Preparation and Molecular Structure of *trans*-Chlorobis(pentane-2,4-dionato)(triphenylphosphine)technetium(III)

By **Giuliano Bandoli, Dore A. Clemente,*** and **Ulderico Mazzi,** Laboratorio di Chimica e Tecnologia dei Radioelementi C.N.R., Corso Stati Uniti, 35100 Padova, Italy

The title complex *trans*-[Tc(pd)$_2$(PPh$_3$)Cl], prepared by reaction of pentane-2,4-dione(pd) with *trans*-[Tc(PPh$_3$)$_2$Cl$_4$], crystallises in the centrosymmetric space group $P\bar{1}$ with a = 13.152(8), b = 15.042(10), c = 15.532(13) Å, α = 112.26(11), β = 91.01(7), γ = 104.70(9)°, and Z = 4. Intensity measurements have been made with Mo-K_α radiation for the 6 601 independent reflections having $2\theta \leqslant 44°$ utilising the θ—2θ scan technique on a diffractometer. The structure has been solved by using the heavy-atom technique and has been refined using full-matrix least-squares procedures to a final R value of 0.063 using 4 950 independent reflections having $I > 3\sigma(I)$. There are two crystallographically independent molecules which differ chiefly in the folding angles of the pd ligands about the O · · · O ' bite ' axis. The octahedral co-ordination polyhedron is tetragonally elongated and approximates idealised D_{4h} symmetry. The four 'short' Tc–O bonds have an average length of 2.01(1) Å, while the two 'long' *trans* Tc–Cl and Tc–P have lengths of 2.42(1) and 2.46(1) Å, respectively. The bonding scheme and *trans* conformation are discussed in terms of the angular-overlap molecular-orbital model.

THE crystal structures of many metal complexes with β-diketones have been solved and the stereochemistry of the chelate rings has been reviewed and discussed.[1] In particular, exceptional interest has been shown [2-10] in the octahedral complexes [M(pd)$_2$X$_2$] and [M(pd)$_2$L$_2$] (pd = pentane-2,4-dionate; X = a mononegative anion ligand such as [N$_3$]$^-$, Cl$^-$, Br$^-$, or [NCS]$^-$; L = a neutral Lewis base such as pyridine or methanol). As part of our investigations into the co-ordination chemistry of technetium in various oxidation states,[11-13] we have studied the structural properties of *trans*-chlorobis(pentane-2,4-dionato)(triphenylphosphine)technetium(III), *i.e.* a complex having the formulation [M(pd)$_2$(X)L]. Pentane-2,4-dionato-complexes have been reported for all the main-group transition elements, except for Tc, and comprise a suitable series to attempt to obtain some information concerning the effect of changing the metal ion. The *trans* preference and bonding scheme of such complexes as a function of *d*-electron configuration will be discussed in terms of the angular-overlap model (a.o.m.).

EXPERIMENTAL

Preparation.— *trans*-Tetrachlorobis(triphenylphosphine)technetium(IV) (1 g) was heated under reflux in anhydrous pentane-2,4-dione (30 cm^3), freshly distilled before use, for 1 h under dry nitrogen. The resulting mixture was evaporated to dryness *in vacuo* and the residue was treated with dry acetone. The solution was filtered, the mother liquid evaporated, and diethyl ether was added. After some hours orange-red crystals were collected from the solution, yield 15% (Found: Cl, 6.3; Tc, 16.3. Calc. for C$_{28}$H$_{29}$ClO$_4$PTc: Cl, 6.0; Tc, 16.6%), ν(CO) at 1 520 cm^{-1}, in agreement with the formulation [Tc(pd)$_2$(PPh$_3$)Cl].

Several multiple crystalline samples were examined photographically before an irregular-shaped specimen was finally obtained. Any attempt to grow better single crystals from alcohol or other solvents failed and thus it was decided to collect the diffraction data on this crystal. The crystal (*ca.* 0.12 × 0.20 × 0.35 mm along the [100], [010], and [001] directions) was glued to a thin glass fibre, coated with a clear epoxy-cement to protect it from air, mounted on a goniometer head (c axis nearly coincident with the diffractometer ϕ axis), and accurately centred on a computer-controlled four-circle Siemens-AED diffractometer.

Crystal Data.—C$_{28}$H$_{29}$ClO$_4$PTc, M = 595.0, Triclinic, a = 13.152(8), b = 15.042(10), c = 15.532(13) Å, α = 112.26(11), β = 91.01(7), γ = 104.70(9)°, U = 2 728.3 Å^3, D_m (by flotation in a solution of CCl$_4$ and hexane) 1.44, Z = 4, D_c = 1.447 g cm^{-3}, $F(000)$ = 1 216. Space group $P1(C_1^1)$ or $P\bar{1}(C_i^1)$; Mo-K_α radiation, λ = 0.710 7 Å, μ(Mo-K_α) = 7.1 cm^{-1}. The reduced Niggli cell was chosen as the unit cell.[14]

Unit-cell parameters, determined initially from X-ray photographs, were adjusted by a least-squares fit of the setting angle of 15 accurately centred reflections. A complete set of θ—2θ scan data having $2\theta \leqslant 44°$ was collected using zirconium-filtered Mo-K_α radiation with a 4° take-off angle and a scan rate of 3° min^{-1}. The intensities of 6 601 independent reflections [within the sphere bounded by $(\sin\theta)/\lambda = 0.53$] were measured with a five-value procedure. Of these, 1 651 (25%) were considered unobserved, having $I \leqslant 3\sigma(I)$ and omitted from further consideration. The net count of the [331] reflection, monitored every 20 reflections, showed no significant crystal decay or change in alignment during the entire

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[1] J. P. Fackler, jun., *Progr. Inorg. Chem.*, 1966, **7**, 361; F. A. Cotton and R. Eiss, *J. Amer. Chem. Soc.*, 1968, **90**, 38; D. P. Graddon, *Co-ordination Chem. Rev.*, 1969, **4**, 1; D. W. Thompson, *J. Chem. Educ.*, 1971, **48**, 79.

[2] H. Montgomery and E. C. Lingafelter, *Acta Cryst.*, 1968, **B24**, 1127; S. Onuma and S. Shibata, *Bull. Chem. Soc. Japan*, 1970, **43**, 2395.

[3] V. W. Day, B. R. Stults, E. L. Tasset, R. O. Day, and R. S. Marianelli, *J. Amer. Chem. Soc.*, 1974, **96**, 2650; B. R. Stults, R. S. Marianelli, and V. W. Day, *Inorg. Chem.*, 1975, **14**, 722.

[4] G. J. Bullen, *Acta Cryst.*, 1959, **12**, 703.

[5] R. C. Elder, *Inorg. Chem.*, 1968, **7**, 1117.

[6] H. Montgomery and E. C. Lingafelter, *Acta Cryst.*, 1964, **17**, 1481.

[7] R. C. Elder, *Inorg. Chem.*, 1968, **7**, 2316.

[8] C. E. Pfluger, T. S. Burke, and A. L. Bednowitz, *J. Cryst. Mol. Structure*, 1973, **3**, 181.

[9] C. J. L. Lock and Che'ng Wan, *Chem. Comm.*, 1967, 1109; I. D. Brown, C. J. L. Lock, and Che'ng Wan, *Canad. J. Chem.*, 1973, **51**, 2073.

[10] P. M. Cook, L. F. Dahl, D. Hopgood, and R. A. Jenkins, *J.C.S. Dalton*, 1973, 294.

[11] G. Bandoli, D. A. Clemente, U. Mazzi, and E. Tondello, *Cryst. Struct. Comm.*, 1974, **3**, 293; U. Mazzi, D. A. Clemente, G. Bandoli, L. Magon, and A. A. Orio, *Inorg. Chem.*, 1977, **16**, 1042.

