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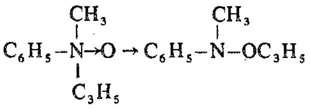

$$C_6H_5\text{–}\underset{C_3H_5}{\overset{CH_3}{N}}\text{→}O \rightarrow C_6H_5\text{–}\overset{CH_3}{N}\text{–}OC_3H_5$$

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Technetium–Phosphonite Complexes. Synthesis of Hexacoordinate Technetium(II) and Technetium(III) Complexes of Diethyl Phenylphosphonite and the Crystal Structure of Dichlorotetrakis(diethyl phenylphosphonite)technetium(II)

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The preparation of the dichlorotetrakis(diethyl phenylphosphonite)technetium(III) complexes $[TcCl_2(C_6H_5P(OC_2H_5)_2)_4]Y$, where $Y^- = Cl^-, ClO_4^-, B(C_6H_5)_4^-$, and dichlorotetrakis(diethyl phenylphosphonite)technetium(II) $[TcCl_2(C_6H_5P(OC_2H_5)_2)_4]$, obtained by the reaction of $(NH_4)_2TcCl_6$ with $C_6H_5P(OC_2H_5)_2$, is described. The complexes have been characterized by elemental analysis, magnetic and conductivity measurements, and IR and electronic spectra. The crystal and molecular structure of the technetium(II) derivative has been determined by three-dimensional x-ray data collected by counter techniques. The compound crystallizes in a monoclinic cell with dimensions $a = 21.740$ (19), $b = 11.750$ (10), $c = 18.312$ (12) Å, and $\beta = 92.92$ (9)°. The space group is $P2_1/c$ (C_{2h}^5) and $Z = 4$. The final R factor for the least-squares refinement is 0.051 (Mo Kα; 5495 observed reflections). The crystal structure consists of discrete molecules each of which has a trans-octahedral configuration as anticipated from IR and proton NMR spectra. The molecule has the following metal–ligand bond lengths and angles: Tc–P = 2.41 (1), Tc–Cl = 2.41 (1) Å; P–Tc–P(trans) = 164.2 (1), P–Tc–P(cis) = 91.9 (1), Cl–Tc–Cl = 178.8 (1)°.

Introduction

Little is known about the coordination chemistry of technetium compared to that of manganese and rhenium, the principal reason being that only recently has the element become available in sufficiently large amounts to be used on a preparative scale. Only a few low-valent technetium complexes have been reported. These are $[TcX_2D_2]Y$ and $[TcX_2D_2]$ ($X^- = Cl^-, Br^-, I^-$; D = *o*-phenylenebis(dimethylarsine), 1,2-bis(diphenylphosphino)ethane; $Y^- = Cl^-, Br^-, I^-, I_3^-, ClO_4^-$),[2,3] carbonyl complexes of the types $Tc_2(CO)_{10}$, $Tc(CO)_4$, $Tc(CO)_5^+$, $Tc(CO)_5^-$,[4-7] $(CO)_3TcMPRe(CO)_3$,[8] and $MP(Tc(CO)_3)_2$[9] (MP = mesoporphyrin IX dimethyl ester), and the compound $(NH_4)_3Tc_2Cl_8{\cdot}nH_2O$.[10-12] No published data, other than our own,[13] exist on technetium(II) and technetium(III) complexes with monodentate phosphine or phosphonite ligands. This lack of information prompted us to synthesize the complexes $[TcCl_2(C_6H_5P(OC_2H_5)_2)_4]Y$ ($Y^- = Cl^-, ClO_4^-, B(C_6H_5)_4^-$) and $[TcCl_2(C_6H_5P(OC_2H_5)_2)_4]$. The diethyl phenylphosphonite ligand was used because of its reducing properties and of its well established[14-17] ability to stabilize low oxidation states of transition metals.

A preliminary account of the structure of the complex $[TcCl_2(C_6H_5P(OC_2H_5)_2)_4]$ has been reported,[18] and the full structure, included in this paper, confirms the structural information obtained from spectroscopic studies.

Experimental Section

Materials. Solid NH_4TcO_4 was obtained by concentration and filtration of its ammonia solution (available from Radiochemical Centre Ltd., Amersham, England). $(NH_4)_2TcCl_6$ was prepared by the electrochemical method,[19] which yields large amounts of product by a simple reduction of NH_4TcO_4 in HCl (6 N) on a platinum electrode. Diethyl phenylphosphonite was synthesized by the method of Rabinowitz and Pellon.[20] All solvents were purified and dried by standard methods.

Apparatus. Magnetic susceptibilities of nitromethane or benzene solutions were measured by the Evans method[21] and corrected for diamagnetism of the ligands from tables given by Figgis and Lewis.[22] ^1H NMR spectra were recorded using a Hitachi Perkin-Elmer R20A instrument with TMS as the internal standard. Conductivities (10^{-3} M solutions in nitromethane at 25 °C) were measured with an LKB conductivity bridge, Model 3116B. Electronic spectra were recorded using a CF4 Optica spectrophotometer. The absorptions of $[TcCl_2L_4]$ complex were measured in the presence of 1 M free phosphonite. Infrared spectra of Nujol samples, using CsI windows, were recorded using Perkin-Elmer 621 (4000–400 cm^{-1}) and Beckman IR-11 spectrophotometers (400–50 cm^{-1}).

Analytical Methods. The technetium was determined by treating a concentrated ethanol solution of the complex with H_2O_2 (30%) and then titrating the TcO_4^- formed with standard $P(C_6H_5)_4Cl$. The equivalent point was determined by measuring the radioactivity of microsamples (0.02 ml) of the solution.[23] Chlorine was determined by potentiometric titration (standard $AgNO_3$) of the ethanol solutions of the complexes after oxidation with H_2O_2 (30%). Only the coordinated chlorine was determined with this method.

Table I

(a) Positional Parameters for the Nonhydrogen Atoms of $[TcCl_2(C_6H_5P(OC_2H_5)_2)_4]$

