J. inorg. nucl. Chem., 1976, Vol. 38, pp. 721–725. Pergamon Press. Printed in Great Britain

COMPLEXES OF TECHNETIUM(IV) AND (III) WITH TERTIARY PHOSPHINES

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(*Received* 10 *June* 1975)

Abstract—The synthesis and characterization of the complexes *trans*-TcX_4L_2 and *mer*-TcX_3L_3 (X = Cl and Br, and L = PMe_2Ph, PEt_2Ph and PPh_3) are reported. Configurations were deduced by far-IR and ^1H NMR studies. Magnetic susceptibility and ^1H NMR results for *mer*-$TcCl_3(PMe_2Ph)_3$ are compared with those for analogues d^4 complexes.

INTRODUCTION

MANY studies have been reported on complexes of the type MX_4L_2 and MX_3L_3 (M, a transition metal; X, a halogen; L, a tertiary phosphine). Chatt *et al.*[1–5], in particular, studied such complexes of elements in the second and third rows, but the only reported technetium complexes of these types are TcX_4L_2 (X = Cl and Br, L = PPh_3 and $AsPh_3$)[6, 7].

We have now synthesized *trans*-TcX_4L_2 and *mer*-TcX_3L_3 (X = Cl and Br and L = PMe_2Ph, PEt_2Ph and PPh_3) and report here some of their properties.

EXPERIMENTAL

Materials. Solid samples of NH_4TcO_4 were obtained by concentration and filtration of ammoniacal solutions (Radiochemical Centre, Ltd Amersham (England)). The tertiary phosphines (MayBridge) were used without further purification. Other materials were reagent grade chemicals.

Apparatus. Magnetic susceptibilities of dichloromethane solutions were measured by the Evans method[8] and corrected for diamagnetism of the ligands[9]. ^1H NMR spectra were recordered on a Bruker HFX-10 instrument with T.M.S. as internal standard. IR spectra of samples in Nujol mulls were recordered on a Perkin-Elmer-621 instrument (4000–400 cm^{-1}) and on a Beckman IR-11 spectrophotometer (<400 cm^{-1}).

Gram amount of technetium were handled in glove-boxes to afford protection against radioactivity.

Analytical methods. ^{99}Tc was determined by a method described elsewhere.(10) Halides were determined by potentiometric titration with standard $AgNO_3$ of a solution of the complex decomposed with the Shoeniger method. Analytical results are in Table 1.

Syntheses of complexes.

Trans - tetrachlorobis(dimethylphenylphosphine)technetium(IV). This complex was obtained by two methods: (i) dimethylphenylphosphine (1·9 g) was added to a mixture of ammonium pertechnetate (0·5 g), concentrated hydrochloric acid (2 ml) and ethanol (50 ml). A yellow solid precipitated immediately, but, on stirring, it rapidly dissolved and the solution became green and deposited a green powder. After refluxing for 10 min the reaction was complete. The precipitate was removed, washed with ethanol and dried. Recrystallization from chloroform gave dark green prisms of *trans*-$TcCl_4(PMe_2Ph)_2$. It is non-electrolyte in nitroethane, soluble in CH_2Cl_2, $CHCl_3$, acetone, slightly soluble in ethanol, and insoluble in non-polar solvents (Yield 92%). (ii) *mer*-trichlorotris-(dimethylphenylphosphine)technetium(III) (0·1 g) was refluxed in CCl_4 (20 ml) for 2 hr. The yellow-orange coloured solution became green and a green solid formed. On cooling a green powder of *trans*-$TcCl_4(PMe_2Ph)_2$ was obtained (Yield 95%).

Mer - trichlorotris(dimethylphenylphosphine)technetium(III). This complex was obtained by two methods: (i) dimethylphenylphosphine (5·9 g) was added to a mixture of ammonium pertechnetate (0·5 g), concentrated hydrochloric acid (2 ml) and ethanol (50 ml). A yellow solid which precipitated immediately dissolved on refluxing to yield a yellow-orange solution. On slow cooling, after refluxing for 1 hr, yellow-orange needles of *mer*-$TcCl_3(PMe_2Ph)_3$ precipitated. By concentrating the mother liquor further product was obtained (Yield 96%). It is a non-electrolyte in nitroethane and soluble in many polar solvents. (ii) the *trans*-tetrachlorobis(dimethylphenylphosphine)technetium(IV) (0·1 g) in ethanol (20 ml) was treated with 5 ml of an ethanol suspension of $NaBH_4$. By concentrating the yellow–orange solution, needles of *mer*-$TcCl_3(PMe_2Ph)_3$ were obtained (Yield 60%).

