517. *State of Niobium Pentachloride in Solution*

By D. L. Kepert and R. S. Nyholm

Niobium pentachloride is found to remain as a dimeric non-electrolyte when dissolved in dry, oxygen-free carbon tetrachloride or nitromethane, although some decomposition occurs at low concentrations due to water as impurity in the solvent. This result is in contrast with the conclusions of other workers which were based on spectroscopic evidence. In acetonitrile, the monomeric non-electrolyte $NbCl_5,CH_3CN$ is formed. Similar results have been obtained for other pentahalides of niobium and tantalum.

The isomorphous pentachlorides and pentabromides of niobium and tantalum are dimeric in the solid, consisting of two octahedra sharing an edge.[1] The pentafluorides are tetrameric, consisting of octahedra sharing corners, with the metal atoms at the corners of a square.[2] In the liquid state, the pentachlorides are virtually non-conducting [3] whereas the pentafluorides are conducting suggesting significant ionisation.[4] In the gaseous state, the pentachlorides and pentabromides are monomeric, and electron diffraction shows them to have a trigonal bipyramidal structure.[5] The decrease in molecular weight on vaporisation is also indicated by the high Trouton constants.

The infrared and Raman spectra of solids, liquids, and solutions have been studied by a number of workers, who found that the spectra of the solid and solutions were similar; they attempted to assign the spectral bands in terms of trigonal bipyramidal structures. No experimental details of solvent purification were included, and the possibility that additional lines in the solution spectra are due to decomposition products cannot be

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[1] A. Zalkin and D. E. Sands, *Acta Cryst.*, 1958, **11**, 615.

[2] A. J. Edwards, R. D. Peacock, and R. W. H. Small, *J.*, 1962, 4486.

[3] W. Biltz and A. Voigt, *Z. anorg. Chem.*, 1922, **120**, 71; W. Biltz and W. Klemm, *ibid.*, 1926, **152**, 267.

[4] F. Fairbrother, W. C. Frith, and A. A. Woolf, *J.*, 1954, 1031.

[5] H. A. Skinner and L. E. Sutton, *Trans. Faraday Soc.*, 1940, **36**, 668.

excluded. Thus Moureau *et al.*[6] found that the Raman spectra of solid $NbCl_5$, solid $TaCl_5$, $NbCl_5$ in carbon disulphide, and liquid $TaCl_5$ were similar, and partially assigned the results on the basis of trigonal bipyramidal structures. Gaunt and Ainscough[7] also interpreted the Raman spectrum of solid niobium pentachloride and the infrared spectrum of niobium pentachloride in carbon disulphide in terms of this structure. Carlson[8] however found that the solid pentachlorides, the pentachlorides in carbon disulphide, and the pentachlorides in carbon tetrachloride had similar, but not identical, infrared spectra, and could only make partial assignments in terms of a trigonal bipyramidal structure. Bader and Westland[9] claimed that solid $NbCl_5$ and $NbCl_5$ in carbon tetrachloride have absorptions at 475 mμ, not present in gaseous $NbCl_5$, and deduced that $NbCl_5$ was dimeric in carbon tetrachloride.

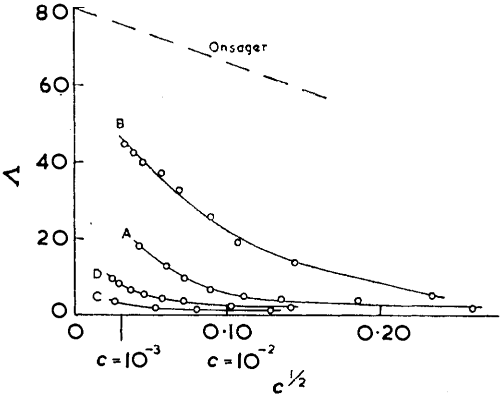
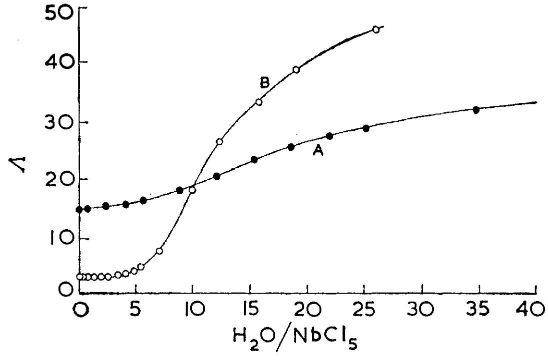