Atom[a]	*x*	*y*	*z*	Atom[a]	*x*	*y*	*z*
Tc	0.2526 (0)	0.0657 (0)	0.2404 (0)	C(10)II	0.0993 (3)	−0.1940 (7)	0.2074 (5)
Cl(1)	0.2683 (1)	0.0723 (2)	0.3719 (1)	PIII	0.2345 (1)	0.2673 (2)	0.2578 (1)
Cl(2)	0.2372 (1)	0.0549 (2)	0.1094 (1)	O(1)III	0.2116 (3)	0.3525 (5)	0.1941 (3)
PI	0.3569 (1)	0.1040 (2)	0.2093 (1)	C(1)III	0.2243 (5)	0.3493 (9)	0.1201 (6)
O(1)I	0.4118 (2)	0.1421 (5)	0.2659 (3)	C(2)III	0.1838 (6)	0.4200 (3)	0.0745 (7)
C(1)I	0.4246 (4)	0.0872 (8)	0.3355 (4)	O(2)III	0.2973 (2)	0.3223 (4)	0.2924 (3)
C(2)I	0.4764 (4)	0.1457 (10)	0.3767 (6)	C(3)III	0.3044 (4)	0.4424 (7)	0.3063 (5)
O(2)I	0.3835 (2)	−0.0054 (4)	0.1692 (3)	C(4)III	0.3559 (6)	0.4615 (10)	0.3617 (7)
C(3)I	0.4453 (4)	−0.0117 (7)	0.1435 (5)	C(5)III	0.1788 (3)	0.3145 (6)	0.3231 (4)
C(4)I	0.4447 (5)	−0.0792 (10)	0.0743 (6)	C(6)III	0.1930 (4)	0.3142 (7)	0.3978 (5)
C(5)I	0.3702 (3)	0.2176 (7)	0.1434 (4)	C(7)III	0.1496 (4)	0.3491 (7)	0.4457 (5)
C(6)I	0.3575 (4)	0.1998 (8)	0.0682 (5)	C(8)III	0.0914 (4)	0.3819 (8)	0.4199 (6)
C(7)I	0.3635 (4)	0.2888 (9)	0.0187 (5)	C(9)III	0.0772 (4)	0.3831 (8)	0.3468 (6)
C(8)I	0.3812 (5)	0.3938 (9)	0.0433 (6)	C(10)III	0.1205 (4)	0.3512 (7)	0.2979 (5)
C(9)I	0.3950 (5)	0.4125 (8)	0.1167 (7)	PIV	0.2749 (1)	−0.1329 (2)	0.2594 (1)
C(10)I	0.3894 (4)	0.3251 (7)	0.1669 (5)	O(1)IV	0.2847 (2)	−0.2224 (5)	0.1949 (3)
PII	0.1437 (1)	0.0272 (2)	0.2356 (1)	C(1)IV	0.2492 (5)	−0.2346 (9)	0.1286 (6)
O(1)II	0.1043 (2)	−0.0055 (5)	0.3041 (3)	C(2)IV	0.2812 (6)	−0.2941 (13)	0.0756 (7)
C(1)II	0.1109 (4)	0.0469 (9)	0.3748 (5)	O(2)IV	0.2215 (2)	−0.1861 (4)	0.3065 (3)
C(2)II	0.0667 (5)	0.0050 (11)	0.4227 (6)	C(3)IV	0.2200 (4)	−0.3046 (8)	0.3263 (6)
O(2)II	0.1082 (2)	0.1352 (4)	0.1993 (3)	C(4)IV	0.1804 (6)	−0.3211 (10)	0.3892 (7)
C(3)II	0.0416 (4)	0.1440 (8)	0.1927 (6)	C(5)IV	0.3448 (3)	−0.1751 (6)	0.3133 (4)
C(4)II	0.0236 (5)	0.2200 (12)	0.1292 (6)	C(6)IV	0.3482 (3)	−0.1658 (6)	0.3892 (4)
C(5)II	0.1128 (3)	−0.0878 (6)	0.1763 (4)	C(7)IV	0.4012 (4)	−0.1944 (7)	0.4284 (4)
C(6)II	0.1041 (3)	−0.0719 (8)	0.1022 (4)	C(8)IV	0.4523 (4)	−0.2317 (8)	0.3947 (5)
C(7)II	0.0834 (4)	−0.1610 (10)	0.0575 (5)	C(9)IV	0.4493 (4)	−0.2428 (7)	0.3193 (5)
C(8)II	0.0710 (4)	−0.2650 (10)	0.0868 (6)	C(10)IV	0.3961 (3)	−0.2144 (7)	0.2784 (4)
C(9)II	0.0785 (4)	−0.2811 (8)	0.1616 (6)				

(b) Positional Parameters for the Hydrogen Atoms of $[TcCl_2(C_6H_5P(OC_2H_5)_2)_4]$

Atom[b]	*x*	*y*	*z*	Atom[b]	*x*	*y*	*z*	Atom[b]	*x*	*y*	*z*
HC(1)I	0.389	0.090	0.363	HC(3)II	0.024	0.071	0.185	HC(6)III	0.232	0.290	0.416
HC(1)I′	0.435	0.010	0.328	HC(3)II′	0.027	0.175	0.236	HC(7)III	0.160	0.351	0.497
HC(2)I	0.484	0.098	0.424	HC(4)II	−0.022	0.219	0.124	HC(8)III	0.061	0.403	0.453
HC(2)I′	0.464	0.225	0.389	HC(4)II′	0.040	0.178	0.082	HC(9)III	0.037	0.406	0.329
HC(2)I″	0.510	0.140	0.346	HC(4)II″	0.042	0.296	0.138	HC(10)III	0.110	0.354	0.247
HC(3)I	0.460	0.063	0.135	HC(6)II	0.112	0.000	0.081	HC(1)IV	0.213	−0.275	0.138
HC(3)I′	0.472	−0.045	0.180	HC(7)II	0.078	−0.150	0.006	HC(1)IV′	0.239	−0.161	0.110
HC(4)I	0.486	−0.088	0.060	HC(8)II	0.057	−0.326	0.056	HC(2)IV	0.320	−0.320	0.095
HC(4)I′	0.415	−0.043	0.036	HC(9)II	0.069	−0.353	0.182	HC(2)IV′	0.280	−0.250	0.036
HC(4)I″	0.433	−0.159	0.088	HC(10)II	0.104	−0.206	0.259	HC(2)IV″	0.250	−0.360	0.060
HC(6)I	0.345	0.127	0.051	HC(1)III	0.265	0.374	0.115	HC(3)IV	0.204	−0.348	0.286
HC(7)I	0.355	0.276	−0.032	HC(1)III′	0.220	0.273	0.103	HC(3)IV′	0.261	−0.330	0.339
HC(8)I	0.384	0.455	0.010	HC(2)III	0.197	0.430	0.023	HC(4)IV	0.179	−0.400	0.400
HC(9)I	0.408	0.486	0.133	HC(2)III′	0.183	0.490	0.098	HC(4)IV′	0.138	−0.300	0.380
HC(10)I	0.400	0.339	0.217	HC(2)III″	0.150	0.380	0.065	HC(4)IV″	0.200	−0.280	0.428
HC(1)II	0.151	0.031	0.395	HC(3)III	0.313	0.480	0.262	HC(6)IV	0.313	−0.139	0.414
HC(1)II′	0.106	0.127	0.369	HC(3)III′	0.267	0.472	0.324	HC(7)IV	0.403	−0.188	0.480
HC(2)II	0.070	0.042	0.471	HC(4)III	0.374	0.388	0.377	HC(8)IV	0.489	−0.250	0.422
HC(2)II′	0.072	−0.078	0.429	HC(4)III′	0.335	0.490	0.410	HC(9)IV	0.484	−0.270	0.295
HC(2)II″	0.025	0.022	0.400	HC(4)III″	0.382	0.520	0.353	HC(10)IV	0.395	−0.222	0.227

[a] Roman numerals refer to the four phosphonite ligands. [b] Hydrogen atoms are numbered so that HC(1)I is attached to C(1) of phosphonite ligand I, etc. Primes are used only if more than one hydrogen atoms are attached to the same carbon atom.

