

I thank Professor A. S. Jones and Drs A. Kumar and R. Walker for suggesting this problem and (AK) for crystalline materials and assistance with the X-ray measurements.

References

DENNEY, D. B. & VARGA, S. L. (1973). *Phosphorus*, **2**, 245–248.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JONES, A. S., KUMAR, A. & WALKER, R. T. (1986). *Tetrahedron Lett.* Submitted for publication.

MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO78*. Program for drawing crystal and molecular structures. Univ. of Cambridge, England.

SHELDRICK, G. M. (1978). *SHELX78*. Program for crystal structure determination. Univ. of Cambridge, England.

SHORT COMMUNICATION

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible.

Acta Cryst. (1986). **C42**, 1463–1464

Structure of the isothiocyanate salt of *trans*-aqua(isothiocyanato)(1,4,8,12-tetraazacyclopentadecane)-chromium(III): a centrosymmetric refinement. By WILLIAM CLEGG, *Department of Inorganic Chemistry, The University, Newcastle upon Tyne NE1 7RU, England*

(Received 2 May 1986; accepted 8 May 1986)

Abstract

Refinement of the structure, previously described in $Pna2_1$, $a = 13.797$ (2), $b = 11.138$ (2), $c = 13.700$ (3) Å [Clegg, Leupin, Richens, Sykes & Raper (1985). *Acta Cryst.* **C41**, 530–532], has been completed in $Pnam$, involving a twofold disorder of the macrocyclic ligand across the mirror plane: $R = 0.049$ for 1861 observed reflections. No restraints were required and all bond lengths and angles adopt reasonable values. The description of the molecular structure and ligand conformation and configuration remain unchanged from the $Pna2_1$ results.

The failure to recognize the true symmetry of a crystal structure is a problem highlighted in recent years by numerous reports of reassignments of space groups for previously reported structures. Schomaker & Marsh (1979) have demonstrated that the non-recognition of a centre of symmetry should lead to matrix singularity problems in least-squares refinement, but these may be masked by specific refinement procedures. A particularly awkward decision is that between an ordered non-centrosymmetric structure and a disordered centrosymmetric one. Marsh (1986) has recently shown that the disordered centrosymmetric description is preferable in many cases. This report has led us to re-examine the structure of the title compound, previously refined in the non-centrosymmetric $Pna2_1$, with the aid of restraints to overcome problems associated with the recognized near-centrosymmetry (Clegg, Leupin, Richens, Sykes & Raper, 1985). We have now achieved a satisfactory refinement in the centrosymmetric $Pnam$ ($Pnma$ reoriented to use the same axes as the $Pna2_1$ refinement) without restraints, but with a twofold disorder across the mirror plane.

Revised results: blocked-cascade refinement on F with no restraints on C and N atoms, $w^{-1} = \sigma^2(F) + 0.00086F^2$. Anisotropic thermal parameters for non-H atoms, H of H_2O freely refined, other H atoms constrained to give $C-H = N-H = 0.96$ Å, $H-C-H = 109.5^\circ$, $U(H) = 1.2 U_{eq}(C)$ or $1.2 U_{eq}(N)$. Disordered atoms assigned fixed occupancy factors of 0.5. Scattering factors from *International Tables for X-ray Crystallography* (1974). 158 parameters, 1861 reflections with $F > 2\sigma(F)$, $R = 0.049$, $wR = 0.055$, slope of normal probability plot 1.21; max. $\Delta/\sigma = 0.015$, mean = 0.002, $(\Delta\rho)_{max} = 0.62$, $(\Delta\rho)_{min} = -0.41$ e Å⁻³. Programs: *SHELXTL* (Sheldrick, 1985). Final coordinates are given in Table 1.*

The unproblematic refinement without geometrical restraints, and the improved agreement of observed and calculated data (lower R and wR despite fewer parameters) clearly indicate that the centrosymmetric disordered description is preferred to the non-centrosymmetric ordered result.

The Cr, H_2O , coordinated NCS^- and one C atom of the macrocyclic ligand lie on the mirror plane, the two other NCS^- anions are related to each other by it. Six of the macrocyclic ligand atoms are twofold disordered. The components of the disorder are shown in Fig. 1, and they correspond to two equivalent arrangements (a,b) of the macrocyclic ligand. Each component shows reasonable geometry of the ligand. A minor contribution of a third

* 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 43042 (13 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 ($\text{\AA}^2 \times 10^3$)

$U_{eq} = \frac{1}{3}$ (trace of the orthogonalized U_{ij} matrix).

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Cr	3411 (1)	1115 (1)	2500	24 (1)
O	2134 (2)	1947 (2)	2500	35 (1)
H(0)	1786 (26)	2156 (31)	3011 (25)	73 (12)
N(01)	4702 (2)	349 (3)	2500	35 (1)
C(01)	5485 (3)	-19 (3)	2500	33 (1)
S(01)	6576 (1)	-534 (1)	2500	61 (1)
N(02)	1061 (2)	2448 (3)	4100 (2)	52 (1)
C(02)	970 (2)	2319 (3)	4936 (2)	39 (1)
S(02)	840 (1)	2143 (1)	6105 (1)	69 (1)
C(1)	4231 (3)	4023 (4)	2500	54 (2)
C(2)	3763 (2)	3590 (2)	3428 (2)	45 (1)
N(3)	3903 (1)	2276 (2)	3579 (2)	32 (1)
C(4)	3559 (2)	1916 (3)	4566 (2)	45 (1)
C(5)	3615 (3)	579 (3)	4693 (3)	60 (1)
N(6)	3144 (5)	-14 (5)	3705 (4)	37 (2)
C(7)	2146 (5)	-425 (6)	3828 (5)	51 (2)
C(8)	1874 (9)	-1269 (7)	3013 (9)	56 (3)
C(9)	1868 (7)	-738 (8)	1982 (9)	51 (3)
N(10)	2824 (4)	-261 (5)	1663 (4)	36 (2)
C(11)	2782 (5)	-56 (6)	579 (4)	46 (2)