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

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

[14] I. Křivý and B. Gruber, *Acta Cryst.*, 1976, **A32**, 297.

data collection (*ca.* 10 d). All the measurements were made at the ambient laboratory temperature of *ca.* 20 °C. Data were adjusted to a common arbitrary scale using the reference reflection, and Lorentz and polarisation, but no absorption, corrections were applied. The relatively large size of the crystal, together with the μ value of 7.1 cm^{-1}, suggested the application of absorption corrections, but it was impossible to derive the equations for the planes of the faces because of the irregular shape of the crystal. Moreover, some approximate tests performed with the aid of the program ABSORP[11] indicated that the original uncorrected data were subject to a relatively low error due to absorption. The solution and refinement of the structure were carried out on the basis of the 4 950 $|F_o|$ observed reflections.

Solution and Refinement of the Structure.—The unit cell is triclinic with space group $P1$ or $P\bar{1}$. The centrosymmetric space group was first assumed and then confirmed from the subsequent refinement of the structure. An unsharpened three-dimensional Patterson revealed the positions of the two independent technetium atoms, refinement of which gave a conventional unweighted residual $R\ [= \Sigma|k|F_o| - |F_c||/\Sigma|F_o|$ (k is the scale factor which places $|F_o|$ on an absolute basis) of 0.40. The chlorine and the phosphorus atoms were located from the resulting difference-Fourier synthesis. A refinement including the positional parameters of these atoms (with individual isotropic thermal parameters) reduced R to 0.27, and two successive structure-factor calculations interspersed with Fourier syntheses revealed the locations of all the 64 remaining non-hydrogen atoms (the pentane-2,4-dionate carbon and oxygen atoms and the phosphine phenyl carbon atoms). The model thus obtained was refined by the method of unit-weighted full-matrix least squares and after four cycles of refinement, in which heavy atoms were allowed to vibrate anisotropically, the R value was 0.076. A difference-Fourier synthesis at this point permitted the location of all the 58 hydrogen atoms in chemically anticipated positions as peaks varying in intensity from 0.30 to 0.75 e$Å^{-3}$. The hydrogen positions gave distances and bond angles of doubtful validity owing to partial overlap of the hydrogen peaks with peaks resulting from anisotropic motion of carbon atoms and therefore the hydrogen atoms were assigned to geometrically reasonable positions which gave best agreement with the observed peaks. In particular, the methyl hydrogen atoms assume a staggered conformation with respect to the γ-carbon atom and their positions were calculated using a tetrahedral carbon model with a C–H bond distance of 0.97 Å. The derived positional parameters of the hydrogen atoms were included as fixed contributions in the subsequent refinement; each hydrogen atom was assigned an isotropic thermal parameter equal to that of the carbon to which it was bonded. The application of a dispersion correction in the two last cycles reduced R to 0.063 and the conventional weighted residual $R' \{= [\Sigma w(k|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ to 0.068. The function minimised in the refinement was $\Sigma w(k|F_o| - |F_c|)^2$. Because of the approximately constant counting statistics in the measurement of the data, unit weight was given to each reflection in the refinement: an analysis of the final distribution of $w\Delta F^2$ did not suggest any appropriate weighting scheme. In fact, no significant differences were observed between the final parameters from least-squares refinement cycles which utilised unit weights and those which utilised empirical weights of the form $w^{-1} = a_i|F_o|^i$. No attempt was made to refine the light atoms anisotropically because the number of observations was insufficient to give a reasonable observation-to-parameter ratio, and chiefly the computational time required to refine 70 anisotropic atoms would have been excessive. Refinement was terminated when no shift of atom parameters greater than 0.1σ was observed. A close examination of the agreement between observed and calculated structure factors gave no indication of the presence of extinction effects. A final difference-Fourier map showed a number of peaks up to a maximum of 1.1 e$Å^{-3}$ in the vicinity of the technetium atoms. The reasons for the noise level here are probably related to an improper treatment of the technetium scattering factors. Non-hydrogen and hydrogen atomic scattering factors were taken from refs. 15 and 16. Scattering factors of Tc, Cl, and P were corrected for the real and imaginary part of anomalous dispersion using Cromer's values.[17]

Final parameters are given in Table 1 with their standard deviations in parentheses: the standard deviations were estimated from full-matrix refinement. Table 2 gives the

TABLE 1

Final atomic positional ($\times$ 10^4) parameters

(*i*) For the heavy atoms

Atom	x/a	y/b	z/c
(a) Molecule (A)			
Tc	−1 982(1)	1 191(1)	1 245(1)
Cl	−3 225(2)	−282(2)	1 284(2)
P	−792(2)	2 750(2)	1 265(2)
(b) Molecule (B)			
Tc	5 165(1)	2 735(1)	5 870(1)
Cl	7 025(2)	3 535(2)	6 467(2)
P	3 245(2)	2 084(2)	5 328(2)

(*ii*) For the light atoms

Atom	x/a	y/b	z/c
(*a*) Molecule (A)			
O(1)	−3 203(5)	1 792(5)	1 261(5)
O(2)	−2 244(5)	559(5)	−161(5)
O(3)	−859(5)	493(5)	1 252(5)
O(4)	−1 766(5)	1 778(5)	2 644(5)
C(1)	−4 830(10)	1 946(9)	793(9)
C(2)	−3 926(8)	1 478(7)	531(7)
C(3)	−3 911(8)	843(8)	−352(7)
C(4)	−3 084(8)	425(8)	−687(7)
C(5)	−3 132(10)	−191(9)	−1 705(9)
C(6)	196(10)	−320(9)	1 740(9)
C(7)	−479(8)	400(8)	1 994(8)
C(8)	−634(9)	885(8)	2 895(8)
C(9)	−1 218(9)	1 570(8)	3 189(8)
C(10)	−1 225(11)	2 146(10)	4 214(10)
C(11)	543(8)	2 783(7)	937(7)
C(12)	896(8)	1 935(8)	705(7)
C(13)	1 895(9)	1 931(9)	431(8)
C(14)	2 548(9)	2 778(9)	394(8)
C(15)	2 239(11)	3 647(10)	638(10)
C(16)	1 221(9)	3 651(9)	908(8)
C(17)	−660(8)	3 780(7)	2 388(7)
C(18)	−1 568(9)	3 838(9)	2 826(8)
C(19)	−1 540(10)	4 576(9)	3 689(9)
C(20)	−622(10)	5 275(10)	4 160(9)
C(21)	292(11)	5 215(10)	3 755(10)
C(22)	281(10)	4 485(9)	2 869(9)
C(23)	−1 333(8)	3 152(8)	431(7)
C(24)	−1 288(10)	2 665(10)	−514(9)
C(25)	−1 693(11)	2 948(11)	−1 174(10)
C(26)	−2 117(11)	3 721(11)	−905(10)
C(27)	−2 224(13)	4 176(12)	5(12)
C(28)	−1 801(11)	3 927(10)	708(10)

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[15] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[16] 'International Tables of Crystallography,' Kynoch Press, Birmingham, 1968, vol. 3, p. 202.

