

Crystal Structure of *trans*-[ReCl₂(dppp)₂]Cl · ½H₂O (dppp = 1,3-bis(diphenylphosphino)propane)

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Rhenium(III), 1,3-bis(diphenylphosphino)propane Complex, Crystal structure

The crystal structure of *trans*-[ReCl₂(dppp)₂]Cl · ½H₂O (dppp = 1,3-bis(diphenylphosphino)propane), a potentially useful radiopharmaceutical agent, was determined by single crystal X-ray diffractometry. It belongs to the tetragonal space group *P*4̄ with *Z* = 2. The Re(III) ion is in a quasi-octahedral environment coordinated to a pair of symmetry related dppp molecules, acting as bidentate ligands, and two axial chloride ions.

Due to the extensive use of the γ -emitter ^{99m}Tc in diagnostic nuclear medicine [1, 2] and the potential usefulness of ¹⁸⁶Re and ¹⁸⁸Re for radiotherapeutic purposes [3, 4], the chemistry of technetium and rhenium has become a very active field of research.

Phosphines occupy a significant role in the development of radiopharmaceuticals [5]. Rhenium and technetium complexes, in low oxidation states, with bidentate phosphine ligands have been extensively studied while searching for suitable ^{99m}Tc complexes for hearth studies [1, 6, 7].

Ligand substitution in suitable precursors is an important route to new rhenium complexes [8,9]. Recently, it has been shown that [Re^{III}L₆]³⁺ complexes, with L = thiourea, N-methylthiourea, N-ethylthiourea, and N,N'-dimethylthiourea are suitable starting materials for the synthesis of

Re(III) complexes with diphenylphosphines as chelating ligands [9]. Following this route, crystals of *trans*-[ReCl₂(dppp)₂]Cl · ½H₂O were obtained and the structure solved by X-ray diffractometry.

The complex was synthesised as previously described [9] and crystals adequate for crystallographic studies were obtained by slow evaporation at room temperature from dichloromethane/methanol/HCl (2 N) solutions.

Crystal data for the complex. – C₅₄H₅₂O_{0.5}Cl₃P₄Re, *M* = 1125.39, *F*(000) = 1132, yellow plates, tetragonal system, *a* = 14.333(3), *c* = 12.688(3) Å, *V* = 2606.8(10) Å³, space group *P*4̄, *Z* = 2, *D*_c = 1.434 g cm⁻³, μ (Mo-K α) = 2.643 mm⁻¹.

The intensities were collected on an Enraf-Nonius CAD-4 diffractometer, with graphite monochromated Mo-K α radiation (λ = 0.71073 Å) and ω -2 θ scan technique [*T* = 292(2) K; -18 ≤ *h* ≤ 10, 0 ≤ *k* ≤ 18, 0 ≤ *l* ≤ 16; θ -range for data collection = 1.41 to 27.95 °].

The structure was solved by Patterson and Fourier methods and the final molecular model obtained by anisotropic full-matrix least-squares refinement (based on 2984 reflections [*I* > 2 σ (*I*)] of non-hydrogen atoms. The dppp hydrogen atoms were positioned and refined with the riding model employing a common isotropic displacement parameter (which converged to *U* = 0.05(1) Å²). Final *R* indices [*I* > 2 σ (*I*)] were *R* = 0.061 and *wR* = 0.159. The FLACK parameter is -0.04(2), confirming that the correct absolute structure has been refined.

Programs used were SDP [10], SHELX-76 [11], SHELX-86 [12] for data reduction and correction and structure solution, and SHELX-93 [13] for structure refinement. Full crystallographic data are available from the authors and have been deposited at the Cambridge Crystallographic Data Centre under deposition number CCDC 191934.

Figure 1 shows an ORTEP plot [14] of the structure, with the labelling of the non-hydrogen atoms. The Re(III) ion is sited on a crystallographic two-fold axis and has a quasi-octahedral coordination with a pair of symmetry related dppp molecules acting as bidentate ligands [Re-P bond distances of 2.515(3) and 2.511(3) Å], which define the equatorial plane, and two axial chloride anions [d(Re-Cl) = 2.311(3) Å]. These bond distances are in good agreement with the values previously reported for the related [ReCl₂(dppe)₂]A complexes (dppe = 1,2 bis(diphenylphosphino)ethane; A = Cl⁻ or BF₄⁻) [15].

