

gave data which were at first interpreted as monoclinic.† It was only after full refinement that this structure turned out to be hexagonal (Wang, Gabe, Calvert & Taylor, 1977). It seems from the DDL report that their 'bloc sphérique' was not ground and furthermore no absorption correction was applied. In this case, the expected variations in absorption would be even larger and an orthorhombic distribution of intensities is possible.

The structure description and the chemical conclusions in DDL remain valid because they recognize the chemical similarity of the now symmetry-related Pb(1) and Pb(4) as well as Pb(2) and Pb(3). In fact, no deviations from the hexagonal structure were discussed by DDL: even the distortions shown in their Fig. 3 are hexagonal in nature and are confirmed by the present refinement.

Dr R. E. Marsh (private communication) raises the point that, in view of the non-singularity of the refinement in the *Cmcm* subgroup, it is disturbing that some Pb atoms in the orthorhombic refinement differ from their refined hexagonal positions by a number of σ 's which is statistically highly significant, especially for the Pb(2) and Pb(3) atoms. To this valid statistical argument, we offer the following comments:

(a) All the atomic deviations between the MH refinement and the hexagonal model, except two, correspond to less than half the r.m.s. thermal-motion amplitude. The exceptions, atoms O(15) and O(16), deviate by about 0.1 Å, i.e. 0.8 r.m.s. amplitude or 4 positional σ 's. If the orthorhombic distortion in MH is assumed to be correct, the room-temperature thermal motion would suffice to establish locally the hexagonal symmetry of the structure and consequently to produce alternate orientations of the orthorhombic structure in the metrically hexagonal lattice, leading to atomic disorder or twinning. The resulting diffraction intensities of a macroscopic sample would therefore mimic hexagonal symmetry.

† In this case, A^* varied by 30% (at $\theta = 15^\circ$) for $r_1 = 0.0063$ and $r_2 = 0.0073$ cm respectively ($\mu\bar{r} = 2.78$).

(b) In the MH refinement, Pb(3) behaves abnormally, and they suggest some disorder. In the hexagonal refinement, Pb(2) and Pb(3) occupy the same site which refines normally.

The normal distribution indicates that 11 out of 85 measurements of systematically absent intensities are expected to be larger than 1.5σ . This is consistent with the seven reported new systematic absences.

The metrically hexagonal lattice, the new class of systematic absences found in the DDL data, the satisfactory refinement in *P6₃/mcm* and the disappearance of the anomaly at the Pb(3) position raise doubts about the space-group symmetries *Cmc2₁* and *Cmcm* proposed for Pb₃Mn₇O₁₅ by DDL and MH respectively. We feel that this compound should be re-examined and the possibility that it is truly hexagonal or twinned should be considered by future investigators. If its orthorhombic character were to be confirmed, its structure should be described in terms of a very slight distortion of the above hexagonal structure. Unfortunately, no single crystal from the original preparation could be found by DDL and we were unable to attempt to synthesize it due to experimental difficulties.

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***trans*-Aquachloro[(1*S*,4*S*,7*S*,8*R*,11*R*,14*R*)-5,5,7*e*,12,12,14*e*-hexamethyl-1,4,8,11-tetraazacyclotetradecane]chromium(III) Nitrate, [CrCl(H₂O)(C₁₆H₃₆N₄)](NO₃)₂**

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Abstract. $M_r = 513.96$, monoclinic, *Cc*, $a = 14.560$ (5), $b = 11.740$ (5), $c = 14.772$ (7) Å, $\beta = 110.83$ (3)°, $Z = 4$, $V = 2360.0$ Å³, $D_x = 1.447$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.632$ mm⁻¹, $F(000) = 1092$, $T = 293$ K, final $R = 0.0614$ for 1894 observed reflections. The macrocyclic ligand, teta, forms a CrN₄

plane with Cl⁻ and H₂O occupying the *trans* positions. The *sec*-NH protons adopt the *meso* (*RSSR*) configuration and the methyl groups attached to C atoms at the 7 and 14 positions of the ligand adopt an equatorial orientation.

