

Synthesis and Structure of the Helicate

(M)-(-)-[Pt₂{(R,R)-tetrachos}₂](CF₃SO₃)₄ · 4.5 H₂O

Heather J. Kitto, A. David Rae, Anthony C. Willis, Johann Zank, and S. Bruce Wild

Research School of Chemistry, Institute of Advanced Studies, Australian National University, Canberra, ACT 0200, Australia

Reprint requests to Prof. S. B. Wild. E-mail: sbw@rsc.anu.edu.au

Z. Naturforsch. **59b**, 1458 – 1461 (2004); received August 24, 2004

Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

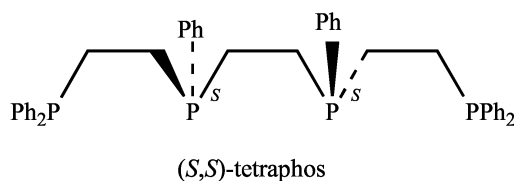
The complex (M)-(-)-[Pt₂{(R,R)-tetrachos}₂](CF₃SO₃)₄ · 4.5 H₂O, where tetrachos = 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetrachosphadecane, has been isolated and structurally characterized. The compound crystallizes in the space group C2 with two crystallographically different, but very similar, cations in the structure, each of which contains a 2-fold axis coincident with the crystallographic 2-fold axis. Each independent cation of the salt consists of a double-stranded, diplatinum(II) helicate that completes a *ca.* one-eighth turn of a double α -helix in the *M* direction, as evidenced by the angle between the two, non-orthogonal PtP₄ square planes in each of the independent molecules. A feature of the structures is the 10-membered ring containing the two platinum atoms and the four chiral phosphorus stereocentres of *R* configuration; this ring has a distorted twist-boat-chair-boat conformation of λ helicity, which is responsible for the *M* twist of the helicate.

Key words: Platinum Complex, Tetrachosphine, Helicate

Introduction

The self-assembly under equilibrium conditions of complex, hierarchical molecular architectures, supramolecular synthesis, is a burgeoning field of modern chemistry [1]. For inorganic systems, the aggregation is facilitated by *dynamic dative bonding* between the donor atoms of the ligands and labile metal ions, which furnishes the thermodynamically most stable complexes [2]. Depending on the binding modes and geometric constraints of the ligands, in particular rigidity, and the preferred coordination geometries of the metal ions, frequently tetrahedral, four-coordinate, a great variety of interesting structural motifs can be assembled, including helicates, metallocatenes, rotaxanes, and molecular grids and knots [1]. Molecular polygons and polyhedra have also been constructed from angular metal components having structures based on the square plane, such as *cis* [Pt(PEt₃)₂]²⁺, and linear and angular bridging groups that form the edges of the two- and three-dimensional structures [3].

The self-assembly of double-stranded di- and trinuclear metal helicates of the type [M₂(tetrachos)₂]X₂ (M = Ag, Au) and [M₃(hexachos)₂]X₃ (M = Cu) has



been accomplished with use of the appropriate polytertiary phosphines in configurationally and enantiomerically pure form, although the corresponding racemates and mixtures of diastereomers of the ligands also give diastereomerically pure helicates by molecular recognition of each ligand strand for itself in the kinetically labile complexes [4, 5]. For the fully flexible tetrachosphine, (S,S)-tetrachos, of known absolute configuration [4], the disilver(I) helicate (M)-(-)-[Ag₂{(R,R)-tetrachos}₂](PF₆)₂ crystallizes with one molecule each of the double α -helix and the parallel helix conformer of the helicate in the unit cell; the corresponding digold(I) helicate contains only the more compact parallel helicate conformer of the complex in its crystal structure [4a]. The *S,S* form of the tetrachosphine generates in each helicate two chiral, tetrahedral metal stereocentres of *M* configuration, which occupy the apical positions of the central, 10-membered

ring [4]. In all of the complexes of this type hitherto characterized by X-ray crystallography, the central 10-membered rings containing adjacent metal centres have the chiral, twist-boat-chair-boat (TBCB) conformation, and it is the relationship between the helicity of this ring (δ or λ) and the configurations of the chiral phosphorus stereocentre therein (R or S) that determines the overall conformation (double α -helix or parallel helix) and helicity (P or M) of the resulting helicate (Fig. 1). The cation of (P)-(-)-[Cu₃{(S,R,R,S)-hexaphos}₂](PF₆)₃ · 4C₆H₆ has the parallel helicate structure in the solid state in which there is a strong cooperative alignment of the three tetrahedral copper stereocentres of P configuration with the two annulated 10-membered TBCB rings of λ conformation [5].

