Fig. 2. The Cu-coordination polyhedra. Broken lines show the hydrogen-bond network.

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Structure of trans-Amminebis(ethylenediamine)fluorochromium(III) Perchlorate, [CrF(NH₃)(C₂H₈N₂)₂](ClO₄)₂

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Abstract. $M_r = 407 \cdot 1$, monoclinic, $P2_1/c$, $a = 14 \cdot 815$ (4), $b = 9 \cdot 526$ (3), $c = 11 \cdot 585$ (3) Å, $\beta = 110 \cdot 95$ (2)°, $V = 1526 \cdot 8$ (7) Å³, $Z = 4$, $D_m = 1 \cdot 776$ (10), $D_x = 1 \cdot 771$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0 \cdot 71069$ Å, $\mu = 11 \cdot 72$ cm⁻¹, $F(000) = 836$, $T = 297$ K, $R = 0 \cdot 058$ for 1423 reflections (all included). Constraints were used to deal with one disordered ethylenediamine group. The bond lengths found were Cr—F, $1 \cdot 862$ (3); Cr—NH₃, $2 \cdot 093$ (6) Å. The bond angles N—Cr—N are $81 \cdot 9°$ (av.) within, and $98 \cdot 1°$ (av.) between, the chelate rings. The other angles at Cr are less than 3° from orthogonality. The shortest of the interionic hydrogen bonds [N···F = $2 \cdot 768$ (9) Å] is from NH₃ to F, between c-glide-plane-related cations.

Introduction. Pseudo-octahedral complexes of the type trans- and cis-[MX(NH₃)(en)₂]²⁺, where X is an acido ligand, are useful analogues of acidopentammines and have been utilized in studies of the stereochemistry of thermal (House, 1977) and, more recently, photochemical kinetics (Kirk, 1981). For the cobalt complexes in particular, a large number of compounds have been synthesized and studied kinetically. In contrast, only recently have a few of the analogous chromium compounds been prepared and characterized (Kirk & Kelly, 1974; Wong & Kirk, 1975) but these have proved important photochemically. The literature

assignment of stereochemistry for these was based on solubilities, chromatographic properties, UV and IR spectroscopy (Wong & Kirk, 1975), and in one instance (Kirk & Kelly, 1974), comparison to the Co^III analogue by X-ray powder photography. In light of the importance of this type of compound in the studies that are currently being used to test and illuminate the nature of ligand labilization in photochemistry and theory of the photostereochemistry of d^3 systems (Vanquickenborne & Ceulemans, 1983), we thought it desirable to undertake a single-crystal-structure determination on at least one of the compounds to confirm that its stereochemistry had been correctly assigned in the previous work. That isomer of [CrF(NH₃)(en)₂](ClO₄)₂ that was previously assigned as trans was chosen for study for several reasons. Firstly, it in particular gave well formed crystals showing good extinction. Several of the other compounds, notably the cis compounds, did not crystallize well. The choice of the fluoro compound also presented the opportunity to investigate the nature of the Cr^III—F bond, an entity little studied in complexes to date. A recent study (Clamp, Connelly, Taylor & Louttit, 1980) of [CrF(NO)(dppe)₂], where dppe = 1,2-bis(diphenylphosphino)ethane, yielded a Cr—F bond length of $1 \cdot 880$ Å, deemed by the authors to involve Cr^III. There may be some suspicion, however, as to whether this

would be a typical Cr^{III}—F bond given the nature of the other ligands. In any event we thought the additional study reported here would provide further useful information on the chromium/fluorine bond. Finally the compound presents an opportunity to study possible hydrogen-bonding interactions between the fluorine atom and the amino protons of the ethylenediamine and ammine ligands in the structure.