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

TABLE 1 (*Continued*)

Atom	*x*/*a*	*y*/*b*	*z*/*c*
(*b*) Molecule (B)			
O(1)	4 852(6)	3 994(5)	6 765(5)
O(2)	5 068(5)	2 233(5)	6 904(5)
O(3)	5 530(6)	1 518(5)	4 999(5)
O(4)	5 332(6)	3 245(5)	4 850(5)
C(1)	4 689(11)	5 273(11)	8 130(10)
C(2)	4 862(9)	4 262(8)	7 644(8)
C(3)	5 000(9)	3 715(9)	8 146(8)
C(4)	5 087(9)	2 734(8)	7 773(8)
C(5)	5 178(10)	2 209(9)	8 392(9)
C(6)	6 055(11)	354(11)	3 712(10)
C(7)	5 779(9)	1 328(9)	4 153(8)
C(8)	5 798(10)	1 921(9)	3 674(9)
C(9)	5 559(9)	2 834(8)	4 017(8)
C(10)	5 504(10)	3 394(9)	3 411(9)
C(11)	2 570(8)	755(7)	4 682(7)
C(12)	3 143(10)	73(9)	4 329(9)
C(13)	2 628(11)	−958(10)	3 865(10)
C(14)	1 540(10)	−1 270(10)	3 760(9)
C(15)	976(10)	−605(10)	4 081(9)
C(16)	1 480(9)	404(9)	4 557(8)
C(17)	2 890(8)	2 683(8)	4 590(7)
C(18)	3 285(9)	3 733(9)	4 907(8)
C(19)	3 103(10)	4 205(9)	4 322(9)
C(20)	2 564(11)	3 675(10)	3 464(10)
C(21)	2 171(12)	2 649(11)	3 134(11)
C(22)	2 335(10)	2 153(9)	3 715(9)
C(23)	2 509(8)	2 389(8)	6 336(7)
C(24)	2 529(9)	1 928(9)	6 942(8)
C(25)	2 008(11)	2 131(10)	7 735(9)
C(26)	1 442(12)	2 817(11)	7 911(10)
C(27)	1 362(12	3 280(11)	7 324(10)
C(28)	1 912(10)	3 078(9)	6 521(9)

atomic parameters for the hydrogen atoms. Since the hydrogen positions in the present structure are of no particular interest for our purpose, no further consideration will be given to them here. Interatomic distances and bond angles with their estimated standard deviations are presented in Table 3. Thermal parameters are calculated and observed structure factors are listed in Supplementary Publication No. SUP 22079 (7 pp.).* The solution and refinement of the structure were carried out by use of the '*X*-Ray '72' program system,[18] on a CDC 7600 computer at the Consorzio Interuniversitario dell'Italia Nord-Orientale, Casalecchio di Reno (Bologna).

RESULTS AND DISCUSSION

Molecular Geometry.—The crystal structure of the complex *trans*-[Tc(pd)$_2$(PPh$_3$)Cl] consists of two independent molecules [labelled (A) and (B)] in the asymmetric unit. Moreover, the complex is monomeric and the conformation of molecules (A) and (B) is shown in Figure 1. Both molecules exhibit a large tetragonal distortion of the octahedral co-ordination polyhedron of Tc^{III} with four short (mean 2.01 Å) Tc–O bonds to each atom in the quasi-planar array of pd oxygen atoms and two long Tc–Cl and Tc–P bonds. Thus, this complex belongs to the class of *trans*-octahedral co-ordination of the metal, *i.e.* the two pd ligands occupy positions *trans* to one another in the co-ordination sphere of the technetium [see Table 5 for *trans*-octahedral bis(pentane-2,4-dionato)-complexes]. Precedents for a *cis*-co-ordination geometry in mononuclear bis(pentane-2,4-dionato)-complexes are provided by the crystal structures of $[Ni(pd)_2(C_5H_5NO)_2]$,[19] $[VO(pd)_2$-

TABLE 2

Positional parameters (× 10^4) for the hydrogen atoms *

Atom	*x*/*a*	*y*/*b*	*z*/*c*
(*a*) Molecule (A)			
H(1)	−4 703	2 379	1 455
H(1′)	−5 490	1 423	665
H(1″)	−4 876	2 336	427
H(3)	−4 530	657	−799
H(5)	−2 501	−420	−1 814
H(5′)	−3 172	210	−2 061
H(5″)	−3 754	−765	−1 902
H(6)	210	−588	1 067
H(6′)	−102	−863	1 934
H(6″)	912	31	2 056
H(8)	−308	739	3 373
H(10)	−1 671	2 589	4 294
H(10′)	−508	2 539	4 504
H(10″)	−1 500	1 684	4 508
H(12)	436	1 334	735
H(13)	2 127	1 331	267
H(14)	3 241	2 771	193
H(15)	2 718	4 248	623
H(16)	992	4 253	1 073
H(18)	−2 237	3 345	2 514
H(19)	−2 190	4 599	3 969
H(20)	−611	5 802	4 765
H(21)	960	5 691	4 093
H(22)	934	4 472	2 590
H(24)	−969	2 116	−722
H(25)	−1 669	2 583	−1 835
H(26)	−2 344	3 949	−1 363
H(27)	−2 598	4 686	188
H(28)	−1 841	4 293	1 366
(*b*) Molecule (B)			
H(1)	4 607	5 554	7 673
H(1′)	5 294	5 711	8 594
H(1″)	4 054	5 208	8 437
H(3)	5 040	4 035	8 823
H(5)	5 232	1 544	8 019
H(5′)	4 555	2 157	8 715
H(5″)	5 805	2 581	8 848
H(6)	6 001	30	4 150
H(6′)	6 774	483	3 556
H(6″)	5 568	−79	3 146
H(8)	5 993	1 691	3 044
H(10)	5 329	4 008	3 771
H(10′)	4 963	2 984	2 878
H(10″)	6 185	3 553	3 190
H(12)	3 910	306	4 401
H(13)	3 033	−1 437	3 625
H(14)	1 174	−1 978	3 451
H(15)	208	−836	3 977
H(16)	1 062	870	4 806
H(18)	3 680	4 125	5 527
H(19)	3 371	4 927	4 541
H(20)	2 448	4 017	3 069
H(21)	1 785	2 270	2 509
H(22)	2 051	1 432	3 490
H(24)	2 924	1 438	6 813
H(25)	2 044	1 795	8 154
H(26)	1 089	2 976	8 470
H(27)	934	3 744	7 450
H(28)	1 874	3 415	6 104

* Hydrogen atoms are numbered according to the carbon atoms to which they are attached. Primes are used only if more than one hydrogen atom is attached to the same carbon atom. Each hydrogen atom was assigned an isotropic thermal parameter equal to that of the carbon atom to which it was attached.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

[18] '*X*-Ray '72,' University of Maryland, Technical Report TR 646, ed. J. M. Stewart.

[19] W. DeW. Horrocks, jun., D. H. Templeton, and A. Zalkin, *Inorg. Chem.*, 1968, **7**, 1552.

$(C_6H_5C_5H_4N)]$,[20] $[Zn(hfpd)_2(py)_2]$,[21] and $[Cu(hfpd)_2(py)_2]$[21] (hfpd = 1,1,1,5,5,5-hexafluoropentane-2,4-dionate, py = pyridine) and also in the polynuclear complexes $[\{Ni(pd)_2\}_3]$,[22] $[\{Co(pd)_2\}_4]$,[23] $[\{Co(pd)_2(OH_2)\}_2]$,[24] and $[\{TiCl(pd)_2\}_2O]\cdot CHCl_3$.[25]

At this point the angular-overlap molecular-orbital method (a.o.m.), developed by Schäffer and Jørgensen[26] and successfully applied by Burdett[27] to the determination of molecular geometries in binary transition-metal complexes, is tentatively used to discuss the bonding scheme and to ascertain which electronic factors are important, if any, in deciding which isomer is formed. The a.o.m. relates the energy *E*, by which a *d* orbital (more exactly, an antibonding orbital that consists

