

In contrast to bpy and phen, the dipyam ligand is strongly distorted from planarity. The angles between the least-squares planes through the two pyridyl rings of each ligand are 36.1 (5) and 37.4 (5)° for the two independent dipyam molecules in the complex. These values are similar to those found for dipyam bound to Cu^{II} (Fuller & Jacobson, 1981; Jensen & Jacobson, 1981) and Pd^{II} (Freeman & Snow, 1965). The axis of intersection of the two least-squares planes passes close to the Co atom and the secondary amine N atom, the amine N atom lying in the obtuse and the Co atom in the reflex angle formed by the two planes. The six-membered chelate ring has a boat conformation, and the Co—N bond makes an average angle of 11.5° with the plane of the pyridyl ring.

The unusually intense transitions in the electronic spectrum of [Co(dipyam)₃]³⁺ are thought to arise from ligand–ligand repulsions (Johnson & Geldard, 1979). In the cation [Co(dipyam)₂(CO₃)]⁺, all the C atoms in the 6-position of the pyridyl rings show some interaction with the other dipyam molecule as shown by short non-bonded distances (C—C or C—N distances less than 3.2 Å, Table 2). For the bpy and phen complexes, in contrast, such short interligand distances are found only between the two mutually *cis* pyridyl groups *trans* to the carbonate. This supports the hypothesis of greater interligand repulsion in complexes of dipyam, and may be attributed to the expansion of the chelate ring which moves the C atoms in the 6-position closer to the centre of the complexes and thus nearer to the other ligands.

The H atoms of the secondary amine groups are involved in hydrogen bonding. One is hydrogen bonded

to the terminal O atom of the carbonate of another cation [distance N(4)···O(3) (−*x*, −*y*, 2−*z*) = 3.018 (12) Å]. The other is hydrogen bonded to an O atom of the perchlorate anion [distance N(1)···O(7) (1−*x*, 1−*y*, 2−*z*) = 3.088 (14) Å]. The other O atoms of the perchlorate anion show much larger atomic displacement parameters, and may be considered as disordered, and this is presumably responsible for the relatively high final *R* factor.

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Fluoro-Containing Coordination Compounds of Chromium(III). IV. Structure of Racemic *cis*-Bis(ethylenediamine)difluorochromium(III) Perchlorate

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Abstract. *cis*-[CrF₂(C₂H₈N₂)₂]ClO₄, *M_r* = 309.65, monoclinic, *P*2₁/*c*, *a* = 5.587 (1), *b* = 11.601 (2), *c* = 17.774 (3) Å, β = 98.07 (1)°, *V* = 1140.6 (6) Å³, *Z* = 4, *D_m* = 1.80 (1), *D_x* = 1.803 Mg m^{−3}, *Mo Kα*, λ = 0.71069 Å, μ = 1.19 mm^{−1}, *F*(000) = 636, *T* = 293 K, *R* = 0.052 for 1569 reflections. The Cr atom is in an octahedral environment coordinated by two bidentate ethylenediamines and two F atoms in a *cis* position. Cations are in the *Aδλ* and *Δλδ* enantiomeric

forms. Cr—F and Cr—N bonds are 1.883 (3), 1.882 (3); and from 2.072 (4) to 2.099 (4) Å. Weak N···F hydrogen bonds exist between cations.

Introduction. Structural studies of fluoro-containing chromium(III) coordination compounds are rare. [CrF₂(en)₂]⁺ (en = NH₂—CH₂—CH₂—NH₂) can exist as *trans* and *cis* isomers. Structures of *trans*-[CrF₂(en)₂]ClO₄ and *trans*-[CrF₂(en)₂]Cl were solved

(Brenčić & Leban, 1981, 1985), but for the *cis* isomer the structural data are not known. Compounds containing *cis*-[CrF₂(en)₂]⁺ can crystallize in racemic form or can be separated in *levo*- or *dextrorotatory* enantiomers.

Table 1. *Positional and equivalent isotropic thermal* ($\times 10^3$) *parameters with e.s.d.'s*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} (Å ²)
Cr	0.4963 (1)	0.5609 (1)	0.2570 (1)	24.5
F(1)	0.7234 (5)	0.4457 (2)	0.2430 (2)	37.3
F(2)	0.7344 (5)	0.6751 (2)	0.2805 (2)	38.3
N(1)	0.4569 (7)	0.6009 (4)	0.1423 (2)	33.9
N(2)	0.2256 (7)	0.4398 (3)	0.2205 (2)	29.7
C(1)	0.3578 (11)	0.4966 (5)	0.0995 (3)	43.7
C(2)	0.1480 (12)	0.4547 (6)	0.1373 (3)	52.1
N(3)	0.2452 (7)	0.6844 (3)	0.2817 (3)	33.0
N(4)	0.5045 (8)	0.5192 (4)	0.3713 (2)	34.4
C(3)	0.2864 (12)	0.6989 (5)	0.3661 (4)	45.9
C(4)	0.3091 (10)	0.5818 (5)	0.4014 (3)	46.8
Cl	0.0846 (2)	0.2174 (1)	-0.0555 (1)	37.4
O(1)	0.2085 (14)	0.1974 (4)	-0.1178 (4)	108.9
O(2)	0.1655 (12)	0.1431 (6)	0.0040 (3)	107.4
O(3)	-0.1631 (10)	0.1932 (5)	-0.0772 (4)	104.1
O(4)	0.1118 (12)	0.3346 (5)	-0.0361 (4)	97.5

