Carbonyltrichlorotris(dimethylphenylphosphine)technetium–Ethanol (1/1), The First Seven-co-ordinate Complex of Technetium; Position of this Molecule in the C_{3v} Family

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The preparation and the crystal and molecular structure of the title complex are reported. The co-ordination polyhedron is that of a distorted capped octahedron (C_{3v} symmetry). The technetium atom is seven-co-ordinate and bonded to three phosphine ligands (capped face), three chlorine ligands (uncapped face), and to the carbonyl group, which occupies the unique capping position. Crystals are monoclinic, space group $P2_1/c$, with cell dimensions a = 11.732(9), b = 11.807(9), c = 23.588(12) Å, and β = 103.42(8)°. The structure has been refined by least squares to a conventional R of 0.093 for 1 794 observed reflections. Metal–ligand bond lengths are: Tc–CO 1.86(2), Tc–Cl 2.48(1), and Tc–P 2.44(1) Å. Seven-co-ordinate complexes are briefly reviewed; in particular, a description of C_{3v} symmetry and its distortions has been developed in terms of repulsion theory and the angular-overlap model.

DURING our studies of technetium chemistry [1-4] the first seven-co-ordinate complex of technetium, $[TcCl_3(CO)(PMe_2Ph)_3]\cdot EtOH$ of C_{3v} symmetry, was prepared. In view of the paucity of data on seven-co-ordination, it seemed interesting to determine the detailed geometry of this complex in an attempt to understand the various factors which dictate the arrangement of the ligands around the central metal atom. The relative importance of these factors, such as the steric and electronic requirements of the ligands, the electronic configuration of the metal atom, and even the crystal packing energy, is not well understood. Thus, complexes containing seven ligands have been re-examined and the technetium complex prompted us to explore complexes of approximately C_{3v} symmetry. Many structural studies have indicated C_{3v} symmetry and provide information

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[1] M. Biagini Cingi, D. A. Clemente, L. Magon, and U. Mazzi, *Inorg. Chim. Acta*, 1975, **13**, 47.

[2] G. Bandoli, D. A. Clemente, and U. Mazzi, *J.C.S. Dalton*, 1976, 125.

[3] U. Mazzi, D. A. Clemente, G. Bandoli, L. Magon, and A. A. Orio, *Inorg. Chem.*, 1977, **16**, 1042.

[4] G. Bandoli, D. A. Clemente, and U. Mazzi, *J.C.S. Dalton*, 1977, 1837.

which suggests that the capped octahedron is a possible associative intermediate in octahedral substitution reactions.[5] The technetium complex has provided an opportunity of using the angular-overlap model (a.o.m.),[6] applied so satisfactorily to binary transition-metal complexes having other geometries,[7] to provide criteria for the choice of geometry in complexes containing seven atoms or groups attached to the central metal atom.

EXPERIMENTAL

Preparation of Carbonyltrichlorotris(dimethylphenylphosphine)technetium–Ethanol (1/1).—Carbon monoxide (1 atm) * was passed through a boiling solution of *mer*-trichlorotris(dimethylphenylphosphine)technetium(III) [2] (0.5 g) in ethanol (30 cm^3) for 7 h. The yellow-orange solution became pale yellow. Evaporation of the solvent and recrystallization of the residue from hot ethanol gave pale yellow plates (0.28 g, 50%) suitable for *X*-ray work. This is the most convenient route for preparation of complexes of the type [ReX$_3$(CO)(PMe$_2$Ph)$_3$] (X = Cl or Br).[8]

Crystal Data.—$C_{25}H_{33}Cl_3OP_3Tc\cdot C_2H_5OH$, $M = 693.8$, Monoclinic, $a = 11.732(9)$, $b = 11.807(9)$, $c = 23.588(12)$ Å, $\beta = 103.42(8)°$, $U = 3\,178.2$, D_m (by flotation in CCl$_4$–C$_6$H$_6$) $= 1.44$, $Z = 4$, $D_c = 1.45$ g cm^{-3}, $F(000) = 1\,424$. Space group $P2_1/c$ (C^5_{2h}, no. 14),[9] from systematic absences, $0k0$ for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$. Unit-cell and orientation parameters were obtained by a least-squares fit [10] to 27 accurately measured θ,χ,ϕ values. Mo-K_α radiation, $\lambda = 0.710\,7$ Å, μ(Mo-K_α) $= 8.7$ cm^{-1}.

Measurements.—Intensity data were collected for a crystal of dimensions *ca.* $0.16 \times 0.28 \times 0.07$ mm mounted on a glass fibre and coated with a clear non-crystalline epoxy cement to prevent decomposition in air. The b axis of the crystal was approximately coincident with the ϕ axis of a Siemens on-line automatic four-circle diffractometer. Mo-K_α radiation at a take-off angle of 4.5°, a Zr-β filter, and a Na(Tl)I scintillation counter were used. 5 589 Independent reflections ($2\theta < 50°$) were then quickly measured by use of the θ—2θ scan technique with the five-value measuring procedure.[11] 1 794 Reflections having $I > 3\sigma(I)$ were used in the subsequent calculations. The net count of the 216 reflection, monitored throughout, decreased by *ca.* 21% during data collection (*ca.* 15 d). The data were adjusted to a common arbitrary scale using the reference reflection, and Lorentz and polarization corrections were applied. An absorption correction [3] was made according to the *m*-points Gaussian-integration formula; the 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 the diffractometer. The following forms were developed: {100}, {001}, {101}, and {010}. The transmission factors ranged from 0.882 to 0.943.