Experimental. Title compound prepared as described previously (Wong & Kirk, 1975). Orange crystals examined using Weissenberg and precession cameras, Cu $K\alpha$ radiation. Chosen crystal mounted on the b axis in a glass tube. Unit cell refined using ten pairs of $\pm 2\theta$ measurements (range 23–34°), Picker four-circle diffractometer. Density measured by flotation in CCl_4/$CHBr_3$. Intensity measurements performed using a stepped scan of 160 steps of 0.01° in 2θ, counting for 0.25 s per step, with a background count for 20 s at each end of the scan. Three standards measured before each batch of 50 reflections, $\pm 3\%$ intensity variation and no crystal decomposition evident. Measurements in 2θ range 0–40° and over two octants, h $\bar{1}4 \rightarrow 13$, k $0 \rightarrow 9$, l $0 \rightarrow 11$. Lorentz, polarization, and absorption corrections applied, numerical-integration method using a $6 \times 8 \times 8$ Gaussian grid; crystal shape specified by following crystal indices and perpendicular distances to origin (mm): $\pm (100)$ 0.1028, $\pm (010)$ 0.2095, $\pm (001)$ 0.2070; calculated transmission range 0.61–0.81. Reflection file sorted and equivalent reflections averaged to give 1423 observations in final data file. Programs used for structure determination mainly *SHELX*76 (Sheldrick, 1976) and *ORTEP* (Johnson, 1965). Structure solved using direct methods, completed with electron density difference maps, and refined by least squares minimizing $\sum w\Delta^2$ where $\Delta = ||F_o| - |F_c||$ with $w = 1/[\sigma^2(F) + 0.001F^2]$ in final stages, $\sigma(F)$ derived from counting statistics. Atomic scattering factors for uncharged atoms those of Cromer & Waber (1974). Anisotropic temperature factors used for all atoms except hydrogen.

The residuals decreased to $R = 0.047$, $wR = 0.056$ but one of the ethylenediamine chelate rings appeared to be approximately planar, with a C—C bond shorter than expected [1.33 (1) Å], and with the thermal vibration ellipsoids of these carbon atoms elongated perpendicular to the ring. Only one hydrogen peak was found for each carbon atom. We consider that the chemical evidence against ethylenic character in this chelate ring is overwhelming and we have explained the diffraction results by assuming that the chelate ring is disordered, either temporally or from unit cell to cell throughout the crystal. The assumption was made that the atomic parameters of N(2) and N(5) are common to both disordered conformers. In retrospect, the temperature parameters have turned out to be similar in magnitude to those of N(6) and N(9) and none of the

four ethylenediamine nitrogen atoms has a particularly elongated thermal ellipsoid. It seems that no gross error was thus introduced. To obtain stability and convergence in the refinement of two superimposed 'half-structures', the constraint facilities of *SHELX*76 were used. The bonds were set to C—C = 1.470 $\pm$ 0.005, C—N = 1.450 $\pm$ 0.005 Å. The angles C—C—N were constrained to 109.5° by C$\cdots$N = 2.380 $\pm$ 0.005 Å. These constraints assist the X-ray intensities rather than completely override them, and are consistent with lengths and angles found in the opposite and normal ethylenediamine ligand. The refinement was finally completed by placing CH_2 and NH_2 hydrogen atoms at their calculated positions assuming N—H, C—H = 0.97 Å, site occupation factors of 0.5 where appropriate, and isotropic thermal parameters of 0.10 Å^2. The coordinates of the hydrogen atoms of the ammonia molecule were found from a difference map and refined.

In final cycle of refinement max. shift/e.s.d. 0.48, final difference map max. 0.42, min. −0.48 e Å^{-3}. Final residuals of chemically reasonable structure $R = 0.058$, $wR = 0.0754$ including all reflections. 197 parameters determined from 1423 reflections and ten constraints.

Discussion. The fractional atomic coordinates and temperature parameters are given in Table 1.* An *ORTEP* drawing of the structure of the cation is given in Fig. 1 with the atomic-labelling scheme. The *trans* geometry of the ion is confirmed. The ethylenediamine ligand N(6)C(7)C(8)N(9) is in a normal non-planar ring conformation and the hydrogen-atom peaks associated with it were evident in the final difference maps, as were those of the ammonia ligand. The ethylenediamine ligand N(2)C(3)C(4)N(5) is given as two superimposed structures each with half occupancy (assumed). Satisfactory hydrogen-atom positions could not be determined from the difference maps for this ligand. All the ethylenediamine hydrogen-atom coordinates were finally calculated for uniformity, and have been omitted from Fig. 1 which would otherwise be too complicated in the disordered region. Corey & Bailar (1959) discussed the stability of the three possible conformations ($\delta\delta$, $\lambda\lambda$, $\lambda\delta$) for *trans*-bis(ethylenediamine) complexes, and suggested on the basis of the interaction between adjacent NH_2 groups that the $\lambda\lambda$ and $\delta\delta$ forms should be ~4 kJ more stable than the $\lambda\delta$ form. Actually *trans*-bis(ethylenediamine) complexes are usually found in the $\lambda\delta$ conformation in the solid state (Purcell & Kotz, 1977), but the difference in

