Reactions of Pertechnetate Anion with Triphenylphosphine. Molecular Structure (at —100 °C) of (1,1-Dimethyl-3-oxobutyl)triphenylphosphonium Pentachloro(triphenylphosphine)technetate(IV)

By **Giuliano Bandoli,* Dore A. Clemente, Ulderico Mazzi,** and **Edoardo Roncari,** Istituto di Chimica e Tecnologia dei Radioelementi del CNR, Area della Ricerca-Corso Stati Uniti, 35100 Padova, Italy

The reactions of the $[TcO_4]^-$ anion with PPh_3 in various concentrations of HCl are reported. $[TcCl_4(PPh_3)_2]$, $[TcCl_5(PPh_3)]^-$, and $[TcCl_6]^{2-}$ were obtained and the anionic complexes were isolated with cations such as $[PPh_3H]^+$, $[AsPh_4]^+$, or $[Ph_3PC(Me)_2CH_2COMe]^+$. The crystal structure of the title complex was determined at —100 °C from 1 761 independent reflections and refined to $R = 0.065$. Crystals are monoclinic, space group $P2_1/n$, $a = 21.909(4)$, $b = 18.963(4)$, $c = 9.896(3)$ Å, $\beta = 103.05(5)°$, and $Z = 4$. The structure consists of well separated units of octahedral $[TcCl_5(PPh_3)]^-$ anions, and tetrahedral phosphonium cations, in which the phenyl groups are in a ' propeller ' configuration around P. Selected bond distances and angles are Tc–Cl (mean) 2.34(1), Tc–P 2.57(1) Å, Cl–Tc–Cl (mean) 90.7(4), Cl–Tc–P 88.7(4)°.

As a part of a program studying the co-ordination chemistry of technetium in various oxidation states,[1-6] we are precisely evaluating the preparation, characterization, properties, and structures of a series of technetium–phosphine complexes and this paper reports the behaviour of the pertechnetate anion with triphenylphosphine, under various experimental conditions.

EXPERIMENTAL

Materials and Apparatus.—Solutions of TcO_4^- in 0.1 mol dm^{-3} NH_4OH were purchased from Radiochemical Centre, Ltd., Amersham and concentrated to obtain solid samples. Other materials were reagent grade chemicals commercially available. Elemental analyses of Tc, P, and Cl were reported elsewhere.[7] Phosphorus in the presence of arsenic was not determined owing to interference of the latter. Infrared spectra of samples in Nujol mulls and CsI pellets were collected on a Perkin-Elmer 580B spectrophotometer. Magnetic susceptibilities of CH_2Cl_2 solutions were determined by the Evans' method on a Varian F.T. 80 n.m.r. instrument and corrected for ligand diamagnetism.

Preparations.—*Tetrachlorobis(triphenylphosphine)technetium*(IV). $[AsPh_4][TcO_4]$ (0.25 g) was stirred in acetone (40 cm^3) with PPh_3 (0.8 g) and HCl (37%, 0.2 cm^3) (1 : 5) at room temperature for 15 min. The green solid obtained was filtered off and recrystallized from CH_2Cl_2 by slow evaporation. Yield 93%.

Tetraphenylarsonium pentachloro(triphenylphosphine)technetate(IV). $[AsPh_4][TcO_4]$ (0.2 g) was stirred in acetone (40 cm^3) with PPh_3 (0.8 g) and concentrated HCl (1 cm^3) at room temperature. Immediately the solution became yellow and on adding diethyl ether (20 cm^3) a yellow powder was obtained. After filtration the sample was washed with EtOH and diethyl ether. Recrystallization from CH_2Cl_2 or acetone gave yellow plates. Yield 92%.

Triphenylphosphonium pentachloro(triphenylphosphine)technetate(IV). $[AsPh_4][TcO_4]$ (0.2 g) was treated in acetone (40 cm^3) with PPh_3 (0.8 g) and HCl (10 cm^3) at room temperature. After 10 min a bright-orange solid precipitated. It was filtered off and washed with EtOH and Et_2O. The solid was recrystallized from acetone–diethyl ether. Yield 90%.

