La Fig. 1 montre que la structure peut être considérée comme formée de couches comprenant chacune un feuillet de cations inséré entre deux feuillets d'anions. Les positions moyennes de ces couches sont les plans $x = 0$ et $x = \frac{1}{2}$. Les liaisons hydrogène unissent les anions et les cations appartenant à une même couche.

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Structure of the Tetra-*n*-butylammonium Salt of the Tetrachloro(methanol)nitrosyltechnetium(II) Anion

By D. S. Brown, J. L. Newman and J. R. Thornback

*Department of Chemistry, Loughborough University of Technology, Loughborough, Leics. LE*11 3*TU, England*

and A. Davison

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, *USA*

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Abstract. $[(C_4H_9)_4N][Tc(NO)Cl_4(CH_3OH)]$, $M_r = 545{\cdot}3$, monoclinic, $P2_1/n$, $a = 11{\cdot}350\,(10)$, $b = 11{\cdot}450\,(5)$, $c = 22{\cdot}154\,(10)$ Å, $\beta = 91{\cdot}5\,(2)°$, $U = 2878{\cdot}85$ Å^3, $Z = 4$, D_m not measured, $D_x = 1{\cdot}256$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 8{\cdot}0$ cm^{-1}, $F(000) = 932$, $T = 293$ K, $R = 0{\cdot}051$ for 2282 observed reflexions with $I > 3\sigma(I)$. The anion $[Tc(NO)Cl_4(CH_3OH)]^-$ has a distorted octahedral geometry with the four Cl atoms lying in an equatorial plane and the other two ligands axial. The nitrosyl group is bonded almost linearly to the Tc and the coordinated methanol *trans* to it was found to be hydrogen-bonded to a methanol of solvation.

Introduction. The use of technetium-99m in the field of nuclear medicine is well established; technetium-99 enables extensive research into the coordination chemistry of the element. We are interested, in particular, in the synthesis of technetium complexes as possible radiopharmaceuticals in which the Tc atom is in a low oxidation state.

The exact structure of the $[Tc(NO)X_{4-5}]^{1-\text{or}\,2-}$ complexes has been a matter of discussion. The ESR data for the complexes where $X = \text{Br}$ or I suggest that the species are five coordinate with no ligand *trans* to the nitrosyl (Kirmse, Stach, Lorenz & Marov, 1984; Kirmse, Stach & Abram, 1985). Since the data for $X = \text{Cl}$ are difficult to assign to either five- or six-coordinated species (Yang, Heitzmann, Ford & Benson, 1982; Orvig, Davison & Jones, 1981), it was decided to undertake a structure determination.

The determination of the structure of the title compound has confirmed the identity of a species prepared by the same methods for both technetium-99 and technetium-99m. The complex may be made in a form amenable to intravenous injection and, since it readily undergoes ligand exchange with amines, arsines, phosphines and Schiff bases, it may find use as a precursor to a novel series of radiopharmaceuticals.

Experimental. Preparation by the method of Cheah, Newman, Nowotnik & Thornback (1987); bright green crystals grown from methanol/diethyl ether; two forms of crystal, rectangular plate and needle; crystal ($0{\cdot}63 \times 0{\cdot}39 \times 0{\cdot}13$ mm) rectangular plate mounted about **a**: Stoe Weissenberg diffractometer, $(\sin\theta)/\lambda <$

