Co-ordination Complexes of Niobium and Tantalum. Part XIII.[1] Thiocyanato-alkoxo-bipyridyl Complexes of Niobium(v) and Tantalum(v)

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Crystalline complexes of the composition $M(NCS)_2(OR)_3$(bipy) (M = Nb or Ta; R = Me or Et) have been prepared. Methoxo- and ethoxo-derivatives, respectively, of niobium and tantalum are isomorphous. Molecular-weight determinations in benzene show that the complexes are dimeric. The presence of two bridging alkoxo-groups, nitrogen-bonded isothiocyanates in the terminal position, and normal bidentate co-ordination of bipyridyl is indicated by spectral evidence. Accordingly, Nb^V and Ta^V are surrounded in these asymmetrical ligand spheres by eight donor atoms.

ALKOXIDES of niobium(v) and tantalum(v) show no tendency to form adducts with nitrogen ligands, and further show reluctance towards substitution by nitrogen ligands.[2] Mixed alkoxo-thiocyanato-bipyridyl complexes have not been prepared so far. We attempted this preparation by using $MCl_2(OR)_3$ as starting material, in order to change the affinity of the central metal towards nitrogen ligands. The chloro-alkoxides are similar in behaviour to the metal pentahalides, which form adducts with bipyridyl quite readily.[3] The choice proved to be correct and thiocyanatoalkoxobipyridyl complexes of Nb^V and Ta^V were prepared. Their properties are of interest with respect to stereochemistry of the central metal, co-ordination number, type of thiocyanato-bonding, and selection of bridging and terminal ligands.

It has been found that dichlorotrisalkoxides of Nb^V and Ta^V in alcohol solution, under anhydrous conditions, undergo exchange with potassium thiocyanate. After removal of insoluble potassium chloride and addition of bipyridyl, crystalline white complexes of the composition $M(NCS)_2(OR)_3$(bipy) can be prepared, which are readily soluble in benzene, chloroform, and some other polar organic solvents, but are insoluble in water. They do not sublime *in vacuo* and decompose when heated. The solids and their solutions decompose in air, developing first a yellow and later a red colour, most probably due to the thiocyanato decomposition and subsequent polymerization. Tantalum derivatives show a greater stability towards decomposition. The methoxo- and ethoxo-metal derivatives, respectively, are isomorphous according to *X*-ray powder photographs.

Analytical data, molecular weight, and pertinent i.r. bands (4000—400 cm^{-1})

	Found						Calc.								Alkoxo-group			
Compound	C (%)	H (%)	N (%)	S (%)	M (%)	*M*	C (%)	H (%)	N (%)	S (%)	M (%)	*M* (dimer)	C=C and C=N ring vibration	Bipy C–H out-of-plane deformation	C–O	M–O	C≡N	NCS def.
$Nb(NCS)_2(OMe)_3$(bipy)	37·8	4·0	12·1	13·3	19·7	1075 1030 980	39·4	3·7	12·2	14·0	20·3	916	1607m 1445s	766s	1090vs 1070sh	541sbr	2084vs 2042vs	465w
$Nb(NCS)_2(OEt)_3$(bipy)	43·0	4·5	11·0	12·7	18·0	1025 1050	43·2	4·6	11·2	12·8	18·6	1000	1606m 1445s	765s	1080vs 1060vs 915s	560sbr	2085vs 2046vs	465w
$Ta(NCS)_2(OMe)_3$(bipy)	33·7	3·8	10·4	11·8	32·2	1140 1080	33·0	3·1	10·3	11·7	33·1	1095	1603m 1440sh	762s	1080vs 1060sh	500sbr	2090vs 2050vs	436w
$Ta(NCS)_2(OEt)_3$(bipy)	37·4	4·0	9·8	11·1	30·3	1170 1210	36·8	3·9	9·6	10·9	30·8	1176	1608m 1440s	765s	1090vs 1060vs 913s	556sbr	2080vs 2035vs	468w

Molecular-weight determinations were carried out in benzene solutions and the results are shown in the Table. Data indicate clearly that all the complexes are dimeric. Molar conductivities of the compounds in nitrobenzene show values in the range 6·7—15·5 Ω^{-1} cm^2. Since 1 : 1 electrolytes are expected to give values in the range 25—33 Ω^{-1} cm^2, these complexes display *ca.* 20—50% lower conductivity. Similar behaviour was observed earlier for Nb^V and Ta^V diarsine complexes;[4] this has been ascribed to a partial decomposition due to the presence of traces of water in the solvent. Very probably, partial decomposition of the complexes is the reason for observed behaviour in this case, too, but the low conductivity may also be due to a weak electrolyte-type dissociation of the thiocyanato-groups. Such ionization, however, does not seem to occur in benzene solutions, as shown by molecular-weight measurements.