Syntheses of Complexes. All of the preparative work was carried out under a nitrogen atmosphere using anhydrous solvents.

Dichlorotetrakis(diethyl phenylphosphonite)technetium(III) Perchlorate and Tetraphenylborate. Ammonium hexachlorotechnetate(IV) (0.5 g), diethyl phenylphosphonite (6 ml), and ethanol (40 ml) were placed in a two-necked, round-bottomed flask fitted with a condenser and inlet and outlet tubes. The apparatus was flushed out with nitrogen and the reaction mixture refluxed for 30 h. During this time, the complete disappearance of solid $(NH_4)_2TcCl_6$ and a color change from yellow to deep red was observed. The addition, at room temperature, of a concentrated ethanol solution of $LiClO_4$ or $NaB(C_6H_5)_4$ to the reaction mixture precipitated the perchlorate or tetraphenylborate salt of the complex cation, respectively. Red crystals were obtained by recrystallization of the perchlorate from ethanol. The yields were high (90–95%) in both cases.

Dichlorotetrakis(diethyl phenylphosphonite)technetium(II). This complex was obtained by the following methods.

(i) $(NH_4)_2TcCl_6$ (0.5 g), diethyl phenylphosphonite (6 ml), and ethanol (40 ml) were placed in a three-necked flask fitted with a condenser, inlet and outlet tubes, and a dropping funnel. Dropwise addition of an ethanol suspension of $NaBH_4$, under magnetic stirring, yielded a yellow precipitate. The reaction mixture was then warmed to the boiling point and immediately filtered by vacuum suction. From the resulting clear yellow solution, yellow crystals of $[TcCl_2(C_6H_5P(OC_2H_5)_2)_4]$ were obtained. A further crop of crystals was recovered by concentration, under vacuum, of the mother liquor (yield 75%).

(ii) The red ethanolic solution of the dichlorotetrakis(diethyl phenylphosphonite)technetium(III) cation was permitted to evaporate slowly (ca. 1 week); some yellow crystals were deposited and a further amount of the final product was obtained by concentration of the mother liquor (yield 48%).

Dichlorotetrakis(diethyl phenylphosphonite)technetium(III) Chloride. Dichlorotetrakis(diethyl phenylphosphonite)technetium(II) (0.2 g) from the previous preparation was stirred with 30 ml of concentrated HCl. A crude product, recrystallized from ethanol–pentane, was obtained from the red suspension (yield 92%).

Crystal Data. The compound $C_{40}H_{60}O_8P_4Cl_2Tc$, mol wt 962.7,

Table II. Thermal Parameters ($\text{Å}^2 \times 10^4$) of the Nonhydrogen Atoms[a]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Tc	282 (3)	321 (3)	426 (3)	−1 (2)	12 (2)	0 (3)
Cl(1)	533 (10)	437 (10)	476 (10)	56 (9)	−17 (8)	−41 (9)
Cl(2)	461 (10)	738 (14)	475 (11)	−99 (10)	−10 (8)	12 (10)
PI	338 (9)	370 (10)	455 (10)	−8 (7)	11 (7)	33 (8)
O(1)I	365 (27)	558 (33)	634 (34)	−99 (24)	−77 (23)	65 (27)
C(1)I	622 (53)	854 (69)	502 (48)	−139 (49)	−108 (39)	118 (47)
C(2)I	624 (60)	1050 (86)	996 (79)	−85 (60)	−300 (55)	41 (67)
O(2)I	394 (27)	417 (29)	626 (33)	1 (22)	123 (23)	15 (24)
C(3)I	435 (44)	517 (51)	919 (67)	−4 (39)	145 (43)	−57 (47)
C(4)I	924 (76)	1029 (85)	825 (69)	186 (67)	290 (59)	−150 (65)
C(5)I	333 (37)	489 (47)	645 (53)	−36 (34)	109 (34)	91 (39)
C(6)I	475 (45)	715 (59)	552 (52)	−4 (42)	124 (38)	117 (44)
C(7)I	630 (56)	851 (72)	630 (58)	58 (51)	112 (44)	289 (53)
C(8)I	873 (71)	606 (66)	963 (80)	17 (54)	237 (60)	351 (58)
C(9)I	728 (64)	531 (61)	1160 (90)	−21 (48)	210 (61)	211 (59)
C(10)I	498 (47)	541 (54)	751 (60)	−12 (40)	130 (42)	120 (45)
PII	331 (9)	439 (11)	484 (11)	−12 (8)	22 (8)	−55 (8)
O(1)II	466 (28)	697 (37)	580 (33)	−182 (27)	153 (24)	−153 (28)
C(1)II	882 (67)	1052 (80)	542 (52)	−366 (61)	209 (47)	−347 (53)
C(2)II	993 (79)	1429 (109)	720 (68)	−335 (76)	351 (59)	−124 (69)
O(2)II	367 (27)	497 (32)	852 (40)	12 (24)	−66 (26)	−63 (28)
C(3)II	339 (43)	680 (62)	1431 (93)	24 (41)	−24 (49)	−179 (61)
C(4)II	755 (68)	1461 (114)	1059 (168)	400 (75)	−298 (62)	83 (82)
C(5)II	284 (33)	549 (48)	520 (44)	−17 (32)	−8 (29)	−137 (36)
C(6)II	457 (43)	753 (58)	548 (49)	−63 (42)	−14 (35)	−130 (46)
C(7)II	551 (54)	1047 (81)	611 (58)	−129 (54)	24 (43)	−249 (56)
C(8)II	672 (62)	999 (86)	1012 (83)	−229 (58)	92 (56)	−565 (70)
C(9)II	613 (57)	685 (64)	1115 (86)	−208 (49)	138 (55)	−290 (60)
C(10)II	424 (42)	535 (50)	685 (55)	−66 (37)	74 (37)	−85 (41)
PIII	392 (10)	372 (10)	560 (12)	32 (8)	−3 (8)	7 (9)
O(1)III	836 (40)	505 (33)	621 (36)	154 (29)	94 (30)	140 (27)
C(1)III	996 (76)	787 (73)	775 (72)	271 (60)	164 (58)	193 (58)
C(2)III	1395 (112)	1436 (126)	819 (88)	654 (101)	−272 (78)	403 (91)
O(2)III	446 (28)	348 (28)	886 (38)	−14 (22)	67 (26)	−62 (25)
C(3)III	621 (52)	431 (48)	1117 (67)	−54 (43)	73 (46)	−98 (48)
C(4)III	1045 (90)	666 (79)	1424 (101)	−231 (68)	−477 (76)	−290 (71)
C(5)III	460 (42)	239 (36)	700 (53)	28 (31)	−28 (36)	−89 (34)
C(6)III	520 (47)	467 (46)	673 (58)	49 (38)	−66 (41)	−157 (41)
C(7)III	807 (63)	516 (53)	673 (57)	19 (47)	54 (47)	−114 (44)
C(8)III	531 (54)	739 (64)	932 (74)	56 (48)	127 (50)	−314 (56)
C(9)III	496 (48)	633 (57)	989 (72)	139 (43)	−41 (46)	−255 (52)
C(10)III	456 (46)	567 (52)	722 (57)	190 (40)	−52 (40)	−129 (43)
PIV	366 (9)	324 (10)	509 (11)	20 (8)	19 (8)	−24 (8)
O(1)IV	646 (34)	498 (33)	681 (36)	65 (27)	−74 (28)	−190 (27)
C(1)IV	822 (66)	729 (69)	890 (73)	137 (55)	−158 (55)	−194 (57)
C(2)IV	1332 (108)	2387 (131)	901 (95)	420 (99)	267 (80)	−812 (92)
O(2)IV	461 (28)	332 (27)	858 (37)	5 (22)	155 (25)	57 (25)
C(3)IV	666 (57)	518 (55)	1128 (73)	−44 (45)	88 (51)	215 (50)
C(4)IV	1101 (91)	803 (80)	1160 (92)	−92 (69)	351 (73)	446 (68)
C(5)IV	416 (39)	278 (36)	565 (48)	10 (30)	50 (33)	31 (32)
C(6)IV	486 (42)	464 (44)	507 (47)	89 (34)	43 (34)	93 (35)
C(7)IV	625 (51)	484 (49)	608 (52)	76 (41)	25 (41)	110 (40)
C(8)IV	467 (45)	659 (57)	785 (62)	81 (41)	−63 (41)	150 (47)
C(9)IV	495 (47)	622 (54)	779 (62)	165 (41)	99 (42)	43 (45)
C(10)IV	408 (40)	480 (46)	662 (51)	101 (35)	111 (35)	36 (38)