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* Lists of structure factors, anisotropic temperature parameters, calculated hydrogen-atom coordinates, bond lengths and angles of the ammonia ligand and selected intermolecular distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42099 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

energy between the alternative forms is probably small. Bonded interatomic distances are given in Table 2(a). The Cr—F length of 1·862 (3) Å is particularly interesting since very few such bonds have been measured by diffraction in Cr^{III} amine complexes, and the value is 0·231 Å shorter than the $trans$-Cr—NH_3 bond length. Such a difference is much greater than the difference between the normal covalent radii (Evans, 1966) for F and N ($r_N = 0.74$, $r_F = 0.72$ Å). The Bragg–Slater (Slater, 1964) radii ($r_N = 0.65$, $r_F = 0.50$, $r_{Cr} = 1.40$ Å)

Table 1. Fractional atomic coordinates and temperature parameters

E.s.d.'s are given in parentheses. Coordinates $\times 10^n$ where $n = 3$ for H and $n = 5$ for Cr, otherwise $n = 4$. Temperature parameters $\times 10^n$ where $n = 4,4,2$ for Cr,Cl,H, otherwise $n = 3$.

U_{eq} is the equivalent isotropic temperature parameter $= \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*(\mathbf{a}_i.\mathbf{a}_j)$. Primed values indicate that U_{iso} is given: $T = \exp(-8\pi^2 U_{iso}\sin^2\theta/\lambda^2)$.

|	x	y	z	$U_{eq}/U_{iso}(\text{Å}^2)$
Cr	74831 (6)	34329 (10)	11995 (8)	401 (5)
F(1)	7542 (3)	2944 (4)	2781 (3)	56 (2)
N(1)	7405 (6)	4066 (9)	−564 (6)	59 (3)
N(2)	8178 (4)	1583 (6)	1069 (7)	63 (3)
N(5)	6277 (4)	2136 (6)	462 (7)	63 (3)
N(6)	6799 (6)	5248 (8)	1395 (8)	63 (4)
N(9)	8707 (4)	4621 (7)	2017 (6)	56 (3)
C(3)	7516 (4)	411 (7)	919 (11)	51 (4)'
C(4)	6559 (4)	823 (9)	38 (11)	59 (4)'
C(3')	7487 (5)	556 (11)	335 (15)	108 (7)'
C(4')	6575 (5)	685 (7)	540 (16)	96 (6)'
C(7)	7504 (7)	6412 (8)	1746 (9)	88 (5)
C(8)	8436 (6)	5894 (10)	2525 (8)	87 (4)
Cl(1)	4480 (1)	3063 (2)	1999 (2)	684 (9)
Cl(2)	232 (1)	2139 (2)	4661 (2)	660 (9)
O(1)	4232 (6)	3764 (9)	2896 (7)	145 (5)
O(2)	4695 (5)	4036 (8)	1203 (6)	125 (4)
O(3)	5300 (6)	2290 (11)	2541 (8)	162 (5)
O(4)	3708 (6)	2219 (11)	1317 (8)	171 (5)
O(5)	−229 (4)	1327 (7)	3562 (5)	109 (3)
O(6)	284 (6)	3526 (7)	4322 (7)	135 (4)
O(7)	1167 (4)	1607 (6)	5271 (5)	88 (3)
O(8)	−308 (4)	2074 (8)	5423 (6)	110 (3)
H(11)	692 (8)	452 (13)	−108 (11)	10'
H(12)	776 (6)	478 (10)	−56 (9)	10'
H(13)	756 (5)	338 (9)	−98 (7)	10'
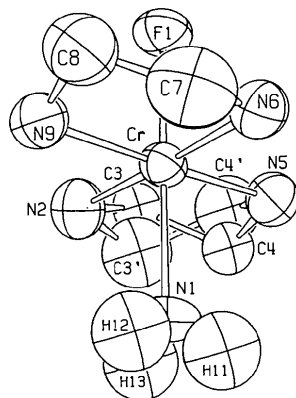
Fig. 1. An *ORTEP* perspective drawing of the cation *trans*-[CrF(NH₃)(en)₂]²⁺ showing the thermal ellipsoids as the 50% equi-probability surface.

