2)	0·9410 (3)	1·91 (10)
C(5)	0·4601 (3)	0·1206 (2)	0·5773 (5)	2·55 (12)
C(6)	0·3279 (3)	0·1148 (2)	0·5703 (4)	2·41 (12)
C(7)	0·5057 (3)	0·2564 (2)	0·4862 (4)	2·37 (11)
C(8)	0·4133 (3)	0·3229 (2)	0·4855 (3)	1·92 (9)
C(9)	0·5841 (3)	0·3428 (2)	0·8138 (4)	2·50 (11)
C(10)	0·6638 (3)	0·2745 (3)	0·7627 (5)	2·93 (13)
C(11)	0·6123 (3)	0·1964 (2)	0·7009 (4)	2·58 (11)
Na	0·0564 (1)	0·4857 (1)	0·8496 (2)	2·53 (5)
O(11)	−0·0640 (3)	0·4993 (2)	1·0733 (4)	3·24 (11)
O(12)	−0·0941 (3)	0·5410 (2)	0·6970 (3)	3·25 (10)
O(13)	0·1834 (3)	0·4539 (2)	0·6518 (3)	3·30 (11)

Table 2. *Bond distances* (Å) *and angles* (°)

Fe—O(1)	1·971 (2)	O(8)—C(8)	1·236 (4)
Fe—O(3)	1·959 (2)	N(1)—C(1)	1·475 (4)
Fe—O(5)	1·980 (2)	N(1)—C(3)	1·479 (4)
Fe—O(7)	1·981 (2)	N(1)—C(9)	1·488 (4)
Fe—N(1)	2·173 (2)	N(2)—C(5)	1·507 (4)
Fe—N(2)	2·177 (2)	N(2)—C(7)	1·464 (4)
O(1)—C(2)	1·298 (4)	N(2)—C(11)	1·490 (4)
O(2)—C(2)	1·219 (4)	C(1)—C(2)	1·531 (4)
O(3)—C(4)	1·292 (4)	C(3)—C(4)	1·525 (4)
O(4)—C(4)	1·233 (4)	C(5)—C(6)	1·523 (5)
O(5)—C(6)	1·277 (4)	C(7)—C(8)	1·534 (4)
O(6)—C(6)	1·217 (4)	C(9)—C(10)	1·529 (5)
O(7)—C(8)	1·273 (4)	C(10)—C(11)	1·530 (5)
O(1)—Fe—O(3)	96·2 (1)	Fe—N(2)—C(5)	102·2 (2)
O(1)—Fe—O(5)	90·9 (1)	Fe—N(2)—C(7)	108·8 (2)
O(3)—Fe—O(5)	105·8 (1)	C(5)—N(2)—C(7)	111·8 (3)
O(1)—Fe—O(7)	169·9 (1)	Fe—N(2)—C(11)	111·9 (2)
O(3)—Fe—O(7)	90·0 (1)	C(5)—N(2)—C(11)	107·7 (3)
O(5)—Fe—O(7)	95·2 (1)	C(7)—N(2)—C(11)	113·8 (3)
O(1)—Fe—N(1)	81·0 (1)	N(1)—C(1)—C(2)	113·8 (2)
O(3)—Fe—N(1)	80·1 (1)	O(1)—C(2)—O(2)	124·6 (3)
O(5)—Fe—N(1)	170·6 (1)	O(1)—C(2)—C(1)	115·7 (3)
O(7)—Fe—N(1)	92·2 (1)	O(2)—C(2)—C(1)	119·6 (3)
O(1)—Fe—N(2)	92·6 (1)	N(1)—C(3)—C(4)	110·2 (2)
O(3)—Fe—N(2)	167·7 (1)	O(3)—C(4)—O(4)	123·4 (3)
O(5)—Fe—N(2)	82·7 (1)	O(3)—C(4)—C(3)	116·0 (3)
O(7)—Fe—N(2)	80·3 (1)	O(4)—C(4)—C(3)	120·5 (3)
N(1)—Fe—N(2)	92·9 (1)	N(2)—C(5)—C(6)	111·7 (3)
Fe—O(1)—C(2)	119·8 (2)	O(5)—C(6)—O(6)	123·4 (3)
Fe—O(3)—C(4)	117·5 (2)	O(5)—C(6)—C(5)	117·0 (3)
Fe—O(5)—C(6)	116·8 (2)	O(6)—C(6)—C(5)	119·4 (3)
Fe—O(7)—C(8)	121·4 (2)	N(2)—C(7)—C(8)	113·7 (2)
Fe—N(1)—C(1)	107·7 (2)	O(7)—C(8)—O(8)	125·0 (3)
Fe—N(1)—C(3)	103·1 (2)	O(7)—C(8)—C(7)	115·7 (3)
C(1)—N(1)—C(3)	110·7 (2)	O(8)—C(8)—C(7)	119·3 (3)
Fe—N(1)—C(9)	113·0 (2)	N(1)—C(9)—C(10)	117·3 (3)
C(1)—N(1)—C(9)	113·5 (2)	C(9)—C(10)—C(11)	120·5 (3)
C(3)—N(1)—C(9)	108·4 (2)	N(2)—C(11)—C(10)	116·1 (3)