[a] The anisotropic thermal parameters are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$.

crystallizes in a monoclinic cell with $a = 21.740$ (19),[24] $b = 11.750$ (10), $c = 18.312$ (12) Å; $\beta = 92.92$ (9)°; $U = 4671.6$ Å^3; d_{measd}(by flotation in carbon tetrachloride–benzene) = 1.38 g cm^{-3}, $Z = 4$, d_{calcd} = 1.363 g cm^{-3}; $F(000) = 2004$; space group $P2_1/c$ (C_{2h}^5; No.14[25]),[26] from systematic absences of $k = 2n + 1$ for $\{0k0\}$ and $l = 2n + 1$ for $\{h0l\}$ data. Unit cell and orientation parameters were obtained by a least-squares fit[27] to 27 accurately measured ϑ, χ, ϕ values.

Data Collection and Processing. Data were initially collected with Cu Kα radiation, but a more accurate set was later measured using Mo Kα radiation. A crystal was carefully measured using a micrometer eyepiece, and the crystal faces were identified by means of an optical goniometer mounted on the head of a Siemens four-circle diffractometer (controlled on-line by a Siemens 303 computer). For this crystal the following forms were developed: $\{110\}$, $\{010\}$, $\{111\}$, $\{11\bar{1}\}$. The crystal of dimensions $0.15 \times 0.29 \times 0.44$ mm (7.08×10^{-3} mm^3) was aligned with the c axis within 2° of the spindle axis, and Zr-filtered Mo Kα radiation (λ 0.7107 Å) was used for the collection of data, at room temperature. The crystal was mounted on glass fiber and coated with a clear epoxy cement to prevent air oxidation; the ϑ–2ϑ scan technique, using a "five-value" measuring procedure,[28] a takeoff angle of 4.5°, and a Na(Tl)I scintillation counter were used. A check reflection ($\bar{2}41$) was remeasured every 20 reflections as a monitor of crystal stability and to normalize the intensities to a common basis. Data in the range $3 \leq 2\vartheta \leq 50°$ ($0.037 \leq (\sin \vartheta)/\lambda \leq 0.595$ Å^{-1}) were collected and 8210 independent reflections were measured, of which 2715 were judged unobserved and omitted from subsequent least-squares treatment (a reflection was classified as unobserved if $I/\sigma(I)$ was less than 3.0). The usual $1/Lp$ corrections were applied to the intensities. The linear absorption coefficient for Mo Kα radiation is 6.01 cm^{-1}; data were corrected for absorption[29] and the transmission factors ranged from 0.891 to 0.945.

Health Precautions. Small amounts of technetium (milligram scale) can be handled without serious health hazard since ^{99}Tc is only a soft β^- emitter (0.3 MeV) with a specific activity of 17 μCi/mg. On the gram scale the hazards increase because the bremsstrahlung of the β^- radiation on the glass leads to production of soft x rays. Con-

Table III. Bond Distances (Å) and Angles (deg) of $[TcCl_2(C_6H_5P(OC_2H_5)_2)_4]$, with Standard Deviations in Parentheses[a]

(a) In the Inner Coordination Sphere of Technetium

Tc–Cl(1)	2.42 (1)	Cl(1)–Tc–Cl(2)	178.8 (1)	Cl(2)–Tc–PIII	99.6 (1)
Tc–Cl(2)	2.41 (1)	Cl(1)–Tc–PI	98.2 (1)	Cl(2)–Tc–PIV	96.3 (1)
Tc–PI	2.41 (1)	Cl(1)–Tc–PII	97.5 (1)	PI–Tc–PIII	90.5 (1)
Tc–PII	2.41 (1)	Cl(1)–Tc–PIII	81.6 (1)	PI–Tc–PIV	91.7 (1)
Tc–PIII	2.42 (1)	Cl(1)–Tc–PIV	82.5 (1)	PII–Tc–PIII	91.3 (1)
Tc–PIV	2.40 (1)	Cl(2)–Tc–PI	81.9 (1)	PII–Tc–PIV	90.8 (1)
		Cl(2)–Tc–PII	82.4 (1)	PI–Tc–PII	164.2 (1)
				PIII–Tc–PIV	164.1 (1)

(b) In the Phosphonite Ligands

Bond	Ligand I	Ligand II	Ligand III	Ligand IV
P–O(1)	1.60 (1)	1.60 (1)	1.60 (1)	1.60 (1)
P–O(2)	1.60 (1)	1.61 (1)	1.61 (1)	1.61 (1)
P–C(5)	1.83 (1)	1.84 (1)	1.83 (1)	1.84 (1)
O(1)–C(1)	1.44 (2)	1.43 (2)	1.40 (2)	1.41 (2)
O(2)–C(3)	1.45 (2)	1.45 (2)	1.44 (2)	1.44 (2)
C(1)–C(2)	1.49 (2)	1.42 (3)	1.44 (3)	1.41 (3)
C(3)–C(4)	1.49 (2)	1.50 (3)	1.49 (3)	1.48 (3)
C(5)–C(6)	1.41 (2)	1.37 (2)	1.39 (2)	1.39 (2)
C(5)–C(10)	1.39 (2)	1.41 (2)	1.39 (2)	1.39 (2)
C(6)–C(7)	1.39 (2)	1.39 (2)	1.38 (2)	1.37 (2)
C(7)–C(8)	1.36 (2)	1.37 (3)	1.38 (2)	1.37 (2)
C(8)–C(9)	1.38 (2)	1.38 (3)	1.36 (2)	1.38 (2)
C(9)–C(10)	1.39 (2)	1.38 (2)	1.38 (2)	1.39 (2)