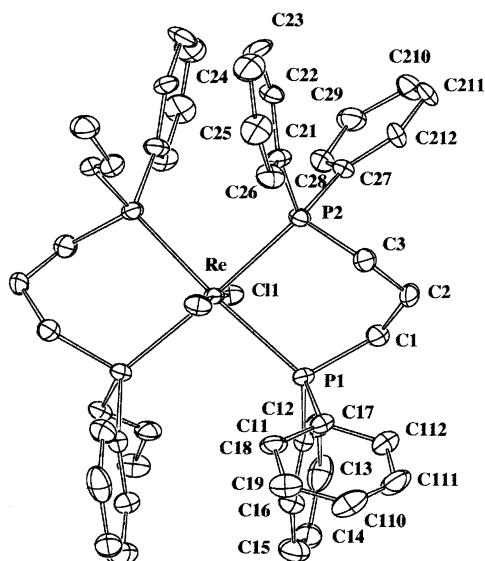


Fig. 1. ORTEP drawing of the $[\text{ReCl}_2(\text{dppp})_2]^+$ complex showing the labelling of the non-H atoms and their displacement ellipsoids at the 30% probability level.

As expected, the phenyl rings are planar within experimental accuracy and the phosphorus atoms bonded to them lay practically on the corresponding phenyl plane. The pair of phenyl groups attached to one of the phosphorus atoms are almost

normal to each other [dihedral angle of $97.6(6)^\circ$] while the pair bonded to other P-atom departs considerably from perpendicularity [$115.0(6)^\circ$]. Both six-membered rings show a twisted conformation. For phosphorus atoms belonging to the same ring, P-Re-P angles ($85.17(11)^\circ$) deviate from the ideal value (90°) expected in an octahedral coordination. This fact also modifies the P-C-C angles within the rings, which increase from the ideal 109.4° value to about 116° . Consequently, the two chelate rings are in a somewhat strained conformation. As expected, in the above mentioned dppe complexes, the strain of the five-membered rings is even higher, as the P-Re-P angle is reduced to $80.43(1)^\circ$ [15].

The chloride counteranion could not be located in the difference Fourier map. This is probably due to large positional disorder. In fact, the packing of the molecule shows interstitial channels along the (0,0,z) direction where residual electron densities of about $2.6 \text{ e} \cdot \text{\AA}^{-3}$ are observed. A disordered water molecule is located on a $\bar{4}$ special position.

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- [1] A. B. Packard, J. F. Kronauge, M. W. Brechbiel, in M. J. Clarke, P. J. Sadler (eds): *Metallopharmaceuticals II*, Springer Verlag, Berlin (1999).
- [2] S. D. Jurisson, J. D. Lydon, *Chem. Rev.* **99**, 2205 (1999).
- [3] K. Hashimoto, K. Yoshihara, *Topics Curr. Chem.* **176**, 277 (1996).
- [4] W. A. Volkert, T. J. Hoffman, *Chem. Rev.* **99**, 2235 (1999).
- [5] K. V. Katti, H. Galy, R. Schibli, T. J. Hoffman, W. A. Volkert, in M. Nicolini, U. Mazzi (eds): *Technetium and Rhenium in Chemistry and Nuclear Medicine 5*, SG Editoriali, Padova (1999).
- [6] W. A. Volkert, S. Jurisson, *Topics Curr. Chem.* **176**, 123 (1996).
- [7] J. D. Kelly, A. M. Foster, B. Kigley, C. M. Archer, F. S. Booker, L. R. Canning, K. W. Chiu, B. Edwards, H. K. Gill, M. McPartlin, K. R. Nagle, I. A. Latham, R. D. Pickett, A. E. Storey, P. M. Webbon, *J. Nucl. Med.* **34**, 222 (1993).
- [8] C. Kremer, E. Kremer, S. Domínguez, E. Chinea, A. Mederos, *Polyhedron* **15**, 4341 (1996).
- [9] D. Gambino, J. Benítez, L. Otero, E. Kremer, E. J. Baran, O. E. Piro, *Polyhedron* **18**, 2099 (1999).
- [10] B. A. Frenz, *Enraf-Nonius Structure Determination Package*, Enraf-Nonius, Delft (1983).
- [11] G. M. Sheldrick, *SHELX-76*, A Program for Crystal Structure Determination, University of Cambridge, Cambridge (1976).
- [12] G. M. Sheldrick, *Acta Crystallogr.* **A46**, 467 (1990).
- [13] G. M. Sheldrick, *SHELX-93*, A Program for Crystal Structure Refinement, University of Göttingen, Göttingen (1993).
- [14] C. K. Johnson, *ORTEP*. Report ORNL-3794, Oak Ridge, TN (1965).
- [15] T. Al-Salih, M. T. Duarte, J. J. R. Frausto da Silva, A. M. Galvao, M. F. C. Guedes da Silva, P. B. Hitchcock, D. L. Hughes, Ch. J. Pickett, A. J. L. Pombeiro, R. L. Richards, *J. Chem. Soc. Dalton Trans.* 3015 (1993).