Solution and Refinement of the Structure.—An unsharpened three-dimensional Patterson map revealed the positions of the technetium atoms, refinement of which gave R 0.35. The chlorine and the phosphorus atoms were located from the resulting difference-Fourier synthesis. Further refinement (with unit weight assigned to each reflection) including these positions reduced R to 0.24, and the positions of the remaining non-hydrogen atoms were found from a subsequent difference synthesis. Four cycles of block-diagonal least-squares refinement of the parameters, with only the 'inner core' anisotropic, lowered R to 0.13. The subsequent difference map showed three peaks higher than background (1.7, 1.9, and 2.1 eÅ^{-3}) which were attributed on a geometrical basis to an ethanol molecule. At this point we became aware of the paper of Manojlović-Muir [12] concerning the structure of [MoCl$_4$(PMe$_2$Ph)$_3$]·EtOH, which is isomorphous and isostructural with our complex and exhibits a similar difficulty for the EtOH molecule. Three cycles of full-matrix least-squares refinement, including the ethanol molecule, lowered R to 0.093. The function minimized in the refinement was $\Sigma w(|kF_o| - |F_c|)^2$, where k is the overall scale factor, and the weighting scheme used was the reciprocal of the best polynomial fitting of ΔF^2 as a function of $|F_o|$; the program PESO used for this step has been described elsewhere.[2,13] One more cycle of full-matrix least squares was accomplished, using $w = 1$ for all the reflections having normalized standard deviations. In all the computations allowance was made for anomalous dispersion; atomic-scattering factors were taken from ref. 14, and the imaginary part of the anomalous dispersion for technetium was taken from ref. 15. A final difference-Fourier map showed two symmetrically disposed peaks around the technetium atom, 1 Å apart with a height of 0.85 eÅ^{-3}, but no other peaks of any importance.

Final positional and thermal parameters, with estimated standard deviations, the structure factors, and details of the least-squares planes and intra- and inter-molecular distances are deposited as Supplementary Publication No. SUP 22157 (27 pp.).†

The atom-numbering system and the configuration of the molecule are illustrated in Figures 1 and 2, and the bond lengths and angles with their standard deviations are given in Tables 1 and 2. The solution and refinement of the structure were carried out by use of the '*X*-Ray '72' program system [16] on the CDC 6 600—7 600 computer at the Consorzio Interuniversitario dell'Italia Nord-Orientale, Casalecchio di Reno, Bologna; other local programs, PESO [13] for the weighting scheme, ABSORB [3] for the absorption correction, and ANGULAR for the angular-overlap calculations, were written by one of us (D. A. C.).

Reliability of the Structure Determination.—The R factor reached in this structure determination is not very low, but we think that the molecular positional parameters are

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* Throughout this paper: 1 atm = 101 325 Pa; 1 eV ≈ 1.60×10^{-19} J.

† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[5] R. D. Archer, *Co-ordination Chem. Rev.*, 1969, **4**, 243 and refs. therein; R. A. D. Wentworth, *ibid.*, 1972—1973, **9**, 171 and refs. therein.

[6] C. E. Schäffer and C. K. Jørgensen, *Mol. Phys.*, 1964, **9**, 401; C. E. Schäffer, *Theor. Chim. Acta*, 1966, **4**, 166.

[7] J. K. Burdett, *J.C.S. Faraday II*, 1974, 1599; *Inorg. Chem.*, 1975, **14**, 375, 931.

[8] P. G. Douglas and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 1491.

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[10] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1967, **22**, 457.

[11] G. Bandoli, C. Panattoni, D. A. Clemente, E. Tondello, A. Dondoni, and A. Mangini, *J. Chem. Soc.* (*B*), 1971, 1407.

[12] L. Manojlović-Muir, *J.C.S. Dalton*, 1976, 192.

[13] G. Bandoli and D. A. Clemente, *J.C.S. Perkin II*, 1976, 413.

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[15] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

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well determined; we are especially interested in the ' inner co-ordination core ' of the technetium, where the errors are surely lower. A systematic comparison with other similar structures (refs. 1—4 and Table 4) gives good agreement (see Discussion section). The reasons for the relatively high R factor are the presence of some disorder or partial occupancy of the EtOH molecule, and the changes in the crystal during data collection. The use of several different crystals did not result in any substantial difference in the positional co-ordinates of the heavy atoms (Tc, Cl, and P).

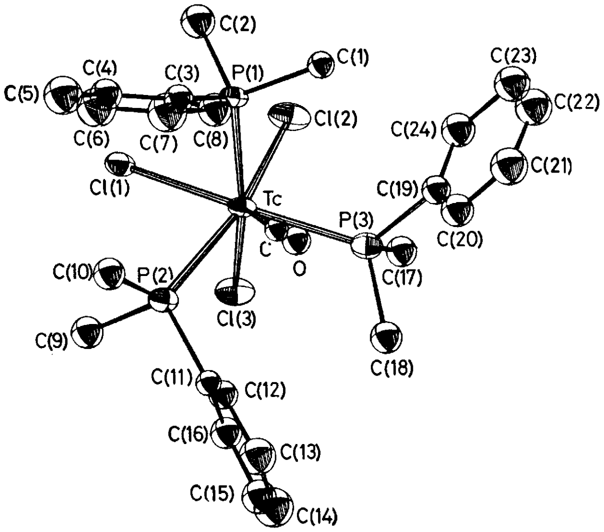


FIGURE 1 A perspective view of the molecular geometry of $[TcCl_3(CO)(PMe_2Ph)_3]$. The thermal-vibration ellipsoids are scaled to enclose *ca.* 40% probability. The numbering system used is also shown

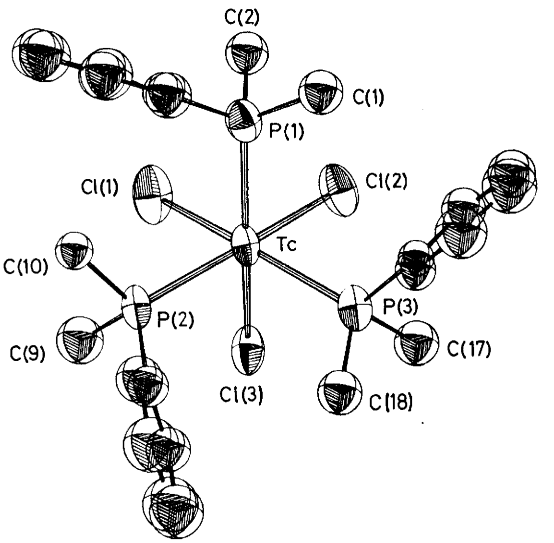


FIGURE 2 Projection of $[TcCl_3(CO)(PMe_2Ph)_3]\cdot EtOH$ viewed down the C_3 vector. The carbonyl group in the capping position and the EtOH molecule are omitted for clarity. The drawings were obtained using the program ORTEP. The thermal-vibration ellipsoids are scaled to enclose 50% probability