TABLE 3

Bond lengths (Å) and angles (°) with standard deviations in parentheses *

	(A)	(B)
(*i*) Lengths		
(*a*) In the inner co-ordination sphere of technetium		
Tc–Cl	2.42(1)	2.42(1)
Tc–P	2.46(1)	2.47(1)
Tc–O(1)	2.03(1)	2.03(1)
Tc–O(2)	2.01(1)	2.01(1)
Tc–O(3)	2.02(1)	2.00(1)
Tc–O(4)	2.00(1)	2.00(1)
(*b*) In the pentane-2,4-dionate ligands		
O(1)–C(2)	1.32(1)	1.27(1)
C(1)–C(2)	1.52(2)	1.50(2)
C(2)–C(3)	1.35(1)	1.37(2)
C(3)–C(4)	1.40(2)	1.40(2)
C(4)–C(5)	1.49(2)	1.48(2)
C(4)–O(2)	1.29(1)	1.27(1)
O(3)–C(7)	1.32(2)	1.30(1)
C(6)–C(7)	1.51(2)	1.51(2)
C(7)–C(8)	1.36(2)	1.36(2)
C(8)–C(9)	1.38(2)	1.39(2)
C(9)–C(10)	1.50(2)	1.49(2)
C(9)–O(4)	1.28(2)	1.28(1)
(*c*) In the triphenylphosphine ligand		
P–C(11)	1.83(1)	1.83(1)
P–C(17)	1.81(1)	1.82(1)
P–C(23)	1.82(1)	1.83(1)
C(11)–C(12)	1.39(2)	1.38(2)
C(12)–C(13)	1.39(2)	1.41(2)
C(13)–C(14)	1.37(2)	1.37(2)
C(14)–C(15)	1.38(2)	1.35(2)
C(15)–C(16)	1.41(2)	1.38(2)
C(16)–C(11)	1.40(2)	1.38(1)
C(17)–C(18)	1.39(2)	1.41(2)
C(18)–C(19)	1.37(2)	1.40(2)
C(19)–C(20)	1.36(2)	1.34(2)
C(20)–C(21)	1.37(2)	1.38(2)
C(21)–C(22)	1.39(2)	1.41(3)
C(22)–C(17)	1.38(1)	1.36(2)
C(23)–C(24)	1.38(2)	1.37(2)
C(24)–C(25)	1.39(2)	1.39(2)
C(25)–C(26)	1.34(2)	1.37(2)
C(26)–C(27)	1.35(2)	1.36(3)
C(27)–C(28)	1.43(3)	1.42(2)
C(28)–C(23)	1.38(2)	1.40(2)
(*ii*) Angles		
(*a*) About technetium	(A)	(B)
Cl–Tc–P	176.3(0.1)	174.4(0.1)
O(1)–Tc–O(2)	89.6(0.3)	88.6(0.3)
O(3)–Tc–O(4)	89.1(0.3)	87.6(0.4)
Cl–Tc–O(1)	88.8(0.3)	88.1(0.3)
Cl–Tc–O(2)	89.1(0.3)	87.1(0.2)
Cl–Tc–O(3)	86.1(0.3)	89.8(0.3)
Cl–Tc–O(4)	88.8(0.3)	90.4(0.3)
P–Tc–O(1)	88.0(0.3)	86.5(0.3)
P–Tc–O(2)	92.8(0.3)	94.4(0.2)
P–Tc–O(3)	97.1(0.3)	95.5(0.3)
P–Tc–O(4)	89.3(0.3)	88.1(0.3)
O(1)–Tc–O(4)	90.0(0.3)	92.1(0.4)
O(1)–Tc–O(3)	174.8(0.3)	177.9(0.3)
O(2)–Tc–O(3)	91.1(0.3)	91.5(0.4)
O(2)–Tc–O(4)	177.9(0.3)	177.4(0.3)
TABLE 3 (*Continued*)		
(*b*) In the pentane-2,4-dionate ligands		
Tc–O(1)–C(2)	123.0(0.6)	126.0(0.8)
Tc–O(2)–C(4)	127.2(0.7)	127.8(0.8)
Tc–O(3)–C(7)	124.6(0.7)	128.1(0.9)
Tc–O(4)–C(9)	128.1(0.7)	129.6(0.8)
O(1)–C(2)–C(1)	111.2(0.8)	113.7(0.8)
C(1)–C(2)–C(3)	121.3(1.0)	120.3(1.1)
O(1)–C(2)–C(3)	127.5(1.1)	126.1(1.1)
C(2)–C(3)–C(4)	126.1(1.0)	126.1(1.1)
C(3)–C(4)–C(5)	120.2(1.0)	120.6(1.1)
C(5)–C(4)–O(2)	116.2(1.0)	115.7(1.1)
C(3)–C(4)–O(2)	123.6(0.9)	123.7(1.3)
O(3)–C(7)–C(6)	112.0(1.0)	113.9(1.3)
C(6)–C(7)–C(8)	121.8(1.3)	120.5(1.2)
O(3)–C(7)–C(8)	126.2(1.2)	125.5(1.2)
C(7)–C(8)–C(9)	125.5(1.3)	125.1(1.2)
C(8)–C(9)–C(10)	120.3(1.3)	121.5(1.1)
O(4)–C(9)–C(10)	114.8(1.2)	114.5(1.2)
C(8)–C(9)–O(4)	124.8(1.1)	123.9(1.3)
(*c*) About phosphorus and other angles in the triphenylphosphine ligand		
Tc–P–C(11)	120.0(0.4)	123.3(0.4)
Tc–P–C(17)	111.4(0.4)	109.9(0.4)
Tc–P–C(23)	111.3(0.3)	109.6(0.3)
C(11)–P–C(17)	107.3(0.5)	104.3(0.5)
C(11)–P–C(23)	101.1(0.5)	101.2(0.5)
C(17)–P–C(23)	104.1(0.5)	107.4(0.6)
P–C(11)–C(12)	120.1(0.8)	120.6(0.8)
P–C(11)–C(16)	121.1(0.9)	121.1(0.9)
C(11)–C(12)–C(13)	121.3(1.1)	120.9(1.2)
C(12)–C(13)–C(14)	119.5(1.3)	118.6(1.4)
C(13)–C(14)–C(15)	121.2(1.2)	120.8(1.2)
C(14)–C(15)–C(16)	119.4(1.3)	120.7(1.2)
C(15)–C(16)–C(11)	119.7(1.3)	120.7(1.2)
C(16)–C(11)–C(12)	118.8(1.1)	118.3(0.9)
P–C(17)–C(18)	117.4(0.7)	118.2(0.8)
P–C(17)–C(22)	125.3(0.9)	122.7(1.0)
C(17)–C(18)–C(19)	121.6(0.9)	119.6(1.0)
C(18)–C(19)–C(20)	121.5(1.2)	120.9(1.2)
C(19)–C(20)–C(21)	118.1(1.1)	120.9(1.2)
C(20)–C(21)–C(22)	121.5(1.1)	119.4(1.3)
C(21)–C(22)–C(17)	120.1(1.2)	120.4(1.2)
C(22)–C(17)–C(18)	117.2(0.9)	118.8(1.3)
P–C(23)–C(24)	119.4(1.1)	119.2(1.0)
P–C(23)–C(28)	122.4(0.9)	122.9(1.1)
C(23)–C(24)–C(25)	121.2(1.4)	122.9(1.4)
C(24)–C(25)–C(26)	120.9(1.3)	118.4(1.6)
C(25)–C(26)–C(27)	119.4(1.8)	121.8(1.5)
C(26)–C(27)–C(28)	121.6(1.7)	119.3(1.6)
C(27)–C(28)–C(23)	118.6(1.3)	119.7(1.5)
C(28)–C(23)–C(24)	118.2(1.4)	117.8(1.1)

* Taking into account the accuracy of the cell parameters.

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[20] M. R. Caira, J. M. Haigh, and L. R. Nassimbeni, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 109.

[21] J. Pradilla-Sorzano and J. P. Fackler, jun., *Inorg. Chem.*, 1973, **12**, 1174.

[22] G. J. Bullen, R. Mason, and P. Pauling, *Inorg. Chem.*, 1965, **4**, 456.

[23] F. A. Cotton and R. C. Elder, *Inorg. Chem.*, 1965, **4**, 1145.