Table 2. *Selected bond lengths (Å) and angles (°) with e.s.d.'s*

Cr-F(1)	1.883 (3)	N(1)-C(1)	1.494 (7)
Cr-F(2)	1.882 (3)	N(2)-C(2)	1.492 (6)
Cr-N(1)	2.072 (4)	C(1)-C(2)	1.511 (9)
Cr-N(2)	2.099 (4)	N(3)-C(3)	1.495 (9)
Cr-N(3)	2.094 (4)	N(4)-C(4)	1.473 (7)
Cr-N(4)	2.083 (4)	C(3)-C(4)	1.494 (8)
F(1)-Cr-F(2)	93.5 (1)	N(2)-Cr-N(4)	93.6 (2)
F(1)-Cr-N(1)	90.5 (2)	N(4)-Cr-N(1)	175.2 (2)
F(1)-Cr-N(2)	87.4 (1)	N(3)-Cr-N(2)	92.7 (1)
F(1)-Cr-N(4)	92.4 (2)	N(3)-Cr-N(1)	94.1 (2)
F(1)-Cr-N(3)	175.3 (2)	N(3)-Cr-N(4)	83.0 (2)
F(2)-Cr-N(3)	86.9 (1)	N(1)-C(1)-C(2)	106.8 (5)
F(2)-Cr-N(1)	92.0 (2)	C(1)-C(2)-N(2)	110.0 (5)
F(2)-Cr-N(4)	91.7 (2)	N(3)-C(3)-C(4)	108.1 (5)
F(2)-Cr-N(2)	174.7 (1)	C(3)-C(4)-N(4)	108.6 (5)
N(2)-Cr-N(1)	82.7 (2)		

Experimental. Red prismatic single crystals were obtained from a solution of 1 g of *cis*-[CrF₂(en)₂]ClO₄ (Vaughn & Yeoman, 1976) and 2 g NaClO₄ in 10 ml water to which 10 ml ethanol were added. The solution was kept at 278 K for 24 h. Density of the crystals was determined by flotation in a mixture of organic solvents. Trigonal prismatic single crystal had dimensions 0.15 × 0.10 × 0.20 mm. The unit-cell dimensions were calculated from 43 reflections ($17 < 2\theta < 37^\circ$) measured on the diffractometer at 293 (1) K. The intensity data were collected at 293 (1) K with an Enraf-Nonius CAD-4 diffractometer. Experimental conditions: graphite-monochromatized Mo K α radiation ($\lambda = 0.71069 \text{ \AA}$), ω - 2θ scan, $\theta_{\min} = 1^\circ$, $\theta_{\max} = 27^\circ$, 2θ scan width = $(0.8 + 0.20 \tan\theta)^\circ$, aperture = $(2.5 + 0.9 \tan\theta)$ mm, variable scan rate, maximum scan time = 45 s, background: 1/4 of the scan time at each of the scan limits. 2175 independent reflections ($0 < h < 7$, $0 < k < 14$, $-22 < l < 22$) were measured, 1569 with $F > 2\sigma(F)$ used for the solution and refinement of the structure. Three standard reflections showed no decay during the data collection and no reorientation of the crystal was necessary.

Structure factors on a relative scale were obtained by applying Lorentz and polarization correction but no absorption correction. *E* map calculated from 250 normalized structure amplitudes, signed by *MULTAN* (Declercq, Germain, Main & Woolfson, 1973) gave the positions of Cr and Cl and of the four N and two F atoms coordinated to Cr. Fourier map gave the positions of the rest of the C and O atoms. H-atom positions calculated with $U_{\text{iso}} = 0.0714 \text{ \AA}^2$. Anisotropic refinement on *F* ended with $R = 0.052$ and $wR = 0.050$. Weighting function of the form $w = 2.74/[\sigma^2(F) + 0.0011F^2]$ from the *SHELX76* (Sheldrick, 1976) system of programs was applied. The maximum shift-to-e.s.d. ratio in the last cycle was 0.11. The final difference Fourier map had maximum and minimum $\Delta\rho$ values 0.20 and -0.26 e \AA^{-3} .