TABLE 1

Dimensions in $[TcCl_3(CO)(PMe_2Ph)_3]\cdot EtOH$

(*a*) Bond distances (Å), with estimated standard deviations in parentheses

Tc–Cl(1)	2.47(1)	Tc–P(2)	2.45(1)
Tc–Cl(2)	2.48(1)	Tc–P(3)	2.44(1)
Tc–Cl(3)	2.49(1)	Tc–C	1.86(2)
Tc–P(1)	2.44(1)		

(*b*) Distances (Å) between the atoms in the co-ordination sphere and angles (°) subtended at the metal atom

	C	P(1)	P(2)	P(3)	Cl(1)	Cl(2)	Cl(3)
C		2.64	2.63	2.63	3.89	3.90	3.86
P(1)	74.6(7)		4.06	4.04	3.09	3.04	4.85
P(2)	73.9(8)	112.7(3)		4.09	3.04	4.84	3.09
P(3)	74.2(8)	112.1(3)	113.9(3)		4.83	3.08	3.06
Cl(1)	127.0(8)	78.1(2)	76.2(3)	158.8(3)		3.43	3.46
Cl(2)	127.5(8)	76.5(3)	158.5(3)	77.6(3)	87.4(3)		3.47
Cl(3)	125.3(7)	160.0(2)	77.4(3)	76.6(3)	88.2(3)	88.5(3)	

TABLE 2

Bond distances (Å) and angles (°) in $[TcCl_3(CO)(PMe_2Ph)_3]\cdot EtOH$, with estimated standard deviations in parentheses; O′, C(25), and C(26) are atoms of the C_2H_5OH molecule

(*a*) Co-ordination sphere and solvent molecule

C–O	1.12(3)	C(1)–P(1)–C(2)	101.4(1.3)
P(1)–C(1)	1.82(3)	C(1)–P(1)–C(3)	105.4(1.2)
P(1)–C(2)	1.80(3)	C(2)–P(1)–C(3)	101.7(1.4)
P(1)–C(3)	1.82(3)	Tc–P(2)–C(9)	118.3(1.0)
P(2)–C(9)	1.89(3)	Tc–P(2)–C(10)	114.8(1.0)
P(2)–C(10)	1.83(3)	Tc–P(2)–C(11)	115.3(0.9)
P(2)–C(11)	1.84(2)	C(9)–P(2)–C(10)	98.4(1.4)
P(3)–C(17)	1.84(3)	C(9)–P(2)–C(11)	103.3(1.2)
P(3)–C(18)	1.85(3)	C(10)–P(2)–C(11)	104.4(1.2)
P(3)–C(19)	1.88(3)	Tc–P(3)–C(17)	117.9(1.0)
O′–C(25)	1.25(7)	Tc–P(3)–C(18)	114.7(1.1)
C(25)–C(26)	1.49(8)	Tc–P(3)–C(19)	115.4(0.9)
Tc–C–O	177.7(2.0)	C(17)–P(3)–C(18)	99.8(1.3)
Tc–P(1)–C(1)	112.8(0.8)	C(17)–P(3)–C(19)	102.8(1.3)
Tc–P(1)–C(2)	117.0(0.9)	C(18)–P(3)–C(19)	104.0(1.3)
Tc–P(1)–C(3)	116.6(0.9)	O′–C(25)–C(26)	98.7(7.0)

(*b*) Dimensions in the phenyl rings *

C(3)–C(4)	1.36	C(4)–C(5)–C(6)	118.4
C(4)–C(5)	1.43	C(5)–C(6)–C(7)	124.3
C(5)–C(6)	1.38	C(6)–C(7)–C(8)	120.1
C(6)–C(7)	1.33	C(7)–C(8)–C(3)	115.5
C(7)–C(8)	1.46	C(8)–C(3)–C(4)	121.2
C(8)–C(3)	1.48	P(2)–C(11)–C(12)	119.8
C(11)–C(12)	1.38	P(2)–C(11)–C(16)	119.6
C(12)–C(13)	1.38	C(11)–C(12)–C(13)	120.4
C(13)–C(14)	1.37	C(12)–C(13)–C(14)	119.0
C(14)–C(15)	1.37	C(13)–C(14)–C(15)	121.6
C(15)–C(16)	1.41	C(14)–C(15)–C(16)	119.4
C(16)–C(11)	1.38	C(15)–C(16)–C(11)	119.0
C(19)–C(20)	1.38	C(16)–C(11)–C(12)	120.6
C(20)–C(21)	1.41	P(3)–C(19)–C(20)	117.6
C(21)–C(22)	1.33	P(3)–C(19)–C(24)	116.4
C(22)–C(23)	1.43	C(19)–C(20)–C(21)	114.8
C(23)–C(24)	1.48	C(20)–C(21)–C(22)	123.5
C(24)–C(19)	1.37	C(21)–C(22)–C(23)	123.1
P(1)–C(3)–C(4)	120.4	C(22)–C(23)–C(24)	114.3
P(1)–C(3)–C(8)	118.3	C(23)–C(24)–C(19)	118.4
C(3)–C(4)–C(5)	120.1	C(24)–C(19)–C(20)	125.8

* Estimated standard deviations average 0.05 Å for distances and 2.6° for angles.