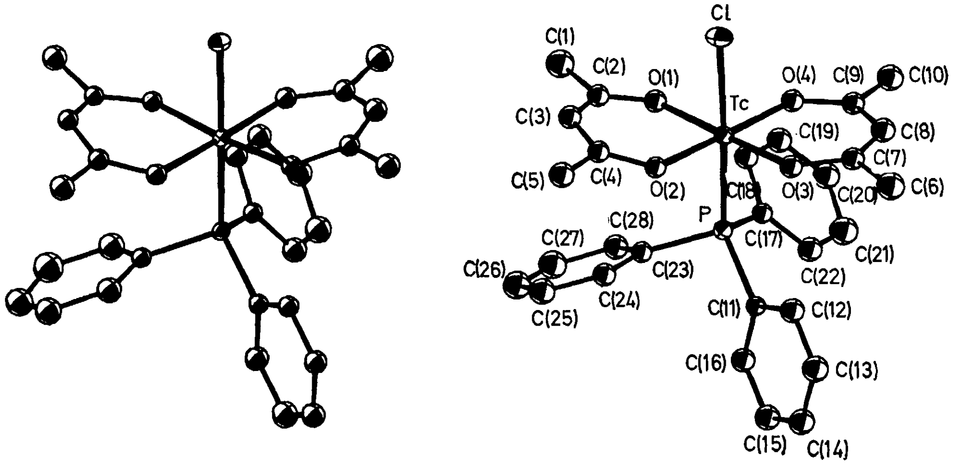
[24] F. A. Cotton and R. C. Elder, *Inorg. Chem.*, 1965, **4**, 423.

[25] K. Watenpaugh and C. N. Caughlan, *Inorg. Chem.*, 1967, **6**, 963.

[26] C. E. Schäffer and C. K. Jørgensen, *Mol. Phys.*, 1964, **9**, 401; C. E. Schäffer, *Theor. Chim. Acta*, 1966, **4**, 166; C. E. Schäffer, *Structure and Bonding*, 1968, **5**, 68; 1971, **5**, 85; C. K. Jørgensen, 'Modern Aspects of Ligand Field Theory,' North-Holland, Amsterdam, 1970 and refs. therein.

[27] J. K. Burdett, *Trans. Faraday Soc.*, 1970, 1599; *Inorg. Chem.*, 1975, **14**, 375, 931; 1976, **15**, 212.

mainly of the d orbital) is raised on interaction with one ligand, to the diatomic overlap integral S *via* $E = \beta S^2$, where β is a constant which can be taken to represent the ligand-field strength of the ligand orbital in question. The total energy of each d orbital is obtained by summing over all the ligands using the angular-overlap matrix appropriate to the complex. The effects of both σ and π interactions are included, while δ bonding is neglected.



Molecule (A) Molecule (B)

FIGURE 1 View of molecules (A) and (B) of *trans*-[Tc(pd)$_2$(PPh$_3$)Cl]. The numbering system used is shown only for molecule (B), since the same holds for (A). For clarity, the hydrogen atoms were omitted. Thermal vibration ellipsoids are shown

With reference to Figure 2, the matrix elements of the d orbitals due to the ligand interaction V are as follows:

trans

$$\langle x^2 - y^2|V|x^2 - y^2\rangle = 3e_\sigma{}^{\mathrm{O}}$$
$$\langle z^2|V|z^2\rangle = e_\sigma{}^{\mathrm{O}} + e_\sigma{}^{\mathrm{Cl}} + e_\sigma{}^{\mathrm{P}}$$
$$\langle xy|V|xy\rangle = 4e_{\pi\|}{}^{\mathrm{O}}$$
$$\langle xz|V|xz\rangle = \langle yz|V|yz\rangle$$
$$= 2e_{\pi\perp}{}^{\mathrm{O}} + e_\pi{}^{\mathrm{Cl}} + e_\pi{}^{\mathrm{P}}$$

cis

$$A_{11} = \langle z^2|V|z^2\rangle = 2.5e_\sigma{}^{\mathrm{O}} + 0.25e_\sigma{}^{\mathrm{Cl}} + 0.25e_\sigma{}^{\mathrm{P}}$$
$$A_{55} = \langle x^2 - y^2|V|x^2 - y^2\rangle =$$
$$1.5e_\sigma{}^{\mathrm{O}} + 0.75e_\sigma{}^{\mathrm{Cl}} + 0.75e_\sigma{}^{\mathrm{P}}$$
$$A_{51} = A_{15} = \langle z^2|V|x^2 - y^2\rangle = \frac{3^{\frac{1}{2}}}{4}(e_\sigma{}^{\mathrm{Cl}} - e_\sigma{}^{\mathrm{P}})$$
$$\langle yz|V|yz\rangle = e_{\pi\perp}{}^{\mathrm{O}} + 2e_{\pi\|}{}^{\mathrm{O}} + e_\pi{}^{\mathrm{Cl}}$$
$$\langle xz|V|xz\rangle = e_{\pi\perp}{}^{\mathrm{O}} + 2e_{\pi\|}{}^{\mathrm{O}} + e_\pi{}^{\mathrm{P}}$$
$$\langle xy|V|xy\rangle = 2e_{\pi\perp}{}^{\mathrm{O}} + e_\pi{}^{\mathrm{Cl}} + e_\pi{}^{\mathrm{P}}$$

Here $e_\sigma{}^{\mathrm{O}}$ means $\beta_\sigma(\mathrm{O})S_\sigma{}^2(\mathrm{O})$,[27] $e_{\pi\perp}{}^{\mathrm{O}}$ refers to π bonding between d_π metal orbitals and p_π pd oxygen orbitals normal to the pd plane, $e_{\pi\|}{}^{\mathrm{O}}$ refers to parallel bonding, and $e_\pi{}^{\mathrm{Cl}}$ refers to bonding between d_π metal orbitals and d_π chlorine orbitals. Then, as expected by Group Theory in octahedral geometry, the $d_{x^2-y^2}$ and d_{z^2} orbitals are exclusively concerned with the σ-bonding effects, while the others are with π. The d^4 system can be described as (11110), (22000), or (21100); because of the large value of the ligand field for the second-row transition-metal atom, the first configuration is unlikely and indeed it will not be further considered. In the *trans* isomer the σ-stabilisation energy[27] for four holes is: $\Sigma(\sigma)_{trans} = 2\langle x^2 - y^2|V|x^2 - y^2\rangle + 2\langle z^2|V|z^2\rangle = 8e_\sigma{}^{\mathrm{O}} + 2e_\sigma{}^{\mathrm{Cl}} + 2e_\sigma{}^{\mathrm{P}}$. Despite the presence of the A_{15} off-diagonal term in the *cis* isomer, $\Sigma(\sigma)_{cis} = \Sigma(\sigma)_{trans}$; in fact, the solution of the secular determinant for σ interactions (broken up into 2×2) is found to be $(E_\sigma', E_\sigma'') = (A_{11} + A_{55})/2 \pm$ other terms, and consequently $\Sigma(\sigma)_{cis} = 2E' + 2E'' = 2A_{11} + 2A_{55} = \Sigma(\sigma)_{trans}$. Thus, π interactions may play an important role in the bonding of this molecule. Assuming as a reasonable ordering choice, $e_{\pi\perp}{}^{\mathrm{O}} \simeq e_{\pi\|}{}^{\mathrm{O}} \gg e_\pi{}^{\mathrm{Cl}}$ (ref. 28) (in fact, pd is capable of forming π bonds[29] of the type $\mathrm{L} \longrightarrow \mathrm{M}$) and taking into account the fact that the metal d orbitals are stabilised by interaction with the empty ligand d orbitals, we propose that, between the π-interacting metal d orbitals, the highest-energy orbital is d_{xy} in the *trans* geometry, while it is d_{yz} in the *cis* isomer. The π-stabilisation energy for configuration (22000) is different for the two geometries. In fact, for this configuration, $\Sigma(\pi)_{trans} = 8e_{\pi\|}{}^{\mathrm{O}} + 4e_\pi{}^{\mathrm{P}}$, while $\Sigma(\pi)_{cis} = 2e_{\pi\perp}{}^{\mathrm{O}} + 4e_{\pi\|}{}^{\mathrm{O}} + 2e_\pi{}^{\mathrm{Cl}} + 4e_\pi{}^{\mathrm{P}}$ and then $\Sigma(\pi)_{trans} - \Sigma(\pi)_{cis} \simeq 2(e_\pi{}^{\mathrm{O}} - e_\pi{}^{\mathrm{Cl}})$. Briefly, the *trans* geometry is in this case the most suitable for overlap

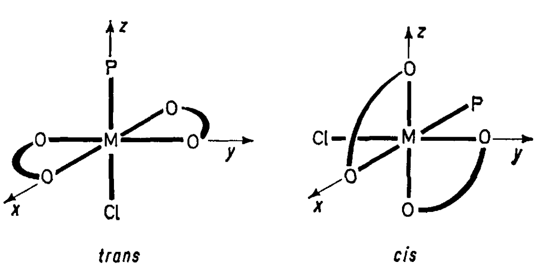


FIGURE 2 Axis system for the *trans* and *cis* isomers. O–O indicates the pentane-2,4-dionate anion

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[28] M. Gerloch and R. C. Slade, 'Ligand-Field Parameters,' Cambridge University Press, 1973, p. 186.