(1,1-Dimethyl-3-oxobutyl)triphenylphosphonium pentachloro(triphenylphosphine)technetate(IV). Triphenylphosphine (1.5 g) dissolved in hot EtOH (60 cm^3) was added to a mixture of $[H_3NC(Me)_2CH_2COMe][TcO_4]$ (0.5 g) and HCl (37%, 15

TABLE 1

Analytical, physical, and i.r. data for technetium complexes

Complex	Colour	Analyses * (%) Tc	P	Cl	ν(Tc–Cl)/cm^{-1}	Other i.r. bands/cm^{-1}
$[TcCl_4(PPh_3)_2]$	Emerald green	12.1 (12.9)	8.7 (8.1)	18.7 (18.5)	339s	1 085m, 738s, 686s
$[AsPh_4][TcCl_5(PPh_3)]$	Yellow	10.3 (10.7)		20.0 (19.2)	331s, 289m	1 080m, 733s, 681s, 470s, 455s, 340m, 333m
$[PPh_3H][TcCl_5(PPh_3)]$	Orange	12.1 (12.3)	7.9 (7.7)	22.7 (22.1)	330s, 287m	2 418w, 1 091m, 750s, 685s
$[Ph_3PC(Me)_2CH_2COMe][TcCl_5(PPh_3)]$	Orange	10.3 (11.0)	7.0 (6.9)	19.8 (19.7)	332s, 293m	1 718m, 1 100m, 748s, 690s
$[PPh_3H]_2[TcCl_6]$	Pale yellow	11.7 (11.8)	7.3 (7.4)	25.5 (25.4)	325s	2 420w
$[AsPh_4]_2[TcCl_6]$	Pale yellow	9.9 (9.2)		19.5 (19.7)	323s	470s, 454s, 341m, 334m

* Calculated values are given in parentheses.

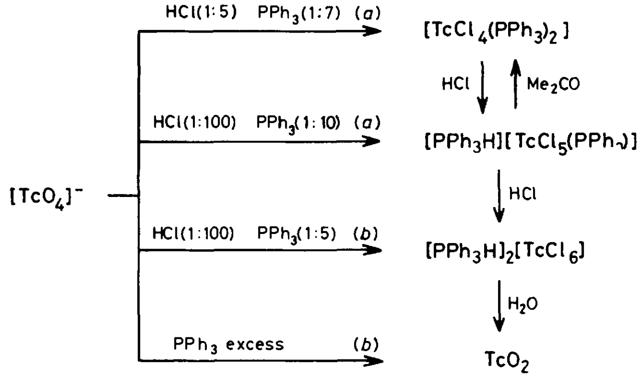
cm^3) in EtOH (10 cm^3). The mixture became red-brown, then changed to yellow-green and a green powder was produced. After refluxing for 10 min, the solution was filtered to separate the green powder, [TcCl$_4$(PPh$_3$)$_2$]. The orange solution was concentrated to dryness *in vacuo* and the residue was washed with water, EtOH, and Et$_2$O. Recrystallization from CH$_2$Cl$_2$ gave crystals suitable for *X*-ray analysis. Yield 45%.

Bis(triphenylphosphonium) hexachlorotechnetate(IV). [AsPh$_4$][TcO$_4$] (0.5 g) in EtOH (30 cm^3) and HCl (37%, 20 cm^3) was treated with PPh$_3$ (0.8 g) dissolved in hot EtOH (40 cm^3). After refluxing for 1 h a yellow solution was obtained with the presence of a small amount of green powder, [TcCl$_4$(PPh$_3$)$_2$]. After filtration the solution was concentrated to dryness. The residue was washed with EtOH and Et$_2$O. The yellow-green powder is slightly soluble in common organic solvents. It was recrystallized from CH$_2$Cl$_2$. Yield 62%. Instead of recrystallization, by adding [AsPh$_4$]Cl to the CH$_2$Cl$_2$ solution and precipitating with Et$_2$O, [AsPh$_4$]$_2$[TcCl$_6$] powder was obtained.