Angle	Ligand I	Ligand II	Ligand III	Ligand IV
Tc–P–O(1)	125.3 (3)	125.5 (3)	124.2 (3)	124.3 (3)
Tc–P–O(2)	108.9 (3)	108.5 (3)	107.7 (3)	108.0 (3)
Tc–P–C(5)	118.3 (3)	119.2 (4)	119.9 (4)	119.6 (4)
O(1)–P–O(2)	104.2 (4)	104.4 (4)	105.2 (4)	105.5 (4)
O(1)–P–C(5)	94.9 (5)	95.3 (5)	95.5 (5)	94.7 (4)
O(2)–P–C(5)	102.1 (5)	100.5 (5)	101.4 (5)	101.9 (5)
P–O(1)–C(1)	123.3 (7)	124.8 (7)	128.4 (9)	127.8 (8)
P–O(2)–C(3)	123.5 (8)	123.1 (7)	122.9 (7)	122.5 (8)
P–C(5)–C(6)	120.4 (9)	120.7 (9)	121.5 (9)	121.0 (8)
P–C(5)–C(10)	120.8 (8)	119.3 (8)	119.8 (9)	120.2 (8)
O(1)–C(1)–C(2)	110.3 (11)	111.6 (12)	113.6 (14)	112.0 (13)
O(2)–C(3)–C(4)	109.5 (10)	109.1 (12)	109.8 (12)	110.1 (12)
C(6)–C(5)–C(10)	118.6 (10)	119.9 (11)	118.7 (11)	118.8 (9)
C(5)–C(6)–C(7)	120.3 (12)	120.2 (12)	120.0 (12)	120.3 (10)
C(6)–C(7)–C(8)	119.9 (13)	120.4 (13)	120.5 (13)	121.5 (11)
C(7)–C(8)–C(9)	120.7 (14)	119.7 (14)	119.8 (14)	118.8 (12)
C(8)–C(9)–C(10)	120.3 (14)	121.1 (14)	120.5 (14)	120.8 (12)
C(5)–C(10)–C(9)	120.1 (12)	118.6 (12)	120.4 (12)	119.8 (11)

[a] Taking into account accuracy of cell parameters

sequently larger quantities of technetium were handled in high-suction boxes equipped with double gloves and a Plexiglas wall. The other manipulations were carried out in a fume cupboard with gloves.

Structure Determination. The solution of the crystal structure was accomplished by conventional heavy-atom techniques, using the Cu Kα radiation data. The Mo Kα data set was later used in the refinement. All atoms were assigned anisotropic thermal parameters, and the phenyl and methylene hydrogen atoms (C–H = 0.95 Å) were included in fixed positions. Six cycles of least-squares refinement were carried out using unit weights yielding a residual index R of 0.053, while the weighted R_w, $[\sum w(K|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, was 0.061. In the last cycle the largest shifts were about half the corresponding standard deviations and there was no evidence for extinction effects. At this point, a difference Fourier map was calculated using only those reflections for which $(\sin\vartheta)/\lambda < 0.35$ Å^{-1} in order to improve the resolution of the missing hydrogen atoms.[30] All hydrogen atoms were clearly visible on this map (0.3–0.6 e Å^{-3}) with the methyl hydrogen atoms staggered with respect to the methylene hydrogen atoms, except those at C(4)III and C(2)IV which were closer to an eclipsed situation. The positional parameters for these methyl hydrogen atoms were included in a structure factor calculation with their isotropic thermal parameters set at 5.0 Å^2 and the usual R factor decreased to 0.051. These hydrogen atom positions were then considered as final. Scattering factors for neutral atoms were used.[31] The real and imaginary parts[31] of the anomalous scattering of Tc, Cl, and P atoms were included. The function minimized in least-squares refinement was $\sum w(K|F_o| - |F_c|)^2$ where $w = 1$ for all reflections.

The final atomic coordinates, together with their estimated standard deviations, calculated by inverting the full-matrix normal equations, are listed in Table I; the thermal parameters are given in Table II.

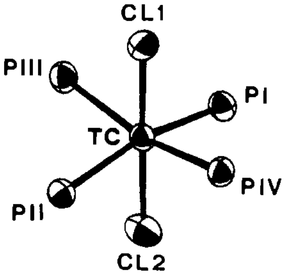

Figure 1. Perspective drawing of the inner coordination sphere of $[TcCl_2(C_6H_5P(OC_2H_5)_2)_4]$.

A table of observed and calculated structure factor amplitudes is available.[32] The atom numbering system and the configuration of the molecule are illustrated in Figures 1 and 2, while bond lengths and bond angles with their standard deviations are given in Table III. Equations of the principal planes, the deviations of atoms therefrom, and selected intramolecular distances are listed in Table IV.

Calculations were performed on the CDC 6600-7600 computer at the Consorzio Interuniversitario Italia Nord-Orientale, Casalecchio (Bologna), using the programs of Stewart et al.[33]

Results and Discussion

The $[TcCl_2L_4]Y$ and $[TcCl_2L_4]$ ($L = C_6H_5P(OC_2H_5)_2$; $Y^- = Cl^-$, ClO_4^-, $B(C_6H_5)_4^-$) complexes were obtained by refluxing ethanol solutions of $(NH_4)_2TcCl_6$ in the presence of an excess of diethyl phenylphosphonite. The observed re-

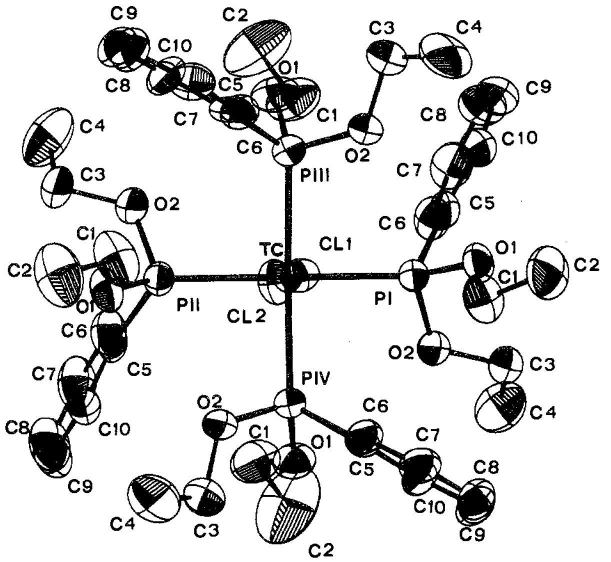

Figure 2. Molecular configuration of [$TcCl_2(C_6H_5P(OC_2H_5)_2)_4$] projected on the *ac* plane. For clarity the hydrogen atoms are omitted. The numbering system used is also shown. The drawings were obtained using the program ORTEP and the thermal vibration ellipsoids are scaled to enclose 50% probability.