[29] R. D. Hancock and D. A. Thornton, *Theor. Chim. Acta*, 1970, **18**, 67.

between the filled π orbitals of pd and the highest-empty technetium π orbital. Otherwise, for the arrangement (21100), $\Sigma(\pi)_{trans} = \Sigma(\pi)_{cis} = 2e_{\pi\perp}^{O} + 4e_{\pi\parallel}^{O} + e_{\pi}^{Cl} + 3e_{\pi}^{P}$ and there is no electronic *d*-orbital energy difference between the two structures with this model. In the unlikely case of $e_{\pi}^{Cl} > e_{\pi\perp}^{O} \simeq e_{\pi\parallel}^{O}$, the a.o.m. yields the conclusion that the *cis* arrangement is more stable whether the configuration is (22000) or (21100).

Although this result encourages extensive use of the a.o.m. model, it is necessary to bear in mind that the method in $[ML'_4L_2]$ complexes is a powerful one when there are four very good σ donors compared to the other two ligands[30] and that the energy differences in systems of the type $[M(pd)_2X_2]$ (M = transition or Group 4 metal with d^{10}; X = halogen, OR, or neutral ligand such as H_2O, py, EtOH, or MeOH) between the *cis* and *trans* alternatives are very small; in fact, the *cis–trans* interconversion is very easy for some of these systems, even at room temperature.

The bond angles about the technetium differ significantly from the 90° expected for symmetrical octahedral co-ordination. These distortions can be seen from Table 3 and the mean planes (Table 4). There are no significant differences in the dimensions (within 0.03 Å for Tc–O bonds) or geometries [within 3° for angle O(1)–Tc–O(3)] of the two technetium octahedra, whereas the pd ligands show some slight differences (see ligand section). The TcO_4 basal ring is slightly (0.03 Å) puckered in molecule (A), but closely planar in (B), with the Tc atom displaced from it by 0.06 Å in (A) and 0.04 Å in (B), always toward the phosphine ligand. The angles between the chelate rings and the TcO_4 plane are 17.0 and 12.5° in molecule (A) and 13.2 and 2.1° in (B) (Table 4). One commonly observed structural feature of pentane-2,4-dionato-complexes is the displacement of the metal atom from the mean plane of the ligand giving rise to a ' chair ' configuration. Cotton and Wood[31] concluded that this observed displacement although a common feature was not an essential one. However, in the present case, three metal displacements are remarkable (0.36, 0.25, and 0.29 Å) and the other is only 0.01 Å. Consequently, only three β-diketonate ligands exhibit the often-noted folding about the O · · · O internuclear axis, such that the plane of the chelate ring makes an angle of 14.4° (9.9 and 11.6°, respectively) with the plane defined by the technetium and two oxygen chelating atoms. Thus the relation between ' normalised bite ' *b* of the chelate, which is defined as the distance between the two donor atoms O · · · O divided by the metal–ligand bond length, *i.e.* $b = d(O \cdots O)/d(M\text{–}O)$, and the angle OMO is shown in Figure 3 for the similar octahedral *trans*-bis(pentane-2,4-dionato)metal complexes listed in Table 5. Although the relation is trigonometric [$b = 2\sin(\widehat{OMO}/2)$], Figure 3 illustrates the large range of the experimental values. We cannot give a simple explanation for the displacement (and ' tilt ') feature. Cotton and Wood[31] were also unable to explain this, although packing forces, intermolecular hydrogen bonds, and inter-ring conjugation have been suggested as its cause. Day *et al.*[3] believe that intra- and inter-molecular steric

TABLE 4

Least-squares planes [with the deviations (Å) of relevant atoms in square brackets] given by $Px + Qy + Rz = S$, where *x*, *y*, and *z* are fractional unit-cell co-ordinates *

	P	*Q*	*R*	*S*
Plane (1): Tc, O(1)—O(4)				
	−6.125 (11.621)	−11.094 (1.567)	5.863 (2.265)	0.674 (7.792)
[Tc −0.05 (−0.03), O(1) 0.04 (0.0), O(2) −0.01 (0.01), O(3) 0.04 (0.0), O(4) −0.01 (0.01), Cl 2.37 (2.39), P −2.50 (−2.49), C(1) 0.59 (0.32), C(2) 0.04 (0.26), C(3) 0.58 (0.45), C(4) 0.34 (0.31), C(5) 0.46 (0.47), C(6) 0.58 (0.14), C(7) 0.34 (0.07), C(8) 0.43 (0.08), C(9) 0.20 (0.02), C(10) 0.17 (−0.09)]				
Plane (2): O(1), C(2), C(3), C(4), O(2) ' chelate ring '				
	−3.257 (12.248)	−12.817 (1.549)	8.877 (−1.018)	−0.135 (5.859)
[O(1) 0.0 (0.01), C(2) −0.01 (−0.02), C(3) 0.02 (0.01), C(4) −0.01 (0.0), O(2) 0.01 (−0.01), Tc 0.36 (0.29), C(1) −0.08 (−0.13), C(5) −0.11 (−0.03), O(3) 0.89 (0.64), C(7) 1.55 (1.00), C(8) 1.78 (1.17), C(9) 1.35 (0.98), O(4) 0.78 (0.68), C(6) 2.03 (1.23), C(10) 1.52 (1.06)]				
Plane (3): O(3), C(7), C(8), C(9), O(4) 'chelate ring '				
	−8.043 (11.429)	−9.071 (1.704)	3.464 (2.695)	0.697 (7.938)
[O(3) −0.02 (−0.01), C(7) 0.02 (0.01), C(8) 0.01 (0.01), C(9) −0.04 (−0.02), O(4) 0.03 (0.01), Tc 0.25 (0.01), C(6) 0.04 (0.04), C(10) −0.20 (−0.15), O(1) 0.69 (0.11), C(2) 1.30 (0.40), C(3) 1.56 (0.60), C(4) 1.16 (0.44), O(2) 0.55 (0.09), C(1) 1.70 (0.51), C(5) 1.40 (0.62)]				
Plane (4): Tc, O(1), O(2)				
	−5.594 (11.724)	−11.532 (1.586)	6.226 (1.870)	0.510 (7.587)
[C(1) 0.44 (0.27), C(2) 0.31 (0.22), C(3) 0.49 (0.39), C(4) 0.30 (0.26), C(5) 0.40 (0.40), O(3) 0.18 (0.07), O(4) 0.07 (0.09), C(7) 0.54 (0.18), C(8) 0.63 (0.20), C(9) 0.35 (0.13)]				
Plane (5): Tc, O(3), O(4)				
	−6.641 (11.509)	−10.630 (1.549)	5.486 (2.659)	0.733 (7.929)
[C(6) 0.43 (0.08), C(7) 0.25 (0.03), C(8) 0.34 (0.02), C(9) 0.16 (−0.02), C(10) 0.11 (−0.16), O(1) 0.18 (0.07), O(2) 0.07 (0.09), C(2) 0.59 (0.36), C(3) 0.77 (0.57), C(4) 0.49 (0.42)]				
Plane (6): C(11)—C(16)				
	−3.800 (0.553)	2.421 (−7.326)	−14.069 (15.414)	−0.857 (6.802)
Plane (7): C(17)—C(22)				
	4.370 (12.160)	−13.459 (−2.781)	11.240 (−5.952)	−2.684 (0.034)
Plane (8): C(23)—C(28)				
	−9.713 (8.185)	−6.888 (5.928)	2.921 (3.954)	−0.741 (5.967)