Characterization of Complexes.—Elemental analyses of the complexes are listed in Table 1. The complexes were characterized also by means of i.r. spectra. [TcCl$_4$(PPh$_3$)$_2$] and [PPh$_3$H]$_2$[TcCl$_6$], already known in the literature,[8–10] show the same data there reported. In particular, the P–H stretching vibration appears at 2 420 cm^{-1} and ν(Tc–Cl) is at 339 and 320 cm^{-1}, respectively. [TcCl$_5$(PPh$_3$)]$^-$ was characterized with three different cations. Bands due to ν(Tc–Cl) were observed at 332—330 and 293—287 cm^{-1}, together with the vibrations characteristic of the PPh$_3$ ligand (*e.g.* 1 085 cm^{-1}). [AsPh$_4$]$^+$ shows characteristic bands at 470, 455, 340, and 333 cm^{-1} and [PPh$_3$H]$^+$ at 2 420 cm^{-1}, while [Ph$_3$PC(Me)$_2$CH$_2$COMe]$^+$ shows a C=O stretching vibration at 1 718 cm^{-1}. The magnetic moment was also measured with this last anionic complex. The value of 3.7 B.M.* suggests the presence of three unpaired electrons in an octahedral environment as in a d^3 ($t_{2g}{}^3$) system. The complex [Ph$_3$PC(Me)$_2$CH$_2$COMe][TcCl$_5$(PPh$_3$)] was characterized by means of the *X*-ray analysis.

Structure Determination.—A first *X*-ray data collection at room temperature gave a set of only 738 observed reflections. To increase the number of observations, *via* a reduction of the vibrational amplitudes, and to improve the precision, it was decided to investigate the complex at low temperature (−100 °C).

Crystal data. C$_{42}$H$_{41}$Cl$_5$OP$_2$Tc; M = 899.7, Monoclinic, space group $P2_1/n$; a = 21.909(4), b = 18.963(4), c = 9.896(3) Å, β = 103.05(5)°, U = 4 005.2 Å^3, Z = 4, D_c = 1.46 g cm^{-3}, F(000) = 1 836, μ(Mo-K_α) = 7.1 cm^{-1}. Diffraction intensities were measured in the θ—2θ scan mode using Mo-K_α radiation (λ = 0.710 69 Å) on a Philips PW1100 automatic diffractometer with a Leyboldt Heraeus NC1D cooling device. A total of 3 610 independent reflections was collected in the range $3 \leqslant 2\theta \leqslant 40°$; of these 1 761 were considered observed [$I > 3\sigma(I)$] and used in the analysis. The structure was solved by the heavy-atom method and refined by full-matrix least-squares with unit weight to each reflection and anisotropic thermal parameters for the heavy atoms. The final R was 0.065. Neutral atomic scattering factors were those of ref. 11 and the effects of anomalous dispersion of the heavy atoms were included.[12] Table 2 reports the final fractional co-ordinates. The more important bond lengths and bond angles are quoted in Table 3. Tables of observed and calculated structure factors and thermal parameters are deposited in Supplementary Publication No. SUP 23294 (20 pp.).† All data processing and computations were carried out using the *X*-RAY 72 program package,[13] on a CDC CYBER 70/model 76 computer system.



SCHEME Reactions of the [TcO$_4$]$^-$ anion with PPh$_3$: (*a*) reaction carried out at room temperature in acetone; (*b*) reaction in refluxing ethanol

