Co-ordination Complexes of Niobium and Tantalum. Part XIV.[1] Alkoxo(2,2'-bipyridine)trichloroniobium(IV) Complexes

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The preparation and properties of crystalline mixed-ligand Nb^{IV} complexes of formula $[NbCl_3(OR)(bipy)]$ (R = Me, Et, Pr^n, or Bu^n; bipy = 2,2'-bipyridine) are described. The complexes were prepared by controlled reduction of $[NbCl_2(OR)_3]$ complexes using (2,2'-bipyridine)lithium in tetrahydrofuran. They are paramagnetic with magnetic moments in the range of 1·4—1·6 B.M. and their i.r. spectra show the presence of co-ordinated 2,2'-bipyridine and alkoxo-groups.

SEVERAL methods have been used to prepare Nb^{IV} complexes: electrolytic reduction in anhydrous alcohols;[2,3] reduction of niobium pentahalide complexes in the presence of pyridine[4] or bidentate nitrogen[5] and arsenic[6] ligands; and the usual synthetic route, formation of adducts by using niobium tetrahalide complexes.[7-9] The method of preparation of the complexes reported here differs from those mentioned above in that red (2,2'-bipyridine)lithium, Li(bipy), is used as reducing agent. Although the corresponding green dilithium-complex Li_2(bipy) has been widely used by Herzog,[10] it is a very powerful reducing agent and reduction may proceed as far as Nb^0 or Nb^{-I}.[11] However, by using Li(bipy) under carefully controlled conditions, reduction can be limited to the stage at which alkoxo(2,2'-bipyridine)trichloroniobium(IV) complexes form. Products of lower oxidation state, if formed as impurities, are removed in the mother liquor.

RESULTS AND DISCUSSION

Trialkoxodichloroniobium(V) complexes[12] were found to be the best starting materials. It has been observed

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that on addition of *ca.* 0·5 equivalents of Li(bipy) to these complexes homogeneous green precipitates formed, which corresponded by composition to the desired pure Nb^{IV} complexes. Further addition of the reducing agent caused the colour of the reaction mixtures to change from dark green to violet, indicating decomposition of the Nb^{IV} complexes and formation of probably several nonstoicheiometric products of Nb^{III} and of lower niobium oxidation states. The synthesis was therefore controlled by adding only 0·5 equivalents of Li(bipy). These observations suggest that the reaction course may be represented by equation (1) (R = Me, Et, Pr^n, or Bu^n).

$$2[NbCl_2(OR)_3] + Li(bipy) \longrightarrow [NbCl_3(OR)(bipy)] + LiCl + [Nb(OR)_5] \quad (1)$$

TABLE 1

Properties of alkoxo(2,2′-bipyridine)trichloroniobium(IV) complexes

Complex	M.p.[a] /°C	Magnetic moment μ_{eff}/B.M.	Analyses/% Found C	H	N	Cl	Nb	Calc. C	H	N	Cl	Nb
$[NbCl_3(OMe)(bipy)]$	115	1·51	34·9	3·25	6·90	27·65	23·85	34·2	2·85	7·25	27·5	24·05
$[NbCl_3(OEt)(bipy)]$	155	1·55	35·5	3·65	7·00	26·45	22·75	35·95	3·30	7·00	26·55	23·2
$[NbCl_3(OPr^n)(bipy)]$	205	1·64	37·8	3·85	6·45	25·6	22·4	37·7	3·65	6·75	25·70	22·4
$[NbCl_3(OBu^n)(bipy)]$	115	1·41	39·85	4·50	6·45	24·55	21·1	39·15	4·00	6·55	24·8	21·7

[a] With decomposition.

TABLE 2

Tentative assignment of characteristic bands (cm^{-1}) in the i.r. spectra of the niobium(IV) complexes

Complex	ν(CH) bipy	ν(CH) OR	ν(CC) and ν(CN) for the bipy rings		ν(CO)	$\nu(CH)_{def}$ out of plane for bipy	ν(MO)
$[NbCl_3(OMe)(bipy)]$	3115	2975			1090vs		
	3080	2925	1605s	1468s		765s	600br
	3060	2825			1060s		
$[NbCl_3(OEt)(bipy)]$	3115	2980			1080vs		
	3090	2940	1605s	1465s	1055vs	765s	600br
	3060	2890			935m		
		2860			905m		
$[NbCl_3(OPr^n)(bipy)]$	3110	2960			1065vs		
	3080	2930	1600s	1465s		765s	570br
	3060	2870			1040s		
$[NbCl_3(OBu^n)(bipy)]$	3110	2940			1060vs		
	3080	2870	1600s	1465s		768s	570br
	3050				1020s		

The alkoxo(2,2′-bipyridine)trichloroniobium(IV) complexes are green crystalline solids, stable in the absence of moisture and oxygen. According to *X*-ray powder photographs the alkoxo-derivatives are not isomorphous. The propoxo-derivative is the most stable towards oxidation and decomposition, in agreement with its thermal stability (Table 1). The complexes are soluble only in polar solvents, where they gradually decompose, thus preventing conductivity and molecular-weight determinations. The oxidation state of niobium was confirmed by iodine titration in the absence of oxygen,[11] values between 4·04 and 4·11 being obtained (indicating the presence of relatively small amounts of impurities).

