

Structure of 5-Hydroxy-2-methoxy-1,3,2λ⁵-dioxaphosphacyclohexane 2-Oxide*

BY T. A. HAMOR

Department of Chemistry, University of Birmingham, Birmingham B15 2TT, England

(Received 11 April 1986; accepted 29 April 1986)

Abstract. C₄H₉O₅P, *M_r* = 168.1, orthorhombic, *Pna*2₁, *a* = 10.825 (5), *b* = 9.342 (4), *c* = 6.839 (4) Å, *V* = 691.6 (6) Å³, *Z* = 4, *D_x* = 1.61 g cm⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 3.00 cm⁻¹, *F*(000) = 352, *T* = 285 K, *R* = 0.035 for 642 observed reflections. The six-membered ring has a distorted chair conformation; the positions of the methoxy and hydroxy groups are established to be axial. Angles at P are within 7.5° of tetrahedral, bond lengths: P–O(ring) 1.564 (2) and 1.560 (2) Å, P–OMe 1.560 (2) Å, P=O 1.455 (3) Å.

Experimental. Crystal size 0.2 × 0.2 × 0.4 mm. Lattice parameters from 25 reflections, Enraf–Nonius CAD-4 diffractometer, data collected using ω–2θ scans, 2 < θ < 25°, index range: *h* 0–12, *k* 0–11, *l* 0–8; two standard reflections measured every 2 h, no significant variation over period of data collection; 661 unique reflections measured, 642 having |*F*| > 5σ(|*F*|) used for analysis; no absorption corrections applied; structure solved by Patterson and Fourier methods; all H atoms located in difference Fourier maps and included in calculations at fixed positions; heavier atoms refined with anisotropic temperature factors, H atoms isotropically; full-matrix least-squares refinement on *F* magnitudes, *R* = 0.035, *wR* = 0.047, *w* = 1/[σ²(*F*) + 0.001*F*²], max. Δ/σ in final cycle 0.017; residual electron density in final difference Fourier map within +0.25 and –0.37 e Å⁻³, atomic scattering factors from *International Tables for X-ray Crystallography* (1974); computations carried out with *SHELX78* (Sheldrick, 1978). The inverse structure gave essentially identical *R* and *wR*.

The molecular structure and atom-numbering scheme are shown in Fig. 1. Atomic coordinates are listed in Table 1,† and bond lengths and angles are in Table 2.

* Contribution from the Crystallography Unit, Universities of Aston and Birmingham.

† Lists of structure amplitudes, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 43015 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Related literature. The title compound was prepared by the method described by Denney & Varga (1973); it is an intermediate in the synthesis of metabolically labile and acid-labile dioxaphospha-heterocycles (Jones, Kumar & Walker, 1986).

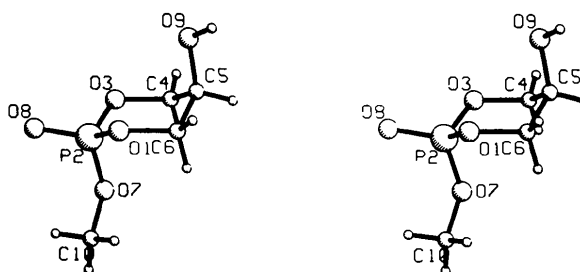


Fig. 1. Stereoscopic view of the molecule, drawn with *PLUTO78* (Motherwell & Clegg, 1978), showing the atom numbering.

Table 1. Fractional atomic coordinates with *e.s.d.*'s in parentheses and equivalent isotropic temperature factors (Å² × 10³)

	$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$			<i>U_{eq}</i>
	<i>x</i>	<i>y</i>	<i>z</i>	
O(1)	0.2368 (2)	0.7710 (2)	0.6802 (4)	38
P(2)	0.3070 (1)	0.7089 (1)	0.5000	33
O(3)	0.4314 (2)	0.6481 (2)	0.5813 (4)	38
C(4)	0.4264 (3)	0.5578 (3)	0.7557 (6)	43
C(5)	0.3570 (3)	0.6284 (3)	0.9187 (5)	39
C(6)	0.2298 (3)	0.6804 (4)	0.8550 (6)	43
O(7)	0.2384 (2)	0.5702 (2)	0.4337 (4)	45
O(8)	0.3239 (2)	0.8174 (3)	0.3498 (4)	48
O(9)	0.4308 (2)	0.7418 (2)	0.9920 (5)	49
C(10)	0.1118 (3)	0.5791 (4)	0.3632 (7)	55

Table 2. Bond lengths (Å) and angles (°)

O(1)–P(2)	1.560 (2)	O(3)–C(4)	1.462 (4)
O(1)–C(6)	1.467 (4)	C(4)–C(5)	1.497 (5)
P(2)–O(3)	1.564 (2)	C(5)–C(6)	1.524 (4)
P(2)–O(7)	1.560 (2)	C(5)–O(9)	1.418 (4)
P(2)–O(8)	1.455 (3)	O(7)–C(10)	1.456 (4)
C(6)–O(1)–P(2)	117.0 (2)	P(2)–O(3)–C(4)	117.9 (2)
O(1)–P(2)–O(3)	105.9 (1)	O(3)–C(4)–C(5)	111.8 (2)
O(1)–P(2)–O(7)	107.8 (1)	C(4)–C(5)–C(6)	112.4 (3)
O(1)–P(2)–O(8)	111.1 (1)	C(4)–C(5)–O(9)	108.1 (3)
O(3)–P(2)–O(7)	102.2 (1)	C(6)–C(5)–O(9)	111.8 (2)
O(3)–P(2)–O(8)	113.3 (1)	C(5)–C(6)–O(1)	111.7 (2)
O(7)–P(2)–O(8)	115.7 (2)	P(2)–O(7)–C(10)	119.8 (2)

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.

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SHORT COMMUNICATION

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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 H₂O freely refined, other H atoms constrained to give C–H = N–H = 0.96 Å, H–C–H = 109.5°, $U(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ or $1.2 U_{\text{eq}}(\text{N})$. 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, $(\Delta\rho)_{\text{max}} = 0.62$, $(\Delta\rho)_{\text{min}} = -0.41 \text{ e } \text{Å}^{-3}$. 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, H₂O, 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.