Introduction. The title compound is one of several possible isomers (House & Yang, 1982; House, Hay & Akbar Ali, 1983). It is formed as orange crystals when green *trans*-[CrCl₂(teta)]ClO₄ is allowed to hydrolyze in water, followed by the addition of NaNO₃. The crystal structure of this isomer allows the assignment of the stereochemistry of the coordinated *sec*-NH centers and the orientation of the methyl groups at the 7 and 14 positions of the macrocycle.

Experimental. Nicolet R3m automated four-circle diffractometer, graphite-monochromated Mo K α . Crystal 0.25 × 0.21 × 0.16 mm. Lattice parameters from 25 reflections in range 28 < 2 θ < 32°; space group *Cc* or *C2/c* from systematic absences; *Cc* confirmed from successful refinement. $\theta/2\theta$ scans, 2 θ_{\max} = 50°. Standard reflections (no variation) 002, $\bar{1}$ 31, $\bar{4}$ 00. 2367 reflections measured, 1894 with $I > 3\sigma(I)$ used in refinement, $h \pm 16$, k 0 to 13, l 0 to 17. No corrections for absorption or extinction. Coordinates of Cr obtained from Patterson calculations. 30 non-hydrogen atoms from difference Fourier maps. Blocked cascade least-squares refinement. All non-hydrogen atoms anisotropic, H atoms (except those of H₂O) included in calculated positions with isotropic thermal parameters equal to 1.2 times the isotropic equivalent of their carrier atoms (C–H = N–H = 0.96 Å); F magnitudes used; $R = 0.0614$, $wR = 0.0473$, $w = [|\sigma^2(F)|]^{-1}$, $S = 4.597$, $(\Delta/\sigma)_{\max} = 0.595$ [C(5) y coordinate], $\Delta\rho = -0.44$ to $+0.64$ e Å⁻³. All calculations on Nova 4X computer using *SHELXTL* (Sheldrick, 1981).

Discussion. Atomic parameters are listed in Table 1,* bond lengths and selected angles in Table 2. The crystal structure consists of independent six-coordinate CrCl(teta)(H₂O)²⁺ cations (Fig. 1) and NO₃⁻ anions. The coordinated Cl⁻ and H₂O ligands are *trans* with respect to the CrN₄ plane and, within the macrocycle, the five-membered rings adopt the *gauche* ($\delta\lambda$) and the six-membered rings the chair (pp)† conformation. The *sec*-NH protons are in the lowest-energy *RSSR* (*meso*) configuration and the (*R,S*)C-methyl groups are in the

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

	x	y	z	U_{eq}^*
Cr	7500	2598 (1)	0	35
N(1)	6817 (6)	2346 (7)	1000 (7)	36
N(2)	6798 (5)	4171 (6)	-256 (5)	39
N(3)	8154 (4)	2813 (6)	-1031 (5)	37
N(4)	8192 (5)	998 (6)	278 (5)	35
C(1)	6436 (7)	1153 (8)	1059 (7)	45
C(11)	5925 (8)	1098 (10)	1785 (8)	68
C(2)	7296 (7)	338 (8)	1347 (7)	47
C(3)	7747 (8)	-29 (9)	565 (8)	50
C(31)	6919 (7)	-628 (9)	285 (7)	71
C(32)	8576 (9)	-914 (9)	1075 (9)	69
C(4)	8513 (8)	817 (9)	-589 (8)	63
C(5)	8887 (7)	1875 (10)	-843 (8)	63
C(6)	8494 (6)	3998 (9)	-1108 (6)	46
C(61)	9044 (7)	4017 (10)	-1856 (7)	62
C(7)	7624 (7)	4793 (8)	-1391 (6)	46
C(8)	7181 (7)	5197 (8)	-636 (7)	43
C(81)	6325 (8)	5983 (9)	-1142 (9)	60
C(82)	7951 (6)	5839 (8)	212 (6)	48
C(9)	6507 (7)	4385 (8)	611 (6)	46
C(10)	6091 (6)	3287 (9)	842 (7)	45
Cl	8848 (2)	3284 (2)	1247 (2)	60
O(1)	6262 (5)	1968 (6)	-1105 (5)	51
N(5)	9002 (5)	2171 (7)	3520 (6)	55
O(2)	8139 (4)	2273 (7)	3232 (5)	70
O(3)	9530 (5)	3122 (6)	3924 (5)	59
O(4)	9465 (5)	1324 (7)	3485 (6)	81
N(6)	1068 (8)	2216 (9)	1597 (7)	75
O(5)	1534 (5)	2884 (7)	2277 (5)	76
O(6)	1127 (8)	2274 (9)	849 (7)	120
O(7)	583 (7)	1408 (7)	1789 (8)	113

