

53. *The Halides of Niobium and Tantalum. Part VII.¹ Dimethyl Ether, Di-n-propyl Ether, and Di-n-propyl Sulphide Complexes of the Pentachlorides; the Relative Strengths of Dialkyl Ether and Dialkyl Sulphide Complexes.*

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The following new crystalline 1 : 1 complexes have been isolated and their compositions established by analysis: $\text{NbCl}_5, \text{Me}_2\text{O}$; $\text{TaCl}_5, \text{Me}_2\text{O}$; $\text{NbCl}_5, \text{Pr}^n_2\text{S}$ (m. p. 27.6°); and $\text{NbCl}_5, \text{Pr}^n_2\text{O}$. The first three distil or sublime unchanged; the fourth decomposes when heated.

The ether is readily replaced from the complexes $\text{NbCl}_5, \text{Et}_2\text{O}$, $\text{TaCl}_5, \text{Et}_2\text{O}$, and $\text{NbCl}_5, \text{Pr}^n_2\text{O}$, by the corresponding dialkyl sulphide, but dimethyl ether is not displaced from $\text{NbCl}_5, \text{Me}_2\text{O}$ by dimethyl sulphide.

A redetermination of the m. p. of $\text{NbCl}_5, \text{Et}_2\text{S}$ gave m. p. 26.5° .

COMPARISON of the properties of some sulphide and diethyl ether complexes of niobium and tantalum pentachlorides and pentabromides, as described in Parts V² and VI¹ of this series, showed that the sulphide complexes were thermally much more stable than the diethyl ether complexes. This has now been confirmed by replacement reactions in which it has been shown that diethyl ether is readily replaced from a complex by diethyl sulphide, and di-n-propyl ether by di-n-propyl sulphide. Moreover, diethyl sulphide is selectively absorbed by niobium pentachloride, with the formation of the complex $\text{NbCl}_5, \text{Et}_2\text{S}$, from a gaseous mixture of diethyl sulphide and ether in which it is present to the extent of only 10%. On the other hand, dimethyl ether is not displaced by dimethyl sulphide from its complex with niobium or tantalum pentachloride, nor is the sulphide displaced by the ether from the complex $\text{TaCl}_5, \text{Me}_2\text{S}$, though in each case at about -30° the second ligand is

¹ Part VI, Fairbrother and Nixon, *J.*, 1962, 150.

² Cowley, Fairbrother, and Scott, *J.*, 1958, 3133.

absorbed by the complex in question but is completely evolved on evacuation at room temperature, leaving the original complex. In the case of the complex $\text{NbCl}_5, \text{Me}_2\text{O}$ an amount of dimethyl sulphide is taken up which corresponds exactly to the composition, $\text{NbCl}_5, \text{Me}_2\text{O}, \text{Me}_2\text{S}$: similarly, at -30° , an amount of dimethyl sulphide is taken up by niobium pentachloride which corresponds to the composition $\text{NbCl}_5, 2\text{Me}_2\text{S}$. In both cases, however, the 1 : 2 complex dissociates into a 1 : 1 complex, with evolution of dimethyl sulphide on evacuation at a temperature well below room temperature.

EXPERIMENTAL

Preparation of Halides.—These were prepared as previously described.²

Ethers and Sulphides.—Dimethyl ether (commercial cylinder product) was passed through alkaline Brady's reagent (a solution of 2,4-dinitrophenylhydrazine) to remove aldehyde, condensed at -78° on to lithium aluminium hydride, roughly fractionated in a closed system, and stored on fine-mesh silica gel which had been degassed at 300° . Dimethyl sulphide, diethyl ether, di-n-propyl ether, and di-n-propyl sulphide were purified by fractional distillation and collected over narrow ranges: final drying was carried out by pre-treatment with the halide under consideration.

Preparation of Complexes.—These were prepared in a vessel having a side-arm from which the halide was sublimed from its ampoule and provided with a tap and B10 joint so that it could be removed from the vacuum-line for weighing.

