Rh₂I₆Cl(CO)₂(CH₃OH)⁻.Ph₃PNPPh₃⁺. Structure Determination of a Very Small Crystal with Synchrotron Radiation

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Abstract

The crystal and molecular structure of the title compound has been established from synchrotron radiation diffraction data recorded with an area detector for a crystal of dimensions $100 \times 50 \times 15 \,\mu m$. Bis-(triphenylphosphoranediyl)ammonium 1,2-dicarbonyl-1-chloro-di-μ-iodo-1,1,2,2-tetraiodo-2-(methanol)dirhodate(1−), [N($C_{18}H_{15}P$)₂][Rh₂ClI₆(CH₄O)-(CO)₂], $M_r = 1629 \cdot 3$, monoclinic, $P2/a$, = $17 \cdot 528$ (10), $b = 13 \cdot 337$ (6), $c = 21 \cdot 410$ (5) Å, $\beta = 100 \cdot 23$ (3)°, $V = 4925 \cdot 5$ Å³, $Z = 4$, $D_x = 2 \cdot 197 \, g \, cm^{-3}$, $\lambda = 0 \cdot 915$ (5) Å, $\mu = 88 \cdot 9 \, cm^{-1}$, $F(000) = 3016$, $T = 295$ K, final $R = 0 \cdot 104$ for 1700 reflections. In the anion two square-planar RhI₄ groups share two I atoms and are tilted at 23° to each other; octahedral coordination around one Rh atom is completed by a Cl atom and a CO group, and about the other by a CH₃OH molecule and a CO group (*cis* to the first).

Introduction

Small crystals of the title compound formed in the reaction mixture (Jacob & Heaton, 1988). They were not large enough for routine diffractometer data collection with a conventional X-ray source, and decomposed when recrystallization was attempted. Crystal structure determination was therefore attempted using the synchrotron radiation source (SRS) at SERC Daresbury Laboratory and the Enraf–Nonius FAST area-detector diffractometer (Andrews *et al.*, 1988).

Structure determination with the FAST diffractometer

A crystal of dimensions $100 \times 50 \times 15 \,\mu m$ was mounted on a single strand of glass wool (~10 μm thick) attached to a stronger glass fibre. Data collection was performed with the on-line version of the *MADNES* software (Messerschmidt & Pflugrath,

1987) implemented on a MicroVAX II, controlling the FAST diffractometer on workstation 9.6 of the SRS. The SRS was operated in single bunch mode, at 2 GeV, 18 mA, wiggler at 5 T. The crystal was rotated about the spindle axis, φ, roughly parallel to the longest dimension of the crystal, and the accumulated intensity on the area detector was recorded for each 'frame', $0 \cdot 5°$ of rotation, in 15 s. The diffraction pattern was thus recorded to a resolution of 1 Å (*i.e.* max. $\sin\theta/\lambda = 0 \cdot 5 \, Å^{-1}$) for $\varphi = 0$–182°, with crystal–detector distance $40 \cdot 4$ mm, and the detector tilted with its normal at $\tau = 28°$ from the beam direction. The beam intensity was monitored at $0 \cdot 5$ s intervals by an ion chamber fitted between the crystal and the end of the collimator, and the readings used for primary scaling of the diffraction pattern. The recorded pattern was processed with the off-line version of the *MADNES* software. The centres of 190 reflections were found, as X, Y and φ, and used in the autoindexing routine to obtain an initial orientation matrix and unit cell, which were refined along with other geometrical parameters. The refined cell and orientation matrix were used to locate and integrate reflection intensities. The 250 most-intense reflections were used for further refinement of unit-cell, orientation-matrix and geometrical parameters. After two cycles, the refinement converged. The standard deviations given for cell parameters were derived from this refinement; in addition, although the wavelength is assumed to have been constant throughout the experiment, there is an uncertainty of *ca* $0 \cdot 5\%$ in its value, which affects all the cell edges.

MADNES then used the refined unit cell and orientation to predict all 7766 reflections in the range of recorded data and integrate their intensities (over X, Y and φ). Reflections to which *MADNES* assigned an error flag ≥ 2, indicating unreasonably high background, edge of detector position, or other errors, were discarded. Diffraction symmetry $2/m$ was evident in the remaining 2821 intensities. These intensity data were separated into six batches in φ,

and were scaled and merged with the programs *ROTAVATA* and *AGROVATA* (Smith & Wonacott, 1979). Merging yielded 1735 unique observed reflection intensities, with merging $R = 0.09$, and a further 506 reflections too weak to measure (*MADNES* assigned error flag 1). All these reflections have $|h| \leq 12$, $|k| \leq 12$, $|l| \leq 21$. Systematic absences indicated the space group unambiguously.