The equation of the least-squares line (*L*) defined by Cl–Tc–P in parametric form is: $X = -0.2000 + 0.0499T$; $Y = 0.1220 + 0.0622T$; $Z = 0.1265 - 0.0004T$ ($X = 0.4145 + 0.0774T$; $Y = 0.2785 + 0.0297T$; $Z = 0.5888 + 0.0233T$) [Tc 0.05 (0.08); Cl 0.03 (0.04); P 0.03 (0.04)]

Angles (°) between the mean planes and the line *L* (for a plane and a line, the angle is to the normal of the plane)

(1)–(2)	17.0(13.2)	(2)–(4)	14.4(11.6)	(6)–(8)	75.8(77.8)
(1)–(3)	12.5(2.1)	(2)–(5)	19.6(14.8)	(7)–(8)	74.2(66.3)
(1)–(6)	88.0(81.4)	(3)–(4)	15.2(3.6)	(*L*)–(1)	3.1(3.1)
(1)–(7)	53.4(44.5)	(3)–(5)	9.9(0.7)	(*L*)–(2)	15.5(14.1)
(1)–(8)	21.2(23.6)	(4)–(5)	5.5(3.1)	(*L*)–(3)	14.6(3.9)
(2)–(3)	29.5(15.2)	(6)–(7)	54.2(71.7)	$(1)_A$–$(1)_B$	45.1

* Values for molecule (B) are in parentheses.

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[30] J. K. Burdett, personal communication.

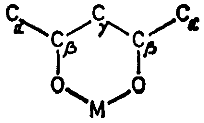
[31] F. A. Cotton and J. S. Wood, *Inorg. Chem.*, 1964, **3**, 245.

constraints are responsible for the major folding along the O · · · O edge of the co-ordination polyhedron, as well as for the distortion of the ligand from planarity which often accompanies such a folding.[32]

Technetium–Ligand Bond Lengths.—A comparison of the Tc–P and Tc–Cl bond lengths in the present complex with those in the closely related six-co-ordinate complexes *trans*-$[Tc^{II}Cl_2\{PPh(OEt)_2\}_4]$,[11] *cis*-$[Tc^{I}(CO)_2\{PPh(OEt)_2\}_4][ClO_4]$,[12] and *mer*-$[Tc^{III}Cl_3(PMe_2Ph)_3]$ [13] shows: (*i*) the Tc–P bond length (2.46) Å is longer than those in refs. 11 and 12 (2.41 and 2.38—2.44 Å), which may be explained by taking into account that phosphite is a better π acceptor than the phosphine ligand [33] and consequently the Tc–P bond will be shortened with the phosphite rather than with the phosphine; (*ii*) the Tc–Cl bond length (2.42 Å) *trans* to the phosphine ligand is longer than the Tc–Cl distances (both 2.33 Å) *cis* to the phosphine ligands in ref. 13, in agreement with the structural *trans* influence;[34] and (*iii*) the Tc–P bond length (2.46 Å) is slightly longer than that observed (2.42 Å) in ref. 13 and approximately the same as the mutual *trans* Tc–P bonds in ref. 13 (2.47 and 2.48 Å). Moreover, the Tc–Cl bond length (2.42 Å) (*trans* to the phosphine ligand) is slightly shorter than those (2.45 and 2.46 Å) in ref. 13. It is hard to ascribe these features to the different behaviour of the two phosphines, since PPh_3 is a better π acceptor than PMe_2Ph,[35] and, in our opinion, the whole bonding scheme of the complexes should be considered, not merely the Cl–Tc–P segment.

TABLE 5

Comparison of molecular dimensions [a] in similar octahedral *trans*-bis(pentane-2,4-dionato)-complexes



		Interatomic distance (Å)					Interatomic angle (°)						
Complex	Ref.	M–O	O · · · O 'bite'	O–C_β	C_β–C_γ	C_β–C_α	OMO	MOC_β	O$C_\beta C_\gamma$	$C_\beta C_\gamma C_\beta$	O$C_\beta C_\alpha$	Metal displacement (Å) from chelate ring	Dihedral angle (°) [b]
$[Mn(pd)_2]\cdot 2H_2O$	2	2.140	2.926	1.287	1.417	1.510	86.3	125.1	124.7	127.5	115.6	0.56	20.9
$[Mn(pd)_2(N_3)]$	3	1.910	2.733	1.274	1.382	1.493	91.4	127.8	124.4	124.4	114.9	0.02	1.0
$[Co(pd)_2]\cdot 2H_2O$	4	2.05	2.94	1.27	1.42	1.48	92.0	123.4	124.7	127.9	116.0	0.41	16.7
$[Co(pd)_2]\cdot 2py$	5	2.034	2.873	1.241	1.393	1.535	89.8	125.9	126.1	125.9	114.5	0.14	5.6
$[Ni(pd)_2]\cdot 2H_2O$	6	2.018	2.913	1.272	1.412	1.510	92.4	123.6	125.5	126.6	115.9	0.34	14.2
$[Ni(pd)_2]\cdot 2py$	7	2.024	2.917	1.247	1.396	1.513	92.3	124.3	125.9	127.4	115.8	0.05	2.2
$[Ni(pd)_2]\cdot 2EtOH$	8	2.011	2.888	1.269	1.395	1.506	91.8	125.0	125.8	126.4	116.0	0.09	3.7
$[Re(pd)_2Cl_2]$	9	1.99	2.80	1.28	1.39	1.53	89.3	127	125	125	115	0.09	3.7
$[Pt(pd)_2I_2]$	10	1.995	2.954	1.269	1.389	1.511	95.4	121.9	126.4	127.8	113.8	0.03	1.3
$[Tc(pd)_2(PPh_3)Cl]$ [c]		2.015	2.830	1.302	1.372	1.505	89.3	125.7	125.5	125.8	113.6	0.36, 0.25	14.4, 9.9
		(2.010)	(2.795)	(1.280)	(1.380)	(1.495)	(88.1)	(127.9)	(124.8)	(125.6)	(114.4)	(0.29, 0.01)	(11.6, 0.7)

[a] Averaged over all the crystallographically inequivalent, but chemically equivalent, bonds or angles. [b] The angle between the OMO plane and the O$C_\beta C_\gamma C_\beta$O mean plane. [c] Values for molecule (B) are in parentheses.

Assuming for our complex a degree of covalency comparable to that of fluorides and oxides, it is possible to derive a value for the Tc^{III}–O bond of 2.08 Å [$r(Tc^{III})$ (c.n.6) 0.68 Å [36]] (mean experimental value 2.01 Å); otherwise, using Pauling's value for the Cl^- radius (1.81 Å),[37] a bond length of 2.49 Å (experimental value 2.42 Å) can be obtained for the Tc^{III}–Cl bond. This indicates an increased covalency, as expected [38] for transition-metal pentane-2,4-dionato-complexes. A plot of the 'bite' oxygen–oxygen separations against the experimentally determined averaged metal–oxygen bond distance [38] for each member of the octahedral *trans*-bis(pentane-2,4-dionato)metal series (Table 5) is not linear, while a good correlation has been found in the $[M^{III}(pd)_3]$ series.[39] It should be mentioned that Lingafelter and Braun [38] also plotted 'bite' separations against crystal radius : charge ratio for many pentane-2,4-dionato-complexes. For the octahedral series the values do not provide convincing support to either correlation.

The Pentane-2,4-dionate and Phosphine Ligands.—The most frequently occurring pd derivatives are those in which the enolate anion is co-ordinated to a central metal atom through both oxygen atoms,[1] as in this work. Chemically equivalent bond lengths and angles within the pd ligands differ by less than two standard deviations, except for the O(1)–C(2) bond lengths [1.32 in molecule (A) and 1.27 Å in (B)]; the longest

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[32] R. B. von Dreele, J. J. Stezowski, and R. C. Fay, *J. Amer. Chem. Soc.*, 1971, **93**, 2887.