Other complexes. The bromo-derivatives of *mer*-TcX_3L_3 and *trans*-TcX_4L_2 with dimethylphenylphosphine, and the chloro- and bromo-derivatives with diethylphenylphosphine were synthesized by the first methods reported above for the two types of complex. *Trans*-$TcCl_4(PPh_3)_2$ was synthesized using the same method, with technetium-phosphine ratios in the 1/5 to 1/30 range.

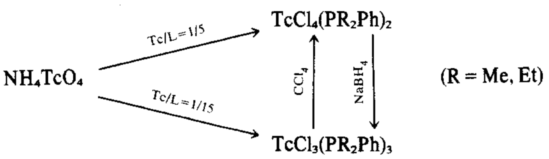
RESULTS AND DISCUSSION

The reactions of pertechnetate with the tertiary phosphines in ethanol yield products with compositions which depend on the phosphines and also the technetium-phosphine ratio. With dialkylphenylphosphines two types of compound are obtained: $TcX_4(PR_2Ph)_2$ (X = Cl, Br and R = Me, Et) if the Tc/PR_2Ph ratio is about 1/5, and $TcX_3(PR_2Ph)_3$ with the same ligands if the Tc/PR_2Ph ratio is above 1/15. With intermediate ratios mixtures of the two complexes are obtained.

With triphenylphosphine only $TcCl_4(PPh_3)_2$ is obtained even if the ratios are very low.

The technetium(IV) chloro derivatives of dialkylphenylphosphines were also obtained from the corresponding technetium(III) complexes by refluxing under carbon tetrachloride. This reaction is a general method for preparation of the rhenium(IV) complexes[2].

The technetium(III) derivatives with the same phosphines, were also prepared by reducing the corresponding technetium(IV) complexes with $NaBH_4$ in ethanol. The reactions are summarized in the following scheme:



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The behaviour of technetium in these reactions is unlike that of rhenium. In fact with dialkylphenylphosphines, when the reaction time is long enough, the complexes ReX_3L_3 can be obtained[2], whilst with triphenylphosphine only $ReOCl_3L_2$ was observed[1]. This behaviour can be attributed to easier reduction to technetium to the tetra- and tri-valent oxidation states. Attempts to prepare $TcOCl_3(PPh_3)_2$ failed.

The technetium(IV) complexes, TcX_4L_2, are all air-stable, green solids. Conductivity measurements show they are non-conducting in nitroethane. Their magnetic moments, from 3·4 to 3·8 B.M., suggest three unpaired electrons in an octahedral environement as in a $d^3(t_{2g}^3)$ system. The far IR spectra of the complexes (Table 2) show one band assignable to ν(Tc–X), suggesting that the complexes have a planar arrangement of halogen and *trans*-phosphine ligands. Owing to the high magnetic moment, the ^1H NMR spectra are very broad and of no use for structural assignment.

Table 1. General properties of the technetium complexes

COMPOUND	M.P.[a]	COLOUR	$\mu_{eff.}$[b]	% Halogen calc.	% Halogen found	% Technetium calc.	% Technetium found
$TcCl_3(PMe_2Ph)_3$	137°	yellow-orange	2.8	17.16	16.97	15.96	16.27
$TcBr_3(PMe_2Ph)_3$	135°	red	2.8	31.84	31.35	13.13	13.15
$TcCl_4(PMe_2Ph)_2$	132°	green	3.4	27.43	27.16	19.13	18.82
$TcBr_4(PMe_2Ph)_2$	193°	green	3.8	46.01	45.90	14.23	14.32
$TcCl_3(PEt_2Ph)_3$	103°	orange	2.8	15.11	14.95	14.06	14.17
$TcBr_3(PEt_2Ph)_3$	100°	red	2.8	28.63	28.57	11.81	11.78
$TcCl_4(PEt_2Ph)_2$	160°	green	3.7	24.75	24.13	17.26	17.41
$TcBr_4(PEt_2Ph)_2$	171°	green	3.7	42.57	42.34	13.17	13.15
$TcCl_4(PPh_3)_2$	215°	green	3.8	18.53	18.90	12.92	13.02

a - Melting points were determined and uncorrected.

b - In M.B. and calculated with Evans method in dichloromethane.

The TcX_3L_3 complexes vary from yellow to red crystals, and are also air-stable. Their solutions in solvents such as dichloromethane or chloroform are not stable and after some hours become greenish. Solutions in non-chlorinated anhydrous solvents are stable.