All calculations were performed on a CDC Cyber-172 computer with the *SHELX76* system. Atomic scattering factors for neutral atoms tabulated by Cromer & Mann (1968) and the values for f' and f'' for the anomalous-dispersion correction compiled by Cromer (1965) were applied. Scattering factors for hydrogen were from Stewart, Davidson & Simpson (1965).

The positional and equivalent thermal parameters are listed in Table 1.* Bond distances and angles are in Table 2. A *yz* projection of the structure including the numbering scheme used in Table 2 is given in Fig. 1.

* 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 43681 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

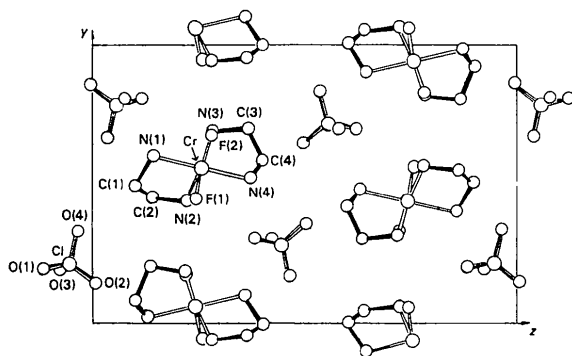


Fig. 1. *yz* projection of the structure and the numbering scheme.

Discussion. Owing to centrosymmetry, both Δ and Λ configurations of the cations are present in the structure (Purcell & Kotz, 1977). Chelate ligands have $\lambda\delta$ conformation with torsion angles around C(1)–C(2) and C(3)–C(4) 52.6 (6) and 56.1 (6)°. Inversion centres and glide planes present in the $P2_1/c$ unit cell transform a $\Delta\lambda\delta$ enantiomer of one cation into the $\Lambda\delta\lambda$ enantiomer of the other. The same situation was found in the structures of *cis*-(\pm)-[CoCl₂(en)₂]Cl·H₂O (Matsumoto, Ooi & Kuroya, 1970) and *cis*-(\pm)-[RhCl₂(en)₂]Cl·HgCl₂ (Podberez'skaja, Beljajev, Bokanin & Bajdina, 1981). By contrast the conformation of the ligands found in the racemic crystal of *cis*-(\pm)-[RhCl₂(en)₂]NO₃ was $\Delta\delta\delta$ and $\Lambda\lambda\lambda$ (Bajdina, Podberez'skaja, Beljajev & Bokanin, 1979). It is known that the energy difference between different conformations of chelate ligands with the same molecular helicity is small and can easily be leveled off by crystal forces (Gollogly & Hawkins, 1970).

Cr–F bond lengths are comparable to the value 1.887 (6) Å found in *cis*-[CrF₂(NH₃)₄]ClO₄ (Brenčič, Čeh & Leban, 1981). Cr–N(en) bonds in the range 2.05 to 2.10 Å were also found in the structures of *trans*-[CrF₂(en)₂]ClO₄ and *trans*-[CrF₂(en)₂]Cl (Brenčič & Leban, 1981, 1985).

Cations are connected by weak hydrogen bonds between N(2), N(3)(*x*, *y*, *z*) and F(1), F(2)(*x*–1, *y*, *z*) at 2.890 (5) and 2.853 (5) Å. Interactions between O atoms of the perchlorate anion and N atoms of the cation are from 3.03 (1) to 3.06 (1) Å, which is on the limit of the sum of the van der Waals radii (Huheey, 1972).

The average Cl–O bond length is 1.40 (1) Å. O–Cl–O angles are from 106.6 (4) to 113.6 (4)°.

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Structure of Merohedrally Twinned Di- μ -fluoro-bis[tris(3,5-dimethylpyrazole-*N*²)-copper(II)] Bis(tetrafluoroborate)

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Abstract. [Cu₂F₂(C₅H₈N₂)₆](BF₄)₂, *M_r* = 915.49, trigonal, $R\bar{3}$, *a* = 28.649 (7), *c* = 17.133 (4) Å, *V* = 12178 (5) Å³, *Z* = 12, *D_x* = 1.498 g cm⁻³, $\lambda(\text{Mo K}\alpha)$ = 0.71073 Å, μ = 10.74 cm⁻¹, 100 K, *F*(000) = 5640,

R = 0.0720 for 1669 observed reflections with *I* > 2.5 σ (*I*). The crystal is twinned by merohedry (α = 0.50). Domains are related by mirror planes of the $R\bar{3}m$ space group. The molecules are dimeric, consisting of two CuF(dmpz)₃(BF₄) units, related by an inversion centre. The two Cu atoms are asymmetrically

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