Here we report the synthesis and structural characterization of the complex (M)-(-)-[Pt₂{(R,R)-tetraphos}₂](CF₃SO₃)₄ · 4.5 H₂O, which is the first double-stranded, dinuclear metal helicate to be structurally characterized in which the metal ions are four-coordinate, square planar. The complex [Pt₂(tetraphos)₂] has been isolated previously and its dimeric nature confirmed by vapour pressure osmometry in benzene, but the diastereomer of the phosphine employed to prepare the complex was not specified [8].

Results and Discussion

The complex (M)-(-)-[Pt₂{(R,R)-tetraphos}₂](CF₃SO₃)₄ was prepared by adding trimethylsilyl triflate (TMSOTf) (4 equiv.) to a dichloromethane solution of [PdCl₂COD] (where COD = cycloocta-1,5-diene) (2 equiv.) and (S,S)-tetraphos (2 equiv.) (eq. (1)) [6]. The solvent and trimethylsilyl chloride by-product were removed from the reaction mixture *in vacuo* and the residue was dissolved in dry acetonitrile; dilution of the solution with diethyl ether afforded the crude product as a colourless powder having m.p. 309–312 °C, $[\alpha]_D^{18} -160$ ($c = 1$, acetone). Yield: 91%. Recrystallization of a small quantity of this material from acetonitrile (undried)–diethyl ether furnished crystals of the 4.5 hydrate suitable for X-ray crystallography. The ³¹P{¹H} NMR spectrum of the complex contains broad singlets of equal intensity for the inner ($\delta = 48.1$, $^1J_{\text{PtP}} = 2359.2$ Hz) and outer ($\delta = 42.8$, $^1J_{\text{PtP}} = 2231.1$ Hz) pairs of phosphorus nuclei.

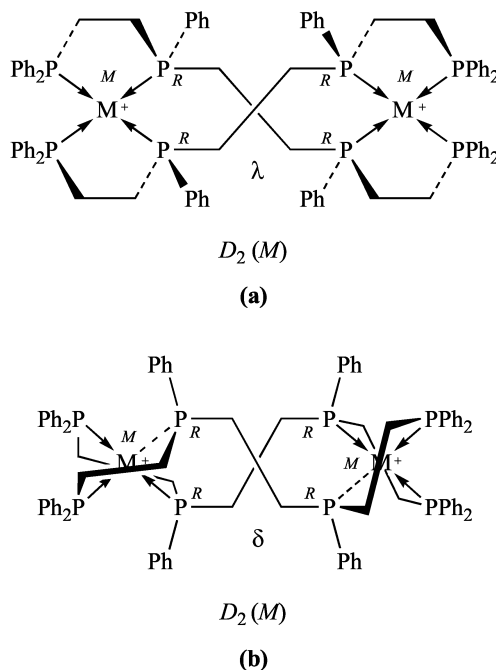
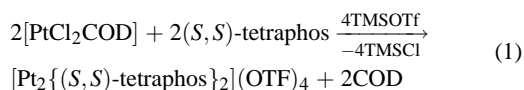


Fig. 1. Schematic side-elevations of double-stranded D_2 -double α -helix (a) and D_2 -parallel helix (b) conformers of the helicates [M]-[M₂{(R,R)-tetraphos}₂]²⁺ (M = Ag, Au).

Crystal Structure Determination

The complex (M)-(-)-[Pt₂{(R,R)-tetraphos}₂](CF₃SO₃)₄ · 4.5 H₂O crystallizes in the space group C2 with 4 formula units in the unit cell. There are two crystallographically different cations in the structure, each containing a 2-fold axis imposed by the crystallographic 2-fold axis parallel to **b**. The structure of the Pt1/Pt1* cation of the complex is depicted in Fig. 2. A view of the Pt1/Pt1* cation down the C₂ axis is shown in Fig. 3. A feature of the structure is the 10-membered ring containing the two platinum atoms and the four chiral, phosphorus stereocentres of R configuration, which has a distorted TBCB conformation. The key torsional angles and their signs are similar for both cations in the structure. The coordination geometry around each platinum is planar within close limits. The dihedral angle between the PtP₄ planes of the Pt1/Pt1* is 49.2° and for the Pt2/Pt2* it is 52.7°. Viewed along the Pt...Pt vector, the PtP₄ planes are rotated to each other as shown in Fig. 4, which corresponds to an M helix. The central 10-membered ring in each cation cannot adopt the more regular TBCB conformation found in the structures of related complexes of tetrahedral metal ions because of the copla-