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Table 1. *Final positional parameters* ($\times 10^4$) *and isotropic thermal parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)\textstyle\sum_i U_{ii}.$$

	x	y	z	B_{eq}
Tc	318 (1)	1095 (1)	−1537 (0)	4·9 (1)
Cl(1)	10667 (3)	582 (2)	1188 (1)	6·4 (2)
Cl(2)	8638 (3)	−2826 (2)	1751 (1)	6·0 (2)
Cl(3)	7865 (3)	−175 (2)	1319 (2)	7·8 (2)
Cl(4)	11470 (3)	−2110 (2)	1632 (2)	7·3 (2)
N(1)	9770 (9)	−628 (8)	2260 (5)	7·0 (6)
O(1)	9901 (13)	−269 (9)	2752 (5)	13·2 (8)
O(2)	9679 (6)	−1595 (7)	612 (3)	6·5 (4)
N(2)	5107 (7)	1074 (6)	7476 (3)	4·7 (4)
C(1)	6014 (9)	1196 (8)	6982 (4)	5·4 (5)
C(2)	5861 (10)	341 (9)	6466 (5)	6·4 (7)
C(3)	6927 (13)	462 (11)	6042 (6)	9·0 (9)
C(4)	6785 (15)	−284 (12)	5477 (6)	9·8 (10)
C(5)	3861 (9)	1131 (8)	7240 (4)	5·0 (5)
C(6)	3514 (10)	2234 (9)	6900 (5)	6·4 (7)
C(7)	2256 (10)	2100 (10)	6597 (5)	6·7 (7)
C(8)	2185 (14)	1181 (13)	6104 (6)	9·9 (9)
C(9)	5387 (9)	2074 (8)	7913 (5)	5·0 (6)
C(10)	4670 (11)	2110 (9)	8478 (5)	6·2 (6)
C(11)	5117 (12)	3144 (10)	8861 (5)	7·4 (7)
C(12)	4464 (15)	3197 (13)	9464 (6)	10·0 (10)
C(13)	5197 (10)	−121 (8)	7783 (4)	5·1 (5)
C(14)	6445 (10)	−401 (9)	8042 (5)	6·6 (7)
C(15)	6362 (12)	−1591 (10)	8370 (7)	8·0 (8)
C(16)	5710 (14)	−1548 (14)	8952 (7)	10·2 (10)
C(17)	8886 (15)	−2302 (12)	269 (6)	10·2 (10)
C(18)	2406 (14)	3844 (15)	4917 (6)	10·1 (10)
O(3)	8577 (9)	1315 (8)	119 (4)	8·9 (6)

0·6 Å^{-1}; lattice parameters by maximizing fit of axial row reflexions in range $(\sin\theta)/\lambda$ 0·2 to 0·5 Å^{-1}; 3797 unique reflexions measured, 2283 with $I > 3\sigma(I)$; h 0→8, k 0→13, l −26→+26; standard check reflexions on each layer with no significant changes; no absorption corrections applied; Tc positions found by Patterson techniques and other atoms by successive difference-Fourier methods, refined by full-matrix least squares on F to $R = 0{\cdot}051$, $wR = 0{\cdot}051$; all atoms anisotropic, unit weighting (based on weight analysis), 15 H atoms located by difference map and not refined; remaining H atoms omitted; max. $\Delta/\sigma = 0{\cdot}009$, $\Delta\rho$ excursions +0·3 to −0·6 e Å^{-3}; scattering factors from *International Tables for X-ray Crystallography* (1974); geometry calculations carried out using the *XRAY*72 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) as implemented on the CDC7600 computer at the University of Manchester Regional Computer Centre and all others with *SHELX*76 (Sheldrick, 1976) as implemented on the Honeywell Multics computer at Loughborough University of Technology.

Discussion. Final atomic coordinates are given in Table 1,* bond lengths and angles in Table 2, and the numbering scheme of the atoms in Fig. 1. A view of the unit cell is shown in Fig. 2. C(18) and O(3) refer to the methanol of solvation.

The X-ray data of the monoclinic crystal show that the anion has a distorted octahedral geometry with the nitrosyl and coordinated methanol mutually *trans* and the four Cl atoms in an equatorial plane with the Tc 0·15 Å above towards the nitrosyl.