Table 2. Molecular geometry

E.s.d.'s are given in parentheses

(a) Interatomic distances (Å)

F(1)—Cr	1·862 (3)	C(4)—C(3)	1·474 (16)
N(1)—Cr	2·093 (6)	C(4')—C(3')	1·459 (10)
N(2)—Cr	2·074 (6)	C(7)—C(8)	1·440 (11)
N(5)—Cr	2·088 (6)	O(1)—Cl(1)	1·390 (7)
N(6)—Cr	2·057 (8)	O(2)—Cl(1)	1·421 (7)
N(9)—Cr	2·059 (5)	O(3)—Cl(1)	1·366 (7)
C(3)—N(2)	1·455 (9)	O(4)—Cl(1)	1·389 (7)
C(3')—N(2)	1·450 (16)	O(5)—Cl(2)	1·437 (6)
C(4)—N(5)	1·459 (10)	O(6)—Cl(2)	1·388 (7)
C(4')—N(5)	1·444 (9)	O(7)—Cl(2)	1·406 (5)
C(7)—N(6)	1·477 (11)	O(8)—Cl(2)	1·388 (5)
C(8)—N(9)	1·466 (10)		

(b) Bond angles (°)

N(2)—Cr—F(1)	90·5 (2)	C(4)—C(3)—N(2)	108·6 (4)
N(5)—Cr—F(1)	89·2 (2)	C(3)—C(4)—N(5)	108·4 (4)
N(6)—Cr—F(1)	87·3 (3)	C(4')—C(3')—N(2)	110·4 (5)
N(9)—Cr—F(1)	87·8 (2)	C(3')—C(4')—N(5)	110·6 (5)
N(5)—Cr—N(2)	80·9 (2)	C(8)—C(7)—N(6)	110·0 (7)
N(9)—Cr—N(6)	82·8 (3)	C(7)—C(8)—N(9)	111·7 (6)
N(6)—Cr—N(5)	99·1 (3)	O(2)—Cl(1)—O(1)	110·6 (5)
N(9)—Cr—N(2)	97·0 (2)	O(3)—Cl(1)—O(1)	110·1 (5)
N(1)—Cr—N(2)	91·7 (3)	O(3)—Cl(1)—O(2)	106·3 (5)
N(1)—Cr—N(5)	91·8 (3)	O(4)—Cl(1)—O(1)	108·6 (5)
N(1)—Cr—N(6)	90·4 (3)	O(4)—Cl(1)—O(2)	109·8 (5)
N(1)--Cr·N(9)	91·3 (3)	O(4)—Cl(1)—O(3)	111·4 (7)
N(6)—Cr—N(2)	177·9 (3)	O(6)—Cl(2)—O(5)	108·6 (4)
N(9)—Cr—N(5)	176·3 (3)	O(7)—Cl(2)—O(5)	108·8 (3)
N(1)—Cr—F(1)	177·7 (3)	O(7)—Cl(2)—O(6)	109·9 (4)
C(3)—N(2)—Cr	109·2 (4)	O(8)—Cl(2)—O(5)	109·9 (4)
C(3')—N(2)—Cr	110·5 (4)	O(8)—Cl(2)—O(6)	109·0 (5)
C(4)—N(5)—Cr	109·8 (4)	O(8)—Cl(2)—O(7)	110·6 (4)
C(4')—N(5)—Cr	110·0 (4)		
C(7)—N(6)—Cr	109·5 (6)		
C(8)—N(9)—Cr	108·5 (4)		

