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New Complexes of Technetium(IV) and -(III) with Dimethylphenylphosphine

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Recently several complexes of the type MX_3L_3 and MX_4L_2 (X = Cl, Br and L = tertiary phosphines) with ruthenium(III), osmium(III) and -(IV), rhenium (III) and -(IV) and iridium(IV) as metals were synthesized and studied,[1-5] but except for the complexes TcX_4L_2 (X = Cl, Br and L = PPh_3 and $AsPh_3$),[6,7] no technetium derivatives were reported.

The reaction of ammonium pertechnetate with dimethylphenylphosphine (1:5) in presence of hydrohalogenic acid (about 1:3) gives, after a few minutes' refluxing in ethanol, the complexes $TcX_4(PMe_2Ph)_2$ (X = Cl, Br) with a yield of 80 - 90%. When the pertechnetate:phosphine ratio was 1:15 or higher, complexes of the type $TcX_3(PMe_2Ph)_3$ (X = Cl, Br) were obtained with about the same yield. Reactant ratios in the range 1:5 to 1:15 afforded mixtures of the two types of complexes.

The characterization of these complexes has shown they are neutral, paramagnetic and octahedral complexes of the $d^4(t_{2g}^4)$ and $d^3(t_{2g}^3)$ systems.

Some informations on the molecular structure of these compounds were obtained from the infrared and p.m.r. spectra (Table I).

The far-infrared spectra of the technetium(IV) compounds show only a stretching vibration which can be attributed to the $\nu(Tc-X)_{e_u}$ indicating that the possible configuration is the *trans*-$TcX_4(PMe_2Ph)_2$.

Three absorptions due to the $\nu(Tc-X)$ are present in the i.r. spectra of the Tc^{III} complexes suggesting a *mer*-configuration for these derivatives.

This structure seems to be further supported by the presence of two signals, with an intensity ratio 1:2, in the p.m.r. of the same complexes. However, the signals are too broad for measuring the coupling constants. The chemical shifts of these complexes are much higher than those found in analogous rhenium and osmium d^4 derivatives,[4,9,10] which exhibit sharp resonance lines. This can be ascribed to the lower magnetic moments (μ_{eff} = 1.5 - 2.4 BM) of the latter compared to that of the technetium(III) complexes (μ_{eff} = 2.6 - 2.8 BM).

Further studies on these compounds and the syntheses of technetium complexes with other tertiary phosphines are in progress.

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TABLE I. Magnetic susceptibility, i.r. and p.m.r. spectra of the complexes

Compounds	μ_{eff}[a]	$\nu(Tc-X)$ (cm^{-1})[b]	proton chemical shifts[c]	
			$-CH_3$	$-C_6H_5$
$TcCl_3(PMe_2Ph)_3$	2.6	330(vs), 274(s), 221(m)	+25.6 +16.5	−6.0, −7.7, −11.5, −12.7, −14.2
$TcBr_3(PMe_2Ph)_3$	2.8	261(vs), 197(m), 166(m)	+27.2 +18.0	−5.1, −6.9, −9.2, −11.5, −12.1
$TcCl_4(PMe_2Ph)_4$	3.4	340(vs)		
$TcBr_4(PMe_2Ph)_4$	3.8	256(vs)		

[a] In solution with Evans technique.[8] [b] In nujol mulls on polyethylene discs.
[c] In $CDCl_3$ with TMS as internal reference.