The bond angles of 172·5 (1) [Cl(1)—Tc—Cl(2)] and 172·8 (2)° [Cl(3)—Tc—Cl(4)] reflect this. In other Tc(NO) complexes, namely $[\mathrm{Tc(NO)(NH_3)_4(H_2O)}]^{2+}$

Table 2. *Bond distances* (Å) *and angles* (°)

Anion		Cation	
Tc—Cl(1)	2·363 (3)	N(2)—C(1)	1·53 (1)
Tc—Cl(2)	2·364 (3)	C(1)—C(2)	1·51 (1)
Tc—Cl(3)	2·355 (3)	C(2)—C(3)	1·56 (2)
Tc—Cl(4)	2·344 (3)	C(3)—C(4)	1·52 (2)
Tc—N(1)	1·689 (11)	N(2)—C(5)	1·50 (1)
Tc—O(2)	2·128 (7)	C(5)—C(6)	1·52 (1)
N(1)—O(1)	1·171 (15)	C(6)—C(7)	1·57 (2)
O(2)—C(17)	1·417 (17)	C(7)—C(8)	1·52 (2)
		N(2)—C(9)	1·53 (1)
Solvent		C(9)—C(10)	1·51 (2)
C(18)—O(3)	1·403 (19) Å	C(10)—C(11)	1·54 (2)
		C(11)—C(12)	1·54 (2)
		N(2)—C(13)	1·53 (1)
		C(13)—C(14)	1·55 (2)
		C(14)—C(15)	1·55 (2)
		C(15)—C(16)	1·50 (2)

Anion		Cation	
O(1)—N(1)—Tc	175·5 (10)	C(1)—N(2)—C(5)	113·2 (7)
Cl(1)—Tc—Cl(2)	172·5 (1)	C(1)—N(2)—C(9)	104·6 (7)
Cl(1)—Tc—Cl(3)	89·4 (1)	C(1)—N(2)—C(13)	111·2 (7)
Cl(1)—Tc—Cl(4)	90·9 (1)	C(5)—N(2)—C(9)	111·6 (7)
Cl(1)—Tc—N(1)	92·1 (3)	C(5)—N(2)—C(13)	104·2 (7)
Cl(1)—Tc—O(2)	83·8 (2)	C(9)—N(2)—C(13)	112·2 (7)
Cl(2)—Tc—Cl(3)	88·6 (1)	N(2)—C(1)—C(2)	114·6 (8)
Cl(2)—Tc—Cl(4)	90·2 (1)	C(1)—C(2)—C(3)	108·8 (9)
Cl(2)—Tc—N(1)	95·3 (3)	C(2)—C(3)—C(4)	112·3 (11)
Cl(2)—Tc—O(2)	88·8 (2)	N(2)—C(5)—C(6)	116·1 (8)
Cl(3)—Tc—Cl(4)	172·8 (2)	C(5)—C(6)—C(7)	110·6 (9)
Cl(3)—Tc—N(1)	94·7 (4)	C(6)—C(7)—C(8)	114·0 (11)
Cl(3)—Tc—O(2)	86·8 (2)	N(2)—C(9)—C(10)	115·9 (8)
Cl(4)—Tc—N(1)	92·4 (3)	C(9)—C(10)—C(11)	107·5 (9)
Cl(4)—Tc—O(2)	86·1 (2)	C(10)—C(11)—C(12)	110·4 (10)
N(1)—Tc—O(2)	175·6 (4)	N(2)—C(13)—C(14)	113·6 (8)
		C(13)—C(14)—C(15)	106·8 (11)
		C(14)—C(15)—C(16)	114·3 (11)

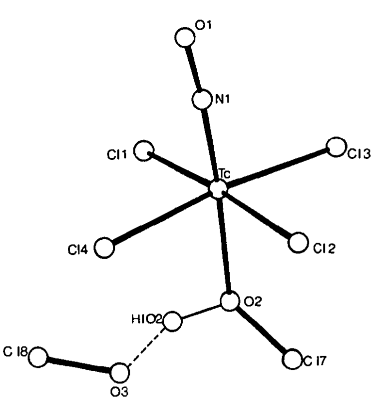

Fig. 1. Molecular structure and atom numbering for the tetrachloro(methanol)nitrosyltechnetium(II) anion and solvated methanol showing hydrogen bonding.

