

Table 2. Comparison of bond distances (Å) and angles (°) involving the formazan nucleus for various formazan complexes

	PDFORM	NIFORM1	NIFORM3	CUFORM	TTFPd
N(1)–N(2)	1.288 (4)	1.281 (9)	1.302 (4)	1.294 (7)	1.310 (7)
N(2)–C(3)	1.340 (7)	1.347 (8)	1.348 (5)	1.348 (7)	1.351 (8)
C(3)–N(4)	1.359 (7)	1.340 (9)	1.337 (3)	1.338 (7)	1.334 (8)
N(4)–N(5)	1.290 (6)	1.312 (9)	1.318 (4)	1.318 (6)	1.304 (7)
N(1)–C(6)	1.436 (7)	1.413 (8)	1.413 (5)	1.394 (7)	1.409 (7)
C(3)–C(15)	1.472 (6)	1.481 (11)	1.486 (5)	1.486 (7)	1.485 (9)
N(5)–C(21)	1.447 (7)	1.475 (9)	1.454 (5)	1.439 (7)	1.420 (8)
N(1)–N(2)–C(3)	123.9 (4)	119.8 (6)	119.1 (2)	119.0 (5)	121.2 (5)
N(2)–C(3)–N(4)	127.3 (4)	127.8 (7)	128.5 (3)	130.1 (5)	124.1 (6)
C(3)–N(4)–N(5)	121.5 (4)	121.3 (6)	121.0 (3)	123.0 (5)	120.9 (5)

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Structure of the Isothiocyanate Salt of *trans*-Aqua(isothiocyanato)(1,4,8,12-tetraazacyclopentadecane)chromium(III), [Cr(NCS)(H₂O)(C₁₁H₂₆N₄)](NCS)₂

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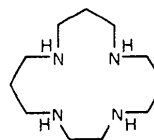
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Abstract. $M_r = 458.6$, orthorhombic, $Pna2_1$, $a = 13.797$ (2), $b = 11.138$ (2), $c = 13.700$ (3) Å, $V = 2105.3$ Å³, $Z = 4$, $D_x = 1.447$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.83$ mm⁻¹, $F(000) = 964$, $T = 291$ K, $R = 0.054$ for 1853 observed reflections. The Cr^{III} atom is coordinated in an equatorial belt by the [15]aneN₄ macrocyclic ligand, and by H₂O and isothiocyanate ligands in mutually *trans* positions. All four N–H bonds are directed to one side of the macrocyclic ligand, away from the H₂O and towards the coordinated NCS⁻. The two uncoordinated NCS⁻ anions are hydrogen bonded to the H₂O ligand.

Introduction. The saturated macrocyclic ligand [15]aneN₄ (1) is one of a series of saturated tetraaza macrocyclic ligands of various ring sizes, complexes of which with various metal ions have been studied structurally. It is found that *cis* isomers are formed by [12]aneN₄ with Co^{III} or Cr^{III}, and by [13]aneN₄ with Cr^{III}, whereas *trans* isomers are formed by [15]aneN₄ or [16]aneN₄ with both metals: for the complexes of [13]aneN₄ and [14]aneN₄ with Co^{III} and of [14]aneN₄

with Cr^{III}, both *cis* and *trans* isomers have been prepared (Collmann & Schneider, 1966; Poon & Tobe, 1967, 1968; Hung, Martin, Jackels, Tait & Busch, 1977; Hung & Busch, 1977; Swisher, Brown, Smierciak & Blinn, 1981). There is evidence of configurational isomerism (different relative orientations of the N–H groups) in [15]aneN₄ complexes of Co^{III} (Hung, Martin, Jackels, Tait & Busch, 1977). We have determined the structure of a [15]aneN₄ complex of Cr^{III} in order to establish the configuration of the macrocyclic ligand in connection with previous kinetic and equilibrium studies in solution (Adzamli, Hender-son, Ong, Sykes, Cammack & Rao, 1982; Richens, Adzamli, Leupin & Sykes, 1984).