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

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

Cr–Cl	2.307 (2)	Cr–N(1)	2.074 (11)	Cr–N(2)	2.079 (7)	
Cr–N(3)	2.078 (8)	Cr–N(4)	2.102 (7)	Cr–O(1)	2.090 (6)	
N(1)–C(1)	1.520 (13)	C(1)–C(11)	1.508 (17)	C(1)–C(2)	1.513 (3)	
C(2)	C(3)	1.578 (17)	C(3)–C(31)	1.565 (13)	C(3)–C(32)	1.569 (15)
C(3)–N(4)	1.500 (14)	N(4)–C(4)	1.526 (15)	C(4)–C(5)	1.458 (17)	
C(5)–N(3)	1.489 (13)	N(3)–C(6)	1.496 (13)	C(6)–C(61)	1.578 (16)	
C(6)–C(7)	1.508 (13)	C(7)–C(8)	1.547 (17)	C(8)–C(81)	1.517 (14)	
C(8)–C(82)	1.547 (12)	C(8)–N(2)	1.517 (13)	N(2)–C(9)	1.506 (13)	
C(9)–C(10)	1.514 (14)	C(10)–N(1)	1.488 (13)	N(5)–O(2)	1.181 (9)	
N(5)–O(3)	1.367 (10)	N(5)–O(4)	1.213 (11)	N(6)–O(5)	1.265 (12)	
N(6)–O(6)	1.139 (15)	N(6)–O(7)	1.274 (15)			
N(3)–Cr–N(2)	94.7 (3)	N(3)–Cr–N(4)	86.5 (3)			
N(2)–Cr–N(4)	178.8 (3)	N(3)–Cr–O(1)	87.9 (3)			
N(2)–Cr–O(1)	86.6 (3)	N(4)–Cr–O(1)	93.3 (2)			
N(3)–Cr–N(1)	178.2 (3)	N(2)–Cr–N(1)	85.8 (3)			
N(4)–Cr–N(1)	93.0 (3)	O(1)–Cr–N(1)	90.5 (3)			
N(3)–Cr–Cl	93.5 (2)	N(2)–Cr–Cl	93.3 (2)			
N(4)–Cr–Cl	86.8 (2)	O(1)–Cr–Cl	178.6 (2)			
N(1)–Cr–Cl	88.2 (2)					

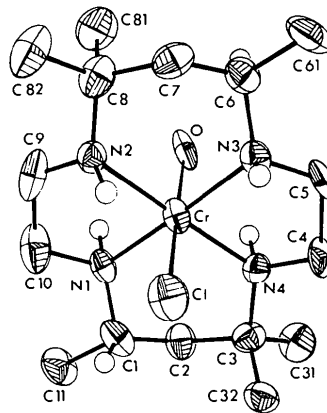


Fig. 1. A general view of the complex cation, *trans*-CrCl(teta)-(H₂O)²⁺.

* Lists of structure amplitudes, anisotropic thermal parameters, bond angles and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39583 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† See Jurnak & Raymond (1972) for the nomenclature used here.

lowest-energy equatorial orientation. The conformation of the macrocycle is entirely similar to that found for the *trans*-Cr(OCONH₂)₂(cyclam) cation (cyclam is 1,4,8,11-tetraazacyclotetradecane) (Bang & Mønsted, 1982).