System, Niobium Pentachloride-Dimethyl Ether.—An excess of dimethyl ether was condensed at -78° on to niobium pentachloride (5.817 g.), and the whole was maintained at 0° for about 10 min. to attain equilibrium, after which the excess of ether was pumped off (Found: Increase of wt., 0.986 g. $\text{NbCl}_5, \text{Me}_2\text{O}$ requires increase, 0.991 g. Found: Cl, 55.0; Nb, 26.1. $\text{NbCl}_5, \text{Me}_2\text{O}$ requires Cl, 56.0; Nb, 29.3%). The complex sublimed unchanged at $105^\circ/\sim 10^{-4}$ mm. It was pale yellow and fairly stable in air.

System, Tantalum Pentachloride-Dimethyl Ether.—This was prepared in the same manner as the niobium pentahalide complex (Found: Cl, 41.7; Ta, 45.95. $\text{TaCl}_5, \text{Me}_2\text{O}$ requires Cl, 44.0; Ta, 44.7%). The complex was white and sublimed unchanged at $93^\circ/\sim 10^{-4}$ mm.

System, Niobium Pentachloride-Di-n-propyl Ether.—An excess of di-n-propyl ether was distilled on to niobium pentachloride (1.673 g.), which dissolved in the ether. After 10 min. the excess of ether was removed under a vacuum, leaving the pale yellow complex [Found: Increase in wt., 0.632 g. $\text{NbCl}_5, (\text{C}_3\text{H}_7)_2\text{O}$ requires increase 0.632 g. Found: Cl, 47.4; Nb, 24.9. $\text{NbCl}_5, (\text{C}_3\text{H}_7)_2\text{O}$ requires Cl, 47.7; Nb, 24.95%]. The complex decomposed when heated in a vacuum, giving a white product, probably mainly oxytrichloride, as in the case of the diethyl ether complex.

System, Niobium Pentachloride-Di-n-propyl Sulphide.—This was prepared in a manner similar to the ether complex [2.033 g. of pentachloride gained 0.894 g. $\text{NbCl}_5, (\text{C}_3\text{H}_7)_2\text{S}$ requires 0.890 g. Found: Cl, 43.9; Nb, 23.85. $\text{NbCl}_5, (\text{C}_3\text{H}_7)_2\text{S}$ requires Cl, 45.6; Nb, 23.8%]. The complex was orange-red and had m. p. 27.6° and sublimed unchanged *in vacuo* at 108° .

All the above complexes had dissociation pressures at room temperature of less than 1 mm.

System, Niobium Pentachloride-Dimethyl Sulphide.—An excess of dimethyl sulphide was condensed on to niobium pentachloride (5.219 g.) and the whole evacuated to 1 mm. at -30° for some hours (2.400 g. of Me_2S were absorbed. $\text{NbCl}_5, 2\text{Me}_2\text{S}$ requires 2.394 g.). The second molecule of sulphide was easily removed by pumping at -20° , leaving the complex $\text{NbCl}_5, \text{Me}_2\text{S}$ reported in Part VI.¹

The complexes $\text{NbCl}_5, \text{Et}_2\text{O}$, $\text{TaCl}_5, \text{Et}_2\text{O}$,² and $\text{NbCl}_5, \text{Et}_2\text{S}$ ¹ were prepared as previously described. The last of these had m. p. 26.5° .

Replacement Reactions.—*System, $\text{NbCl}_5, \text{Et}_2\text{O} + \text{Et}_2\text{S}$.* An approximately equimolar quantity (0.329 g.) of diethyl sulphide was condensed on to the complex $\text{NbCl}_5, \text{Et}_2\text{O}$ (1.281 g.) at -195° in a vacuum system. The complex changed from pale yellow to dark red immediately on contact with the diethyl sulphide vapour. (Reaction occurred even at room temperature, the vessel becoming warm as the sulphide was absorbed.) After completion of the condensation the mixture was allowed to warm to room temperature, forming a deep red viscous liquid. After 10 min., volatile products were pumped off, condensed, and identified by refractive

index, vapour pressure, and molecular weight (vapour density) as diethyl ether and estimated by the loss in weight of the system (0.267 g.: Et_2O requires 0.274 g.). The remaining product sulphide complex was deep red and had m. p. 24.5° .

