Table 2. *Bond distances* (Å) *and selected bond angles* (°) *with e.s.d.'s in parentheses*

Ir—C(1)	1.841 (5)	C(3)—C(7)	1.435 (7)
Ir—C(2)	1.847 (6)	C(3)—C(8)	1.518 (7)
Ir—C(3)	2.240 (5)	C(4)—C(5)	1.424 (7)
Ir—C(4)	2.276 (5)	C(4)—C(9)	1.509 (7)
Ir—C(5)	2.239 (4)	C(5)—C(6)	1.446 (7)
Ir—C(6)	2.278 (5)	C(5)—C(10)	1.519 (7)
Ir—C(7)	2.278 (5)	C(6)—C(7)	1.424 (7)
O(1)—C(1)	1.157 (7)	C(6)—C(11)	1.513 (8)
O(2)—C(2)	1.147 (7)	C(7)—C(12)	1.509 (7)
C(3)—C(4)	1.431 (7)		
RC*—Ir—C(1)	135.4 (2)	C(3)—C(7)—C(6)	107.7 (4)
RC—Ir—C(2)	135.6 (2)	C(4)—C(3)—C(7)	109.1 (4)
C(1)—Ir—C(2)	89.0 (2)	C(3)—C(4)—C(5)	106.8 (4)
Ir—C(1)—O(1)	178.6 (5)	C(4)—C(5)—C(6)	109.0 (4)
Ir—C(2)—O(2)	179.1 (5)	C(5)—C(6)—C(7)	107.4 (4)

* RC is the centroid of the pentamethylcyclopentadienyl ring.

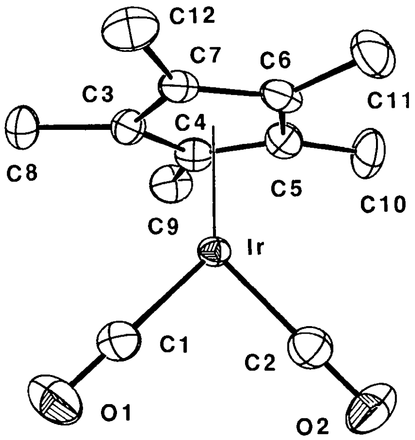

Fig. 1. *ORTEP* drawing of $Cp^*Ir(CO)_2$, with ellipsoids drawn at the 50% probability level.

of the Ir atom in $Cp^*Ir(CO)_2$ toward protonation by CF_3SO_3H as compared with the basicity of $(\eta^5\text{-}C_5H_5)Ir(CO)(PPh_3)$ (Sowa, Zanotti, Facchin & Angelici, 1991).

The cyclopentadienyl C atoms [C(3) through C(7)] of the Cp* ring lie in one plane (± 0.02 Å); the five methyl C atoms are an average of 0.10 Å out of this plane away from the Ir atom. The perpendicular distance from the Ir atom to the Cp* ring plane is 1.906 (5) Å. The plane of the Cp* ring is essentially perpendicular [89.1 (2)°] to the plane defined by O(1)—C(1)—Ir—C(2)—O(2).

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Structure of *cis*-(1,2-Ethanediamine)(1,4,8,11-tetraazacyclotetradecane)chromium(III) Perchlorate

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Abstract. *cis*-(1,2-Ethanediamine-κ^2N,N')(1,4,8,11-tetraazacyclotetradecane-κ^4N,N',N'',N''')chromium(III) triperchlorate, $[Cr(C_2H_8N_2)(C_{10}H_{24}N_4)](ClO_4)_3$, $M_r = 610.77$, orthorhombic, *Pbna* (nonstandard setting of *Pbcn*), $a = 12.145$ (2), $b = 13.832$ (3), $c = 14.624$ (4) Å, $V = 2456.8$ Å^3, $Z = 8$ (half molecules), $D_m = 1.643$, $D_x = 1.651$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 8.47$ cm^{-1}, $F(000) = 1172$, $T = 293$ K, $R = 0.073$ for 1635 independent observed reflections. When coordinated to Cr^{III} in a *cis* configuration, the cyclam ligand (1,4,8,11-tetraazacyclotetradecane) adopts the *RRRR* and

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SSSS conformations with the two five-membered rings possessing δ or λ configurations and the six-membered rings in the chair form. The ethanediamine (en) ring has a geometry similar to that in the $[Cr(en)_3]^{3+}$ ion. There are significant angular distortions of the coordination sphere from ideal octahedral geometry, and these play an important role in the spectroscopic and photophysical properties of this type of complex.