The relevant i.r. frequencies observed for these compounds are given in the Table. The presence of three different ligands, all displaying characteristic vibrations in the i.r. region makes empirical assignments somewhat difficult. Nevertheless, on comparing the spectra of these mixed ligands complexes with the spectra of corresponding free molecules and analogous simple complexes [*e.g.* $Nb(OR)_5$, $NbCl_5$(bipy), *etc.*], characteristic bands may be reliably assigned and conclusions can be drawn on the type of ligand co-ordination present.

Of diagnostic value in the i.r. spectra is the absence of bipyridinium cation bands, expected to occur [3,5] near 2400 cm^{-1}. Normal co-ordination of bipyridyl is deduced from the CC and CN stretching bands, and CH out-of-plane vibrational mode, appearing in the spectra in the

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[3] C. Djordjević and V. Katović, *J. Chem. Soc.* (*A*), 1970, 3382.

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range 1608—1603, and near 765 cm^{-1}, respectively. In free bipyridyl[3,5] these modes appear at 1580 and 750 cm^{-1}.

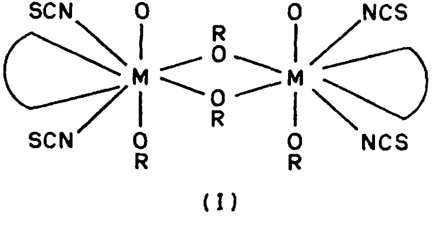
Characteristic vibrational modes of co-ordinated alkoxo-groups appear in the range 1100—900 cm^{-1}. They have been found of diagnostic value with regard to the terminal or bridged position of ethoxo-groups.[6,7] On comparison with parent alcohols, the CO modes are usually shifted to higher frequencies, and are split in the presence of bridged and terminal groups. In dimeric pentaethoxides for example,[7] corresponding frequencies appear at 1066, 1030 and 914, 880 cm^{-1}. Spectra of dithiocyanatotrisalkoxobipyridyl Nb^V and Ta^V complexes show splitting of the corresponding bands too, occurring at 1090, 1058, and 915 cm^{-1}. In corresponding methoxo-thiocyanato-bipyridyl derivatives this splitting does not occur, but i.r. data on bridged methoxo-derivatives are not available. M–O Modes appear in the expected region in the range 560—500 cm^{-1}.

Assignments of main thiocyanato-group vibrations and their significance in these spectra is straightforward. Based on several literature reports[8,9] the following observations can be made. CN Stretchings which appear below 2100 cm^{-1}, exclude the presence of bridging groups, whilst indicating the presence of *N*-bonded isothiocyanates. Splitting of this 2085, 2065 band, observed previously for the $NbO(NCS)_5^{2-}$ anion,[10] indicates the presence of bent M–NCS bonds; the latter have been confirmed for oxopentaisothiocyanatoniobate(V) by the structural determination.[11] Although bipyridyl and alkoxo-groups do not show strong bands in the region near 800 cm^{-1}, the CS stretching band, usually of small intensity,[9] cannot be assigned with certainty in the complex spectra of these compounds. A very weak band appears in all the complexes at *ca.* 850 cm^{-1}, probably originating in this vibrational mode. However, bands appearing in all the complexes between 480 and 460 cm^{-1} are obviously due to the NCS bending; this provides supporting evidence for the presence of nitrogen bonded terminal isothiocyanates.

Preliminary methoxo-group proton resonance studies have been carried out on the methoxoniobium(V) derivative. They reveal an interesting behaviour of the dimer in deuteriated chloroform solutions. One peak, suggesting a rapid intramolecular exchange of methoxo-groups (τ 5·68, relative to internal Me_4Si standard) is observed at 40 °C. At temperatures in the range 30—10 °C, the spectrum is split into the two bands of the intensity ratio 2 : 1, indicating that the new (higher field) peak is due to the bridging groups in the dimer. Below 0° further splitting occurs, and at −40° a third band forms (higher field still) at the expense of the two previous peaks. The three equal intensity bands (ratio 1·0 : 1·0 : 1·0) in the spectrum suggest the presence of bridging and two distinguishable types of terminal methoxo-groups, as expected in the co-ordination spheres involved. In agreement with the i.r. spectra, which exclude the possibility of a thiocyanato-bridge, this preliminary n.m.r. evidence therefore suggests the presence of two bridging and four terminal (nonequivalent) methoxo-groups.