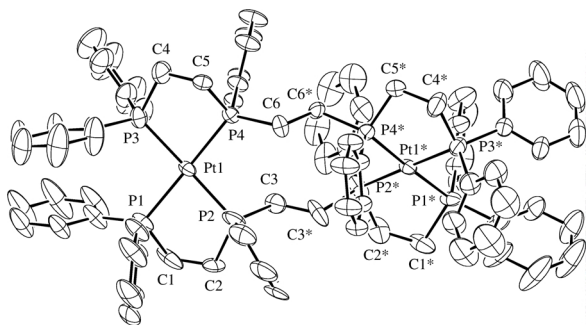


Fig. 2. ORTEP view of cation Pt1/Pt1* of (M)-(–)-[Pt₂{(*R,R*)-tetraphos}₂](CF₃SO₃)₄ · 4.5H₂O with 30% probability ellipsoids. Asterisks denote atoms generated by crystallographic two-fold symmetry. Selected bond lengths [Å] and angles [°]: Pt1–P1 2.323(3), Pt1–P2 2.327(3), Pt1–P3 2.324(3), Pt1–P4 2.328(3), P1–Pt1–P2 81.5(2), P(1)–Pt1–P3 97.5(2), P2–Pt1–P4 99.3(2), P3–Pt1–P4 81.7(2).

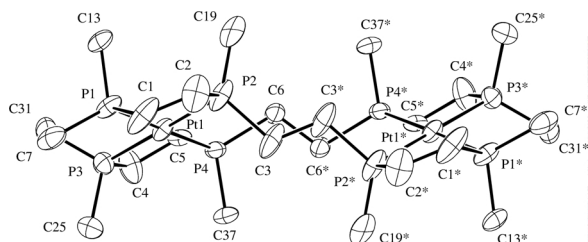


Fig. 3. Side elevation of core structure of Pt1/Pt1* cation showing λ twist of central TBCB 10-membered ring (30% probability level).

narity of the three heteroatoms at each end of the ring, viz. P2, Pt1, P4 (and symmetry related P2*, Pt1*, P4*), and P6, Pt2, P8 (and P6*, Pt2, P8*) and the relatively small angles between them, viz. 99.3(2)° in the Pt1/Pt1* cation and 97.3(2)° in the Pt2/Pt2* cation. These constraints are responsible for the *ca.* 45° twist between the two PtP₄ planes in the cations, which corresponds to a *ca.* one-eighth turn of a double α-helix. When the coordination geometry around the metal ions is tetrahedral, the two MP₂ groups at each end of the 10-membered ring (and the exocyclic MP₂ groups) are approximately coplanar [2, 4, 5]. Further perturbations to the structures concern the helicities of the four chiral, 5-membered chelate rings in the structures, and the angular distortions about the four inner-*P* stereocentres around the platinum atoms in each cation. The two carbon atoms of each 5-membered chelate ring in the cations are either above or below the PtP₄ planes, as shown in Fig. 5. For the Pt1/Pt1* molecule: C1 and C2 are below the Pt1P₄ plane by –1.01 and –0.62 Å, respectively; C4 and C5 are above the Pt1P₄ plane by

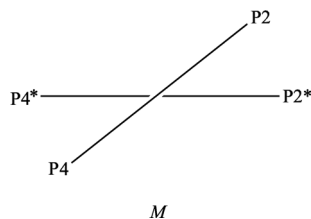


Fig. 4. Non-orthogonal skew lines representing Pt₄ planes of helicate cation.

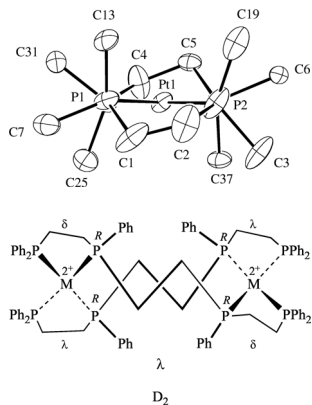


Fig. 5. Side elevation of Pt₄ plane of Pt1/Pt1* cation of helicate cation showing chiral conformations of terminal chelate rings (30% probability ellipsoids).

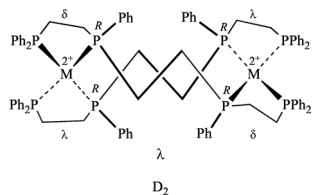


Fig. 6. Schematic side elevation of Pt1/Pt1* cation of Pt1/Pt1* helicate showing configurational and conformational elements.

0.53 and 1.09 Å, respectively. Thus, the torsion angles P1–C1–C2–P2 and P3–C4–C5–P4 (and P5–C43–C44–P6 and P7–C46–C47–P8) are similar, but their signs are opposed. This situation, one ring λ, the other δ at each platinum, together with the regular angular distortions of the geometries about each inner-*P* stereocentre, reduces the overall, idealized symmetries of the helicate ions from *D*₂ to *C*₂. A schematic side-elevation of the Pt1/Pt1* cation of the helicate showing the configurational and conformational elements of the structure is shown in Fig. 6. The Pt1...Pt1* distance is 7.240(2) Å and the Pt2...Pt2* distance is 7.327(2) Å.