The Rh- and I-atom positions could be found by Patterson methods. Heavy-atom refinement and difference syntheses then revealed all the remaining non-H atoms. Least-squares refinement on $|F(hkl)|$ used two blocks (101 parameters for the anion in one, 85 for the cation in the other) and unit weights, allowed anisotropic vibration parameters for Rh and I only, constrained all phenyl groups as regular hexagons, and did not include H atoms; it converged to $R = 0.104$, for 1700 reflections with $F > 6\sigma(F)$. The largest shift/e.s.d. in the final round of least squares was 0.1; the maximum and minimum heights in the final difference synthesis were $+2$ and -1 e Å^{-3}; all the highest peaks were near Rh- or I-atom positions. f' and f'' for Rh and I were -0.770, 1.450 and -0.3975, 2.826 e (Cromer & Liberman, 1970). The program *SHELX* (Sheldrick, 1976) was used throughout. The atom parameters are given in Table 1.*

The structure

This X-ray analysis established the chemical constitution of the crystals, previously quite uncertain. The C and O atoms of the methanol molecule were the least well defined in the electron density syntheses, even at the final stage when all other atoms had been refined; a carbonyl group would have been a possible though less good interpretation on crystallographic evidence alone; the interpretation as methanol uses the knowledge that methanol was present in the reaction mixture.

The Rh-containing anion is illustrated in Fig. 1. Bond lengths and angles in it and in the PNP cation do not differ significantly from expected values. The Rh_2I_6 skeleton is slightly folded; the angle between the two RhI_4 planes is 23°. The coordination around each Rh atom does not differ significantly from octahedral, thus the Cl atom approaches the methanol O atom at a distance of 2.92 (7) Å, suggestive of a weak hydrogen bond. If the Rh_2I_6 skeleton were planar this Cl···O contact would be *ca* 3.98 Å. The similar, but chemically symmetrical ion, [Rh₂I₆-

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* Lists of structure factors and thermal vibrational parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52420 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and thermal parameters with e.s.d.'s in parentheses*

	x	y	z	U_{eq}/U_{iso}*(Å²)
Rh(1)	0·2896 (4)	0·2914 (4)	0·1021 (3)	0·067 (4)
I(2)	0·2132 (3)	0·2922 (4)	0·2023 (2)	0·070 (4)
I(3)	0·4196 (3)	0·2998 (4)	0·1908 (2)	0·075 (4)
Rh(2)	0·3441 (4)	0·2397 (4)	0·2845 (3)	0·058 (4)
I(5)	0·2610 (4)	0·1958 (5)	0·3743 (3)	0·098 (5)
I(6)	0·1591 (4)	0·2814 (5)	0·0191 (3)	0·108 (5)
I(7)	0·3737 (4)	0·2915 (6)	0·0104 (3)	0·121 (6)
I(8)	0·4757 (4)	0·1866 (4)	0·3585 (3)	0·093 (5)
Cl(1)	0·3286 (13)	0·0692 (15)	0·2442 (10)	0·085 (7)
C(1)	0·2846 (42)	0·4183 (44)	0·0931 (31)	0·06 (2)
O(1)	0·2797 (32)	0·5028 (38)	0·0892 (24)	0·08 (2)
C(2)	0·3573 (48)	0·3651 (50)	0·3204 (35)	0·08 (3)
O(2)	0·3704 (30)	0·4407 (39)	0·3398 (23)	0·08 (2)
O(3)	0·2961 (37)	0·1330 (46)	0·1115 (30)	0·11 (2)
C(3)	0·2811 (72)	0·0668 (93)	0·0631 (59)	0·17 (5)
P(1)	0·0185 (11)	0·2432 (12)	0·7813 (8)	0·043 (5)
P(2)	−0·0184 (11)	0·2615 (12)	0·6371 (8)	0·044 (5)
N(1)	0·0216 (29)	0·2535 (34)	0·7104 (21)	0·041 (13)
C(12)	−0·0070 (30)	0·4397 (40)	0·7956 (16)	0·06 (2)
C(13)	−0·0226 (30)	0·5287 (40)	0·8252 (16)	0·09 (3)
C(14)	−0·0358 (30)	0·5272 (40)	0·8875 (16)	0·09 (3)
C(15)	−0·0334 (30)	0·4366 (40)	0·9203 (16)	0·08 (2)
C(16)	−0·0178 (30)	0·3475 (40)	0·8908 (16)	0·05 (2)
C(11)	−0·0046 (30)	0·3491 (40)	0·8285 (16)	0·10 (3)
C(22)	0·0227 (22)	0·0968 (34)	0·8762 (21)	0·05 (2)
C(23)	−0·0053 (22)	0·0134 (34)	0·9043 (21)	0·10 (3)
C(24)	−0·0743 (22)	−0·0321 (34)	0·8755 (21)	0·09 (3)
C(25)	−0·1152 (22)	0·0058 (34)	0·8185 (21)	0·08 (2)
C(26)	−0·0872 (22)	0·0892 (34)	0·7904 (21)	0·07 (2)
C(21)	−0·0182 (22)	0·1347 (34)	0·8192 (21)	0·06 (2)
C(32)	0·1431 (32)	0·1431 (30)	0·7679 (20)	0·08 (3)
C(33)	0·2222 (32)	0·1239 (30)	0·7728 (20)	0·11 (3)
C(34)	0·2764 (32)	0·1913 (30)	0·8046 (20)	0·13 (3)
C(35)	0·2516 (32)	0·2780 (30)	0·8315 (20)	0·11 (3)
C(36)	0·1725 (32)	0·2972 (30)	0·8267 (20)	0·06 (2)
C(31)	0·1183 (32)	0·2297 (30)	0·7949 (20)	0·04 (2)
C(42)	−0·0445 (27)	0·0598 (34)	0·6334 (15)	0·06 (2)
C(43)	−0·0745 (27)	−0·0304 (34)	0·6067 (15)	0·08 (2)
C(44)	−0·1114 (27)	−0·0335 (34)	0·5433 (15)	0·08 (2)
C(45)	−0·1182 (27)	0·0536 (34)	0·5067 (15)	0·10 (3)
C(46)	−0·0881 (27)	0·1439 (34)	0·5335 (15)	0·06 (2)
C(41)	−0·0513 (27)	0·1470 (34)	0·5968 (15)	0·04 (2)
C(52)	0·1180 (27)	0·2068 (25)	0·5929 (19)	0·07 (2)
C(53)	0·1945 (27)	0·2245 (25)	0·5861 (19)	0·07 (2)
C(54)	0·2320 (27)	0·3120 (25)	0·6106 (19)	0·05 (2)
C(55)	0·1930 (27)	0·3817 (25)	0·6419 (19)	0·05 (2)
C(56)	0·1164 (27)	0·3640 (25)	0·6487 (19)	0·04 (2)
C(51)	0·0789 (27)	0·2765 (25)	0·6242 (19)	0·05 (2)
C(62)	−0·0647 (24)	0·4015 (33)	0·5453 (19)	0·04 (2)
C(63)	−0·1059 (24)	0·4835 (33)	0·5162 (19)	0·11 (3)
C(64)	−0·1561 (24)	0·5364 (33)	0·5479 (19)	0·07 (2)
C(65)	−0·1651 (24)	0·5074 (33)	0·6087 (19)	0·09 (3)
C(66)	−0·1239 (24)	0·4254 (33)	0·6379 (19)	0·04 (2)
C(61)	−0·0737 (24)	0·3725 (33)	0·6062 (19)	0·06 (2)

