resonance could also lie among the several exchangeable resonances that appear in the spectrum recorded in H_2O (Figure 1c).[28,34–36] The magnetic anisotropy of the siroheme could lead to the presence of numerous exchangeable resonances that frequently arise from proximal or distal histidine, arginine, and backbone NH protons. The data can be interpreted as indicative of a histidine residue as the sixth ligand to the siroheme in sulfite reductase. A methionine as axial ligand is unlikely since there is no evidence for a characteristic three-proton signal due to the iron-bound methionine ε-methyl group found at low frequencies (−8 to −25 ppm) in several *c*-type cytochromes.[33,37–40]

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Registry No. His, 71-00-1; siroheme, 52553-42-1; sulfite reductase, 37256-51-2.

(33) Wuthrich, K.; Senn, H.; Eugster, A. *Biochim. Biophys. Acta* **1983**, *743*, 58.
(34) Cutnell, J. D.; La Mar, G. N.; Kong, S. B. *J. Am. Chem. Soc.* **1981**, *103*, 3567.
(35) Sheard, B.; Yamane, T.; Shulman, R. G. *J. Mol. Biol.* **1970**, *53*, 35.
(36) Kong, S. b.; Cutnell, J. D.; La Mar, G. N. *J. Biol. Chem.* **1983**, *258*, 3843.
(37) Senn, H.; Guerlesquin, F.; Bruschi, M.; Wuthrich, K. *Biochim. Biophys. Acta* **1983**, *748*, 194.
(38) Senn, H.; Wuthrich, K. *Biochim. Biophys. Acta* **1983**, *743*, 69.
(39) Senn, H.; Wuthrich, K. *Biochim. Biophys. Acta* **1983**, *746*, 48.
(40) Timkovich, R.; Cork, M. S.; Taylor, P. V. *Biochemistry* **1984**, *23*, 3526.

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Unusual Synthesis and X-ray Structure of *cis*-Dichloro[1,2-bis(*o*-(diphenylphosphino)phenyl)ethane-1,2-diolato(2−)]technetium(IV) Hemiethanol Solvate

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Technetium phosphine complexes are stable and thus are useful in the design of ^{99m}Tc radiopharmaceuticals.[1,2] In this context the most important properties of phosphine ligands are their ability to reduce the pertechnetate(VII) ion and their ability to stabilize low oxidation states by means of π-back-bonding.[3–6] Technetium-99m phosphine complexes have been investigated for biological purposes,[1,7,8] and a few are very close to being used as radiopharmaceuticals. Chelating ligands containing both phosphorus(III) and other coordinating atoms offer new possibilities in the development of this field.

The ligand *o*-(diphenylphosphino)benzaldehyde ($Ph_2PC_6H_4CHO$) is one of the simplest possible bidentate O,P-chelating phosphine ligands. We have studied the reaction of this ligand with oxotetrachlorotechnetate(V) and observed an unexpected Tc(IV) product containing an O_2P_2-tetradentate ligand. The synthesis and X-ray structural characterization of this unusual product are now reported.

Table I. Crystallographic Data for *cis*-$TcCl_2(Ph_2PC_6H_4CHO)_2\cdot{}^1/_2EtOH$

formula: $C_{38}H_{30}Cl_2O_2P_2Tc\cdot{}^1/_2EtOH$
fw 773.4
space group: $P\bar{1}$ (No. 2)
$a = 12.460\ (8)$ Å
$b = 15.140\ (4)$ Å
$c = 10.753\ (5)$ Å
$\alpha = 86.98\ (4)°$
$\beta = 106.88\ (7)°$
$\gamma = 111.67\ (6)°$
$V = 1800.5\ (2.7)$ Å^3
$Z = 2$

diffractometer: Philips PW1100
$T = 22$ °C
$\lambda = 0.7107$ Å
$\mu = 6.5$ cm^{-1}
ρ(obsd) = 1.44 (3) g cm^{-3}
ρ(calcd) = 1.426 g cm^{-3}
no. of obsd ($I > 3\sigma(I)$) rflcns: 1369 (up to $2\vartheta = 36$)
anisotropy for atoms in "inner core"
$R(F_o) = 0.075$
$w = 1$