give a better prediction of the bond lengths. The recent observations by Vaughn (1981) on [CrF(NH₃)(tn)₂]²⁺, where tn = 1,3-propanediamine, give Cr—F = 1·872 (3) Å and Cr—NH₃ = 2·080 (6) Å in agreement with this work. The short Cr—F bond length suggests a strong bond. The Cr—N lengths are normal, agreeing with many literature values. The bond angles at Cr given in Table 2(b) show that within the ethylenediamine rings the N—Cr—N bond angles are approximately 8° less than 90°, whereas between the ethylenediamine ligands there is a similar compensatory increase in the N—Cr—N angles. The other angles are close to 90° (max. deviation 2·4, mean deviation 1·4°). Approximately tetrahedral geometry about the C and N centres is expected and observed, and puckering of the five-membered rings is necessary to achieve this. The puckering is clearly seen for the N(6)C(7)C(8)N(9) ligand.

The perchlorate ions have angles close to the tetrahedral value. The chlorine atoms have normal temperature parameters, and the oxygen atoms have higher values, presumably due to librational motion, but no difficulty was experienced in the structure determination on this account.

The interionic distances calculated suggest that a number of weak hydrogen bonds exist between the

perchlorate ions and the amine groups. The deposited material (Table *S5*) shows four O$\cdots$N contacts in the range 2·9–3·1 Å for the second perchlorate ion, which are shorter than any of the O$\cdots$C contacts. The shortest interionic hydrogen bond, N(1) to F(1) at *x*, 0·5–*y*, *z*–0·5, has a length of 2·768 (9) Å, involves H(13) [F$\cdots$H = 1·90 (8) Å, angle F$\cdots$H–N = 163 (7)°], and is between *c*-glide-plane-related cations. The hydrogen bonds of this kind therefore run continuously through the crystal structure.

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Structure of Bis(pyridine)(5,10,15,20-tetraphenylporphyrinato)iron(II)–Pyridine Solvate, [Fe(C₄₄H₂₈N₄)(C₅H₅N)₂].2C₅H₅N

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Abstract. $M_r = 985 \cdot 0$, triclinic, $P\bar{1}$, $a = 9 \cdot 472$ (5), $b = 10 \cdot 325$ (2), $c = 13 \cdot 545$ (8) Å, $\alpha = 80 \cdot 25$ (3), $\beta = 77 \cdot 79$ (4), $\gamma = 77 \cdot 79$ (3)°, $V = 1254 \cdot 5$ Å³, $Z = 1$, $D_x = 1 \cdot 304$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0 \cdot 7107$ Å, $\mu = 3 \cdot 65$ cm⁻¹, $F(000) = 514$, $T = 298$ K, $R = 0 \cdot 034$ for 3577 observed reflections. The structure consists of Fe(tetraphenylporphyrin)(py)₂ and two pyridine molecules of solvation. The average Fe–N(pyrrole) distance is 1·993 Å, while the axial Fe–N(pyridine) distance is 2·039 (1) Å. Because of the center of symmetry the Fe atom is located exactly in the plane of the porphinato ring, but is displaced by 0·064 Å from each of the pyridine planes.

Introduction. The relevance of porphyrin stereochemistry in biology is well documented (see, for example, Lever & Gray, 1983). The study of the title compound was undertaken as part of a program to map the electron density in iron porphyrins as a function of oxidation state, coordination number and spin state (Lecomte, Chadwick, Coppens & Stevens, 1983; Coppens & Li, 1984).

Experimental. Fe^{II} tetraphenylporphyrin [Fe(tpp)] was prepared from Fe^{III} tetraphenylporphyrin chloride by reduction with chromous acetylacetonate in a benzene–ethanol mixture (Collman, Hoard, Kim, Lang & Reed, 1975). The crystals were subsequently recrystallized from a benzene–heptane mixture. The bis(pyridine) complex was prepared by dissolving 100 mg of Fe(tpp) in boiling dry pyridine. The reaction mixture was rapidly filtered through a medium-porosity sintered

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