FIGURE 1. Conductances (cm.^{2} ohm^{-1} mole^{-1}) as function of concentration in nitromethane

A, Niobium pentachloride in dry nitromethane. B, Niobium pentachloride in nitromethane containing 0·005M water. C, Hydrogen chloride in dry nitromethane. D, Chlorine in dry nitromethane

FIGURE 2. Conductometric titration of water against niobium pentachloride in nitromethane



We have studied the pentahalides dissolved in nitromethane, acetonitrile, carbon tetrachloride, and carbon disulphide.

Nitromethane as Solvent.—The conductivity of niobium pentachloride in nitromethane increases markedly with dilution (Figure 1, curve A), indicating either that it is a weak electrolyte in this solvent and dissociates to solvated species in dilute solutions, or that reaction with impurities in the solvent is occurring, which becomes increasingly important in more dilute solutions. The broken line is that calculated from the Onsager limiting law. The conductivity is very dependent upon the water concentration of the solvent (curve B), indicating that at least part of the conductance arises from hydrolysis of

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[6] H. Moureau, P. Sue, and M. Magat, " Contribution a l'étude de la structure moleculaire. Vol. Commemoratif Victor Henri," 1947—1948, p. 125.

[7] J. Gaunt and J. B. Ainscough, *Spectrochim. Acta*, 1957, **10**, 52.

[8] G. L. Carlson, *Spectrochim. Acta*, 1963, **19**, 1291.

[9] R. F. W. Bader and A. D. Westland, *Canad. J. Chem.*, 1961, **39**, 2306.

niobium pentachloride. The results obtained are not very reproducible; those quoted are the lowest values of the conductivity which were obtained. Within experimental error, identical curves have been obtained with $TaCl_5$, $TaBr_5$, NbF_5, and $NbBr_5$.

The conductivity of these solutions falls slowly with time, and even more markedly on heating. The initial partial hydrolysis of the niobium pentachloride probably forms: (*a*) hydrogen chloride, which is conducting only if there remains some water in solution. Dry hydrogen chloride has a low conductivity (curve C). On heating or standing however, the $NbCl_5$ further dehydrates the solvent and the aquated hydrogen chloride, and the conductivity falls; (*b*) partially hydrolysed niobium species, $(NbCl_{5-x})^{x+}Cl_x^{x-}$, which may also be conducting. Heating may cause some coagulation of these species, although no precipitation is observed.

This effect of water and heating is also shown in the conductometric titration of water against $NbCl_5$ in nitromethane (Figure 2). In a fairly rapid titration in the cold (curve A), the $NbCl_5$ incompletely reacts with water impurities to form conducting solutions, and the conductance changes only slightly with increase in water concentration. However in a titration which is heated between each addition of water (curve B), at low concentrations of water the conductivity is very low because of the low conductivity of anhydrous hydrogen chloride, the hydrolysed $NbCl_5$, and the unchanged $NbCl_5$. After an end point at $H_2O : NbCl_5 :: \sim 5 : 1$, complete hydrolysis of the pentachloride occurs and the solution completely loses its yellow colour; then the conductivity rapidly increases upon addition of water due to the aquation of the free hydrogen chloride. In the latter titration, a heavy precipitate forms at $H_2O : NbCl_5 :: \sim 20 : 1$, while in the former titration, the niobium species do not precipitate until $H_2O : NbCl_5 :: \sim 100 : 1$.