Scheme I

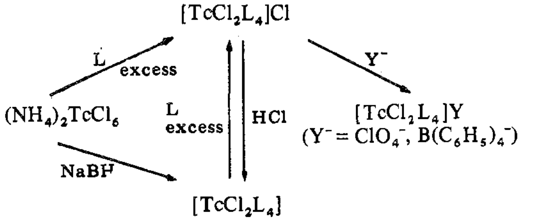

Table IV. Molecular Geometry

(a) Least-Squares Planes and Equations of Planes in Direct Space Given by $Px + Qy + Rz = S^a$

Plane	Atoms	*P*	*Q*	*R*	*S*
1	Tc, PI, PII, PIII, PIV	2.134	0.285	18.103	4.911
2	Tc, Cl(1), Cl(2), PI, PII	−4.183	11.527	−0.250	−0.364
3	Tc, Cl(1), Cl(2), PIII, PIV	21.276	2.137	−2.663	4.874
4	C(5)I–C(10)I	20.881	−2.995	−2.939	6.664
5	C(5)II–C(10)II	20.678	−3.377	−2.949	2.100
6	C(5)III–C(10)III	7.150	11.080	−1.254	4.366
7	C(5)IV–C(10)IV	7.175	11.053	−1.744	−0.012

Deviations (Å) of Atoms from Planes

Plane 1	Tc, 0.0; PI, −0.33; PII, −0.33; PIII, 0.33; PIV, 0.33; Cl(1), 2.41; Cl(2), −2.41; O(1)I, 0.82; O(2)I, −1.03; O(1)II, 0.81; O(2)II, −1.03; O(1)III, −0.84; O(2)III, 1.11; O(1)IV, −0.84; O(2)IV, 1.06
Plane 2	Tc, 0.0; Cl(1), −0.02; Cl(2), −0.02; PI, 0.02; PII, 0.02; PIII, 2.40; PIV, −2.38; O(1)I, 0.21; O(2)I, −1.34; O(1)II, −0.21; O(2)II, 1.42
Plane 3	Tc, 0.0; Cl(1), 0.0; Cl(2), 0.0; PIII, 0.0; PIV, 0.0; PI, 2.38; PII, −2.38; O(1)III, −0.13; O(2)III, 1.36; O(1)IV, 0.19; O(2)IV, −1.37
Plane 4	C(5)I, 0.0; C(6)I, 0.0; C(7)I, 0.01; C(8)I, −0.01; C(9)I, 0.0; C(10)I, 0.0; PI, −0.14; O(1)I, 0.73; O(2)I, 0.86
Plane 5	C(5)II, 0.01; C(6)II, −0.01; C(7)II, 0.0; C(8)II, 0.01; C(9)II, 0.0; C(10)II, 0.0; PII, 0.08; O(1)II, −0.82; O(2)II, −0.91
Plane 6	C(5)III, −0.01; C(6)III, 0.0; C(7)III, 0.01; C(8)III, −0.01; C(9)III, 0.0; C(10)III, 0.01; PIII, −0.05; O(1)III, 0.81; O(2)III, 0.96
Plane 7	C(5)IV, 0.0; C(6)IV, 0.0; C(7)IV, 0.0; C(8)IV, 0.01; C(9)IV, 0.0; C(10)IV, 0.0; PIV, 0.06; O(1)IV, −0.74; O(2)IV, −0.99

(b) Dihedral Angles between the Planes

Planes	Angle, deg	Planes	Angle, deg	Planes	Angle, deg	Planes	Angle, deg
1–2	88.9	1–6	89.8	4–5	1.9	5–6	87.3
1–3	89.7	1–7	88.7	4–6	85.3	5–7	87.0
1–4	88.7	2–3	89.6	4–7	85.1	6–7	1.5
1–5	88.5						

(c) Selected Intramolecular Distances Less Than 3.4 Å

Tc–O(2)I	3.30	Cl(2)–C(6)I	3.24	O(2)II–O(1)III	3.41
Tc–O(2)II	3.29	Cl(2)–C(6)II	3.25	O(2)II–C(6)II	3.01
Tc–O(2)III	3.29	PI–O(2)III	3.28	O(2)II–C(10)III	3.12
Tc–O(2)IV	3.28	PII–O(2)IV	3.26	O(1)III–C(10)III	2.81
Cl(1)–PIII	3.16	PIII–O(2)II	3.29	O(2)III–C(10)I	3.12
Cl(1)–PIV	3.18	PIV–O(2)I	3.31	O(2)III–C(6)III	3.05
Cl(1)–O(2)III	3.35	O(1)I–O(2)III	3.32	O(1)IV–C(10)IV	2.80
Cl(1)–O(2)IV	3.40	O(1)I–C(10)I	2.84	O(2)IV–C(10)II	3.14
Cl(1)–C(6)III	3.33	O(2)I–O(1)IV	3.38	O(2)IV–C(6)IV	3.08
Cl(1)–C(6)IV	3.30	O(2)I–C(6)I	3.07	C(3)I–C(6)I	3.38
Cl(2)–PI	3.16	O(2)I–C(10)IV	3.17	C(3)II–C(6)II	3.36
Cl(2)–PII	3.17	O(1)II–O(2)IV	3.31	C(3)III–C(6)III	3.37
Cl(2)–O(2)I	3.39	O(1)II–C(10)II	2.83	C(3)IV–C(6)IV	3.38

(d) Selected Intermolecular Distances Less Than 3.8 Å^b

C(3)III- - -C(3)IV^{A}	3.52	C(10)I- - -C(8)IV^{B}	3.74
C(10)I- - -C(9)IV^{B}	3.59	C(9)I- - -C(8)IV^{B}	3.74
C(7)III- - -Cl(2)^{C}	3.65	C(2)I- - -C(7)I^{C}	3.74
Cl(1)- - -C(7)I^{C}	3.69	C(2)I- - -C(4)I^{B}	3.75
O(1)I- - -C(9)IV^{B}	3.72		

[a] x, y, and z are in fractional unit-cell coordinates. [b] Superscripts refer to molecules in the following equivalent positions relative to the reference molecule at x, y, z: (A) $x, 1 + y, z$; (B) $1 - x, {}^1/_2 + y, {}^1/_2 - z$; (C) $x, {}^1/_2 - y, {}^1/_2 + z$.