The magnetic moments of the niobium(IV) complexes, measured at room temperature in an argon atmosphere, were in the range 1·4—1·6 B.M. (Table 1). These values, slightly lower than those expected for the spin-only case of the d^1 electron configuration, may arise for various reasons. Reproducible values obtained in several determinations show that decomposition is not the cause of this small, but consistent lowering of the moment observed previously. A high spin-orbit coupling constant for niobium(IV) or metal–metal interaction is the most probable origin of this deviation. Metal–metal interactions, however, usually cause much more drastic decreases in the moments. More elaborate magnetic measurements and *X*-ray structure analyses of these compounds is needed to explain this behaviour, generally observed for Nb^{IV} derivatives that are expected to be octahedral.[3-9]

Some useful information is provided by the i.r. spectra of the niobium(IV) complexes, and tentative assignments of the relevant vibrational modes is given in Table 2. In general, these spectra were too complicated to allow detailed assignments, but it was possible to recognize empirically some characteristic bands appearing in critical regions [13-16] by comparing spectra of analogous complexes. An important feature of these spectra is the absence of absorption bands expected for the bipyridinium cation (*ca.* 2400 cm^{-1}) and of an alcoholic OH stretching (>3100 cm^{-1}) which, together with

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tentative assignments given in Table 2, demonstrates the presence of co-ordinated alkoxo- and 2,2′-bipyridine groups.[3] In mixed-ligand complexes of this type, absorption in the region between 3500 and 2500 cm^{-1} is of great significance. Aromatic and aliphatic C–H stretching frequencies may be clearly resolved, and for the alkoxo-complexes these bands differ in shape and intensity from those found in spectra of the parent alcohols. For the 2,2′-bipyridine ligand the C–H stretching bands were shifted towards higher frequencies with respect to the free molecule (3075, 3050, and 3000 cm^{-1}). Other regions of interest are those of 1620—1450 cm^{-1}, where C=C and C=N ring stretchings appear (shifted on co-ordination to higher frequencies), and 1100—900 cm^{-1}, where ring deformation modes and alkoxo-group C–O stretching frequencies are anticipated.

Although the i.r. spectra of these complexes are very well resolved and clear, in the regions where both alkoxo- and 2,2′-bipyridine ligands are expected to absorb, the choice of a given band for a particular assignment was rather arbitrary. This was especially the case for C–O stretching frequencies, which occur between 1100 and 1000 cm^{-1}, along with some bands of 2,2′-bipyridine. The tentative assignments given were based on comparison of the spectra of alkoxo(2,2′-bipyridine)chloro-complexes with those of the parent alcohols and niobium complexes where alkoxo-modes only are present {$[NbCl_2(OR)_3]_2$ and $[Nb(OR)_5]$}.[16] As observed previously,[3,16] there are more bands in the C–O stretching region for an ethoxo-group complex than for any other alkoxo-group complex. Thus additional bands appear near 900 cm^{-1} and probably originate in the splitting of an extra band which is found in ethanol itself on comparison with other alcohols. In the complexes $[NbCl_2(OEt)_3]_2$ and $[Nb(OEt)_5]_2$ additional bands are found at 920 and 845 and 914 and 880 cm^{-1}, respectively. As shown in Table 2, two additional bands (above 900 cm^{-1}) were found for the complex $[NbCl_3(OEt)(bipy)]$. The absence of a strong band between 1000 and 900 cm^{-1} in all the other alkoxo-derivatives reported here may indicate that the 2,2′-bipyridine ligand is not negatively charged in these complexes.[17] Reliable evidence for the presence of a terminal or a bridging alkoxo-group cannot be deduced from i.r. spectra only. Most probably, alkoxo(2,2′-bipyridine)trichloroniobium(IV) complexes are six-co-ordinate and stereochemically similar to the analogous mixed-ligand complex of Nb^V, $[Nb(O)Cl_2(OR)(bipy)]$.[3,18]