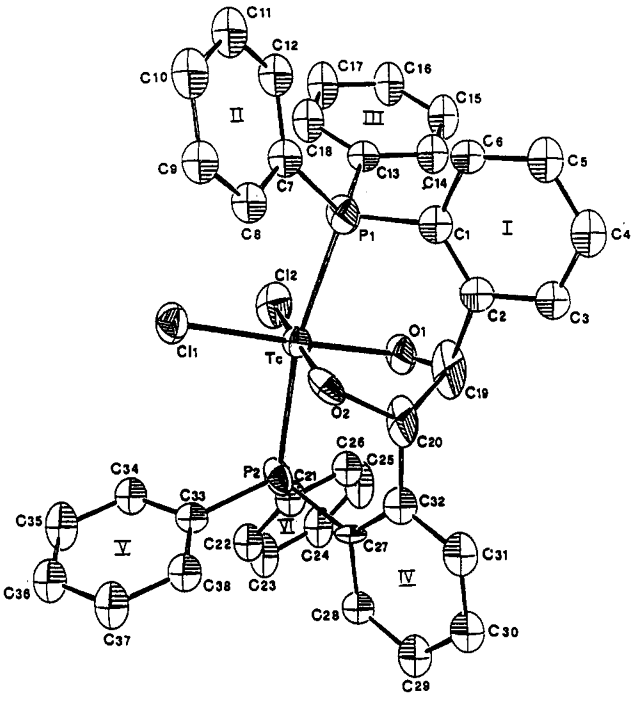

Figure 1. ORTEP drawing of the structure of $TcCl_2(Ph_2PC_6H_4CH(O^-)-CH(O^-)C_6H_4PPh_2)$. The EtOH molecule has been omitted for clarity.

Synthesis

$N(CH_2CH_2CH_2CH_3)_4[TcOCl_4]$ (50 mg, 0.1 mmol) was dissolved in the minimum amount (2 mL) of ethanol. *o*-(Diphenylphosphino)benzaldehyde (94 mg, 0.35 mmol) was added to this solution. The initial pale green color turned deep purple; after the solution was stirred for 10 min at room temperature, the solids dissolved and the solution was left to evaporate slowly overnight. Red-purple crystals were obtained, and after filtration, they were washed with two 1-mL portions of ethanol and dried under a nitrogen stream (yield: 95% with respect to $[TcOCl_4]^-$).

Elemental analyses, conductivity and magnetic susceptibility measurements, and ^{1}H NMR and IR spectra are consistent with the formulation $TcCl_2L$ ($L = (Ph_2PC_6H_4CHO-)_2$).[9]

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(1) Deutsch, E. A.; Glavan, K. A.; Sodd, V. J.; Nismiyama, H.; Ferguson, D. L.; Lukes, S. J. *J. Nucl. Med.* **1981**, *22*, 897.
(2) Dean, R. T.; Wester, D. W.; Nosco, D. L.; Adams, M. B.; Coveney, J. R.; Robbins, M. S.; McElvany, K. D.; De Jong, R. In *Technetium in Chemistry and Nuclear Medicine 2*; Nicolini, M., Bandoli, G., Mazzi, U., Eds.; Cortina International: Verona, Italy, 1986; pp 147–154.
(3) Bandoli, G.; Clemente, D. A.; Mazzi, U.; Roncari, E. *J. Chem. Soc., Dalton Trans.* **1982**, 1381.
(4) Bandoli, G.; Clemente, D. A.; Mazzi, U. *J. Chem. Soc., Dalton Trans.* **1976**, 125.
(5) Mazzi, U.; De Paoli, G.; Traverso, O. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1090.
(6) Wester, D. W.; White, D. H.; Miller, F. W.; Dean, R. T. *Inorg. Chem.* **1984**, *23*, 1501.
(7) Dean, R. T.; Adams, M. D.; Miller, F. W.; Robbins, M. S.; Wester, D. W.; White, D. H. *J. Nucl. Med.* **1984**, *25*, 15.
(8) Gerson, M. C.; Deutsch, E. A.; Libson, K. F.; Adolph, R. J.; Ketring, A. R.; Vanderheyden, J. L.; Williams, C. C.; Saenger, E. L. *Eur. J. Nucl. Med.* **1984**, *9*, 403.

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Table II. Relevant Bond Lengths (Å) and Angles (deg) with Esd's in Parentheses

Tc–Cl1	2.355 (8)	P1–C1	1.83 (2)	C2–C19	1.53 (3)
Tc–Cl2	2.344 (9)	P2–C21	1.82 (2)	C32–C20	1.55 (3)
Tc–P1	2.495 (8)	P1–C7	1.83 (2)	O1–C19	1.44 (3)
Tc–P2	2.505 (9)	P2–C27	1.84 (2)	O2–C20	1.43 (3)
Tc–O1	1.95 (2)	P1–C13	1.79 (2)	C19–C20	1.53 (3)
Tc–O2	1.94 (2)	P2–C33	1.79 (2)		