[15]aneN₄

(1)

Experimental. Preparation from $[\text{Cr}(\text{[15]aneN}_4)(\text{H}_2\text{O})_2][\text{ClO}_4]_3$ (Samuels & Espenson, 1979) yielded red crystals (Richens *et al.*, 1984). Crystal $0.2 \times 0.2 \times 0.1$ mm mounted on glass fibre. Enraf-Nonius CAD-4 diffractometer. Unit-cell parameters from 25 centred reflections ($18 < 2\theta < 28^\circ$). Systematic absences: $0kl$ for $k+l$ odd, $h0l$ for h odd; space group $Pna2_1$ or $Pnam$ ($Pnma$ reoriented). 2396 non-extinguished reflections with $2\theta < 54^\circ$, index ranges: $h 0 \rightarrow 17$, $k 0 \rightarrow 14$, $l 0 \rightarrow 17$. No significant intensity variation for three standard reflections. No absorption or extinction corrections. 1853 reflections with $F > 2\sigma(F)$.

Structure solved from Patterson and difference syntheses in $Pnam$. Refinement with anisotropic thermal parameters converged at $R = 0.10$. Unsatisfactory features were (i) high temperature-factor components, typical of disorder problems, for some macrocyclic-ligand atoms, and (ii) the crystallographic mirror plane bisecting the $\text{NCH}_2\text{CH}_2\text{N}$ section of the ligand and thus imposing an eclipsed conformation. Refinement in $Pna2_1$, imposing no crystallographic symmetry on the cation, required restraints on the macrocyclic ligand to prevent a drift towards a centrosymmetric solution: soft restraints applied by the *SHELXTL DFIX* instruction (Sheldrick, 1978) to impose near equality on all C—C bond lengths, on all N—C bond lengths, on C—C—N angles and on C—N—C angles. Restraints also applied to H atoms of the coordinated H_2O , to maintain approximately equal O—H with near tetrahedral H—O—H. Other H atoms constrained to give $\text{N—H} = \text{C—H} = 0.96 \text{ \AA}$, $\text{H—C—H} = 109.5^\circ$, $U(\text{H}) = 1.2U_{\text{eq}}(X)$ with $X = \text{C, N or O}$.

Blocked-cascade refinement on F , $w^{-1} = \sigma^2(F) + 0.00177F^2$. Anisotropic thermal parameters for non-H atoms. Scattering factors from *International Tables for X-ray Crystallography* (1974). 246 parameters, $R = 0.054$, $wR = 0.067$, slope of normal probability plot 1.11. Max. $\Delta/\sigma = 0.075$, mean = 0.010. Largest peak in final difference map 0.51 e \AA^{-3} , largest hole -0.34 e \AA^{-3} with no indications of disorder. An attempt to refine η (Rogers, 1981) was inconclusive [$\eta = 0.6(3)$], not surprisingly, in view of the pseudo-centrosymmetry.

Discussion. Atomic coordinates are given in Table 1, bond lengths and angles in Table 2.* The structure of the asymmetric unit is shown in Fig. 1. The coordination of the Cr atom is distorted octahedral, the deviations from ideal angles of 90° and 180° being caused mainly by the presence of one short

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39982 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$)