System, $\text{NbCl}_5 + \text{Et}_2\text{O} + \text{Et}_2\text{S}$. An excess of a gaseous 9:1 mixture of diethyl ether and sulphide was admitted to an evacuated vessel containing niobium pentachloride (1.214 g.). There was again immediate production of a red colour due to absorption of the sulphide vapour, even at room temperature; the mixture was condensed on to the halide and warmed again to room temperature; the excess of volatile compounds was pumped off; the red crystals remaining had a dissociation pressure of less than 1 mm., melted 26.5° , and there was an increase of weight of 0.405 g. ($\text{NbCl}_5, \text{Et}_2\text{S}$ requires increase, 0.405 g.).

Systems, $\text{NbCl}_5, \text{Me}_2\text{O} + \text{Me}_2\text{S}$; $\text{TaCl}_5, \text{Me}_2\text{S} + \text{Me}_2\text{O}$; and $\text{TaCl}_5, \text{Me}_2\text{O} + \text{Me}_2\text{S}$. By contrast with the foregoing, dimethyl ether is not replaced by dimethyl sulphide, or *vice versa*, in these systems. An excess of dimethyl sulphide was condensed on to the complex $\text{NbCl}_5, \text{Me}_2\text{O}$ (0.744 g.) in a closed system. Even after 1 hr. at room temperature, no increase in pressure was observed, such as would indicate a liberation of ether. After removal of the volatile components, the weight and composition of the original complex were unchanged. That some labile compound was formed was indicated by a change of colour from pale yellow to salmon-pink and by the increase of weight to 0.880 g., which corresponds to the formation of $\text{NbCl}_5, \text{Me}_2\text{O}, \text{Me}_2\text{S}$, on removal of the excess of dimethyl sulphide by pumping at -30° during 2 days; but the sulphide was readily removed at room temperature, the complex returning to its pale yellow colour, and is probably held as lattice sulphide.

When an excess of dimethyl sulphide was condensed on to the complex $\text{TaCl}_5, \text{Me}_2\text{O}$ or an excess of the ether on to the complex $\text{TaCl}_5, \text{Me}_2\text{S}$ the complexes were recovered unchanged, as shown by the absence of a permanent change in colour or weight.

System, $\text{TaCl}_5, \text{Et}_2\text{O} + \text{Et}_2\text{S}$. Diethyl sulphide (0.260 g., ~ 1 mol.) was condensed at -195° on to the grey complex (1.229 g., ~ 1 mol.). There was little reaction between the solid complex and the sulphide vapour; this occurred only when the sulphide was liquefied. The mixture was allowed to warm to room temperature, forming a dark red liquid from which the volatile component was pumped off, condensed, and identified as diethyl ether by its vapour pressure, refractive index, molecular weight (vapour density), and mass (Found: 0.210 g.; $\text{TaCl}_5, \text{Et}_2\text{O}$ requires Et_2O , 0.210 g.).

System, $\text{NbCl}_5, \text{Pr}^n_2\text{O} + \text{Pr}^n_2\text{S}$. Di-n-propyl sulphide (0.732 g., ~ 1 mol.) was condensed on to the niobium pentachloride-di-n-propyl ether complex (2.305 g., ~ 1 mol.). After 5 min. at room temperature the volatile fraction was removed, condensed under vacuum, and identified as di-n-propyl ether by its refractive index; completion of the reaction was indicated by the mass of ether displaced (0.632 g.; $\text{NbCl}_5, \text{Pr}^n_2\text{O}$ requires Pr^n_2O 0.632 g.). The orange-red product had m. p. 22.5° ($\text{NbCl}_5, \text{Pr}^n_2\text{S}$, m. p. 27.6°).