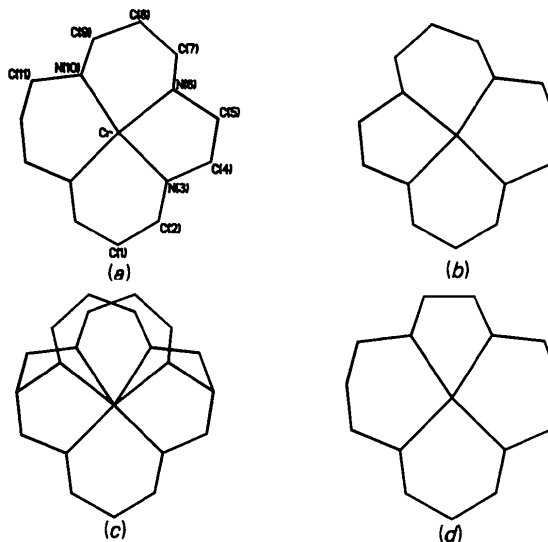


Fig. 1. (a), (b) The two equal-weight disorder components. Unlabelled atoms in (a) are mirror-related to labelled atoms. (c) The combined disordered ligand. (d) A possible third disorder component.

Table 2. Bond lengths (\AA) and angles ($^\circ$)

Cr—O	1.991 (3)	Cr—N(01)	1.975 (3)
Cr—N(3)	2.077 (2)	Cr—N(6)	2.107 (6)
Cr—N(10)	2.078 (6)	O—H(0)	0.880 (35)
N(01)—C(01)	1.155 (5)	C(01)—S(01)	1.611 (4)
N(02)—C(02)	1.161 (4)	C(02)—S(02)	1.623 (3)
C(1)—C(2)	1.505 (4)	C(2)—N(3)	1.491 (4)
N(3)—C(4)	1.489 (4)	C(4)—C(5)	1.501 (5)
C(5)—N(6)	1.641 (7)	N(6)—C(7)	1.462 (9)
C(7)—C(8)	1.506 (13)	C(8)—C(9)	1.531 (17)
C(9)—N(10)	1.488 (12)	N(10)—C(11)	1.504 (8)
C(11)—C(5')	1.401 (7)		
O—Cr—N(01)	177.9 (1)	O—Cr—N(3)	90.0 (1)
N(01)—Cr—N(3)	88.5 (1)	O—Cr—N(6)	97.1 (2)
N(01)—Cr—N(6)	84.2 (2)	N(3)—Cr—N(6)	82.6 (2)
O—Cr—N(10)	89.9 (2)	N(01)—Cr—N(10)	91.9 (2)
N(3)—Cr—N(10)	168.1 (2)	N(6)—Cr—N(10)	85.6 (2)
N(3)—Cr—N(3')	90.7 (1)	N(6)—Cr—N(3')	170.3 (2)
N(10)—Cr—N(3')	101.2 (2)	Cr—O—H(0)	127.3 (23)
H(0)—O—H(0')	105.3 (46)	Cr—N(01)—C(01)	175.2 (3)
N(01)—C(01)—S(01)	180.0 (3)	N(02)—C(02)—S(02)	179.8 (3)
C(2)—C(1)—C(2')	115.3 (4)	C(1)—C(2)—N(3)	112.1 (3)
Cr—N(3)—C(2)	118.1 (2)	Cr—N(3)—C(4)	112.1 (2)
C(2)—N(3)—C(4)	110.4 (2)	N(3)—C(4)—C(5)	110.8 (3)
C(4)—C(5)—N(6)	106.4 (3)	Cr—N(6)—C(5)	109.7 (3)
Cr—N(6)—C(7)	116.3 (4)	C(5)—N(6)—C(7)	113.8 (5)
N(6)—C(7)—C(8)	110.1 (7)	C(7)—C(8)—C(9)	116.4 (7)
C(8)—C(9)—N(10)	113.8 (9)	Cr—N(10)—C(9)	116.6 (5)
Cr—N(10)—C(11)	116.6 (4)	C(9)—N(10)—C(11)	108.0 (6)
N(10)—C(11)—C(5')	107.9 (5)		

The prime denotes an atom related by the mirror plane (symmetry operation $x, y, \frac{1}{2}-z$).

arrangement (d) is not necessary in explanation of the observed disordered structure, and would require occupancy factors different from 1 and 0.5, but cannot be ruled out.

The description of the molecular geometry, ligand conformation and configuration, and hydrogen bonding previously given (Clegg *et al.*, 1985) remains unaffected, but the geometrical parameters of the disordered structure are slightly different and are actually *more* precisely determined (Table 2).

I thank SERC for a research grant.

References

- CLEGG, W., LEUPIN, P., RICHENS, D. T., SYKES, A. G. & RAPER, E. S. (1985). *Acta Cryst.* **C41**, 530–532.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- MARSH, R. E. (1986). *Acta Cryst.* **B42**, 193–198.
- SCHOMAKER, V. & MARSH, R. E. (1979). *Acta Cryst.* **B35**, 1933–1934.
- SHELDRIK, G. M. (1985). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*. Revision 5. Univ. of Göttingen, Federal Republic of Germany.