The presence of water in the solvent is also indicated by the significant conductivity of dry chlorine (Figure 1, curve D); since chlorine does not react with nitromethane under these conditions, the most plausible reaction of chlorine to form conducting species is with trace amounts of water.

Confirmation that an irreversible reaction occurs on dilution of niobium pentachloride was shown after removal of the solvent and examination of the residue by *X*-ray powder photography; above approximately 0·1 molar the residue was partly $NbCl_5$, but below approximately 0·01 molar, no $NbCl_5$ was observed in the residue. Infrared spectra and carbon, hydrogen, and nitrogen analyses showed that the latter residue contains no nitromethane.

The diffuse reflectance spectra of $NbCl_5$, $NbBr_5$, and $TaBr_5$ ($TaCl_5$ is white and forms colourless solutions) and solution spectra in nitromethane show strong absorptions with edges at approximately 420, 620, and 490 mμ, respectively. The spectra at lower wavelengths could not be determined as the high extinction coefficients require low concentrations, which lead to decomposition. The extinction coefficient at various wavelengths on the edge of this absorption band does not follow Beer's law, but falls sharply at low concentrations due to decomposition (Figure 3).

The molecular weight of $NbCl_5$ in boiling nitromethane shows it to be dimeric above 0·1 molar, but less than monomeric below about 0·05 molar. Figure 4 shows the experimentally observed elevation of boiling point as a function of concentration, with theoretical slopes for both dimer and monomer.

In order to examine the feasibility of a reversible dissociation occurring on dilution of $NbCl_5$ to form either $NbCl_4^+$ and Cl^-, or $NbCl_4^+$ and $NbCl_6^-$, attempts have been made to prepare these ions.

(*a*) $NbCl_4^+$. Attempts were made to observe the existence of $NbCl_4^+$ by conductometric titration of silver perchlorate against niobium pentachloride in nitromethane. Only an end point at $AgClO_4 : NbCl_5 :: 5 : 1$ is shown (Figure 5). This result can be interpreted as showing that either all the partially dechlorinated products have the same conductivity, or the removal of one chlorine causes complete decomposition of the molecule with the liberation of the remaining chlorine atoms. $NbCl_4F$ has recently been prepared by the partial fluorination of $NbCl_5,PCl_5$.[10] Although non-conducting in the melt, it was formulated as $(NbCl_4)^+F^-$ on the basis of the formation of conducting solutions in acetonitrile and glacial acetic acid. Using the quoted values for the specific conductances, molar conductivities can be calculated which clearly show the non-existence of stable ionic species (Table 1).

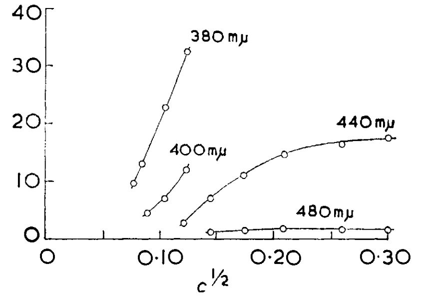

FIGURE 3. Extinction coefficient of niobium pentachloride in nitromethane as function of concentration at different wavelengths

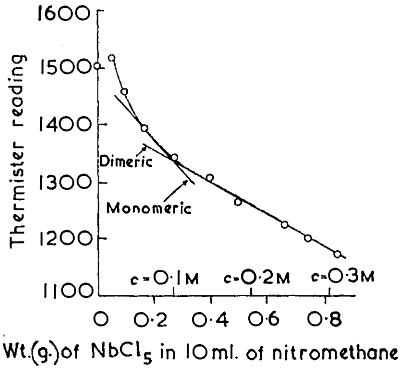

FIGURE 4. Elevation of boiling point by niobium pentachloride in nitromethane

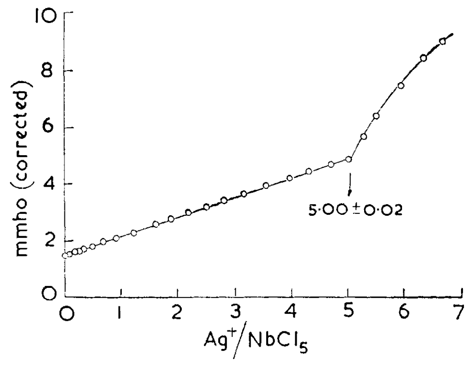

FIGURE 5. Conductometric titration of silver perchlorate (0·207M) against niobium pentachloride (130 ml. of 0·0252M) in nitromethane