RESULTS AND DISCUSSION

Pertechnetate ion reacts with PPh$_3$ producing different compounds, which depend on the reaction conditions. In neutral or basic acetone or EtOH solution PPh$_3$ reacts only as a reducing agent. In HCl media it reacts also as a complexing agent. In the Scheme all the performed reactions are reported; those in acetone are more 'clean.' When HCl is used in a stoicheiometric ratio [TcCl$_4$(PPh$_3$)$_2$] is obtained in almost quantitative yield. The [TcCl$_5$(PPh$_3$)]$^-$ complex is obtained in good yield at room temperature by increasing the ratio of HCl to Tc. On decreasing the excess of PPh$_3$, formation of the [TcCl$_6$]$^{2-}$ complex increases. This suggests that the PPh$_3$ ligand in [TcCl$_5$(PPh$_3$)]$^-$ is weakly bound. Starting from the product obtained by concentration of residues containing acetone of the solution of [NH$_4$][TcO$_4$] in 0.1 mol dm^{-3} in NH$_4$OH, the compound [Ph$_3$PC(Me)$_2$CH$_2$COMe][TcCl$_5$(PPh$_3$)] was collected, refluxing in EtOH with a high excess of PPh$_3$ and 37% HCl. An explanation of the production of the strange cation can be found in the presence of acetone in ammoniacal solution.[14] [H$_3$NC(Me)$_2$CH$_2$COMe][TcO$_4$] was collected and, when the reaction with excess PPh$_3$ ligand in acid media was performed, the cation [Ph$_3$PC(Me)$_2$CH$_2$COMe]$^+$ was produced. From all these data we can observe that the pertechnetate anion is reduced by PPh$_3$ to the 4+ oxidation state and no intermediate compound in higher oxidation state can be isolated. In particular, the Tc=O group, in contrast to the per-rhenate analogue, was never obtained in all the reported conditions. Since the Tc=O group and Tc$^{\mathrm{V}}$ complexes are well known,[15–17] we have to conclude that the reduction mechanism of TcO$_4{}^-$ with PPh$_3$ is different from ReO$_4{}^-$, and it does not pass through the formation of any species containing a Tc=O bond.

---

* Throughout this paper: 1 B.M. = 9.274×10^{-24} J T^{-1}.

† For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

The structure of $[Ph_3PC(Me)_2CH_2COMe][TcCl_5(PPh_3)]$ is formed by the juxtaposition at van der Waals distances of well separated anions and counter cations. Thus, the individual structural elements are clearly discernible in the crystal (Figure). The anion has approximately octahedral symmetry with an average Tc–Cl bond length of 2.34(1) Å (range 2.32—2.36 Å), a Tc–P distance of 2.57(1) Å, and with an average of the Cl–Tc–Cl angles of 90.7(4)° (range 87.8—93.8°). A survey of the Tc–Cl and Tc–P lengths indicates that the Tc–Cl distance does not vary systematically with oxidation state and that no Tc–P distances as long as 2.57 Å have previously been reported. The lengthening of the Tc–P bond can be related to the high reactivity of the PPh_3 moiety in leaving the co-ordination sphere, as already emphasised, and to the fact that the phosphine does not participate in π-bonding, as anticipated by Mason and co-workers.[18] The phosphonium ion is very nearly a perfect tetrahedron with all C–P–C angles within two standard deviations (*ca.* 4°) of being tetrahedral. The three planar phenyl groups arrange them-