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43966 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

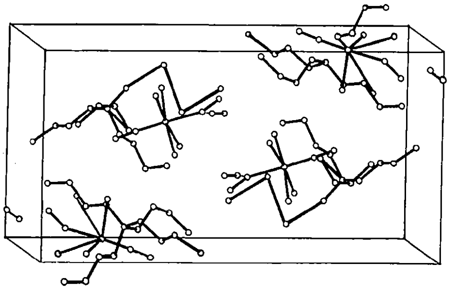

Fig. 2. A view of the unit-cell contents.

(Radonovich & Hoard, 1984) and $Tc(NO)Br_2(CNCMe_3)_3$ (Linder, Davison, Dewan, Costello & Maleknia, 1986) similar distortions have been observed. The Tc—N—O bond angle of 175·5 (10)° confirms that the ligand should be considered as NO^+ rather than NO^-. The Tc—N bond length of 1·689 (11) Å appears shorter than in the two complexes above which are 1·716 (4) and 1·726 (15) Å respectively (though this is barely statistically significant) while the N—O bond is intermediate between the other two, 1·203 (6) and 1·136 (17) Å. The Tc—O bond is probably elongated owing to the *trans* effect of the nitrosyl, although a lack of comparable Tc complexes prevents a quantitative assessment of the effect. However a long axial bond has been observed in the analogous rhenium complex (Ciano, Guisto, Manassero & Sansoni, 1975). The contact distance of 2·610 (2) Å for O(2)—O(3) is attributed to hydrogen bonding between coordinated and solvated methanols.

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cis-Dichloro[trimethylenebis(diphenylphosphine)]platinum(II)

BY GLEN B. ROBERTSON AND WASANTHA A. WICKRAMASINGHE

Research School of Chemistry, The Australian National University, GPO Box 4, Canberra, Australia

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Abstract. $[PtCl_2\{P_2(C_3H_6)(C_6H_5)_4\}]$, $M_r = 678{\cdot}4$, triclinic, $P\bar{1}$, $a = 14{\cdot}424$ (1), $b = 10{\cdot}686$ (1), $c = 8{\cdot}580$ (1) Å, $\alpha = 72{\cdot}61$ (1), $\beta = 79{\cdot}80$ (1), $\gamma = 88{\cdot}31$ (1)°, $U = 1241{\cdot}6$ Å^3, $Z = 2$, $D_m = 1{\cdot}80$ (1), $D_x = 1{\cdot}81$ g cm^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0{\cdot}71069$ Å, $\mu = 63{\cdot}0$ cm^{-1}, $F(000) = 660$, $T = 294$ (1) K, $R = 0{\cdot}025$, $wR = 0{\cdot}029$ for 6195 unique reflections [$I \geq 3\sigma(I)$]. Crystals are isomorphous with those of their palladium analogue and molecular dimensions differ only in detail. The Pt—P bond distances are equivalent to within experimental error [av. 2·2321 (6) Å] but the Pt—Cl distances are inequivalent [2·3559 (8) and 2·3687 (8) Å]. The alkyl backbone of the phospine ligand exhibits substantial angular strain.

Introduction. The title compound was obtained, as the only crystalline product formed, while attempting to recrystallize *cis*-$[PtCl(COC_6H_9)\{(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2\}]$ (Bennett & Rokicki, 1983). Data collection and structure solution were commenced on the basis of apparently satisfactory density agreement found, later, to be due to a numerical error. Nevertheless, precise molecular dimensions for the title compound are of interest, both for comparison with related molecules and because it provides a further example of length differences between chemically equivalent Pt—Cl bonds.

Experimental. Tabular colourless crystals from dichloromethane solution of *cis*-$[PtCl(OCC_6H_9)\{(C_6$-

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