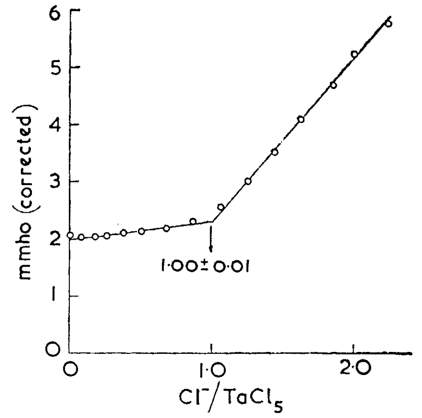

FIGURE 6. Conductometric titration of tetraphenylarsonium chloride (0·0408M) against tantalum pentachloride (100 ml. of 0·0132M) in nitromethane

TABLE 1

Conductance of $NbCl_4F$

Acetonitrile (molarity × 10^3)	2	4	10	20	55	83
Λ ($cm.^2$ ohm^{-1} $mole^{-1}$)	1000	400	100	10	2	0·02
Acetic acid (molarity × 10^3)	$1{\cdot}_5$	5	25	45		
Λ ($cm.^2$ ohm^{-1} $mole^{-1}$)	$0{\cdot}01_5$	0·2	0·1	0·2		

(*b*) $NbCl_6^-$. Conductometric titration of tetraphenylarsonium chloride against niobium pentachloride in nitromethane shows an end point due to $NbCl_6^-$ only (Figure 6). The first addition of tetraphenylarsonium chloride always produces a slight lowering of conductivity due to suppression of dissociation of free hydrochloric acid. The slight turbidity which is sometimes present in the $NbCl_5$ solution due to $NbOCl_3$ disappears at

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[10] L. Kolditz and G. Furcht, *Z. anorg. Chem.*, 1961, **312**, 11.

the end point due to the formation of $NbOCl_4^-$. There are no subsequent end points ($Cl : NbCl_5 :: <3{\cdot}5 : 1$). Similar results have been obtained by others using benzoyl chloride,[11] phosphorous oxychloride,[12] and iodine monochloride [13] as solvents.

TABLE 2

Conductance of $NbCl_5$ in acetonitrile

Molarity $\times 10^3$	58·9	29·4	19·5	14·3	9·4	6·9	4·8	3·5	2·5	1·8	1·2
Λ (cm.^{2} ohm^{-1} mole^{-1})...	12	23	26	33	42	50	59	70	85	101	124

Acetonitrile as Solvent.—The pentahalides form conducting solutions in acetonitrile in an analogous manner to that described for nitromethane (Table 2). In these cases however pumping off the solvent leaves the isomorphous, diamagnetic complexes MX_5,CH_3CN.