TABLE 2

Fractional atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

	x/*a*	*y*/*b*	*z*/*c*
Tc	1 726(1)	2 045(1)	2 687(2)
Cl(1)	1 083(3)	2 882(3)	1 289(5)
Cl(2)	1 150(3)	2 244(3)	4 363(5)
Cl(3)	2 471(3)	2 892(3)	3 762(6)
Cl(4)	2 267(3)	1 163(3)	4 095(6)
Cl(5)	2 285(3)	1 838(3)	994(6)
P(1)	921(3)	1 137(3)	1 452(5)
P(2)	1 201(3)	4 397(3)	6 899(5)
O	3 022(6)	3 064(7)	8 810(13)
C(1)	957(9)	967(11)	−361(20)
C(2)	931(10)	1 583(12)	−1 234(22)
C(3)	961(11)	1 486(12)	−2 640(23)
C(4)	1 022(10)	802(12)	−3 162(22)
C(5)	1 055(9)	221(11)	−2 256(21)
C(6)	984(9)	318(10)	−922(20)
C(7)	131(9)	1 376(10)	1 380(20)
C(8)	−298(9)	1 508(10)	110(19)
C(9)	−925(10)	1 708(11)	65(21)
C(10)	−1 134(9)	1 791(10)	1 303(20)
C(11)	−706(10)	1 678(11)	2 593(21)
C(12)	−92(10)	1 473(11)	2 624(21)
C(13)	1 042(9)	259(11)	2 240(21)
C(14)	−608(10)	−50(11)	2 849(21)
C(15)	742(10)	−714(12)	3 473(22)
C(16)	1 318(10)	−1 055(12)	3 412(23)
C(17)	1 747(10)	−736(11)	2 775(23)
C(18)	1 621(9)	−58(11)	2 196(19)
C(19)	928(9)	5 128(10)	7 811(19)
C(20)	301(9)	5 177(10)	7 829(20)
C(21)	86(9)	5 776(11)	8 434(21)
C(22)	507(10)	6 296(11)	9 014(21)
C(23)	1 129(9)	6 226(11)	9 094(20)
C(24)	1 372(10)	5 650(12)	8 470(22)
C(25)	582(9)	3 775(11)	6 555(21)
C(26)	262(9)	3 605(11)	5 173(21)
C(27)	−222(10)	3 137(11)	4 958(21)
C(28)	−408(10)	2 796(12)	6 067(22)
C(29)	−107(10)	2 970(12)	7 429(21)
C(30)	408(10)	3 418(11)	7 681(22)
C(31)	1 330(9)	4 737(10)	5 275(19)
C(32)	1 483(10)	4 252(11)	4 289(22)
C(33)	1 632(10)	4 536(11)	3 085(21)
C(34)	1 606(10)	5 260(11)	2 839(23)
C(35)	1 419(10)	5 723(11)	3 769(21)
C(36)	1 277(10)	5 465(11)	5 013(22)
C(37)	1 959(9)	4 013(11)	7 886(20)
C(38)	1 951(9)	4 043(10)	9 480(20)
C(30)	2 513(12)	4 454(13)	7 561(25)
C(40)	1 956(9)	3 233(11)	7 417(20)
C(41)	2 547(9)	2 832(10)	8 028(19)
C(42)	2 548(10)	2 048(12)	7 547(22)

