Some Metal Halide–Phosphorus Halide–Alkyl Halide Complexes. Part II.[1] Reactions with Niobium and Tantalum Pentachlorides and Tungsten Hexachloride

By **Joseph I. Bullock,*** The Joseph Kenyon Laboratories, University of Surrey, Guildford
Frederick W. Parrett and **Nicholas J. Taylor**, Chemistry Department, Royal Military College of Canada, Kingston, Ontario, Canada

The reaction systems RCl + R'PCl$_2$ + MCl$_x$ (R = t-butyl, R' = chloride or methyl) have been investigated with the metal halides NbCl$_5$, TaCl$_5$, and WCl$_6$. In each case, complexes of the type (RR'PCl$_2$)(M^{V}Cl$_6$) have been characterised by vibrational spectroscopy. Magnetic susceptibility measurements are reported for the tungsten complexes.

WE have previously reported[1] complexes of the type (Bu^{t}PCl$_3$)$^+$(MCl$_{x+1}$)$^-$ as products of the reaction system Bu^{t}Cl + PCl$_3$ + MCl$_x$ (MCl$_x$ = BCl$_3$, AlCl$_3$, and SnCl$_4$), and of the type (Bu^{t}MePCl$_2$)$^+$(MCl$_{x+1}$)$^-$ for the system Bu^{t}Cl + MePCl$_2$ + SnCl$_4$. We here extend the range of metal chlorides which fit into these general reaction schemes. Both phosphine systems have been found to give ionic complexes with NbCl$_5$, TaCl$_5$, and WCl$_6$. The vibrational spectra reported here are readily interpreted in terms of either of the cations Bu^{t}PCl$_3^+$ or Bu^{t}MePCl$_2^+$ associated with one of the hexachloro-anions NbCl$_6^-$, TaCl$_6^-$, and WCl$_6^-$. In addition, magnetic data and u.v.–visible spectra are reported for the tungsten complexes, the oxidation state v being confirmed by these results.

RESULTS AND DISCUSSION

The compounds were air and water sensitive. Analytical data are given in Table 1.

Cation Spectra.—The C_{3v}, Bu^{t}PCl$_3^+$ cation with $\Gamma_{vib} = 3A_1$ (i.r., Raman) + $3E$ (i.r., Raman) and the C_s, Bu^{t}MePCl$_2^+$ cation with $\Gamma_{vib} = 6A^1$ (i.r., Raman) + $3A^{11}$ (i.r., Raman) have been discussed[1] for the AlCl$_3$, BCl$_3$, and SnCl$_4$ complexes. The spectra associated with these cations are listed in Supplementary Publication No. 20616 (5 pp.).†

Anion Spectra.—A regular octahedral species MX$_6$, which is centrosymmetric, has six fundamentals. Two of these, $\nu_3(T_{1u})$ and $\nu_4(T_{1u})$, are i.r.-active and three, $\nu_1(A_{1g})$, $\nu_2(E_g)$, and $\nu_5(T_{1g})$, are Raman-active. The sixth mode, $\nu_6(T_{2g})$, is inactive but may be calculated as may the Raman-active fundamentals from the i.r.-active combinations of these with ν_3 and ν_4.

The vibrational spectra of the metal chloride anions were all consistent with octahedral hexachloro-species. The assigned fundamentals were in good agreement with reported values[2-7] for NbCl$_6^-$ and TaCl$_6^-$ and for[2,8] WCl$_6^-$. We were unable to observe any Raman spectra for the tungsten compounds because of pyrolysis in the laser beam. The formation of tungsten(v) species was not unexpected considering the reported[9] instability of the hexachloride in organic solvents. The spectra associated with the anions are listed in the Supplementary Publication.†

The compounds had additional i.r. bands, most of which were weak, which could not be assigned to

---

† For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[1] Part I, J. I. Bullock, F. W. Parrett, and N. J. Taylor, *J.C.S. Dalton*, 1972, 1843.

[2] D. M. Adams, J. Chatt, J. M. Davidson, and J. Gerratt, *J. Chem. Soc.*, 1963, 2189.

[3] K. W. Bagnall and D. Brown, *J. Chem. Soc.*, 1964, 3021.

[4] J. E. D. Davies and D. A. Long, *J. Chem. Soc.* (*A*), 1968, 2560.