All bond lengths and angles within the cation are normal for such compounds (Bang & Mønsted, 1982) with Cr–N(mean), Cr–Cl and Cr–O distances of 2.083, 2.307 and 2.090 Å, respectively.

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Structure of Bis(η^5 -trimethylsilylcyclopentadienyl)titanium(IV) Pentasulfide, [Ti(C₅H₁₃Si)₂]S₅

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Abstract. $M_r = 482.78$, monoclinic, $P2_1/c$, $a = 7.884$ (5), $b = 14.018$ (14), $c = 22.352$ (24) Å, $\beta = 96.28$ (7)°, $Z = 4$, $V = 2455.4$ (39) Å³, $D_x = 1.30$ g cm⁻³, $F(000) = 1008$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 8.44$ cm⁻¹, room temperature, $R = 0.10$ for 2382 reflexions. The six-membered heterocycle TiS₅ has a chair conformation. The Ti atom has an irregular tetrahedral environment comprising the bidentate pentasulfide fragment [Ti–S = 2.416 (5) and 2.450 (5) Å] and the two centroids (*R*'s) of the substituted cyclopentadienyl rings (Ti–*R* = 2.076 and 2.059 Å).

Introduction. The comparison of the structure of Ti(η^5 -C₅H₅)₂Cl₂ with that of Ti(η^5 -C₅H₄CH₃)₂Cl₂ demonstrates that the substitution of the H atom by a CH₃ group on each cyclopentadienyl ring has a negligible effect on the basic molecular configuration. Specifically, the corresponding bond distances and angles differ by less than 0.01 Å and 1.3°, respectively (Petersen & Dahl, 1975). Moreover, the two cyclopentadienyl rings are symmetrically disposed with respect to the TiS₂ fragment in Ti(η^5 -C₅H₅)₂(SC₆H₅)₂: The TiS₂ plane approximately bisects the *R*–Ti–*R* angle (Epstein, Bernal & Köpf, 1971; Muller, Petersen & Dahl, 1976). In contrast, no symmetrical positioning of the Ti(η^5 -C₅H₅)₂ fragment relative to TiS₂ (which is part of the TiS₅ ring) has been observed in Ti(η^5 -C₅H₅)₂S₅ (II). The normal to the TiS₅ plane forms angles of 32 and 17° with the Ti–*R* ring vectors.

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The purpose of the present work is to elucidate the disposition of the two substituted cyclopentadienyl rings relative to the six-membered TiS₅ ring system in the title compound (I).

Experimental. The title compound was prepared by the reaction of Ti[η^5 -C₅H₄Si(CH₃)₃]Cl₂ (Köpf & Klouras, 1982) with excess (NH₄)₂S₅ in methanol, using a method similar to that described by Köpf & Block (1969) and Köpf & Kahl (1974). After recrystallization from CHCl₃/CH₃OH (1:1), dark-red glistening crystals were obtained. The compound is air-stable, m.p. 382 K. Composition: found: C = 39.72, H = 5.31 wt% [$M_r = 482$ (mass spectrum)]; calculated: C = 38.80, H = 5.43 wt%. ¹H NMR peaks were found at τ (p.p.m.) 3.97 (*m*) and 4.17 (*m*) (C₅H₄, relative intensity 4), 9.77 (*s*) and 9.84 (*s*) [Si(CH₃)₃, relative intensity 9].

Syntex diffractometer, 2θ range 0–47°, graphite-monochromatized Mo *K* α radiation. 3807 reflections measured; after averaging, 2382 independent observed reflections [$I > 2.5\sigma(I)$] remained. Intensities not corrected for absorption or extinction. Structure solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), and refined by blocked full-matrix least squares using *SHELX* (Sheldrick, 1976); all atoms except H considered to be anisotropic. All H atoms placed in geometrically calculated positions. Refinement converged with unit weights to $R = 0.1034$.