RESULTS AND DISCUSSION

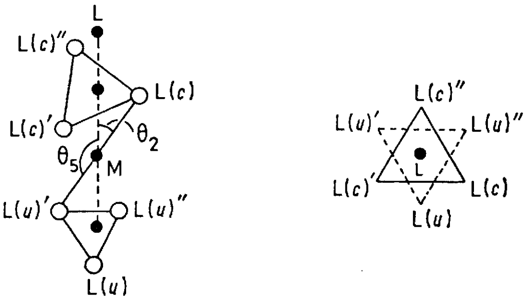
Description of the Structure.—The crystal structure is built up of discrete molecular units of $[TcCl_3(CO)(PMe_2Ph)_3]$ (Figure 1) and EtOH; the ethanol molecule, unlike some other ethanol adducts, appears to show no significant interaction *via* the oxygen atom with any adjacent entity. The molecular structure shows approximately C_{3v} symmetry. (The degree of the distortions will be discussed in a separate section.) A perspective drawing of the inner co-ordination sphere is shown in Figure 2. Thus, the co-ordination polyhedron around Tc^{III} can be described as a distorted capped octahedron, with the capped face (abbreviated as *c*) formed by the three phosphorus atoms and the uncapped face (*u*) formed by the three chlorine atoms; the carbonyl group occupies the unique capping position (*C*). Means of the interbond angles subtended at technetium are: C–Tc–P(*c*) 74.2, C–Tc–Cl(*u*) 126.6, P(*c*)–Tc–P(*c*) 112.9, Cl(*u*)–Tc–Cl(*u*) 88.0, Cl(*u*)–Tc–P(*c*) (*cis* to Cl) 77.3, and Cl(*u*)–Tc–P(*c*)(*trans* to Cl) 159.1° (Table 1). In the ' inner core ', the carbonyl group lies along the C_3 axis, while the three phosphorus and chlorine atoms lie on the three mirror planes σ_v, with the chlorine atoms on the opposite side to the *xy* plane. (In this description the *x*, *y*, *z* Cartesian axes point in directions given for the C_{3v} point group in ref. 17.) Insertion of the carbonyl group into *mer*-$[TcCl_3(PMe_2Ph)_3]$ leads to a monomeric diamagnetic complex with 18 metal valence electrons and precludes formation of a metal–metal bond.

Amongst the C_{3v} complexes in Table 3, those having a d^4 configuration achieve 18 electrons in the valence shell and are diamagnetic, while the two complexes having a d^2 configuration achieve only 16 electrons because of their diamagnetism, *i.e.* the two unpaired electrons occupy two separate degenerate orbitals. In each case the 16–18-electron rule[18] is satisfied; this rule also holds for $[W(CO)(RC{\equiv}CR)_3]$ C_{3v} complexes, which seem to have 20 valence electrons ($6 + 2 + 12$) as pointed out by Tate *et al.*[19] According to King,[20] the A_2 molecular orbital cannot overlap with the tungsten atomic orbitals, none of the metal orbitals having A_2 symmetry.

The interatomic distances and angles within the ethanol show somewhat higher standard deviations, a consequence of the high thermal motion of the O′, C(25), and C(26) atoms, due either to some degree of disorder or to partial occupancy of the solvent molecule.

TABLE 3

Observed and normalized angles (°) for seven-co-ordinate complexes with a C_{3v} capped octahedron as the reference polyhedron



Complex	θ_2 (mean)	θ_5 (mean)	$\delta_{obs.}$			$\delta_{norm.}$			Ref.
C_{3v} ideal-repulsion model ($n = 6$)	74.6	130.3				16.2	16.2	16.2	25, 37
$[MoCl_4(PMe_2Ph)_3]{\cdot}EtOH$	74.6	127.3	15.3	18.5	19.7	10.9	14.1	15.4	12
$[MoBr_2(CO)_2(Ph_2AsCH_2AsPh_2)_2]$	73.4	128.0	9.3	21.6	25.0	1.7	21.7	25.1	*a*
$[MoBr_2(CO)_3(Ph_2PCH_2CH_2PPh_2)]$	73.6	125.5	5.9	12.1	10.4	5.4	13.2	18.9	58
$[MoCl_2(CO)_2(PMe_2Ph)_3]$	71.9	128.6	24.6	22.4	20.8	9.1	18.5	22.0	56
rac-$[MoI_2(CO)_3\{o\text{-}C_6H_4(AsMePh)_2\}]{\cdot}CHCl_3$	73.5	127.8	16.7	21.3	3.8	2.0	17.4	24.6	*b*
meso-$[MoI_2(CO)_3\{o\text{-}C_6H_4(AsMePh)_2\}]$	73.4	127.7	8.2	10.3	17.5	7.0	17.4	19.7	*b*
$[WI_2(CO)_3\{Me_2AsC(CF_3)C(CF_3)AsMe_2\}]$	73.4	127.7	7.5	9.8	13.5	18.8	11.8	13.5	*c*
$[MoCl(CO)_3(bipy)(SnCl_2Me)]$ [d]	68.5	128.4	4.5	12.5	21.7	2.7	25.3	28.7	*e*
$[WCl(CO)_3(dth)(SnCl_2Me)]$ [f]	69.8	126.0	31.5	25.3	6.7	42.8	14.9	17.2	55
$[TcCl_3(CO)(PMe_2Ph)_3]{\cdot}EtOH$	74.2	126.6	21.4	24.3	25.1	11.0	13.7	14.7	This work
$[MoBr_4(PMe_2Ph)_3]$	74.5	127.4							57
$[NEt_4][WBr_3(CO)_4]$	74.1	125.5							*g*

[a] M. G. B. Drew, *J.C.S. Dalton*, 1972, 626. [b] J. C. Dewan, K. Henrick, D. L. Kepert, K. R. Trigwell, A. H. White, and S. B. Wild, *J.C.S. Dalton*, 1975, 546. [c] A. Mercer and J. Trotter, *Canad. J. Chem.*, 1974, **52**, 3331. [d] bipy = 2,2′-Bipyridyl. [e] M. Elder and D. Hall, *Inorg. Chem.*, 1969, **8**, 1268. dth = 2,5-dithiahexane. [g] M. G. B. Drew and A. P. Wolters, *J.C.S. Chem. Comm.*, 1972, 457.