[33] A. A. Orio, B. J. Chanstain, and H. B. Gray, *Inorg. Chim. Acta*, 1969, **3**, 8.

[34] E. M. Shustorovich, M. A. Porai-Koshits, and Yu. A. Buslaev, *Co-ordination Chem. Rev.*, 1975, **17**, 1 and refs. therein.

[35] C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 2953 and refs. therein.

[36] R. H. Shannon and C. T. Prewitt, *Acta Cryst.*, 1969, **B25**, 925.

[37] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, pp. 224 and 521.

[38] E. C. Lingafelter and R. L. Braun, *J. Amer. Chem. Soc.*, 1966, **88**, 2951.

[39] P. K. Hon and C. E. Pfluger, *J. Co-ordination Chem.*, 1973, **3**, 67.

C–O distance is associated with the short adjacent C–C bond and attempts to find a better position for the C(2) atom in that region resulted in refinement to the same final position. Thus, it is likely that C(2) is slightly misplaced, its position being somewhat closer to O(1) and further from C(3). The mean C–O (1.291 Å) and non-methyl C–C distances (1.376 Å) are slightly longer and shorter, respectively, than the averaged values listed in Lingafelter and Braun's survey[38] of monomeric pentane-2,4-dionato-structures and in Table 5 for nine similar octahedral complexes. The methyl groups in molecules (A) and (B) lie significantly out of the chelate ring (Table 4). In view of the larger positional error of the methyl carbon atoms this is hardly significant; the carbon atoms show greater thermal motion, as can be seen in Figure 1; on the other hand, such displacements have been observed previously in β-ketoenolato-complexes.[38]

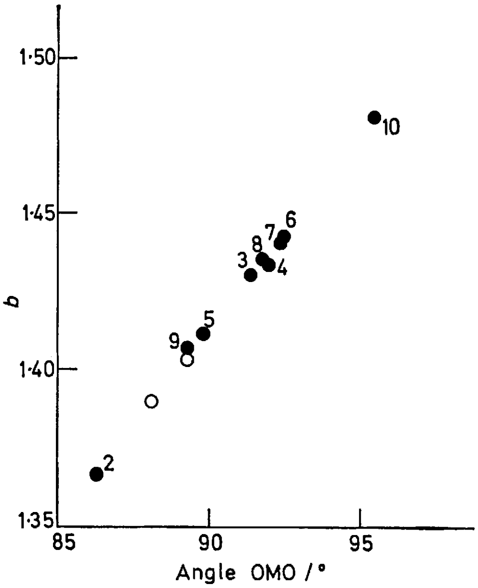

FIGURE 3 Relation between the 'normalised bite' b and the angle OMO (°) [see Table 5 for identification of points; (○) refer to the present complex]

The angles at C and O are >120° reflecting the strain imposed by the small angle at the metal and the requirement, for maximum electron delocalisation, of the ring planarity. The angle between the normals to the plane defined by each of the pd fragments is 29.5° in molecule (A) and 15.2° in (B). The mean P–C(sp^2) bond length is normal [1.82(1) Å], while all the Tc–P–C angles are larger, especially those in molecule (A), than the tetrahedral value and consequently all the C–P–C angles are smaller. These features are common in transition-metal complexes of phosphine ligands and have been attributed to contraction of the metal–phosphorus bond due to π effects.[40] The rings are closely planar, the maximum deviation of an individual atom being 0.02 Å, while the phosphorus atoms are significantly (up to 0.16 Å) out of the benzene planes. Figure 1 provides a view of the different orientations of the phenyl rings. In these rings some distances differ from the expected value by more than two standard deviations, probably because of the partial refinement (anisotropy was not introduced for the light atoms), so that the least-squares standard deviations are underestimates.[41]

Crystal Packing.—The different conformations of the entire *trans*-bis(pentane-2,4-dionato)technetium(III) part of molecules (A) and (B) cannot be the result of van der Waals interactions; moreover, it is not possible for hydrogen-bond interactions (Table 6) with O(1) and O(3) to perturb the ring conformation. In fact, similar interactions are present in molecules (A) and (B) and it is difficult to see how this can result in a different conformation. Finally, all the other intra- and inter-molecular distances (Table 7) can be explained in terms of van der Waals contacts.

TABLE 6

Hydrogen bond distances and angles *

Bond (D–H · · · A)	Distances (Å) D–H	H · · · A	D · · · A	Angle (°) D–H · · · A
C(18)–H(18) · · · O(1)	0.97	2.41	3.28	149.5
	(0.97)	(2.54)	(3.35)	(141.6)
C(12)–H(12) · · · O(3)	0.97	2.21	3.11	154.6
	(0.97)	(2.32)	(3.22)	(153.4)

* Values for molecule (B) are in parentheses.

TABLE 7

Selected non-bonded distances (Å)

(*i*) Contacts within the same complex (⩽3.6 Å) *

Cl · · · O(1)	3.13(3.11)	O(3) · · · C(12)	3.11(3.22)
Cl · · · O(2)	3.12(3.07)	O(4) · · · C(17)	3.17(3.08)
Cl · · · O(3)	3.04(3.14)	O(4) · · · C(18)	2.94(2.96)
Cl · · · O(4)	3.10(3.15)	C(4) · · · C(24)	3.50(3.32)
P · · · O(1)	3.13(3.10)	C(11) · · · C(17)	2.93(2.88)
P · · · O(2)	3.25(3.30)	C(11) · · · C(22)	3.22(3.08)
P · · · O(3)	3.37(3.32)	C(11) · · · C(23)	2.82(2.82)
P · · · O(4)	3.14(3.12)	C(11) · · · C(24)	3.19(3.29)
O(1) · · · O(2)	2.84(2.82)	C(16) · · · C(17)	3.40(3.44)
O(1) · · · O(4)	2.85(2.90)	C(16) · · · C(22)	3.23(3.24)
O(1) · · · C(18)	3.28(3.35)	C(16) · · · C(23)	3.26(3.15)
O(1) · · · C(23)	3.38(3.27)	C(16) · · · C(24)	3.57(3.56)
O(2) · · · O(3)	2.87(2.87)	C(17) · · · C(23)	2.87(2.94)
O(2) · · · C(23)	3.52(3.55)	C(17) · · · C(28)	3.09(3.19)
O(2) · · · C(24)	3.35(3.26)	C(18) · · · C(23)	3.51(3.53)
O(3) · · · O(4)	2.82(2.77)	C(18) · · · C(28)	3.35(3.41)

(*ii*) Intermolecular distances (⩽3.6 Å)

C(5B) · · · C(26A^{I})	3.59	C(6B) · · · O(2B^{III})	3.53
O(4B) · · · C(19B^{II})	3.57	C(20A) · · · C(20A^{IV})	3.51
C(12B) · · · C(6B^{III})	3.53	C(5B) · · · Cl(A^{V})	3.55
O(3B) · · · C(13B^{III})	3.42	C(13A) · · · O(3A^{VI})	3.48

Roman numerals as superscripts denote the following equivalent positions relative to the reference molecule at x, y, and z:

I $1 + x, y, 1 + z$
II $1 - x, 1 - y, 1 - z$
III $1 - x, -y, 1 - z$
IV $-x, 1 - y, 1 - z$
V $-x, -y, 1 - z$
VI $-x, -y, -z$

* Values for molecule (B) are in parentheses.

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[40] R. Mason and A. D. C. Towl, *J. Chem. Soc.* (*A*), 1970, 1601; L. Manojlović-Muir, *ibid.*, 1971, 2796.

[41] R. L. Belford, N. D. Chasteen, M. A. Hitchman, P. K. Hon, C. E. Pfluger, and I. C. Paul, *Inorg. Chem.*, 1969, **8**, 1312.