Cl1–Tc–Cl2	92.2 (3)	O1–Tc–O2	80.6 (8)
Cl2–Tc–O1	94.3 (6)	Cl1–Tc–O2	93.2 (5)
Cl2–Tc–O2	173.1 (6)	Cl1–Tc–O1	172.4 (6)
P1–Tc–O1	80.1 (6)	P1–Tc–O2	88.9 (5)
P2–Tc–O2	80.7 (6)	P2–Tc–O1	89.7 (6)
P1–Tc–Cl1	95.5 (3)	P2–Tc–Cl1	93.6 (3)
P1–Tc–Cl2	94.7 (3)	P2–Tc–Cl2	94.7 (3)
P1–Tc–P2	166.6 (3)		
Tc–O1–C19	114.9 (1.6)	Tc–O2–C20	116.6 (1.5)
O1–C19–C20	106.7 (2.0)	O2–C20–C19	104.6 (2.1)
C2–C19–O1	113.3 (2.1)	C32–C20–O2	112.0 (1.9)
C2–C19–C20	110.1 (2.2)	C19–C20–C32	110.0 (2.1)
Tc–P1–C1	108.6 (7)	Tc–P2–C21	116.9 (7)
Tc–P1–C7	116.7 (7)	Tc–P2–C27	108.3 (6)
Tc–P1–C13	114.8 (6)	Tc–P2–C33	115.8 (7)

Crystallography

Several attempts in various solvents (CH_2Cl_2, $CHCl_3$, or CH_3OH) to obtain single crystals of good quality for the purpose of an X-ray structure were unsuccessful. Some small crystals were obtained from an ethanol solution. Details of crystal data, measurement of intensities, and data processing are summarized in Table I. The intensities were processed in the normal fashion (2468 independent reflections were measured, of which only 1369 were judged to be observed), and no absorption correction was made since the crystal was very small and the μ value was rather low. The structure was solved by standard heavy-atom methods and refined by least-squares methods. Since observed reflections were limited in number, anisotropic thermal parameters were assigned only to the atoms of the "inner core" of the complex and the six phenyl rings were treated as rigid bodies (C–C = 1.395 Å, C–C–C = 120°). Peaks in the final ΔF map were up to 0.9 e Å^{-3} in the vicinity of the ethanol molecule. The programs used were those of the SHELX package.[10] The molecular structure is shown in Figure 1, which also defines the atom-numbering scheme. The bond distances and angles are listed in Table II, while other geometrical entities (equatorial mean plane, dihedral angles, torsion angles, and interatomic contacts) are given in Table III.

Results and Discussion

The paucity of diffraction data (mainly the scarcity of high-angle data) did not allow a more accurate structure determination, but the stereochemistry of the Tc atom is unambiguously well defined. The structure consists of discrete molecules of $Tc^{IV}Cl_2L$, with the Tc coordination environment as a distorted octahedron. Ethanol of crystallization is also present in the lattice. The quadridentate ligand presents the two trans phosphorus atoms bonded to technetium with a P1–Tc–P2 angle of 166.6 (3)° and the Tc^{IV}–P bond distances (2.495 (8) and 2.505 (9) Å) ca. 0.06 Å longer than the Tc^{III}–P distances found in analogous complexes,[11] while the two anionic O1 and O2 atoms of the ligand occupy two equatorial positions. The Tc–O1 and Tc–O2 distances (1.95 (2) and 1.94 (2) Å, respectively) correlate well with those found previously for 1,2-diolato–technetium complexes,[12] whereas C19–C20 (1.53 (3) Å) and both C–O distances (1.44 (3) and 1.43 (3) Å) are longer than those normally found in similar oxo-technetium[12] and oxo–molybdenum complexes.[13] Also the C2–C19 and C20–C32 distances (1.53 (3) and 1.55 (3) Å, respectively) are abnormally long, if compared with the value of 1.48 Å for the parent compound *o*-(diphenylphosphino)benzaldehyde.[14]

Table III. Other Geometrical Entities

(i) Deviations from Plane (Å)

distances of relevant atoms from the least-squares "equatorial" mean plane (E) defined by Cl1, Cl2, O1, and O2: Cl1, −0.02; Cl2, +0.02; O1, −0.14; O2, +0.11; Tc, −0.01; C19, −0.39; C20, +0.35

(ii) Dihedral Angles (deg)

(E)–(I)	78.2	(E)–(IV)	79.7
(E)–(II)	66.8	(E)–(V)	151.5
(E)–(III)	22.1	(E)–(VI)	119.4
(I)–(II)	92.2	(IV)–(V)	71.9
(I)–(III)	98.7	(IV)–(VI)	95.4
(II)–(III)	57.4	(V)–(VI)	62.8