C_{3v} Capped-octahedral Geometry.—Seven-co-ordinate complexes reported to possess C_{3v} capped-octahedral geometry are listed in Table 3. {The complexes $[W(CO)(PhC{\equiv}CPh)_3]$ [21] and $[TaH(CO)_2(Me_2PCH_2CH_2PMe_2)_2]$ [22] have not been included because there are insufficient structural data to carry out the calculations relative to the ' normalized geometry ' (see the next section).} Although the repulsive-energy differences between the various ideal seven-co-ordinate geometries (pentagonal bipyramidal D_{5h}, capped trigonal prism C_{2v}, and capped

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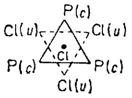
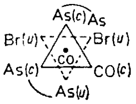
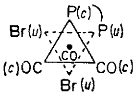
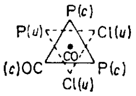
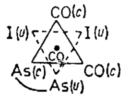
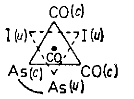
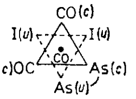
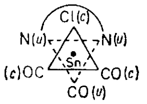
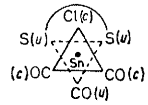
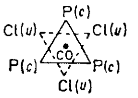
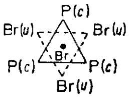
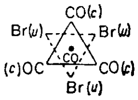
[22] P. Meakin, L. J. Guggenberger, F. N. Tebbe, and J. P. Jesson, *Inorg. Chem.*, 1974, **13**, 1025.

octahedron C_{3v}) are quite small,[23–25] D_{5h} geometry seems to be found most frequently. Moreover, another type, the tetragonal base–trigonal base, while considered to have a repulsive energy comparable to that of the first three, is found much less frequently.[26]

TABLE 4

Mean values of distances (Å) in seven-co-ordinate complexes having the C_{3v} capped-octahedral structure

						
M–X	2.399					
M–X(u)	2.447	2.662	2.661	2.523	2.855	2.868
M–L(c)	2.575	2.600	2.500	2.514	2.603	2.595
M–L(u)		2.651	2.618	2.623	2.663	2.645
M–CO		1.92	1.895	1.76	1.87	1.92
M–CO(c)		1.90	1.946	1.97	2.02	2.00
Ref.	12	*a*	58	56	*b*	*b*

						
M–X					2.425	
M–X(c)		2.557	2.517			
M–X(u)	2.852			2.480	2.560	2.638
M–L(c)	2.556			2.443	2.580	
M–L(u)	2.618	2.23	2.558			
M–CO	1.94			1.86		1.93
M–CO(c)	1.985	1.97	1.985			1.97
M–CO(u)		2.01	1.92			
Ref.	*c*	*e*	55	This work	57	*g*

[a–c,e,g] As in Table 3. Although no structural data are available, we believe that the following complexes also have C_{3v} geometry: $[M(CO)_2(pdma)_2X]X$ [M = Cr, Mo, or W; pdma = *o*-phenylenebis(dimethylarsine)] (J. Lewis, R. S. Nyholm, C. S. Pande, S. S. Sandhu, and M. H. B. Stiddard, *J. Chem. Soc.*, 1964, 3009); $[M(CO)_6(SnPh_3)]$ and $[M(CO)_5(PPh_3)(SnPh_3)]$ (M = V, Nb, or Ta), $[M(CO)_5(PPh_3)(AuPh_3)]$ (M = V or Ta), and $[Ta(CO)_6(AuPh_3)]$ (A. Davison and J. E. Ellis, *J. Organometallic Chem.*, 1970, **23**, C1); and $[FeH_4L_3]$ (L = $PEtPh_2$ or $PBuPh_2$) (M. Aresta, P. Giannoccaro, M. Rossi, and A. Sacco, *Inorg. Chim. Acta*, 1971, **5**, 115).

A characteristic of C_{3v} complexes is that the capped face is occupied by ligands which exhibit σ and/or π interactions with the central metal atom and that the uncapped face is occupied by ligands such as halogens, with the exceptions of the complexes exhibiting strong steric constraints between the central atom and multidentate ligands, or whose stoicheiometry does not correspond to $[MX_3L_3C]$ (X = halogen, L = phosphine or arsine derivative and/or CO; C = capping ligand). In the latter stoicheiometry the C ligand, as shown in Table 4, is always strongly π bonding (CO or $SnCl_2Me$) or a bulky halogen atom. The C ligand, capping the face formed by the ligands which exhibit σ and/or π interactions, is in a position to minimize the *trans*-labilizing effect of these ligands and it is π accepting, *i.e.* the electron density is delocalized from the central metal atom to the ligands to reduce the charge on the metal.

It is interesting to note that the examples of C_{3v} seven-co-ordination are restricted to metals with no more than four *d* electrons, and almost all the d^4 complexes are low spin (our complex, in particular, is diamagnetic), while d^2 complexes are paramagnetic with two unpaired electrons.[27] A simplified electronic scheme, based on Group Theory,[16] can be used to explain the first feature; if C_{3v} symmetry is assumed, the σ-hybridized metal orbitals can be shown to transform as $3A_1 + 2E$. The technetium orbitals which transform as A_1 are $5s$, $5p_z$, and $4d_{z^2}$, and as E are $(5p_x, 5p_y)$, $(4d_{xz}, 4d_{yz})$, and $(4d_{x^2-y^2}, 4d_{xy})$. Thus the most reasonable hybridization scheme for the technetium orbitals in this capped-octahedral geometry is $(5s)(5p_x)(5p_y)(5p_z)$-$(4d_{z^2})(4d_{x^2-y^2})(4d_{xy})$ or the equivalent hybridization . . . $(4d_{z^2})(4d_{xz})(4d_{yz})$, which are abbreviated sp^3d^3, as demonstrated by Kimball.[28a] Three *d* orbitals must be available for C_{3v} symmetry (always the d_{z^2} orbital if the *z* axis is along the C_3 axis) and therefore the maximum electronic configuration must be d^4. The angular-overlap method (a.o.m.), already applied to the determination of some geometries of binary transition-metal complexes,[7] leads to the same result and the most likely ordering of the technetium *d*-orbital destabilization energy is reported in the simplified electronic scheme in Figure 3. This scheme takes into account only the σ energy; it has been verified for a wide range of θ_2 values and is illustrated here for $\theta_2 = 74.6°$ [θ_2 is the CML angle and 74.6° the ' ideal ' value obtained from a ' hard-sphere model '