*For Rh and I atoms, $U_{eq} = (U_{11} + U_{22} + U_{33})/3$; for other atoms the refined isotropic displacement parameter is given.
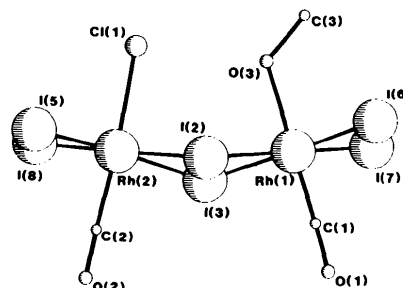

Fig. 1. The $Rh_2I_6Cl(CO)_2(CH_3OH)^-$ anion. The Rh—I(terminal) bond lengths are 2·64 to 2·68 (2) Å, and the Rh—I(bridging) bond lengths are 2·70 to 2·72 (2) Å; the angles I(2)—Rh(1)—I(3) and I(2)—Rh(2)—I(3) are 85·3 (2) and 85·0 (2)°; all other angles around the Rh atoms are within 3° of 90 or 180°.

$(MeCO)_2]^{2-}$, shows no fold (Adamson, Daly & Forster, 1974).

Problems with small crystals

The difficulties encountered in recording X-ray diffraction data for structure determination from very small crystals arise from the poor crystal quality as well as from the low intensity of the diffraction pattern. The poor crystal quality is indicated by the large mosaic spread, evaluated as *ca* 3° by *MADNES*. The diffraction spots become very extended in reciprocal space, and the derivation of good integrated intensities, especially for the weaker spots is difficult, as already described by Andrews *et al.* (1988). Improvements in the experimental strategy and processing software may allow somewhat better intensity measurements and structure determination in the future, but it is clear that even with the present procedures sufficient data can be recorded from such a small poor crystal to establish the chemical structure and stereochemistry.

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Hydration in Protein Crystals.
A Neutron Diffraction Analysis of Carbonmonoxymyoglobin*

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Abstract

In protein crystallography, it has been customary to ignore the contribution of bulk solvent by omitting the low-order diffraction data in refinement procedures. However, these data contain important information on both the structure of the solvent and the gross features of the unit-cell contents. The contribution of the solvent to the low-order structure-factor terms can be evaluated by dividing the solvent volume into shells extending outward from the surface of the protein. Two hydration layers in myo-globin crystals were characterized, allowing a better evaluation of the surface structure of the protein, improved placement of bound water and ion molecules, and a better overall fit to the observed data. A reciprocal-space least-squares refinement program was modified to include restraints on the configuration of water binding in water-to-protein and water-to-water associations. The inclusion of the solvent contribution allows all structure factors to be used in the refinement procedure. Eighty-seven water and five ion molecules were localized in carbonmonoxy-myoglobin. All water molecules that are bound to protein bind to polar or charged groups, and the final R factor is 11·5%.