duction of technetium(IV) to technetium(III) and -(II) further supports the previously reported[12-16] ability of the phosphonite ligand to reduce transition metals and to stabilize their low oxidation states, by delocalization of electron density from the metal to the phosphonite ligands. The rate of formation of the technetium(II) complex, which is obtained slowly by the above method, can be increased by reduction of the hexachlorotechnetate(IV) cation with $NaBH_4$ in the presence of the phosphonite ligand. Whereas solid [$TcCl_2L_4$]Cl is obtained by treating the Tc(II) complex with hydrochloric acid, the perchlorate and tetraphenylborate derivatives can be precipitated by adding the corresponding salt to the [$TcCl_2L_4$]$^+$ cation in ethanol solution as shown in Scheme I. Solutions of the technetium(III) complexes in polar organic solvents such as ethanol, acetone, dichloromethane, nitromethane, etc., are stable in the presence of free phosphonite. However, under the same conditions, [$TcCl_2L_4$] undergoes slow decomposition with oxidation to the technetium(III) complex, the rate of which is only decreased by the presence of free diethyl phenylphosphonite. Neutral [$TcCl_2L_4$] is a nonelectrolyte, but the conductivity measurements (Table V) of 10^{-3} M nitromethane solutions of [$TcCl_2L_4$]Y (Y^- = Cl^-, ClO_4^-, $B(C_6H_5)_4^-$) at 25 °C indicate that the complexes are 1:1 electrolytes. The measured magnetic moments are also in agreement with the formula proposed for the technetium(III) derivatives, the values being very close to that reported by Fergusson et al.[2,3] for the [$TcCl_2D_2$]Cl (D = 1,2-bis(diphenylphosphino)ethane) complex but lower than the spin-only value for an nd^4 configuration in octahedral symmetry. This is a usual feature of a d^n configuration with $n < 5$ owing the orbital coupling. The magnetic moment found for the [$TcCl_2L_4$] complex in benzene solution is 1.4 μ_B. Again this value is lower than that corresponding to one unpaired electron, but in this case partial decomposition of the complex seems to be responsible for the difference. However these results are not incompatible with the proposed formula, which is substantiated also by other properties. The presence of the phosphonite ligands is supported by the IR spectra which show characteristic absorption bands. Absorptions at 1030, 634 cm^{-1} and at 3050, 1575 cm^{-1} can be observed in the IR spectra of

Table V. Some Properties of $[TcCl_2L_4]$ and $[TcCl_2L_4]^+$ Complexes

Oxidn states	Compd	Mp, °C	Color	% Cl		% Tc		μ_{eff},[a] μ_B	Λ_{eq},[b] mho mol^{-1} cm^2	ν_{Tc-Cl}, cm^{-1}
				Calcd	Found	Calcd	Found			
III	$[TcCl_2L_4]Cl$[c]	96	Red	10.66	11.54	9.92	10.12	2.6	80.3	350 s
III	$[TcCl_2L_4]BPh_4$	104	Red	5.53	5.38	7.73		2.7	76.1	348 s
III	$[TcCl_2L_4]ClO_4$	115 dec	Red	6.68[d]	6.32	9.32		2.7	75.9	346 s
II	$[TcCl_2L_4]$	86	Yellow	7.37	7.13	10.29	10.93	1.4[e]	Insol	306 m

[a] Magnetic moment at 306 K. [b] Conductivity of 10^{-3} M nitromethane solutions. [c] L = diethyl phenylphosphonite. [d] The ClO_4^- chlorine was not included because of the analytical method used (see Experimental Section). [e] With decomposition.

Table VI. Electronic Spectra

Compd	Solvent	λ_{max}, Å[a]
$[TcCl_2D_2]$[b]	DMF	4210 (2980), 3180 (5050)
$[TcCl_2D_2]Cl$[b]	Acetone	4820 (1600), 4480 (1230)
$[TcCl_2L_4]$[c]	Penthane	4380 (2050), 3620 sh
$[TcCl_2L_4]Cl$[c]	Ethanol	4940 (2500), 3620 sh

[a] Extinction coefficients in parentheses. [b] Complexes synthesized by Fergusson et al.[2] D = 1,2-bis(diphenylphosphino)ethane. [c] L = diethyl phenylphosphonite.

the $[TcCl_2L_4]Y$ (Y^- = ClO_4^-, $B(C_6H_5)_4^-$) due to noncoordinated anions.[34] The band at 306 cm^{-1} for the $[TcCl_2L_4]$ complex can be assigned to the asymmetric stretching of the trans Tc–Cl bands. The corresponding absorption for the $[TcCl_2L_4]^+$ cations falls in the 346–350-cm^{-1} range. Similar frequencies, at 304 cm^{-1} for $[TcCl_2D_2]$ (D = *o*-phenylenebis(dimethylarsine)) and at 335, 343 cm^{-1} for $[TcCl_2D_2]^+$, have been reported previously.[35] The electronic spectra show bands at 4950 (2500), 3620 (sh) Å and at 4390 (2050), 3600 (sh) Å for the $[TcCl_2L_4]^+$ and the $[TcCl_2L_4]$ complexes, respectively. These absorptions, compared with the data for the analogous complexes with 1,2-bis(diphenylphosphino)ethane,[3] reported in Table VI, may be assigned to the intraligand or charge-transfer transitions.

The x-ray structure analysis confirms that the conformation of the ligands around the technetium atom is that of a distorted octahedron, with four phosphorus atoms in the equatorial plane and two chlorine atoms in the apical positions, i.e., mutually trans (Figures 1 and 2).

The distances of the ligand donor atoms from the mean equatorial plane (PI and PII (trans to it), −0.33 Å; PIII and PIV (trans to it), +0.33 Å) may be taken as a measure of the distortion from the ideal octahedral geometry (Table IV, plane 1). The dihedral angle between planes 2 and 3 (ca. 90°) (Table IVb) and bond distances and angles (Table III) suggest that such distortion is of the type octahedron → tetrahedron; in fact, the two P–Tc–P angles (trans phosphorus) of 164.2° (instead of 180° for a regular octahedron) are explained by a movement of a pair of two trans phosphorus atoms from one side and of the other pair from the opposite side with respect to the equatorial plane, but remaining still perfectly contained in planes 2 and 3 (Table IVa); then the phosphorus atoms are out of the equatorial plane by an alternate step arrangement, with the technetium atom in the middle. The idealized molecular symmetry of the coordination polyhedron is $\bar{4}2m$, a subgroup of $4/mmm$ (D_{4h}), the highest symmetry allowed without distortion. The idealized S_4 ($\bar{4}$) axis passes through the Cl(1), Tc, and Cl(2) atoms and the C_2 (2) axes are contained in the equatorial plane and pass midway between the cis phosphorus atoms. The inclusion of the whole molecule destroys the symmetry elements, but not completely; in fact, the S_4 ($\bar{4}$) axis is still approximately maintained. This feature has not been found in a similar complex *trans*-$[RuH_2(PPh(OEt)_2)_4]$,[36] where an idealized S_4 ($\bar{4}$) axis, passing through the trans hydride atoms, is present only for the inner coordination of Ru atom, since this molecule has space group imposed C_2 (2) point symmetry, not coincident with the S_4 ($\bar{4}$) axis, between the phosphonite ligands.