	x	y	z	U_{eq}
Cr	3411 (1)	6115 (1)	5000	23 (1)
O	2129 (3)	6947 (3)	4980 (7)	34 (1)
H(a)	1840 (26)	7267 (59)	4449 (25)	41
H(b)	1713 (29)	6993 (56)	5490 (26)	41
N(1)	3142 (5)	4996 (6)	3789 (5)	49 (2)
C(2)	3594 (10)	5523 (6)	2875 (7)	59 (4)
C(3)	3554 (7)	6874 (6)	2942 (5)	36 (3)
N(4)	3868 (6)	7269 (5)	3928 (5)	34 (3)
C(5)	3771 (8)	8598 (8)	4045 (6)	46 (3)
C(6)	4228 (4)	9011 (5)	4976 (5)	54 (2)
C(7)	3754 (7)	8589 (6)	5899 (6)	47 (4)
N(8)	3933 (5)	7287 (6)	6084 (5)	32 (3)
C(9)	3573 (7)	6975 (6)	7059 (7)	53 (4)
C(10)	3621 (6)	5655 (6)	7267 (6)	55 (4)
C(11)	2771 (5)	4938 (6)	6909 (4)	51 (2)
N(12)	2837 (5)	4734 (6)	5848 (4)	50 (2)
C(13)	1872 (7)	4222 (12)	5534 (7)	74 (5)
C(14)	1862 (8)	3784 (11)	4528 (7)	83 (5)
C(15)	2132 (5)	4566 (7)	3691 (6)	56 (3)
N(01)	4704 (3)	5350 (4)	4985 (9)	35 (1)
C(01)	5490 (4)	4981 (4)	4987 (10)	34 (1)
S(01)	6574 (1)	4466 (2)	4998 (4)	60 (1)
N(02)	1069 (4)	7423 (7)	6616 (5)	51 (2)
C(02)	975 (5)	7306 (6)	7440 (6)	41 (2)
S(02)	854 (2)	7152 (2)	8601 (2)	69 (1)
N(03)	1057 (4)	7468 (7)	3406 (5)	54 (2)
C(03)	958 (4)	7335 (7)	2573 (5)	39 (2)
S(03)	832 (2)	7133 (3)	1392 (2)	68 (1)

Table 2. Freely refined and restrained bond lengths (\AA) and angles ($^\circ$)

Cr—O	1.997 (4)	Cr—N(1)	2.108 (6)
Cr—N(4)	2.050 (7)	Cr—N(8)	2.104 (7)
Cr—N(12)	2.084 (6)	Cr—N(01)	1.976 (4)
O—H(a)	0.903 (41)	O—H(b)	0.906 (39)
N(1)—C(2)	1.516 (11)	N(1)—C(15)	1.480 (10)
C(2)—C(3)	1.508 (9)	C(3)—N(4)	1.486 (10)
N(4)—C(5)	1.495 (11)	C(5)—C(6)	1.496 (11)
C(6)—C(7)	1.499 (11)	C(7)—N(8)	1.493 (10)
N(8)—C(9)	1.467 (12)	C(9)—C(10)	1.499 (10)
C(10)—C(11)	1.501 (11)	C(11)—N(12)	1.474 (8)
N(12)—C(13)	1.511 (13)	C(13)—C(14)	1.462 (14)
C(14)—C(15)	1.488 (13)	N(01)—C(01)	1.160 (6)
C(01)—S(01)	1.603 (5)	N(02)—C(02)	1.145 (10)
C(02)—S(02)	1.607 (8)	N(03)—C(03)	1.158 (9)
C(03)—S(03)	1.643 (7)		
O—Cr—N(1)	96.2 (3)	O—Cr—N(4)	88.4 (3)
N(1)—Cr—N(4)	82.0 (3)	O—Cr—N(8)	91.4 (3)
N(1)—Cr—N(8)	169.3 (3)	N(4)—Cr—N(8)	90.7 (3)
O—Cr—N(12)	90.8 (3)	N(1)—Cr—N(12)	86.3 (2)
N(4)—Cr—N(12)	168.1 (3)	N(8)—Cr—N(12)	101.2 (2)
O—Cr—N(01)	177.5 (3)	N(1)—Cr—N(01)	84.0 (3)
N(4)—Cr—N(01)	89.2 (3)	N(8)—Cr—N(01)	88.1 (3)
N(12)—Cr—N(01)	91.7 (3)	Cr—O—H(a)	125.8 (26)
Cr—O—H(b)	125.3 (30)	H(a)—O—H(b)	108.6 (36)
Cr—N(1)—C(2)	110.4 (5)	Cr—N(1)—C(15)	115.4 (5)
C(2)—N(1)—C(15)	115.9 (7)	N(1)—C(2)—C(3)	108.7 (7)
C(2)—C(3)—N(4)	109.9 (6)	Cr—N(4)—C(3)	112.1 (5)
Cr—N(4)—C(5)	121.1 (5)	C(3)—N(4)—C(5)	111.4 (6)
N(4)—C(5)—C(6)	110.9 (7)	C(5)—C(6)—C(7)	116.0 (6)
C(6)—C(7)—N(8)	112.1 (6)	Cr—N(8)—C(7)	115.2 (5)
Cr—N(8)—C(9)	112.3 (5)	C(7)—N(8)—C(9)	109.2 (6)
N(8)—C(9)—C(10)	113.0 (7)	C(9)—C(10)—C(11)	115.2 (7)
C(10)—C(11)—N(12)	110.9 (6)	Cr—N(12)—C(11)	117.3 (5)
Cr—N(12)—C(13)	117.1 (5)	C(11)—N(12)—C(13)	106.5 (6)
N(12)—C(13)—C(14)	113.7 (8)	C(13)—C(14)—C(15)	121.9 (10)
N(1)—C(15)—C(14)	110.8 (7)	Cr—N(01)—C(01)	175.1 (5)
N(01)—C(01)—S(01)	179.5 (12)	N(02)—C(02)—S(02)	179.3 (7)
N(03)—C(03)—S(03)	179.2 (6)		