Introduction. As part of ongoing studies (Kirk & Heyd, 1991) of the spectroscopic, photochemical and photophysical properties of macrocyclic ligand complexes of Cr^{III}, we have determined the structure of $[Cr(cyclam)(en)](ClO_4)_3$. There are other structure reports of *cis* cyclam Cr^{III} complexes (Forsellini, Parasassi, Bombieri, Tobe & Sosa, 1986), but none of these concerns the coordination of Cr^{III} to six amine ligands. Such amine complexes have played an important role in photochemical and photophysical studies, and their properties are anomalous in ways that seem to relate to the angular distortions of the coordination sphere at Cr^{III} (Kirk & Guedel, 1992). The structural features are important in this context.

Experimental. $[Cr(cyclam)(en)]^{3+}$ was prepared by reaction of 1,2-ethanediamine dried over molecular sieves, with *cis*-$[Cr(cyclam)(NO_3)_2]NO_3$ as described in the literature (Kane-Maguire, Wallace & Miller, 1985). After recrystallization from perchloric acid solution, analysis of the yellow compound obtained showed it to be a mixture of the triperchlorate and the diperchlorate nitrate, paralleling the behaviour of hexafluorophosphate and tetrafluoroborate salts reported earlier (Kane-Maguire, Wallace & Miller, 1985).

Yellow crystals suitable for X-ray study were grown by slow evaporation in the dark of 3M $HClO_4$ solutions of the complex that had been rendered nitrate ion free by repeated precipitation from aqueous perchloric acid solutions.

Symmetry and approximate unit-cell dimensions were established by preliminary photographic work with Weissenberg and precession cameras using Cu $K\alpha$ radiation. The crystal used for intensity data collection was 0.86 × 1.01 × 0.32 mm. Density measurement was by flotation in $CCl_4/CHBr_3$. Using a Picker four-circle diffractometer, eight pairs of centering measurements in the 2θ range 21–50° were used in a least-squares procedure to refine the unit cell.

The Picker system used a $\theta/2\theta$ scan with 160 steps of 0.010° in 2θ, with counting for 0.25 s at each step. Background measurements were for 20 s at the beginning and end of each scan. Each batch of 50 reflections was preceeded by the measurement of three standards: ±3% variation in these standards was observed, and there was no crystal decomposition. Measurements were in the 2θ range 0 to 50°, with h 0 to 14, k 0 to 16, l 0 to 17. Lorentz, polarization and absorption corrections were applied using a numerical integration method on a 10 × 10 × 10 Gaussian grid with crystal shape (mm) ±(110) 0.4293, ±($\bar{1}$10) 0.5039, ±(001) 0.1594; calculated transmission range 0.496 to 0.760. 2169 reflections reduced by the criterion $I > 3\sigma(I)$ to 1635 observed.

Table 1. *Fractional atomic coordinates* ($\times 10^5$ Cr, Cl; $\times 10^4$ *others*) *and temperature parameters* (Å$^2 \times 10^4$ Cr, Cl; Å$^2 \times 10^3$ *others*)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cr(1)	21874 (10)	25000	50000	325 (4)
Cl(1)	−1543 (13)	46853 (12)	32480 (11)	459 (5)
Cl(2)	12700 (23)	25000	0	813 (13)
O(1)	666 (5)	4929 (4)	3908 (4)	75 (2)
O(2)	259 (5)	3949 (5)	2681 (4)	82 (2)
O(3)	−481 (4)	5510 (4)	2759 (4)	58 (2)
O(4)	−1067 (6)	4344 (6)	3741 (6)	107 (3)
O(5)	666 (12)	3226 (14)	379 (14)	238 (9)
O(6)	2017 (15)	2160 (17)	612 (12)	324 (15)
N(1)	3330 (4)	1480 (4)	4573 (4)	47 (2)
N(2)	2319 (5)	3221 (4)	3747 (4)	48 (2)
N(3)†	887 (4)	1633 (4)	4563 (4)	39 (2)
C(1)	3281 (7)	1103 (6)	3600 (6)	66 (3)
C(2)	3414 (7)	1942 (6)	2897 (6)	69 (3)
C(3)	2427 (7)	2631 (6)	2879 (5)	63 (3)
C(4)	3206 (6)	3960 (6)	3805 (6)	61 (3)
C(5)	3216 (7)	4382 (6)	4802 (6)	60 (3)
C(6)	−198 (5)	2188 (5)	4569 (5)	46 (2)