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with $n = 6$) (ref. 25)]. However, it is reasonable that entrance of a seventh ligand into a regular (θ_2 54.74°) capped octahedron will destabilize mainly the d_{z^2} orbital (the z axis was chosen as that along the capped ligand, *i.e.* along the ternary axis), and the destabilization depends on the e_σ (ref. 28*b*) value of the seventh ligand. Taking into account also the π delocalization from the lowest e orbitals (occupied by d^4 electrons) to the π^* orbitals of CO ligand or the 3d orbitals of the phosphine ligands, only those e orbitals show a stabilization which increases the separation in electronic energy between the occupied and unoccupied orbitals. Thus, in the present case there is a degenerate pair of low-lying levels, insensitive to pyramidalization; furthermore, Figure 3 accounts for the observed diamagnetism of C_{3v} seven-co-ordinate d^4 complexes and for the paramagnetism of C_{3v} seven-co-ordinate d^2 complexes of the type $[MX_4(PMe_2Ph)_3]$.[27]

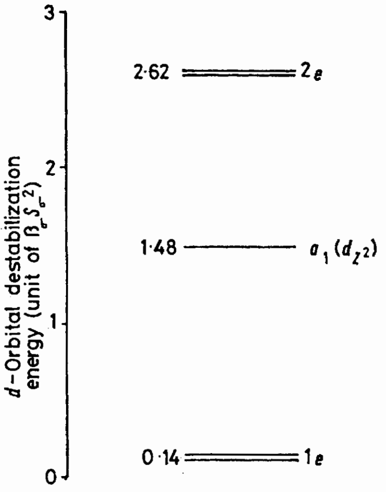

FIGURE 3 Orbital destabilization energy in C_{3v} capped octahedral geometry for $\theta_2 = 74.6°$

A practical, if crude, scheme for carrying out extended-Hückel molecular-orbital (m.o.) calculations on complexes of D_{5h} and C_{3v} geometry was used to confirm the ordering of the levels and to obtain quantitative information on orbital energies. Although more accurate atomic-orbital functions are available, the single-exponent Slater-type orbitals were chosen in the calculations, using the ξ single exponents derived by Slater's rules [29] or those defined by Burns.[30] Calculations were made on $[ZrF_7]^{3-}$,[31] whether in D_{5h} (experimental) or C_{3v} geometry (guessed), with valence-orbital ionization potentials (v.o.i.p.s) for zirconium of *ca.* 1.25 eV smaller [32] than those of titanium [33] or else using its v.o.i.p. obtained by Slater–Condon parameters.[34] A neutral fluorine function was chosen for the 2p orbital,[35] neglecting the 2s orbital. The trend in the m.o. energy levels was then evaluated by the slightly modified QCPE program no. 256.[36] The results are in agreement with those found previously and are briefly reported in Figure 4.

Available structural data are difficult to parameterize for the prediction of the geometries of seven-co-ordinate species,[37] and also for $[ML_7]$ compounds (M = d metal, L = unidentate ligand), *i.e.* in the absence of strong ligand–ligand interactions. These molecules are usually non-rigid and thus show high distortions from the regular polyhedra so that a change in geometry may occur in the liquid and solid phases. For example, among the d^0 compounds the $[ZrF_7]^{3-}$ anion in $[NH_4]_3$-$[ZrF_7]$ [31] is approximately pentagonal bipyramidal (disordered by the presence of N–H • • • F hydrogen bonds which are formed and broken during the ionic reorientation); in $Rb_5Zr_4F_{21}$ [38] there are four crystallographically independent Zr atoms with two independent ZrF_7 polyhedra having a structure midway between C_{3v} and D_{5h}.[37] An electron-diffraction study [39] of ReF_7 has shown that a small but significant departure from D_{5h} symmetry occurs in the gas phase, while the $[NbF_7]^{2-}$ anion in $K_2[NbF_7]$ [40] and the $[TaF_7]^{2-}$ anion in $K_2[TaF_7]$ [41] have a distorted capped trigonal-prismatic structure. It is interesting to note that technetium does not form a heptafluoride,[39] while $OsF_7(d^1)$ is very unstable. The $[Ti(CN)_7]^{4-}$ anion (d^1) in $K_4[Ti(CN)_7]$·$K[CN]$ [42] presents a capped trigonal-prismatic structure

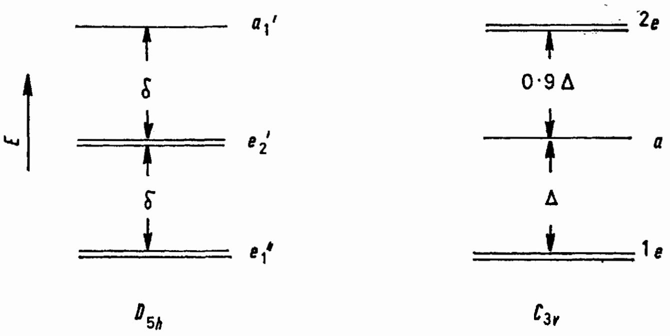

FIGURE 4 Molecular-orbital energy levels for D_{5h} and C_{3v} (θ_2 74.6, θ_5 130.3°) seven-co-ordinate geometries. Only the orbitals with large d contributions are shown

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in the solid state, while the analogous $[V(CN)_7]^{4-}$ anion (d^2) in $K_4[V(CN)_7]\cdot 2H_2O$[43] has D_{5h} geometry in the liquid and solid phases. Among the d^3 complexes the $[Mo(CN)_7]^{4-}$ anion[44] is D_{5h} in solution, but in $K_4[Mo(CN)_7]\cdot 2H_2O$ it is C_{2v} in the solid state. Finally, in IF_7 (d^{10}) a significant departure from D_{5h} symmetry occurs[45] in the gas phase. In our opinion, this feature is due to the fact that the various polyhedra of importance in seven-co-ordination do not differ greatly in energy, whether in terms of repulsive energy (' hard-sphere model '[25]) or electronic energy. Repulsive energy has been widely discussed by several workers.[23-25,46-51]