Experimental Section

The ³¹P{¹H} NMR spectrum was recorded on a Varian VXR 500 spectrometer; chemical shifts are quoted with reference to 85% H₃PO₄. The electrospray mass spectrum was recorded in acetonitrile on a VG Quattro II mass spectrometer with a cone potential of 25 V. The optical rotation was measured on the specified solution with a Perkin–Elmer Model 241 spectropolarimeter; the specific rotation was estimated to be within ±0.05 deg. cm² g^{–1}. [PdCl₂(COD)] was prepared by the literature method [11].

(M)-(–)-Bis[(*4R,7R*)-1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane]diplatinum(II)trifluoromethylsulfonate

A solution of (*S,S*)-tetraphos (0.5 g, 0.745 mmol) in dichloromethane (75 ml) was treated with a solution of

[PtCl₂COD] (0.28 g, 0.745 mmol) in the same solvent (25 ml) followed by trimethylsilyl triflate (0.33 g, 1.5 mmol). After several minutes, the reaction mixture was evaporated to dryness. The colourless residue was purified by recrystallization from dry acetonitrile (20 ml) by the addition of diethyl ether (30 ml). The pure *anhydrous* product separated from the solution as a colourless, microcrystalline solid (0.79 g, 91%). M.p. 309–312 °C. – $[\alpha]_D^{18}$ (*c* = 1, Me₂CO): +160 (589 nm). – ³¹P {¹H} NMR: (500.14 MHz, Me₂CO-*d*₆): δ = 48.1 (¹J_{PtP} = 2359.2 Hz, 4 P, outer-P), 42.8 (¹J_{PtP} = 2231.1 Hz, 4 P, inner-P). – MS (ES): *m/z* = 1165.2 [M + 2H]²⁺. – C₈₈H₈₄F₁₂O₁₂P₈Pt₂S₄ (2327.81): calcd. C 45.41, H 3.64; found C 45.02, H 3.68. A small quantity of this material was recrystallized from acetonitrile (undried) by the addition of diethyl ether, whereupon the 4.5-hydrate crystallized (as determined by X-ray crystallography).

Crystal structure determination

Crystal data were collected and integrated using a Nonius Kappa CCD area detector diffractometer with monochromated Mo-K α (λ = 0.7107 Å) at 200 K. Data were corrected for absorption (transmission factors 0.495–0.686). The structure contains two, half cations in the asymmetric unit. There are two crystallographically different cations in the structure, each with 2-fold rotational symmetry imposed by crystallographic operations, *viz.* 1 – *x*, *y*, 1 – *z*, and 2 – *x*, *y*, 2 – *z*. The cations are related by a pseudo *F*-centring. The structure contains an extended solvation region: five water sites were detected, O13–O17; O17 was disordered about a 2-fold axis and O16 had such a large thermal motion that its position was found from a map and fixed. The large displacement parameters on some phenyl ring and anion atoms, together with the dominance of the platinum atom in the

diffraction pattern, made constrained refinement an attractive option. The programme RAELS00 was used to refine 339 independent variables [9]. This program allows extensive use of constraints and restraints. The phenyl rings were constrained to have the same local C_{2v} symmetry centred on the phosphorus atom to which they are attached as local origin. The anions were constrained to have identical bond lengths and angles while retaining local 3-fold rotational symmetry, one end being allowed to rotate relative to the other using a multiple local axis system [10]. The platinum and methylene carbon atoms were refined as isolated atoms but restraints were imposed to make differences in chemically equivalent bond lengths approach zero. Single atom anisotropic thermal parameterization was used for the platinum and water oxygen atoms only; O16 was refined isotropically. The thermal motion of the anions were refined using *TLX* rigid body parameterizations, the centres of libration initially lying on the sulfur atoms [9, 11]. Thermal parameters for the phosphorus atoms and attached phenyl and methylene groups were refined using *TL* rigid body parameterizations, the centres for libration being the platinum atoms to which the phosphorus atoms were attached. More details of the constrained refinement may be found in the CIF.

Crystal data for C₈₈H₈₄F₁₂O₁₂P₈Pt₂S₄ · 4.5 H₂O: *M* = 2408.88, colourless plate, *a* = 25.6537(5), *b* = 10.8058(3), *c* = 36.7503(8) Å, β = 105.659(1)°, space group *C*2, *Z* = 4, *V* = 9809.4(4) Å³, μ (Mo-K α) = 31.38 cm^{–1}, 31756 measured and 8082 unique reflections [*R*_{int} = 0.078], *R* = 0.085, *wR* = 0.135 for 7800 reflections [*I* > 3 σ (*I*)] and 339 parameters.

Displacement parameters and complete tables of interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. The data are available on request on quoting CCDC–24830.

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