† Indicates an N atom of ethanediamine.

Table 2. *Interatomic distances* (Å), *bond angles* (°) *and torsion angles* (°)

N(1)—Cr(1)	2.075 (6)	C(1)—N(1)	1.517 (10)
N(2)—Cr(1)	2.093 (6)	C(3)—N(2)	1.515 (10)
N(3)—Cr(1)	2.083 (5)	C(4)—N(2)	1.488 (9)
O(1)—Cl(1)	1.428 (5)	C(6)—N(3)	1.525 (8)
O(2)—Cl(1)	1.406 (6)	C(2)—C(1)	1.559 (12)
O(3)—Cl(1)	1.403 (5)	C(3)—C(2)	1.531 (11)
O(4)—Cl(1)	1.404 (6)	C(5)—C(4)	1.570 (12)
O(5)—Cl(2)	1.362 (14)	C(6)—C(6)	1.528 (14)
O(6)—Cl(2)	1.359 (15)		
N(2)—Cr(1)—N(1)	90.5 (2)	C(4)—N(2)—Cr(1)	109.4 (5)
N(3)—Cr(1)—N(1)	91.4 (2)	C(6)—N(3)—Cr(1)	111.4 (4)
N(3)—Cr(1)—N(2)	93.6 (2)	C(4)—N(2)—C(3)	110.8 (6)
O(2)—Cl(1)—O(1)	108.7 (3)	C(3)—C(2)—C(1)	113.2 (6)
O(3)—Cl(1)—O(1)	110.5 (3)	C(2)—C(1)—N(1)	111.0 (7)
O(3)—Cl(1)—O(2)	112.9 (4)	C(2)—C(3)—N(2)	112.9 (7)
O(4)—Cl(1)—O(1)	106.4 (5)	C(5)—C(4)—N(2)	108.3 (6)
O(4)—Cl(1)—O(2)	109.9 (5)	N(1)—Cr(1)—N(1′)	96.0 (5)
O(4)—Cl(1)—O(3)	108.2 (4)	N(2)—Cr(1)—N(1′)	83.6 (5)
O(6)—Cl(2)—O(5)	110.3 (11)	N(3)—Cr(1)—N(1′)	172.1 (4)
O(5)—Cl(2)—O(5)	114.8 (15)	N(2)—Cr(1)—N(2′)	171.2 (5)
O(6)—Cl(2)—O(6)	96.2 (20)	N(2)—Cr(1)—N(3′)	93.0 (4)
C(1)—N(1)—Cr(1)	119.3 (4)	N(3)—Cr(1)—N(3′)	81.4 (4)
C(3)—N(2)—Cr(1)	118.9 (5)	N(3)—C(6)—C(6′)	106.8 (4)
N(1)—C(5′)—C(4′)—N(2′)	54.8	N(3)—C(6)—C(6′)—N(3′)	50.9
N(2)—C(4)—C(5)—N(1′)	54.8		

The structure was found and refined using *SHELX*76 (Sheldrick, 1976), and illustrations were generated using *ORTEP* (Johnson, 1965). The atomic scattering factors were for neutral atoms, with corrections for anomalous dispersion (Ibers & Hamilton, 1974). The structure was solved by direct methods, developed by standard Fourier synthesis procedures using difference maps and refined by the method of least squares. H atoms were not located. In the final refinement, the max. shift/e.s.d. = 0.48, the final difference map, max. $\Delta\rho$ 0.8, min. $\Delta\rho$ -0.5 e Å^{-3}. Final residuals were $R = 0.073$, $wR = 0.080$ using 1635 reflections and 155 parameters, $S = 2.9055$.