TABLE 3

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

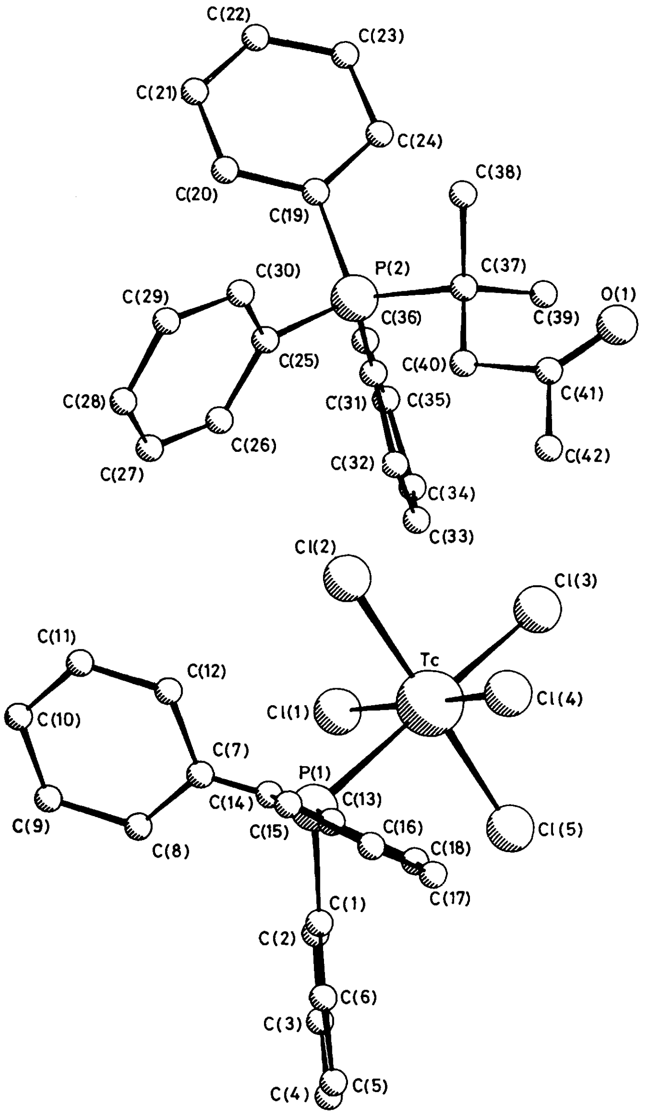
(*a*) In the technetate anion

Tc–Cl(1)	2.35(1)
Tc–Cl(2)	2.33(1)
Tc–Cl(3)	2.36(1)
Tc–Cl(4)	2.32(1)
Tc–Cl(5)	2.32(1)
Tc–P(1)	2.57(1)
P(1)–C(1)	1.84(2)
P(1)–C(7)	1.78(2)
P(1)–C(13)	1.83(2)
C–C (Ph)	mean 1.40
Cl(1)–Tc–Cl(2)	87.8(0.4)
Cl(1)–Tc–Cl(3)	93.8(0.4)
Cl(1)–Tc–Cl(4)	174.1(0.5)
Cl(1)–Tc–Cl(5)	91.9(0.4)
Cl(1)–Tc–P(1)	85.2(0.4)
Cl(2)–Tc–Cl(3)	90.0(0.4)
Cl(2)–Tc–Cl(4)	88.6(0.4)
Cl(2)–Tc–Cl(5)	179.0(0.4)
Cl(2)–Tc–P(1)	91.3(0.4)
Cl(3)–Tc–Cl(4)	90.7(0.4)
Cl(3)–Tc–Cl(5)	90.9(0.4)
Cl(3)–Tc–P(1)	178.4(0.4)
Cl(4)–Tc–Cl(5)	91.7(0.4)
Cl(4)–Tc–P(1)	90.3(0.4)
Cl(5)–Tc–P(1)	87.8(0.4)
Tc–P(1)–C(1)	113.9(1.3)
Tc–P(1)–C(7)	113.9(1.3)
Tc–P(1)–C(13)	112.9(1.2)
C(1)–P(1)–C(7)	105.2(1.3)
C(1)–P(1)–C(13)	102.9(1.9)
C(7)–P(1)–C(13)	107.2(1.5)
P(1)–C(Ph)–C(Ph)	mean 120.1
C–C–C (Ph)	mean 120.0

(*b*) In the phosphonium cation

P(2)–C(19)	1.83(2)
P(2)–C(25)	1.77(2)
P(2)–C(31)	1.81(2)
P(2)–C(37)	1.87(2)
C(37)–C(38)	1.58(4)
C(37)–C(39)	1.57(4)
C(37)–C(40)	1.55(3)
C(40)–C(41)	1.51(3)
C(41)–O	1.23(2)
C(41)–C(42)	1.56(3)
C–C (Ph)	mean 1.40
C(19)–P(2)–C(25)	106.1(2.0)
C(19)–P(2)–C(31)	107.6(1.8)
C(19)–P(2)–C(37)	112.9(1.7)
C(25)–P(2)–C(31)	109.4(1.8)
C(25)–P(2)–C(37)	113.0(1.8)
C(31)–P(2)–C(37)	107.7(1.9)
P(2)–C(37)–C(38)	107.3(2.7)
P(2)–C(37)–C(39)	108.8(2.7)
P(2)–C(37)–C(40)	105.8(2.4)
C(38)–C(37)–C(40)	109.4(3.1)
C(39)–C(37)–C(40)	113.6(3.6)
C(37)–C(40)–C(41)	114.6(3.0)
C(40)–C(41)–O	126.9(3.6)
O–C(41)–C(42)	118.3(3.4)
C(40)–C(41)–C(42)	114.8(3.0)
P(2)–C(Ph)–C(Ph)	mean 119.7
C–C–C (Ph)	mean 119.9

* Taking into account the accuracy of the cell dimensions.