three intensity standards monitored every 2 h of X-ray exposure time; orientation (for the same three reflections) monitored after every 200 scans; 2821 unique reflections, $2\theta \leq 60°$ $(0 \leq h \leq 16,\ 0 \leq k \leq 23,\ 0 \leq l \leq 12)$; 2686 reflections with $|F_o| > 3\sigma(|F_o|)$ used for structure determination; intensities corrected for Lorentz and polarization, not for absorption. The Fe-, three O- and N-atom positions determined by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and successive difference Fourier maps. All the H atoms were fixed by geometrical constraints (C—H = 0·97 Å) and isotropic thermal parameters $(U = 0·05\ \text{Å}^2)$. The water hydrogens were not included in the calculation. The structure was refined on F by full-matrix least squares using anisotropic thermal parameters for non-H atoms; for atomic parameters containing the Λ configuration of the complex anion, $R = 0·0416$ and $wR = 0·0488$, $w = 1/[\sigma^2(F_o) + 0·009789|F_o|^2]$, $S = 0·703$, and for those containing the Δ configuration $R = 0·0543$ and $wR = 0·0652$, $w = 1/[\sigma^2(F_o) + 0·010141|F_o|^2)$, $S = 0·873$; $|\Delta\rho|_{max}$ in the final difference Fourier map = $0·66\ \text{e Å}^{-3}$. $(\Delta/\sigma)_{max} = 0·005$. The enantiomeric structure could be rejected at the 0·005 significance level by the Hamilton (1965) test $(R_{1,2409,0·005} = 1·002)$. All calculations were performed with *SHELX*76 (Sheldrick, 1976) and molecular illustrations were drawn using *ORTEP* (Johnson, 1976) on a FACOM M-780/20 computer. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

The optical activity of the complex was checked in an aqueous solution with a JASCO J-600 spectropolarimeter.

Discussion. The final atomic parameters are listed in Table 1.* The molecular structure and numbering scheme are illustrated in the *ORTEP* plot given in Fig. 1. Bond distances and angles are listed in Table 2.

The coordination geometry around the Fe$^{\text{III}}$ atom is approximately octahedral. The tdta ligand acts as a hexadentate ligand. For this complex, therefore, two optical isomers, Δ and Λ, are possible. The single crystal used in the present work was spontaneously resolved by the crystallization and the absolute configuration of the complex anion is estimated from the residual values to be the Λ configuration, although its optical activity could not be observed in aqueous
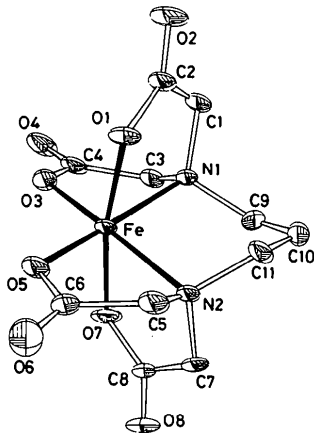
Fig. 1. *ORTEP* (Johnson, 1976) drawing of the [Fe(tdta)]$^-$ anion (50% probability thermal ellipsoids) with the atom-numbering scheme. H atoms are omitted for clarity.

solution because of rapid racemization or rearrangement. The trimethylenediamine moiety takes a symmetric skew-boat form with δ conformation. This differs from Li[Fe(tdta)] (Li salt) and other metal–tdta complexes, which have a twist-boat conformation (Yamamoto, Mikata, Miyoshi & Yoneda, 1988, and references therein).

The Fe—N [av. 2·175 (2) Å] and Fe—O [av. 1·973 (2) Å] distances in the present complex (Na salt) are shorter than those of the Li salt [2·194 (3) and 1·989 (3) Å, respectively]. The deviations of the bond angles around the Fe^{III} atom from 90 and 180° in the Na salt are smaller than those in the Li salt,

e.g. O(3)—Fe—O(5), 105·8 (1)° [112·5 (1)° in the Li salt]; N(1)—Fe—N(2), 92·9 (1)° [94·3 (1)°]; in-plane, O—Fe—N, 80·1 (1) and 82·7 (1)° [77·8 (1) and 78·8 (1)°], and so on. This fact seems to indicate that in the Na salt the molecular geometry of the Fe^{III} complex has less steric hindrance in the solid in comparison with the Li salt.

The Na atom is surrounded octahedrally by three O atoms of the tdta moiety [O(2) ($-\frac{1}{2} + x, \frac{1}{2} - y, 2 - z$), O(4) and O(8) ($\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$)] and three water O atoms. The Na—O distances are in the range 2·343 (3)–2·515 (3) Å. Hydrogen bonds also exist between the water molecules and the O atoms in the tdta moiety, O(1)···O(11) [2·817 (4) Å], O(6)···O(11) [2·792 (4) Å] and O(7)···O(13) [2·882 (4) Å].

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Structure of
[2,6-Bis(2-benzimidazolyl)pyridine]dichlorocopper(II) Dimethylformamide

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Abstract. [CuCl$_2$(C$_{19}$H$_{13}$N$_5$)].C$_3$H$_7$NO, $M_r = 518\cdot9$, monoclinic, $P2_1/n$, $a = 9\cdot150$ (1), $b = 12\cdot908$ (3), $c = 18\cdot964$ (4) Å, $\beta = 93\cdot33$ (1)°, $V = 2236\cdot0$ (7) Å^3, $Z = 4$, $D_m = 1\cdot54$ (2), $D_x = 1\cdot54$ Mg m^{-3}, λ(Mo Kα) = 0·71069 Å, $\mu = 1\cdot25$ mm^{-1}, $F(000) = 1060$, room temperature, $R = 0\cdot069$ for 1918 reflections. The structure shows Cu^{II} in a square-pyramidal environment with the planar tridentate ligand and one chloride in the equatorial plane, and the second chloride more weakly bound (as shown by the