EXPERIMENTAL

Niobium pentachloride (Koch–Light) was used without further purification (Found: Cl, 65·2. Calc. for $NbCl_5$: Cl, 65·6%). Absolute methanol, ethanol, n-propanol, and n-butanol (all from Merck), containing 0·01—0·02% H_2O, were dried over molecular sieves 3A and 4A and distilled in a vacuum line to reduce the water content to 0·01—0·001%. The ligand 2,2′-bipyridyl was recrystallized from ethanol and sublimed *in vacuo*. Tetrahydrofuran was purified by the usual method with copper(I) chloride to remove the bulk of the peroxides present, dried over KOH, and heated under reflux over metallic sodium for 4 h. Remaining traces of water and peroxides were removed by the following procedure in the vacuum line, using $Li_2(bipy)$. Tetrahydrofuran was poured into an argon-filled flask containing 2,2′-bipyridine (0·5 g) and lithium chips. The solution turned green and was then distilled on the vacuum line in the presence of 2,2′-bipyridine (100 mg) and lithium chips (*ca.* 1 g). Traces of water, oxygen, or peroxides decompose the green $Li_2(bipy)$ complex by forming red Li(bipy) according to equation (2).

$$2Li_2(bipy) + H_2O \longrightarrow Li_2O + 2Li(bipy) + H_2 \quad (2)$$

Preparations.—All preparative manipulations were carried out on the vacuum line or in a dry-box filled with argon.

The complex $Li_2(bipy)$ was prepared according to the method of Herzog.[11] The formation of a bright green colour indicated quantitative conversion to $Li_2(bipy)$. Since impurities convert $Li_2(bipy)$ to Li(bipy) and change the colour to brown or red, an excess of lithium metal must always be present to reverse this reaction. The complex Li(bipy) cannot be obtained directly from lithium and 2,2′-bipyridine since a mixture of green $Li_2(bipy)$ and red Li(bipy) ensues. However, by filtering a solution of pure $Li_2(bipy)$ in tetrahydrofuran into an equivalent amount of 2,2′-bipyridine, in absence of moisture and oxygen, a pure red solution of Li(bipy) was obtained. The amount of the complex formed can be calculated from the amount of 2,2′-bipyridine used.

Alkoxo(2,2′-bipyridine)trichloroniobium(IV) *complexes.* A flask, containing niobium pentachloride (*ca.* 1·5 g), was evacuated, cooled with liquid nitrogen, and the appropriate alcohol (ROH; R = Me, Et, Pr^n, or Bu^n) distilled into it. The HCl gas formed on warming up the solution was removed and evacuation continued until a crystalline residue, corresponding in composition to a trisalkoxodichloro-complex of Nb^V, remained. To remove the last traces of alcohol, the residue was dissolved in tetrahydrofuran (1—2 ml) and re-evacuated to dryness. This treatment was repeated, and the flask finally evacuated to 10^{-3} mmHg. The residue was then dissolved in tetrahydrofuran (*ca.* 15 ml) and the resulting solution cooled to *ca.* −10 °C. A solution of Li(bipy) was added dropwise, under vigorous stirring, to the reaction mixture to give a Li : Nb ratio of 1 : 2. A green precipitate appeared after about half the reducing agent had been added. The reaction mixture was then stirred (15 h for the methoxo-, ethoxo-, and propoxo-derivatives, 1—2 h for the butoxo-derivative) after which the green *precipitate* was filtered off, washed twice with tetrahydrofuran, and dried *in vacuo* (yield: 40, 35, 35, and 30% for the methoxo-, ethoxo-, propoxo-, and butoxo-derivatives, respectively). Oxidation states of 4·04, 4·06, 4·08, and 4·11 were obtained for the methoxo-, ethoxo-, propoxo-, and butoxo-derivatives, respectively by iodine titration. Analyses are given in Table 1.

Analytical Procedures.—Niobium was determined by ignition of the complexes in a platinum crucible at 950 °C after first oxidizing Nb^{IV} with 4—5 drops of hydrogen peroxide and precipitating the metal hydroxide with a few drops of ammonia. Chloride was determined potentio-

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metrically by titration with 0·02M-silver(I) nitrate. Carbon, hydrogen, and nitrogen analyses were obtained from the Central Microanalytical Laboratory, Institute 'Rudjer Bošković.' The oxidation state of niobium was determined by titrating a known amount of complex, dissolved in tetrahydrofuran on the vacuum line, with a standard iodine solution [11] in tetrahydrofuran. The solution of the complex gradually lost its green colour, turning yellow just before the equivalence point where the colour sharply turned brown.

Physical Measurements.—I.r. spectra were recorded on a Perkin-Elmer model 221 spectrometer in the range 4000—400 cm^{-1}, as Nujol and hexachlorobutadiene mulls. *X*-Ray powder photographs were obtained in 0·3 mm capillaries with Philips 57·54 and 114·6 mm cameras and exposure times of 1·5 and 3 h, respectively, using Cu-K_α radiation. The magnetic susceptibilities of the solid complexes were determined at room temperature by the Gouy method in an argon atmosphere.

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