Discussion. The title compound crystallizes in the orthorhombic space group *Pbna*, as does the trichloride trihydrate of its Co^{III} analogue (Lai & Poon, 1976). The unit cell contains molecules of both chiralities related by the *a*, *b* and *n* glide planes. The main X-ray results are presented in Tables 1 and 2.*

The structure of the cation is shown in Fig. 1. The twofold symmetry axis bisects the ethanediamine ring, passing through the Cr^{III} centre. Applying the substituent hierarchy $Cr > NH(CH_2)_2NH > NH(CH_2)_3NH > H$ to the conformations at the four N atoms, the cation shown is the *cis*-(*RRRR*), and this cation shares crystal sites alternately with its enantiomeric *cis*-(*SSSS*). No other conformers are present. In the *cis*-(*RRRR*) species, the diaminoethane ring is in the δ conformation, as are the two five-membered rings of the cyclam, while the six-membered rings are in the chair form and have a λ conformation when viewed along the twofold axis of the cation. For these chair rings, the conformations and interrelationships are the same as reported (Jurnak & Raymond, 1974) for the two chair-form rings found in $[Cr(tn)_3][Ni(CN)_5].2H_2O$ (tn = 1,3-propanediamine). Analogous geometrical relationships are seen in the Co^{III} analogue, but note that the molecule depicted (Lai & Poon, 1976) is *cis*-(*SSSS*) not its enantiomer as stated.

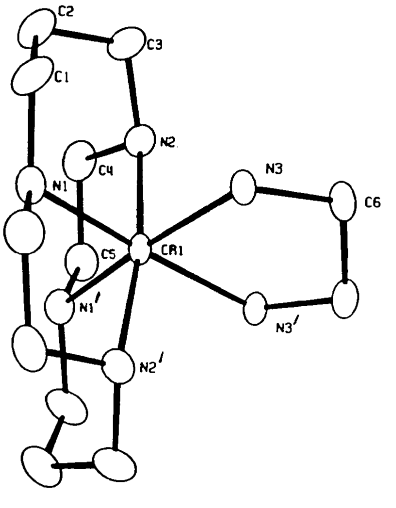

Fig. 1. Molecular structure of the *cis*-(*RRRR*)-[Cr(cyclam)(en)]$^{3+}$ ion.

The cyclam ligand is folded at an angle of 96.0° along a diagonal of the tetragon formed by the four N atoms, the same angle, within experimental error, as seen in the Co^{III} species, but differing from the corresponding angles in *cis*-[Cr(cyclam)Cl$_2$]$^+$ of 92.8° in the chloride and 94.3° in the perchlorate.

There is no difference between the average Cr—N bond lengths to the cyclam and en ligands (Table 2). The average length of 2.084 Å in [Cr(cyclam)(en)]$^{3+}$ is close to the average length, 2.080 Å, in *cis*-[Cr(cyclam)Cl$_2$]ClO$_4$ (House & McKee, 1984). This bond length is significantly longer than the value of 1.986 ± 0.003 Å reported for the *M*—N bonds in the cobalt(III) analogue. As predicted by Hawkins (1971), this results in a smaller N—*M*—N angle and a larger N—C—C—N torsion angle in the Cr(en) ring. Again, comparison of Cr with Co shows that the five-membered rings of the cyclam have a significantly longer C—C bond [1.570 (12) *vs* 1.488 Å]. The data also reveal small bond length and angle distortions in the five-membered rings of the cyclam, relative to the lone Cr(en) ring. In particular, the N—C—C—N torsion angle is increased to 55° from the 51° value in the Cr(en) case (Table 2).

Finally, note that the temperature factors and bond length and angle uncertainties for the perchlorate ion occupying a special position are rather large, suggesting that there may be some disorder present. This may well account for the failure of the structure to converge to a better *R* value.