The general properties of these complexes, reported in Table 1, confirm the proposed formulation. Their magnetic moments, in particular, suggest a $d^4(t_{2g}^4)$ configuration in an octahedral environement. Their far IR spectra are complicated by the presence of the metal-ligand stretching vistations. Thus, even after identifying ν(M–Cl) by comparison with spectra of bromo-derivatives and vice versa, some bands are not assigned. In Table 2 the bands attributed to metal-halogen are dashed lines. In same cases, three bands are assignable to ν(M–X) stretching suggesting a *mer*-configuration.

This structure is confirmed by the NMR studies. The ^1H NMR of some complexes (Table 3) show for every type of proton, two signals in the ratio 1/2; this is consistent only with a *mer*-configuration.

A recent X-ray analysis[11] of *mer*-$TcCl_3(PMe_2Ph)_3$ has also confirmed the *mer*-configuration and the monomeri nature of the complex.

Specific studies were carried out on $TcCl_3(PMe_2Ph)_3$. The temperature variation of the magnetic susceptibility of this complex, shows normal Curie-Weiss behaviour above 200°K with no temperature independent paramagnetism (Table 4). This contrasts with results for the d^4 systems studied previously[3, 4, 12], and can be explained by assuming that the energy separation of the higher state from the ground state is $\ll$KT[9].

The ^1H NMR spectra of $TcX_3(PMe_2Ph)_3$ (X = Cl, Br) and of $TcCl_3(PEt_2Ph)_3$ complexes are also very dissimilar from those of rhenium and osmium d^4 complexes. While the signals for the complexes with these metals are sharp (line width *ca.* 1 Hz), for technetium d^4 complexes the signals are broad (line width *ca.* 30 Hz for methyl groups). The shift for the methyl groups is very far upfield for technetium derivatives (δ *ca.* −25 ppm compared with *ca.* −4 ppm for other d^4 systems). The phenyl proton shifts are of the same order for all the d^4 complexes but for technetium the order of increasing downfield shift is *ortho* < *para* ≤ *meta*; that is, nearly opposite to rhenium and osmium complexes. The behaviour of $TcCl_3(PMe_2Ph)_3$ is similar to that of tungsten d^2 complexes[12], the only difference being that the ^1H NMR signals are sharp, but less than the other d^4 complexes (line width *ca.* 3 Hz). If we consider the magnetic moment of the tungsten derivatives, 1·8–2·2 B.M., compared with 2·8 B.M. for technetium(III) complexes, we can presumably explain the ^1H NMR behaviour as proceeding from the permanent paramagnetism of the complexes.

The ^1H NMR signals were assigned to the corresponding protons by general comparison and by measurement of relative peak areas. The two doublets (1:2 ratio; areas 2) were assigned to *ortho*, the two triplets (1:2 ratio; areas 2) to the *meta* and the two multiplets (1:2 ratio; areas 1) to the *para* phenyl protons. The two very broad signals (1:2 ratio; areas 6) in high field were attributed to the methyl protons (Table 5).

We have also studied the effect of temperature on the ^1H NMR spectra of *mer*-$TcCl_3(PMe_2Ph)_3$. As theory suggests[13] the chemical shift of the methyl groups changes inversely with temperature, (Table 5), but if we observe the phenyl protons the direction of change of chemical shift is variable. Only for the *ortho* protons is a slight dependence shown.

Table 2. Far-IR spectra (cm^{-1}) of *mer*-TcX_3L_3 and *trans*-TcX_4L_2 (X = Cl, Br and L = PMe_2ph, PEt_2Ph and PPh_3). The absorptions attributed to ν(Tc–X) are dashed lines