[5] S. M. Horner, R. J. H. Clark, B. Crociani, D. B. Copley, W. W. Horner, F. N. Collier, and S. Y. Tyree, *Inorg. Chem.*, 1968, **7**, 1859.

[6] I. R. Beattie, T. R. Gilson, and G. A. Ozin, *J. Chem. Soc.* (*A*), 1968, 2765.

[7] J. MacCordick, G. Kaufmann, and R. Rohmer, *J. Inorg. Nuclear Chem.*, 1969, **31**, 3059.

[8] K. W. Bagnall, D. Brown, and J. G. H. du Preez, *J. Chem. Soc.* 1964, 2603.

[9] Z. V. Shirokshina and N. V. Suikovskaya, *Zhur. priklad. Khim.*, 1960, **33**, 1001.

allowed fundamentals. Some of the stronger ones have been assigned to allowed T_{1u} combinations and ν_6 was calculated in all cases. Of those bands remaining several appeared to be weakly activated forbidden modes. These and a weak band corresponding to ν_1 may have arisen from low crystal site symmetry.

TABLE 1

Analytical results

System	Analyses % P	 % Metal	 % Cl	Colour	Notes	Suggested structure
$NbCl_5 + PCl_3 + Bu^tCl$	6·2	18·5	63·7	Yellow	$C_4H_9PNbCl_9$ requires P, 6·2; Nb, 18·6; Cl, 63·8%	$(Bu^tPCl_3)(NbCl_6)$
$NbCl_5 + MePCl_2 + Bu^tCl$	6·2	19·4	59·0	Yellow	$C_5H_{12}PNbCl_8$ requires P, 6·45; Nb, 19·35; Cl, 59·15%	$(Bu^tMePCl_2)(NbCl_6)$
$TaCl_5 + PCl_3 + Bu^tCl$	*	30·7	54·3	White	$C_4H_9PTaCl_9$ requires Ta, 30·75; Cl, 54·25%	$(Bu^tPCl_3)(TaCl_6)$
$TaCl_5 + MePCl_2 + Bu^tCl$	*	31·9	50·0	White	$C_5H_{12}PTaCl_8$ requires Ta, 31·85; Cl, 49·95%	$(Bu^tMePCl_2)(TaCl_6)$
$WCl_6 + PCl_3 + Bu^tCl$	5·3	31·1	54·1	Dark green	$C_4H_9PWCl_9$ requires P, 5·25; W, 31·1; Cl, 54·0%	$(Bu^tPCl_3)(WCl_6)$
$WCl_6 + MePCl_2 + Bu^tCl$	5·4	32·2	49·9	Green	$C_5H_{12}PWCl_8$ requires P, 5·45; W, 32·2; Cl, 49·7%	$(Bu^tMePCl_2)(WCl_6)$

* The presence of tantalum severely interfered with phosphorus analysis.

The complex $(Bu^tMePCl_2)(WCl_6)$ had many strong bands in its i.r. spectrum. Of the strong bands at 750, 731, 645, and 603 cm^{-1}, only the last may be assigned to an allowed first order combination ($\nu_2 + \nu_3$). It is worth noting that in comparison, the combination $\nu_1 + \nu_3$ at 698 cm^{-1} was only weakly observed. The other three strong bands could be hitherto unobserved cation bands or even, possible, ternary combinations. There was no evidence that hydrolysis had taken place.

TABLE 2

Magnetic data * for the tungsten(V) complexes

$(Bu^tPCl_3)(WCl_6)$ Diamagnetic correction $-255·6 \times 10^{-6}$ c.g.s.u. $\theta = 900°$; Néel temperature 125 K

Temp. (K)	295	266·5	236	204	186	165
$10^6\chi_A$	200·5	204·2	209·8	215·4	219·1	224·7
μ_{eff}(B.M.)	0·69	0·66	0·63	0·59	0·57	0·55
Temp. (K)	146	135·5	126	114	102	89
$10^6\chi_A$	235·9	254·6	267·6	254·6	235·9	215·4
μ_{eff}(B.M.)	0·53	0·53	0·52	0·48	0·44	0·39

$(Bu^tMePCl_2)(WCl_6)$ Diamagnetic correction $-249·3 \times 10^{-6}$ c.g.s.u.; $\theta = 150°$; Néel temperature 104 K

Temp. (K)	295	264·5	234·5	204	174	145·4
$10^6\chi_A$	179·8	192·7	208·1	231·3	249·3	269·8
μ_{eff}(B.M.)	0·65	0·64	0·62	0·61	0·59	0·56
Temp. (K)	125·5	115	107·5	102	96	90·5
$10^6\chi_A$	290·4	303·3	323·8	334·1	316·1	303·3
μ_{eff}(B.M.)	0·54	0·53	0·53	0·52	0·49	0·47

* Atomic magnetic susceptibilities in c.g.s.u.