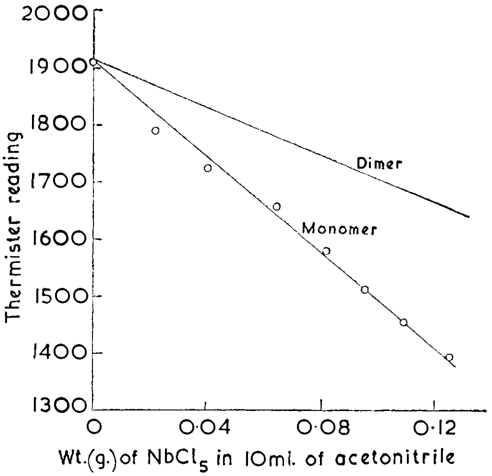

FIGURE 7. Elevation of boiling point by niobium pentachloride in acetonitrile

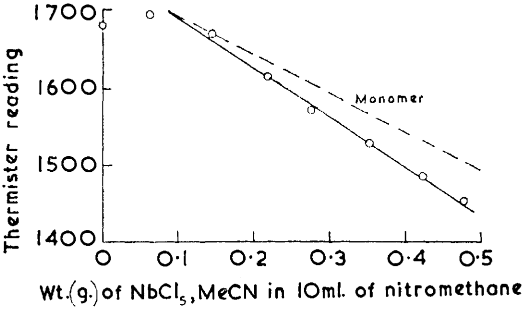

FIGURE 8. Elevation of boiling point by $NbCl_5$,MeCN in nitromethane

The molecular weight in boiling acetonitrile shows the complexes to be monomeric (Figure 7), and to be partially dissociated in boiling nitromethane (Figure 8). The infrared spectra of these compounds are normal for co-ordinated acetonitrile (Table 3). There are two important bands in the region of 2300 cm.$^{-1}$. One is a combination band of the symmetric CH_3 deformation (ν_3) and the symmetric C–C stretch (ν_4),[14] both of which can be measured independently; the second band is due to the symmetric C–N stretch (ν_2) (Table 3). The increase of ν_2 on co-ordination is normal for co-ordinated acetonitrile.

TABLE 3

Infrared spectra of acetonitrile complexes

	ν_3	ν_4	$\nu_3 + \nu_4$	$\nu_3 + \nu_4$ (obs.)	ν_2	$\Delta\nu_2$
$CH_3{\cdot}CN$	1375	917	2292	2290	2254	
$NbCl_5,CH_3{\cdot}CN$	1357	947	2304	2306	2283	29
$NbBr_5,CH_3{\cdot}CN$	1360	947	2307	2310	2288	34
$TaCl_5,CH_3{\cdot}CN$	1362	952	2314	2314	2290	36
$TaBr_5,CH_3{\cdot}CN$	1359	950	2309	2314	2290	36

Carbon Tetrachloride as Solvent.—The diffuse reflectance spectrum of niobium pentachloride and the absorption spectrum in carbon tetrachloride show the edge of a strong

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[11] V. Gutmann and H. Tannenberger, *Monatsh.*, 1957, **88**, 292.
[12] V. Gutmann and F. Mairinger, *Monatsh.*, 1958, **89**, 724.
[13] V. Gutmann, *Z. anorg. Chem.*, 1951, **264**, 151.
[14] P. Venkateswarlu, *J. Chem. Phys.*, 1951, **19**, 293.

absorption at about 420 mμ. The absorption maximum at 475 mμ observed by Bader and Westland could not be found.

Although of limited solubility, the molecular weight of niobium pentachloride in boiling carbon tetrachloride shows it to be dimeric; Figure 9 shows the experimentally observed elevation of boiling point as a function of concentration, with theoretical slopes for monomer and dimer. No significant decomposition occurs at low concentrations indicating the more effective purification of this solvent.

The small differences between the infrared and Raman spectra of the pentahalides in carbon tetrachloride compared with the solid state, observed by other workers (see above), are possibly due to decomposition products arising from oxygen or water impurities in the solvent.

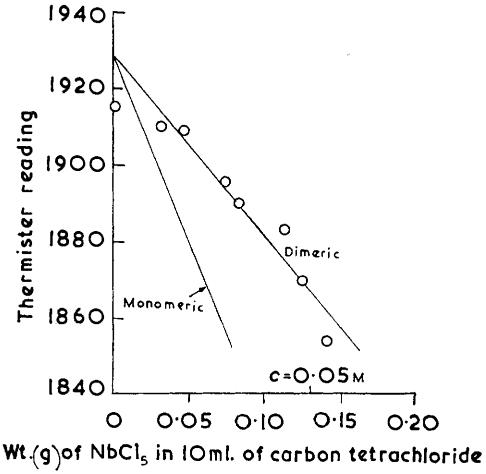

FIGURE 9. Elevation of boiling point by niobium pentachloride in carbon tetrachloride

Carbon Disulphide as Solvent.—Niobium pentachloride forms an orange solution in carbon disulphide, and the edge of the absorption is shifted to about 510 mμ, clearly indicating reaction with the solvent.