System, $\text{NbCl}_5, \text{Pr}^n_2\text{S} + \text{Pr}^n_2\text{O}$.—An excess of di-n-propyl ether was condensed on to the sulphide complex (2.923 g.), and the volatile fraction was later removed. No change took place in either the mass or other properties of the complex.

DISCUSSION

The results leave no room for doubt that the heats of formation of the diethyl and di-n-propyl sulphide complexes from their components are greater than those of the corresponding ether complexes, especially when one considers that the replacement reactions are exothermic and the resulting sulphide complexes low-melting solids. They also suggest that the bond energy of the metal-sulphur bond in these complexes is greater than that of the metal-oxygen bond, though in the absence of quantitative thermochemical data a direct comparison is not possible. The relatively greater strength of the metal-sulphur bond is at first sight rather surprising in view of the avidity of these metal atoms for oxygen and the way in which metal-oxygen bonds dominate much of their chemistry, and it is possible that the order $\text{SR}_2 > \text{OR}_2$ may be reversed in other series of compounds.

One cannot accept as an explanation of the strength of the metal-sulphur bond a simple back-co-ordination of unshared *d*-electrons from a penultimate shell, as has been postulated to account for this effect in the case of adducts with copper, zinc, and the later transition

elements, especially platinum and palladium,³ since in the case of niobium and tantalum all the *d*-electrons beyond those in the inert-gas type cores are used in bonding with halogen. It seems possible that steric and electrostatic effects may have more influence in determining the stabilities of these adducts than supplementary π -bonding. There are three factors to be considered: (*a*) the steric effect, (*b*) the dipole moment of the ligand, and (*c*) the polarisability of the sulphur or oxygen atom. The steric effect is probably chiefly responsible for the greater stabilities of the dimethyl adducts and the formation of 1:2 complexes with the sterically unhindered tetrahydrothiophen whilst diethyl ether forms only 1:1 complexes. We shall, also, report later the formation of 1:2 complexes between the pentafluorides and dimethyl ether. The chief cause of the greater stabilities of the sulphides, however, probably lies with factors (*b*) and (*c*). The dipole moments of the dialkyl sulphides are greater than those of the ethers (Et₂O, 1.15 D; Et₂S, 1.58 D),⁴ though the difference is much less with the dimethyl compounds (Me₂O, 1.29 D; Me₂S, 1.40 D).⁴ These are the dipole moments of the undistorted gaseous molecules and chiefly determined by their orientation polarisations. When, however, the oxygen or sulphur atom approaches the metal atom in these halides, it encounters a strong field. That such a strong field exists is shown by the excellent Friedel-Crafts-type catalytic properties of these penta-halides.⁵ This field will further enhance the dipole moment of the ligand by polarisation of the electrons of the sulphur or oxygen atom, and the more so the greater the electron polarisability of these atoms. Here again the advantage is in favour of sulphur, which has the greater polarisability in these compounds (sulphur in Et₂S, 9.1 c.c.; oxygen in Et₂O, 2.8 c.c.)⁴. Other systems also have been reported in which the order of donor strength is SR₂ > OR₂ and in which supplementary π -bonding to the sulphur appears to be precluded, *viz.*, SnCl₄ and SbCl₅.⁶ A similar explanation may apply also to them.

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³ Ahrland, Chatt, and Davies, *Quart. Rev.*, 1958, **12**, 265.

⁴ Bailar, "Chemistry of the Coordination Compounds," Reinhold, New York, 1956, p. 129.

⁵ Fairbrother and Frith, *J.*, 1951, 3051.

⁶ Lindqvist and Zackrisson, *Acta Chem. Scand.*, 1960, **14**, 453.