Co-ordination Complexes of Niobium and Tantalum. Simple and Polymeric Oxy-chloro-alkoxy-bipyridyl Derivatives

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WE have examined the interaction of niobium- and tantalum-(V) chlorides with bipyridyl under various conditions and isolated several types of complexes.

From solutions in ethanol and n-propanol containing small, controlled amounts of water, we have prepared stable, colourless crystalline compounds of formula $NbOCl_2(OR)bipy$ ($R = Et, Pr^n$). The infrared spectra of these complexes show, besides the vibrational modes associated with co-ordinated bipyridyl and alkoxy-groups, sharp doublets at 910 and 890 cm.$^{-1}$ and at 905 and 880 cm.$^{-1}$ respectively, which can be attributed to a niobium–oxygen vibrational mode. In the Nb–Cl stretching region the ethoxy-derivative shows strong bands at 333 and 313 cm.$^{-1}$, and the n-propyloxy-derivative a strong band at 323 cm.$^{-1}$ These values are comparable with the frequencies observed in chloro-acetylacetonato-alkoxy-complexes of niobium and tantalum.[1]

From an ethanol solution of Nb^{IV} [2] under an atmosphere of argon a paramagnetic blue–green crystalline compound of formula $Nb_2Cl_5(OEt)_3$-$bipy_2$ was obtained. It has a magnetic moment of 1·39 B.M. at 20°C.[3] Some properties of this compound suggest the existence of ionic complex forms of the type $[Nb(OEt)_2bipy_2]^{2+}$ $[NbCl_5(OEt)]^{2-}$.

From ether solutions, under anhydrous conditions, a yellow crystalline complex of formula $Nb_2OCl_8bipy_2$ was prepared.[4] This compound is very sensitive to moisture. In addition to the vibrational absorption bands due to co-ordinated bipyridyl, the infrared spectrum of the complex shows a strong band at 940 cm.$^{-1}$, undoubtedly arising from an Nb=O stretching mode. Under similar conditions the pale yellow complex $Ta_4OCl_{18}bipy_4$ was prepared, which has similar properties and a similar infrared spectrum to the niobium complex, and which shows a Ta=O stretching frequency at 930 cm.$^{-1}$ The complex $NbOCl_3bipy$ has been isolated from benzene suspensions of $NbOCl_3$ and bipyridyl; it is less sensitive to moisture than the two last-mentioned complexes.

The oxy-chloro-bipyridyl complexes are insoluble in nonpolar solvents, so we were unable to determine their molecular weights. The infrared spectra of the three oxy-chloro-bipyridyl complexes all show the presence of co-ordinated bipyridyl and the absence of the bipyridinium cation. (The bipyridinium cation is, however, formed in the presence of traces of moisture, and under these conditions bands associated with it can be observed in the infrared spectra.)

TABLE[a]

Complex	Colour	m.p. (°c)	i.r. bands (cm.$^{-1}$)	Assignment of i.r. bands (stretching)	Magnetic moment (B.M. at 20°c)
$NbOCl_2(OEt)bipy$ ..	colourless	210 (dec.)	910, 890	Nb=O	
			333, 313	Nb-Cl	
$NbOCl_2(OPr^n)bipy$ ..	colourless	163 (dec.)	905, 880	Nb=O	
			323	Nb-Cl	
$Nb_2Cl_5(OEt)_3bipy_2$ ..	green–blue	140 (dec.)			1·39
$Nb_2OCl_8bipy_2$	yellow	40 (dec.)	940	Nb=O	
			341, 318	Nb-Cl	
$Ta_4OCl_{18}bipy_4$	pale yellow	40 (dec.)	930	Ta=O	
			348, 320	Ta-Cl	
$NbOCl_3bipy$	colourless	120 (dec.)	940	Nb=O	
			342, 316	Nb-Cl	

[a] The compounds were analysed for C, H, N, Cl, metal, and bipy. The analyses are in good agreement with the formulae, *e.g.*, $NbOCl_2(OEt)bipy$ ($C_{12}H_{13}O_2N_2Cl_2Nb$) requires: C, 37·8; H, 3·4; N, 7·4; Cl, 18·6; Nb, 24·4; bipy 41·0. Found: C, 38·2; H, 3·4; N, 7·2; Cl, 18·9; Nb, 24·9; bipy, 41·2.

The following polymeric complexes (empirical formulae based upon analytical and spectroscopic evidence) have been obtained by precipitation from 96%-ethanol solutions with chloroform: $Nb_4O_6(OH)_2Cl_4(OEt)_2bipy_2$ and $Ta_6O_2(OH)_{18}Cl_6(OEt)_2bipy_2$. They are colourless and amorphous, soluble in methanol, ethanol, and water. They can be re-precipitated from alcohol solutions. Their infrared spectra show hydrogen bonding, co-ordinated alkoxy- and bipyridyl groups, M–O–M vibrational bands, and the absence of bipyridinium cation. The complexes are not thermally stable; this may imply the occurrence of linear polymerisation rather than ring formation. The chains presumably terminate with a bipyridyl ligand at either end. Compounds with polymeric cationic species of niobium and tantalum were isolated from ethanol solutions containing large anions (*e.g.*, tetraphenylborate and Reinecke salt). The cations in these compounds have oxy-, hydroxy-, alkoxy-, and bipyridyl ligands, the metal atoms having positive charges (1+ and 2+ for niobium, 1+ for tantalum), the niobium cation consisting of four, and the tantalum cation of six, metal ions. The cationic forms of niobium and tantalum are believed to be stabilised by co-ordinated bipyridyl. The complexes formed by niobium and tantalum with bipyridyl in these systems are not of identical type.

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[1] C. Djordjević, *Spectrochim. Acta*, 1965, **21**, 301.
[2] R. A. D. Wentworth and C. H. Brubaker, *Inorg. Chem.*, 1963, **2**, 551.
[3] R. E. McCarley and J. C. Boatman, *Inorg. Chem.*, 1963, **2**, 540.
[4] R. J. H. Clark, D. L. Kepert, and R. S. Nyholm, *J. Chem. Soc.*, 1965, 2877.