EXPERIMENTAL

Physical Measurements.—The halides and acetonitrile complexes were stored in vacuum manifolds. The preparation of the acetonitrile complexes, and all measurements of conductance and spectra on the pentahalides and complexes were carried out in a conventional vacuum line. " Oxygen-free " nitrogen was further purified by passing through a column containing activated copper at 400°, and scrubbing with chromous solutions (0·4M) in sulphuric acid (0·1M). The gas was then dried with sulphuric acid and magnesium perchlorate. The solvents were dried over calcium hydride for several weeks, de-oxygenated with the purified nitrogen, and then fractionally distilled. The apparatus was of such a design as to allow quantitative dilution of halide solutions so that measurements could be made over a wide concentration range.

The conductances were measured with bright platinum electrodes sealed into the flask, and a Wayne–Kerr universal bridge type B221. The solution spectra were measured using 0·1 cm. or 1 cm. silica cells joined to the apparatus with graded seals, with a Unicam S.P. 500 spectrophotometer. Reflectance spectra were measured using the manufacturer's attachment to a Unicam S.P. 500 spectrophotometer with samples prepared in a conventional dry-box. Magnetic measurements were made using the conventional Gouy method with tubes packed in the dry-box. Molecular weight determinations were carried out by using a Gallenkamp ebulliometer modified so that it could be used on the vacuum line, with sample pellets prepared in the dry-box. The apparatus was calibrated with naphthalene.

Niobium and tantalum were determined by ignition of the complexes to the oxides, and halogen by potentiometric titration with silver nitrate after a sealed, weighed ampoule of the compound had been broken under the surface of an alkaline solution. Carbon, hydrogen, and nitrogen were determined by the Max Planck Institut für Kohlenforschung, Mülheim, Germany.

Halides.—Preparation and analyses of the halides have been described elsewhere.[15]

Acetonitrile Complexes.—The metal pentahalide (*ca.* 2 g.) was dissolved in hot acetonitrile (*ca.* 20 ml.), and the solution evaporated to a small volume, cooled, filtered, washed with small quantities of acetonitrile, and pumped dry. The crystalline complexes are very unstable to air and water. All the complexes are isomorphous. Typical analyses are given: for pentachloro(acetonitrilo)niobium(V) (Found: C, 7·3; H, 2·1; N, 4·8; Cl, 55·6; Nb, 30·0. $C_2H_3NCl_5Nb$ requires C, 7·7; H, 1·0; N, 4·5; Cl, 57·0; Nb, 29·9%); and for pentabromo(acetonitrilo)niobium(V) (Found: C, 4·2; H, 1·7; N, 1·5; Br, 74·1. $C_2H_3NBr_5Nb$ requires C, 4·5; H, 0·6; N, 2·6; Br, 74·9%).

The niobium complexes show a slight paramagnetism. The magnetic susceptibility (χ) of pentachloro(acetonitrilo)niobium(V) is $0{\cdot}06 \times 10^{-6}$, therefore χ'_{Nb} is 147×10^{-6} cgsu, and the magnetic moment (μ_{eff}), 0·59 B.M. Similarly, for pentabromo(acetonitrilo)niobium(V), χ, χ'_{Nb}, and μ_{eff} are $-0{\cdot}07 \times 10^{-6}$, 143×10^{-6} cgsu, and 0·59 B.M., respectively.

The reflectance spectra are virtually identical with the pure halides.

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[15] R. J. H. Clark, D. L. Kepert, J. Lewis, and R. S. Nyholm, preceding Paper.