The octahedral → tetrahedral distortion is the result of packing requirements of the bulky ligands.[36] The magnitude of the distortion is probably less in $[TcCl_2(PPh(OEt)_2)_4]$ than in *trans*-$[RuH_2(PPh(OEt)_2)_4]$ (P–Tc–P(trans) = 164.2° and P–Ru–P(trans) = 161.4°; distances of the P atoms from the best equatorial plane are 0.33 Å for the Tc complex and 0.37 Å for the Ru complex) and the reason seems to be the M–P distance, which is larger for Tc–P (2.41 Å) than for Ru–P (2.27 Å). Moreover, the TcP_4 skeleton assumes a flattened stereochemistry similar to that of ReP_4 in $[ReCl(N_2)(PPhMe_2)_4]$,[37] $[(PMe_2Ph)_4ClReN_2MoCl_4(OMe)]$,[38] and $[ReH_3(PPh_2CH_2CH_2Ph_2P)_2]$;[39] in this last case the binary axis, subgroup of $\bar{4}$, is coincident with a crystallographic axis. The observed Tc–P distances (2.41 Å) are short when compared with those of the trans phosphine ligands in the complex *mer*-$[TcCl_3(PPhMe_2)_3]$[13b] (2.47 Å) but are similar to that observed in the trans phosphonite complex *cis*-$[Tc(CO)_2(PPh(OEt)_2)_4]$.[13a] The shortening of the Tc–P distance is ascribed to a rather substantial Tc–P π-type interaction, because diethyl phenylphosphonite is a better π acceptor than the phosphine ligand.[14]

The standard Tc–Cl distance for the linear Cl–Tc–Cl fragment is expected to be 2.39 Å (see Table II of ref 40); this is similar to our reported Tc–Cl bond length of 2.41 Å. The Tc–Cl distance is not strictly comparable to those found in $[K_2TcCl_6]$ (2.35 Å),[41] $[TcCl_4]_n$ (2.24–2.49 Å),[42] and $[TcCl_8]^{3-}$ (2.36 Å),[12] owing to the different bonding situation. At first sight, it seems possible to compare our data with those of the compound *trans*-$[MnCl_2(o\text{-}C_6H_4(PMe_2)_2)_2]$,[43] but the Mn–Cl (2.502 Å) and Mn–P (2.625 Å) distances are much longer than ours. This is because the Mn(II) complex is high spin, while Tc(II) is a low-spin compound, allowing a different bonding situation and hybridization.[44]

Parameters reported for the phosphonite ligands in Table III are similar to those in other $PhP(OEt)_2$ derivatives; the mean C–C distances in the ethoxy group (1.48 Å) and the relatively high thermal parameters for C(2) and C(4) atoms parallel similar situations for this ligand.[13a,36] The intermolecular contacts are of the normal van der Waals type as is usual for this kind of compounds.

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Registry No. $[TcCl_2(C_6H_5P(OC_2H_5)_2)_4]Cl$, 61202-78-6; $[TcCl_2(C_6H_5P(OC_2H_5)_2)_4]BPh_4$, 61202-79-7; $[TcCl_2(C_6H_5P(OC_2H_5)_2)_4]ClO_4$, 55671-21-1; $TcCl_2(C_6H_5P(OC_2H_5)_2)_4$, 53042-18-5; $(NH_4)_2TcCl_6$, 18717-26-5.

Supplementary Material Available: Listing of structure factor amplitudes (31 pages). Ordering information is given on any current masthead page.

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Crystal Structure of $[(NH_3)_5RuSSRu(NH_3)_5]Cl_4\cdot 2H_2O$. A Structural Trans Effect and Evidence for a Supersulfide S_2^- Bridge

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The structure of $[(NH_3)_5RuSSRu(NH_3)_5]Cl_4\cdot 2H_2O$ has been determined using single-crystal x-ray diffraction. The crystal is of the orthorhombic class, space group *Pnma*, with unit cell constants $a = 11.673$ (2), $b = 7.216$ (1), and $c = 25.782$ (4) Å. The reflection data measured on an automated diffractometer have been refined by least-squares to $R_1 = 0.024$ and $R_2 = 0.033$. The dimeric cation contains two pentaammineruthenium moieties joined in a rigorously trans conformation by a two sulfur atom bridge. Evidence is adduced for the formulation of the bridging species as a supersulfide ion, S_2^-. A trans effect of 0.058 (9) Å is observed with the trans Ru–N bonds lengthened relative to the cis Ru–N bonds.

Introduction

Taube and co-workers[2] have reported the synthesis and characterization of a dimeric cation which they postulate to be $[(NH_3)_5RuSSRu(NH_3)_5]^{4+}$, two pentaammineruthenium groups joined by a two sulfur atom bridge. The electronic structure of the RuSSRu core may be described as two ruthenium(II) atoms bridged by a singlet disulfur, two ruthenium(III) atoms bridged by a disulfide ion, S_2^{2-}, one ruthenium(III) and one ruthenium(II) atom bridged by a supersulfide ion, S_2^-, or some hybrid combination of these, where each formulation is expected to lead to a rather different structure. Siebert and Thym[3] have reported the synthesis of $[(CN)_5CoSSCo(CN)_5]^{6-}$ and also proposed a two sulfur atom bridge. Recently, Sykes[4] and co-workers have described the preparation of $[(H_2O)_5CrSSCr(H_2O)_5]^{4+}$. In an effort to further characterize the geometrical and electronic structures of this class of complexes and also to examine whether the coordinated sulfur atom of the bridge causes a structural trans effect similar to those we have investigated in $[(NH_3)_5CoX]^{n+}$ complexes,[5] we have determined the single-crystal structure of $[(NH_3)_5RuSSRu(NH_3)_5]Cl_4\cdot 2H_2O$ and report it here.

Experimental Section

Preparation and Crystallization of $[(NH_3)_5RuSSRu(NH_3)_5]Cl_4\cdot 2H_2O$, I. The trans chloro complex $[Cl(NH_3)_4RuSSRu(NH_3)_4Cl]Cl_2$, prepared according to method 2 of Brulet, Isied, and Taube,[2,6] was converted to I by warming in a solution of 3 N NH_3 and 0.6 N NH_4Cl. Solid was obtained on addition of ethanol with sufficient aqueous ammonia added to give an indication of pH ~9 on test paper. Recrystallization of I was effected by dissolving the solid in a solution of 3 N NH_3 and 0.6 N NH_4Cl at room temperature and then adding ethanol/NH_3 solution. Some difficulty was encountered in growing crystals suitable for x-ray diffraction. If crystallization was rapid, the resultant crystals were too small; if crystallization took more than 1 day, decomposition took place and the crystals were of poor quality. The visible–UV absorption spectrum of I dissolved in 3 N NH_3/0.6 N NH_4Cl and measured on a Cary 14 spectrophotometer is essentially the same as that reported previously.

The IR spectrum (Nujol mull, KBr plates, Perkin-Elmer 337) exhibits a relatively sharp water stretching band at 3400 cm^{-1}, several ill-defined N–H stretches between 3270 and 3130 cm^{-1}, and bands at 1610, 1290, 1280, 1250, 1235, and 790 cm^{-1} in close parallel to those for a sample of $[(NH_3)_5RuS]_2Br_4$ provided by C. Kuehn and H. Taube. An additional band was observed at 1265 cm^{-1} for I. The Raman spectrum of a crystalline sample of I was run by L. J. Basile