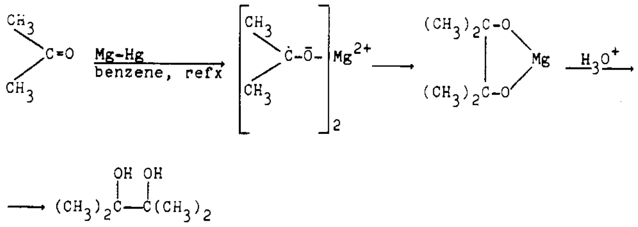
(iii) Torsion Angles (deg)

Tc–O1–C19–C20	35.3	Tc–O2–C20–C19	34.9
O1–C19–C20–O2	−42.6	C2–C19–C20–C32	−158.9
C1–C2–C19–C20	−86.4	C27–C32–C20–C19	−87.0

(iv) Interatomic Contacts (Å)

O1- - -Cl2	3.16	O2- - -Cl1	3.14
O1- - -O2	2.51	Cl1- - -Cl2	3.39
P1- - -O1	2.89	P2- - -O2	2.91
P1- - -O2	3.13	P2- - -O1	3.16

There seems to be an overall lengthening of the distances in the ethanediolate moiety, although, owing to poor accuracy in positional parameters, little significance can be attributed to this trend. The remaining equatorial positions are occupied by the two chlorine atoms (mean Tc–Cl distance of 2.35 (1) Å). The technetium lies on the mean Cl1, Cl2, O1, O2 equatorial plane (Table III), while O1 and O2 are out in the opposite direction by −0.14 and +0.11 Å, respectively. As evidenced by X-ray analysis, the technetium(IV) center is bonded to a tetradentate ligand in which the glycolate linkage bridges two O,P-bidentate moieties. The formation of this tetradentate ligand from bidentate *o*-(diphenylphosphino)benzaldehyde can be explained only by means of catalytic assistance by the technetium center in promoting bimolecular reduction of two aldehyde groups. This general reaction in which a metal catalyzes the formation of a carbon–carbon bond is known for aldehydes and ketones:[15]



While no data are available to support the hypothesis that catalysis occurs when the two phosphine ligands are bonded to the technetium center, this is a reasonable possibility, since $TcCl_4P_2$ complexes (P = tertiary phosphine) are easily obtained.[5] With both aldehydes and ketones the bimolecular reduction is performed by magnesium, which oxidizes to form a coordination complex, while with technetium the reducing effect must be attributed to the ligand.

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Supplementary Material Available: A listing of fractional coordinates and anisotropic and isotropic thermal parameters (Table A) (1 page); a complete listing of structural data (Table B) (8 pages). Ordering information is given on any current masthead page.

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(9) Anal. Calcd for $C_{38}H_{30}O_2P_2Cl_2Tc{\cdot}CH_3CH_2OH$: C, 60.31; H, 4.55; N, 0.0; Cl, 8.90. Found: C, 59.40; H, 4.35;, N, 0.0; Cl, 8.42. Magnetic susceptibility measurements performed in dichloromethane by the Evans method yield a value of μ = 3.5 μ_B in agreement with a high-spin d^3 system typical for Tc(IV). The ^1H NMR spectrum in chloroform shows nine distinct signals in the range δ = 1–23 ppm (δ(TMS) = 0.0 ppm).

(10) Sheldrick, G. M. *SHELX 76, Programs for Crystal Structure Determination*; University of Cambridge: Cambridge, England, 1976.

(11) Bandoli, G.; Mazzi, U.; Roncari, E.; Deutsch, E. *Coord. Chem. Rev.* **1982**, *44*, 191. Duatti, A.; Marchi, A.; Luna, S. A.; Bandoli, G.; Mazzi, U.; Tisato, F. *J. Chem. Soc., Dalton Trans.* **1987**, 867.

(12) Davison, A.; De Pamphilis, B. V.; Franklin, K. J.; Jones, A. G.; Lock, C. J. L. *Inorg. Chim. Acta* **1987**, *128*, 161 and references therein.

(13) Jones, A. G.; De Pamphilis, B. V.; Davison, A. *Inorg. Chem.* **1981**, *20*, 1617.

(14) Landvatter, E. F.; Rauchfuss, T. B. *Organometallics* **1982**, *1*, 506.

(15) Allinger, N. L.; Cava, M. P.; De Jongh, D. C.; Johnson, C. R.; Lebell, N. A.; Stevens, C. L. *Organic Chemistry*; Worth Publishers Inc.: New York, 1971; p 493.