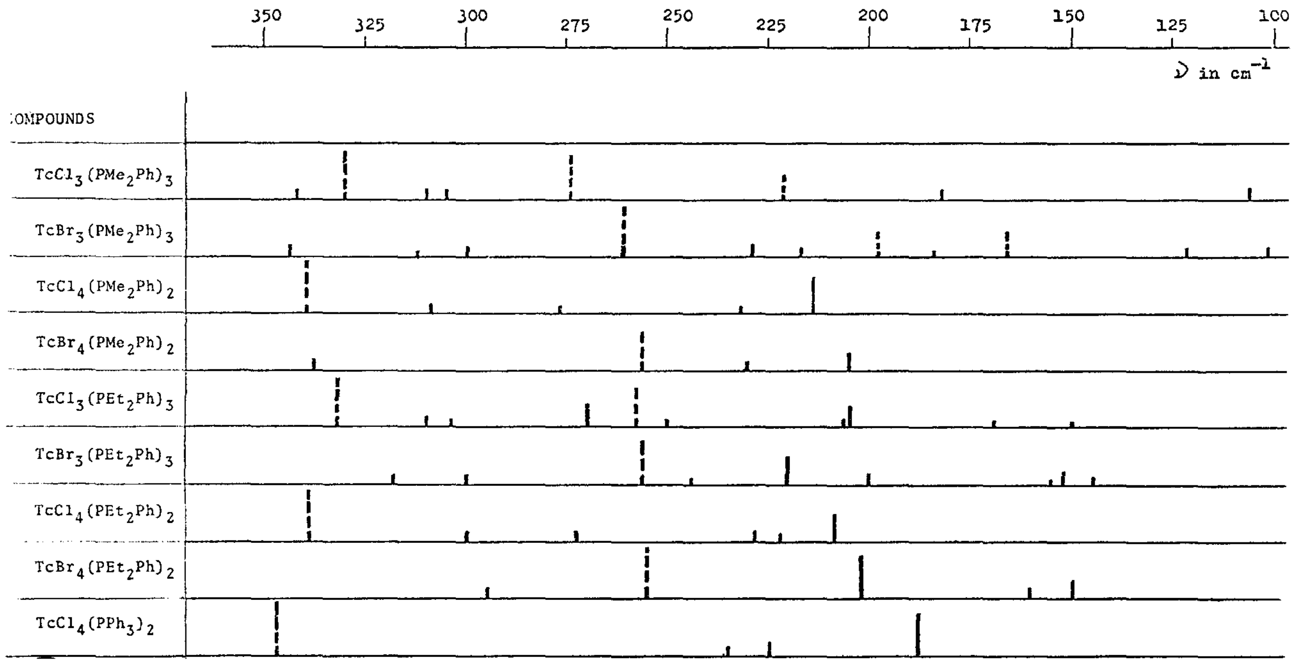

Table 3. Proton chemical shifts of some technetium(III) complexes at 30°C (δ in ppm on respect to T.M.S.)

COMPLEXES	PROTONS		
	- METHYL	- METHYLEN	- PHENYL
$TcCl_3(PMe_2Ph)_3$	+27.5 +18.2		-5.1 -6.8 -9.3 -11.2 -12.0 -12.2
$TcBr_3(PMe_2Ph)_3$	+25.6 +16.5		-6.0 -7.7 -11.5 -12.7 -14.4
$TcCl_3(PEt_2Ph)_3$	+10.4 +2.8	+15.1 +5.9	-5.1 -6.2 -8.7 -11.6 -12.0 -12.4

Table 4. Dependence of magnetic susceptibility (cgsu) of *mer*-$TcCl_3(PMe_2Ph)_3$ in CH_2Cl_2 solution in the 300 ÷ 193°K range

Δf	$\chi_M^{corr.}$	$1/\chi_M^{corr.} \cdot 10^{-4}$	$\mu_{eff.}$	$1/T \cdot 10^{-3}$
74.4	3356	2.979	2.82	3.33
86.1	3919	2.552	2.92	3.66
89.8	4098	2.440	2.93	3.80
94.6	4329	2.310	2.96	3.95
102.9	4728	2.115	3.03	4.11
109.4	5041	1.984	3.06	4.29
116.9	5402	1.851	3.10	4.48
124.0	5744	1.744	3.13	4.69
130.4	6057	1.651	3.14	4.93
139.5	6485	1.542	3.16	5.18

Table 5. Proton chemical shifts of *mer*-$TcCl_3(PMe_3Ph)_3$ complex in $CDCl_3$ solution (ppm on respect to Me_2Si)

PROTONS		27 °C	0 °C	-20 °C	-40 °C	-60 °C
- methyl	1	+27.5	+30.2	+32.7	+36.2	+39.6
	2	+18.2	+20.0	+21.8	+24.0	+26.4
- phenyl						
-ortho	1	-5.1	-4.7	-4.7	-4.5	-4.3
	2	-6.8	-6.8	-6.8	-6.5	-6.8
-meta	1	-12.2	-12.8	-13.4	-14.2	-15.0
	2	-11.2	-11.7	-12.2	-12.8	-13.5
-para	1	-9.3	-9.2	-9.0	-8.9	-8.7
	2	-12.0	-12.3	-12.7	-13.2	-13.8

We could clarify the absorption pattern of the aryl protons from the different temperature effects on the proton chemical shift. In fact, at room temperature the *meta 1* and the *para 2* protons are not distinct, but at −20°C the *meta 1* protons show a triplet while the *para 2* protons are a multiplet and are near to the triplet assigned to the *meta 2* protons.

Acknowledgements—We thank Dr. G. J. Leigh for valuable suggestions and discussions and Mr. A. Berton for elemental analyses.

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