For the tungsten compounds the frequencies of the Raman-active fundamentals ν_1, ν_2, and ν_5 were calculated from the i.r. combination bands. The fundamentals for WCl_6^- were, as expected, very similar in frequency to those of the neighbouring species $TaCl_6^-$.

U.v.–Visible Spectra of Tungsten Compounds.—The electronic spectra of $(Bu^tPCl_3)(WCl_6)$ and $(Bu^tMePCl_2)(WCl_6)$ at 90 and 295 K were consistent with the results reported [10,11] for the complex $(Et_4N)(WCl_6)$.

Magnetic Susceptibility Measurements of Tungsten Complexes.—Complexes of the hexachlorotungstate(V) ion are known [12] to be antiferromagnetic. Plots of the reciprocal atomic susceptibilities against temperature show Néel points in the range 100—140 K and the upper parts of the curves can be extrapolated to give large positive values of θ, the Curie–Weiss constant. Magnetic moments at room temperature [2,8,12] are less than 1 B.M.

The compounds $(Bu^tPCl_3)(WCl_6)$ and $(Bu^tMePCl_2)(WCl_6)$ show very similar behaviour (Table 2) confirming the presence of the WCl_6^- ion. The vibrational spectra indicate that the ion has octahedral structure but the mechanism of the antiferromagnetic exchange is unknown.

EXPERIMENTAL

Purification of Reagents.—Methyldichlorophosphine, phosphorus trichloride, and t-butyl chloride were purified by fractional distillation under a nitrogen atmosphere. Carbon disulphide was dried over phosphorus pentoxide and distilled under nitrogen. All liquids were degassed before use. Niobium and tantalum pentachlorides and tungsten hexachloride were used as supplied.

Preparation of Samples.—Because of the nature of the compounds investigated, all preparations and manipulations were carried out in a glove-box continuously flushed with dried, high purity nitrogen.

The metal chloride was initially dissolved in carbon disulphide. Then slight excesses of the phosphine and t-butyl chloride were added, in that order, to prevent formation of hydrocarbon polymers. Excesses of the reagents were used to minimize the chance formation of polymeric anions. The complexes were filtered, washed with carbon disulphide to remove any unreacted metal chloride, and then dried *in vacuo*. The analytical results for the six complexes reported here are listed in Table 1.

Raman Spectroscopy.—Raman spectra were obtained

---

[10] R. A. Walton, P. C. Crouch, and B. J. Brisdon, *Spectrochim. Acta*, 1968, **24A**, 601.

[11] B. J. Brisdon, D. A. Edwards, D. J. Machin, K. S. Murray, and R. A. Walton, *J. Chem. Soc.* (*A*), 1967, 1825.

[12] B. J. Brisdon and R. A. Walton, *J. Inorg. Nuclear Chem.*, 1965, **27**, 1101.

using a Spex 1401 spectrometer with either helium–neon or argon-ion laser excitation. Sample presentation was in sealed capillary tubes.

Infrared Spectroscopy.—The spectral region 400—1000 cm^{-1} was examined using the Grubb-Parsons Spectromaster; sample presentation was as Nujol mulls between potassium bromide plates. The R.I.I.C. FS-720 interferometer was utilised for the region 30—400 cm^{-1}; Nujol mulls between Polythene plates were used for sample presentation.

U.v.–Visible Spectroscopy.—U.v. and visible spectra were recorded using the Unicam SP 700C spectrophotometer. Solid state spectra were obtained at room temperature and liquid-nitrogen temperature by the diffuse reflectance method, lithium fluoride being used as the reference.

Magnetic Susceptibility Measurements.—Magnetic data were obtained using the Newport Instruments variable temperature Gouy balance over the temperature range 90—300 K. Sample presentation was in precalibrated quartz tubes.

[2/2080 *Received, 4th September*, 1972]