We have used the data of Thompson and Bartell[25] to generate ideal co-ordination geometries based on the ' hard-sphere model ' and the $n = 6$ exponent for the repulsive potentials ($\sum_{i \neq j} R_{ij}^{-n}$) ($n$ lies between 1, for a purely coulombic interaction, and 12). For $n < 2.5$, a D_{5h} symmetry seems to be favoured; for high n a C_{3v} structure is stable, but the minimum energies for these two alternatives are very close. In particular, for $n = 6$ and a C_{3v} geometry, the θ_2 and θ_5 values are 74.6 and 130.3°, respectively,[25] where θ_2 and θ_5 are shown in Table 3. The enlargement of θ_2 from 54.74° (ideal capped octahedron) is due to the entrance of the seventh ligand into the co-ordination sphere, while θ_5 is slightly greater than the octahedral value (125.26°); thus, θ_5 does not attain the value of 130.3° and it is practically independent of the entrance of the seventh ligand (see Table 3).

The electron-energy aspect has been investigated by the a.o.m. based on the interaction of ligand electron pairs and holes in the central metal charge distribution.[7] Thus, we evaluated the total stabilization energy due to the interaction of the orbitals of the central atom with the ligand orbitals, with inclusion of σ and π bonding, in $[ML_7]$ complexes. In our case the angular-overlap equations cannot be easily applied, because the complex is not orthonormal (*i.e.* there is d orbital mixing) and some elements (off-diagonal) of the secular determinant are different from zero.[52,53] (Appendix 1).* The relation between the function $\Sigma(\sigma)$ and the angle θ_2 is shown in Figure 5 for a d^4 system, like Tc^{III}. The term $\Sigma(\sigma)$ is defined by Burdett[7] as $\Sigma(\sigma) = \beta_\sigma \sum_j h_j S_\sigma^2[d(\Gamma_j);\sigma(\Gamma_j)]$, where h_j is the number of holes (empty orbitals) in the d-orbital manifold ($h_j = 6$ for Tc^{III}), S_σ is the group overlap integral between the two orbitals, β is a measure of the strength of the interaction between the two orbitals, and $d(\Gamma_j)$ and $\sigma(\Gamma_j)$ are respectively a group of orbitals located on the central atom and the ligand group of σ orbitals transforming under the jth representation of the molecular point group. The above equation is important, since the observed structure seems to be determined (taking into account only the σ interactions) by the maximum overlap between the empty d orbitals of the metal and the linear combinations of the appropriate symmetry orbitals from the σ ligands. For a d^4 system in D_{5h} symmetry, the $\Sigma(\sigma)$ value is 14 $\beta_\sigma S_\sigma^2$, resulting from Group Theory[54] (Appendix II).* The same value is shown by an ideal octahedron, capped to represent the $[ML_7]$ complexes (C_{3v} symmetry). In fact, the two highest levels are destabilized by $12\beta_\sigma S_\sigma^2$ ($3\beta_\sigma S_\sigma^2$ per each of four holes) and the entrance of the seventh ligand in the d_{z^2} orbital results in an additional destabilization of $2\beta_\sigma S_\sigma^2$. (In this description the z axis is along C_3.)

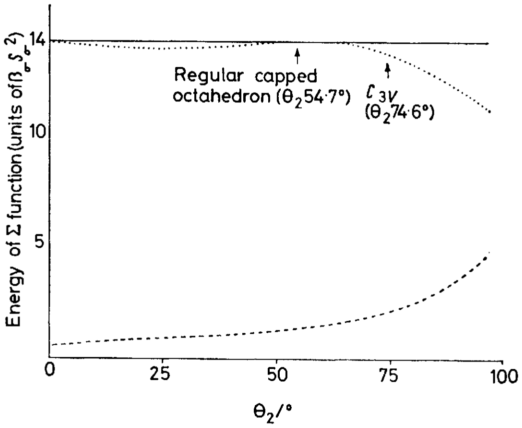

FIGURE 5 Plot of the energy of the Σ function (in units of $\beta_\sigma S_\sigma^2$) against the angle θ_2: (——) D_{5h}; (· · · ·) $\Sigma(\sigma)$; (– – – –) $\Sigma(\pi)$

As shown in Figure 5, the C_{3v} symmetry is slightly less favoured compared to D_{5h} and the ideal capped octahedron, in agreement with its results of Muetterties and Guggenberger.[37] Consequently, the slight difference in repulsive potential and electronic energy can explain the distortions, so often found, from D_{5h} to C_{3v}. Weak van der Waals forces may also play an important role in the crystal in determining such distortions. It is of interest that in the C_{3v} complexes (Tables 3 and 4) the capped face is formed by atoms or groups which undergo π interactions with d orbitals of the central metal atom. Although the function $\Sigma(\pi)$ is expected to be smaller than $\Sigma(\sigma)$ and therefore to exert a correspondingly smaller influence on the molecular geometry, in these C_{3v} complexes the π counterparts can be of great importance. In fact, while $\Sigma(\sigma)$ slightly

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* Deposited as SUP 22157.

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decreases with increasing θ_2, $\Sigma(\pi)$ $\{ = \beta_\pi \sum_j n_j S_\pi^2[d(\Gamma_j); \pi(\Gamma_j)]$ (n_j is the number of electrons occupying the bonding orbitals; in our complex, $n_j = 4$, the electrons of the two $1e$ orbitals)$\}$ somewhat increases and may counterbalance the slight σ loss (Figure 5). Many calculations were performed with some values of e_π;[52] the function $\Sigma(\pi)$ is shown, as an example, in Figure 5 (dotted line) for $e_\pi = 0.15$ for the carbonyl and the phosphine groups. Unfortunately, these calculations give only an approximate trend in the π contribution, since the e_σ/e_π values are not well known for all the ligands in question. Finally, the observed θ_2 values approach that of Thompson and Bartell,[25] because they are determined by the mutual repulsions of the ligands (Table 3).