View of the $[Ph_3PC(Me)_2CH_2COMe]^+[TcCl_5(PPh_3)]^-$ molecule showing the atom numbering

selves around P(2) as ' propeller paddles,' as reported,[19] but the P(2)–C(37) bond is not a formal three-fold axis of these groups, as required for an overall C_{3v} symmetry. The features of the geometry of the organic portion of the cation are in good agreement with the literature values of organophosphonium ions,[20] although the accuracy of the atomic co-ordinates in this part of the crystal is not great enough for a strict comparison.

[1/1537 *Received, 5th October,* 1981]

REFERENCES

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

[2] G. Bandoli, D. A. Clemente, and U. Mazzi, *J. Chem. Soc., Dalton Trans.*, 1976, 125.

[3] G. Bandoli, D. A. Clemente, and U. Mazzi, *J. Chem. Soc., Dalton Trans.*, 1977, 1837.

[4] G. Bandoli, D. A. Clemente, U. Mazzi, and E. Roncari, *Acta Crystallogr., Sect. B*, 1978, **34**, 3359.

[5] G. Bandoli, D. A. Clemente, and U. Mazzi, *J. Chem. Soc., Dalton Trans.*, 1978, 373.

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

[7] U. Mazzi, E. Roncari, G. Bandoli, and L. Magon, *Transition Met. Chem.*, 1974, **4**, 151.

[8] J. E. Fergusson and J. H. Hickford, *J. Inorg. Nucl. Chem.*, 1966, **28**, 2293.

[9] J. E. Fergusson and J. H. Hickford, *Aust. J. Chem.*, 1970, **23**, 453.

[10] U. Mazzi, G. De Paoli, P. Di Bernardo, and L. Magon, *J. Inorg. Nucl. Chem.*, 1976, **38**, 721.

[11] D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, 1965, **18**, 104.

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

[13] *X*-RAY 72, System of Programs, Technical Report TR-192, University of Maryland, 1972.

[14] J. D. Roberts and M. C. Caserio, ' Basic Principles of Organic Chemistry,' Benjamin Inc., New York, 1965, p. 479.

[15] A. Davison, B. V. De Pamphilis, A. G. Jones, and M. A. Davis, *J. Am. Chem. Soc.*, 1978, **100**, 5570.

[16] J. E. Smith, E. F. Byrne, F. A. Cotton, and J. C. Sekutowlki, *J. Am. Chem. Soc.*, 1978, **100**, 5571.

[17] H. Spies and B. Johanesen, *Inorg. Chim. Acta*, 1979, **33**, L113.

[18] L. Aslanov, R. Mason, A. G. Wheeler, and P. O. Whimp, *Chem. Commun.*, 1970, 30.

[19] M. Foulon, F. Baert, J. P. Henichart, and R. Houssin, *Cryst. Struct. Commun.*, 1977, **6**, 587; A. T. McPhail, G. M. Semeniuk, and D. B. Chesnut, *J. Chem. Soc. A*, 1971, 2174; F. J. Hollander, D. H. Templeton, and A. Zolkin, *Inorg. Chem.*, 1973, **12**, 2262; R. M. Wing, *J. Am. Chem. Soc.*, 1968, **90**, 4828; N. N. Greenwood, J. A. McGinnety, and J. D. Owen, *J. Chem. Soc. A*, 1971, 809; C. J. Fritchie, *Acta Crystallogr.*, 1966, **20**, 107; G. A. Bowmaker, G. R. Clark, and D. K. Paul Yuen, *J. Chem. Soc., Dalton Trans.*, 1976, 2329; J. Hjortas, *Acta Crystallogr., Sect. B*, 1973, **29**, 767; C. Couldwell and K. Prout, *Acta Crystallogr., Sect. B*, 1978, **34**, 2312.

[20] ' Perspectives in Structural Chemistry,' eds. J. J. Daly, J. D. Dunitz, and J. A. Ibers, J. Wiley and Sons, New York, 1970, vol. 3, p. 165 and refs. therein; A. C. Skapski and F. A. Stephen, *J. Cryst. Mol. Struct.*, 1977, **4**, 77.