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* Tables of anisotropic thermal parameters, structure factors and selected intermolecular distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55945 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1007]

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Tetrakis(2-chlorobenzyl)lead

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Abstract. [Pb(C_7H_6Cl)$_4$], $M_r = 709.51$, monoclinic, $P2_1/c$, $a = 10.871$ (6), $b = 21.962$ (10), $c = 11.650$ (6) Å, $\beta = 110.11$ (4)°, $V = 2612$ (2) Å^3, $Z = 4$, $D_x = 1.804$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.710730 Å, $\mu = 6.94$ mm^{-1}, $F(000) = 1368$, $T = 169$ (1) K, final $R = 0.040$ for 2391 unique observed [$F \geq 5\sigma(F)$] X-ray diffractometer data. The C atoms of the four benzyl CH_2 groups form a slightly distorted tetrahedron around the central atom of the title compound. The four Pb—C distances [2.25 (1) to 2.26 (2) Å] are not significantly different. Pb—C distance data of symmetric tetraalkyllead or benzyllead compounds are not available for comparison. The C—C distances are in the usual range.

Introduction. Tetrabenzyllead and substituted symmetric tetrabenzyllead compounds differ from common tetraorganolead compounds by being coloured (yellow) and being very air sensitive. One requirement for understanding this unusual behaviour is a detailed knowledge of the molecular structure of such compounds. We report here on the solid-state structure of (2-$ClC_6H_4CH_2$)$_4$Pb. This is the first published single-crystal structure determination of a symmetric tetraalkyllead compound.

Experimental. The compound was prepared by reaction of 2-$ClC_6H_4CH_2MgBr$ with $PbCl_2$ under total exclusion of air (Bähr & Zoche, 1955). Single, yellow, clear crystals from ethanol, m.p. 372 K. Crystal size ≃ 0.14 × 0.14 × 0.16 mm, $\omega/2\theta$ scans, variable scan speed 2.5–15° min^{-1} in θ, Nicolet *R3m/V* diffractometer, graphite-monochromated Mo $K\alpha$ radiation; lattice parameters from least-squares fit with 26 reflections in the range $2\theta = 15$–30°; six standard reflections (200, $\bar{2}00$, 040, $0\bar{4}0$, 004, $00\bar{4}$) recorded every 2.5 h, showed up to 8.54% intensity loss during data collection; 6781 reflections measured; $1 \leq \theta \leq 25°$; $-12 \leq h \leq 3$, $-1 \leq k \leq 27$, $-14 \leq l \leq 14$. The data were corrected for Lorentz–polarization, but not for absorption effects. After averaging 4620 unique reflections, $R_{\rm int} = 0.0236$, from which 2391 have [$F \geq 5\sigma(F)$]; no ψ scans; systematic absences ($h0l$) $l = 2n + 1$, ($0k0$) $k = 2n + 1$ conform with space group $P2_1/c$ (No. 14); structure solution *via* direct

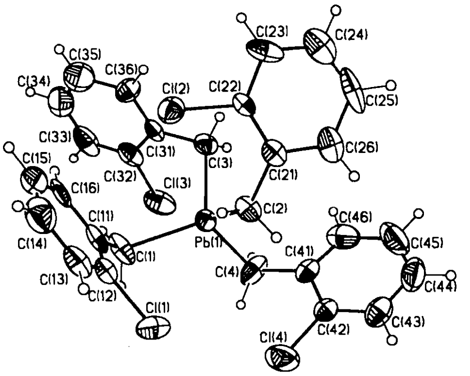

Fig. 1. General view (*SHELXTL-Plus*) of the molecule, showing the atom-numbering scheme.

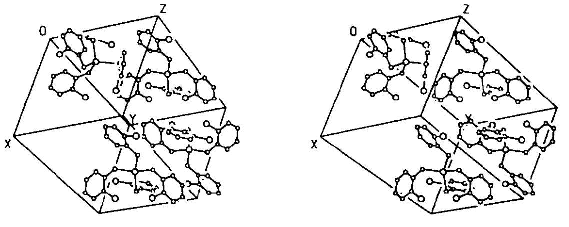

Fig. 2. Stereoscopic view (*SHELXTL-Plus*) of the unit cell.

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