Assessment of the Molecular Shape with Reference to C_{3v} Symmetry.—The question arises as to whether the ligand atoms in the complexes in Table 3 may nearly describe the vertices of some idealized polygon with seven vertices and, in particular, a C_{3v} capped-octahedral polyhedron. As pointed out by Muetterties and Guggenberger,[37] the best way to determine this is to obtain the dihedral angles. A difficulty in these calculations is that the values of the metal–ligand distances are different, and it was necessary to construct an orthogonal set of co-ordinates which constrains the M–L distances to one value (1.0 Å) and yet preserves the values of the bond angles, *i.e.* it freezes the angular disposition of the ligands (Appendix III).* The $\delta_{\text{obs.}}$ terms in Table 3 are the three dihedral angles between the L(c),L,L(c)′ and L(c),L(u),L(c)′ faces, while the $\delta_{\text{norm.}}$ values refer to the corresponding angles evaluated for the 'normalized' model, *i.e.* with the same M–L distances.

The ideal-repulsion model of C_{3v} (with $n = 6$) [37] predicts the dihedral angles to be 16.2°.† The departure of $\delta_{\text{norm.}}$ values from 16.2° is remarkable only for the first column, and is lower in the two last columns. In the first column, most of the complexes show a dihedral angle smaller than 16.2°, while one of the two remaining complexes shows [55] a considerably greater angle. This type of distortion cannot be ascribed to a displacement of the capping atom from the C_3 pseudo-axis, but to the fact that the angle θ_5 is $<130.3°$ when $\delta < 16.2°$ and $>130.3°$ when $\delta > 16.2°$.[55] The complexes listed in Table 3 can be described as distorted C_{3v} on the basis of $\delta_{\text{norm.}}$ values. Moreover, despite the fact that the complex in ref. 56, $[\mathrm{MoCl_2(CO)_2(PMe_2Ph)_3}]$, was said to have C_s molecular symmetry (since there is only a pseudo-mirror plane), our test certifies it as C_{3v}, with three non-equivalent $\mathrm{PMe_2Ph}$ ligands (ref. 27, p. 597), because two phosphines are in the capped face while the third is in the uncapped face.

Technetium–Ligand Bond Lengths.—The $\mathrm{Tc^{III}}$–P distances in the present complex average 2.44 Å, the three phosphine ligands being equivalent. This value can be compared with the corresponding distances in *mer*-$[\mathrm{TcCl_3(PMe_2Ph)_3}]$,[2] where the Tc–P(*trans* to chlorine) and Tc–P(*trans* to phosphorus) distances are 2.42 and 2.475 Å, respectively. Our value should strictly be compared with the first of these values (the mean value of the P–Tc–Cl angles in 159.1°) and the small lengthening of this distance in the present complex is generally ascribed to the increase in co-ordination number from six to seven. The $\mathrm{Tc^{III}}$–P distances can also be compared with $\mathrm{Mo^{IV}}$–P {in $[\mathrm{MoCl_4(PMe_2Ph)_3}]\cdot\mathrm{EtOH}$ [12] and $[\mathrm{MoBr_4(PMe_2Ph)_3}]$ [57]} and $\mathrm{Mo^{II}}$–P distances {in $[\mathrm{MoBr_2(CO)_3(Ph_2PCH_2CH_2PPh_2)}]$ [58] and $[\mathrm{MoCl_2(CO)_2(PMe_2Ph)_3}]$ [56]}. There is a shortening of the metal–phosphorus distance in going from $\mathrm{Mo^{IV}}(d^2)$ to $\mathrm{Mo^{II}}(d^4)$ and then to $\mathrm{Tc^{III}}(d^4)$ (Table 4); this feature cannot be related to the electronic configuration, but it is quite reasonable when compared with other similar complexes.[59]

The $\mathrm{Tc^{III}}$–Cl distances average 2.48 Å, as found in *mer*-$[\mathrm{TcCl_3(PMe_2Ph)_3}]$,[2] in agreement with the Tc–Cl bond being essentially ionic. The $\mathrm{Tc^{III}}$–CO distance (1.86 Å) is shorter than the corresponding one in *cis*-$[\mathrm{Tc(CO)_2\{P(OEt)_2Ph\}_4}]\cdot\mathrm{ClO_4}$,[1] but in the latter complex the carbonyl group is *trans* to a phosphonate ligand and thus the lengthening is reasonable. In C_{3v} capped-octahedral molybdenum(II) complexes the $\mathrm{Mo^{II}}$–CO(capping) distances are restricted to the range 1.87—1.94 Å (Table 4), except the surprisingly short distance (1.76 Å) given in ref. 58 which cannot be easily justified. The lengthening of the $\mathrm{Mo^{II}}$–CO(capping) distance, compared to that of $\mathrm{Tc^{III}}$–CO, is in agreement with literature data; it is of the same amount as that of $\mathrm{Mo^{II}}$–P(c) compared with $\mathrm{Tc^{III}}$–P(c) and takes into account the difference between the metallic radii.

Finally, the geometry of the phosphine ligands reveals no unexpected features and there are no abnormally short contacts, a C(1) · · · O contact of 3.51 Å being the minimum value.‡

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[*] Deposited as SUP 22157.

[†] We thank E. L. Muetterties and L. J. Guggenberger for suggesting this correct value instead of the published [37] value of 24.2°.

[‡] Two very interesting studies on seven-co-ordinate geometries have recently appeared,[60,61] and the structures of two C_{3v} complexes $[\mathrm{MoCl_2(CO)_3(PEt_3)_2}]$ [62] and $[\mathrm{MoBr_2(CO)_2(PMe_2Ph)_3}]\cdot\mathrm{Me_2CO}$ [63] have recently been determined.

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