NCH₂CH₂N arm of the macrocyclic ligand with a consequent small N—Cr—N angle. The macrocyclic ligand forms an equatorial belt, with H₂O and one NCS⁻ ligand in axial positions, *trans* to each other. The two NCS⁻ counterions are hydrogen bonded to the H₂O ligand [O...N = 2.73 (1) and 2.68 (1) Å], thus forming an electrically neutral unit.

A search of the Cambridge Structural Database (1984) showed that structures have been determined for complexes of the [*n*]aneN₄ ligands and their substituted derivatives with ions of most of the first transition series, Ni being present in about half of the complexes studied. For Cr^{III}, only [14]aneN₄ complexes have been reported, and these have been found in both *cis* and *trans* forms with essentially octahedral coordination (Bang & Mønsted, 1982, 1984).

One complex of [15]aneN₄ has been reported, [Cu([15]aneN₄)(ClO₄)₂] (Fabrizzi, Mealli & Paoletti, 1979). As is the case for the compound in the present study, a *trans* structure is observed. In both structures, the five-membered chelate ring has a *gauche* conformation, the two adjacent six-membered rings are chairs, but the third ring has an envelope type of conformation with a single CH₂ flap, the coordinated metal atom lying much closer to the mean plane of the two N and two closest C atoms (Fig. 1).

Of particular interest is the configurational arrangement of the macrocyclic ligand. All four N—H bonds are directed to one side of the ligand, away from H₂O and towards the coordinated NCS⁻. This is in contrast to the Cu complex, in which two N—H bonds are directed to each side of the ligand.

The packing of the hydrogen-bonded ion triple units is shown in projection in Fig. 2, which also demonstrates the near mirror symmetry.

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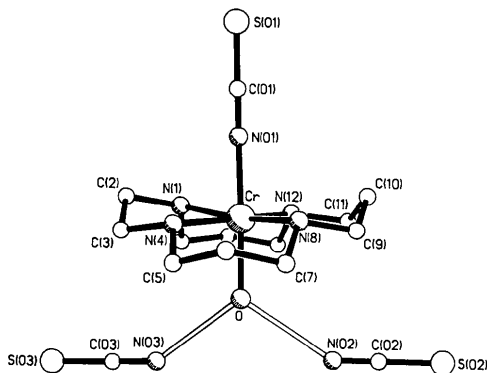


Fig. 1. Structure of the cation and anions, showing the atom labelling and hydrogen bonding. H atoms are omitted. Labels are not shown for C(6), C(13), C(14) and C(15).

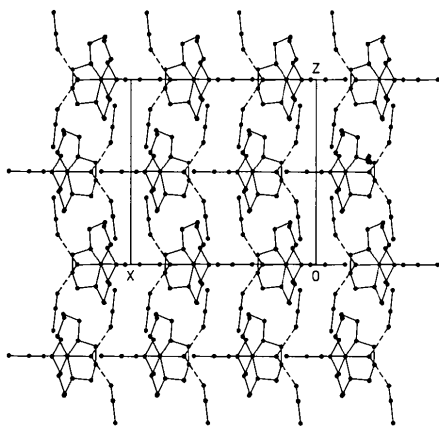


Fig. 2. Parallel projection down the *b* axis.