Bradley *et al.* have proved, by variable-temperature n.m.r. studies, the existence of double alkoxo-bridged octahedral dimers in the penta-alkoxides of niobium and tantalum. It is interesting that in pentamethoxides the splitting, corresponding to the difference between terminal and bridging group resonances, occurs below 40°, and further splitting, reflecting a distinction between the two types of terminal groups, is observed at −56°. Temperature ranges are therefore similar to those observed for the mixed ligand complex, in a different solvent. However, in these eight-co-ordinated mixed ligand spheres, the variable-temperature n.m.r. spectra may reflect different phenomena. The intramolecular exchange of inequivalent alkoxo-groups is certainly one of the more important. In addition, temperature-dependent equilibria between possible structural isomers must not be ruled out, nor must the temperature and possibly concentration-dependent dimer–monomer equilibria be forgotten. To understand fully the spectra of the dithiocyanatotrismethoxobipyridylniobium(V) dimer, which we have examined, a more thorough investigation is needed, including the study of analogous tantalum complexes and ethoxo-derivatives, preferably in a wide temperature and concentration range, and in different solvents.

Alkoxo-bridging is common, and it is not surprising that in these compounds, containing thiocyanato- and alkoxo-groups, the former assume only terminal positions. With the two alkoxo-groups in the bridge, as indicated by spectral evidence, Nb^V and Ta^V achieve eight-co-ordination. Formula (I) indicates the possibility of several structural isomers with regard to the distribution of terminal monodentate ligands and chelated bipyridyl. The most probable distorted dodecahedral arrangements of different isomers probably differ little in energy, and therefore in solutions the occurrence of rearrangement is plausible.



(I)

It is of interest to compare the stereochemistry of these isothiocyanatoalkoxobipyridyl compounds with some

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analogous known complexes of Nb^V and Ta^V. Octahedral arrangements have been found in dimeric pentaalkoxides,[12] dimeric pentachlorides,[13] polymeric oxotrichloroniobium(V),[13] and the oxodichloroethoxobipyridylniobium(V).[11] Seven co-ordination has been reported for spheres involving electronegative oxygen and fluoride ligands only, such as NbF_7^{2-}, $NbOF_5^{2-}$,[13] $NbO(C_2O_4)_3^{3-}$,[14,15] $H_2NbO(OH)(C_2O_4)_2(H_2O)$,[1,16] and for MX_5(diarsine).[4] The highest Nb^V co-ordination in a niobyl derivative, containing the Nb=O group in the ligand sphere, observed so far is thus seven. Complexes with ligand spheres involving four chelated peroxo-groups, are eight-co-ordinated. The same is the case for substituted peroxo-derivatives, involving three or two peroxides, and one or two, respectively, bidentate nitrogen (bipy, *o*-phen) or oxygen ($C_2O_4^{2-}$) ligands.[17,18] An *X*-ray structure analysis of adducts of the type MX_5(bipy) has not been done, but a polymeric nature is suggested by chemical and spectral properties,[3] as bridging halides may raise the co-ordination above seven.

Structural information available on the stereochemistry of Nb^V and Ta^V complexes therefore seem to indicate that eight-co-ordination occurs only in compounds where most of the participating ligands are fairly electronegative, and do not allow a large charge transfer to the central metal ion. To a certain extent, in mixed ligands spheres, this charge transfer, or, orbital overlap, can be modified easily by the bond angles and bond distances. The niobyl group, however, is unique in possessing strong double-bond character. Structural evidence obtained so far shows, that in the presence of the Nb=O group in mixed ligand spheres, involving other electronegative unidentate (hydroxo, fluoro, chloro, thiocyanato) or chelated (oxalato) ligands, the co-ordination number does not exceed seven. As for bipyridyl, by accommodating the bond length and accordingly the orbital overlap, it can be adjusted to ligand fields of lower or higher co-ordination numbers, as illustrated by existence of six-co-ordinated $NbOCl_2(OEt)(bipy)$, and eight-co-ordinated $[M(O_2)_3(bipy)]^-$ and $[M(NCS)_2(OR)_3(bipy)]_2$ complexes.

EXPERIMENTAL

Reagents.—Metal pentachlorides, obtained commercially (Koch–Light Laboratories) were used without further purification, since the chlorine analysis showed 65·2 and 49·3%, for $NbCl_5$ and $TaCl_5$, respectively (Calc. 65·6 and 49·5%). Absolute methanol and ethanol (Merck) containing 0·01—0·2% H_2O were dried over molecular sieves 3A and 4A and distilled in a vacuum line. In this way the water content was reduced to 0·01—0·001%. 2,2′-Bipyridyl was recrystallized from ethanol and sublimed *in vacuo*. Potassium thiocyanate was dried over $MgClO_4$, and before use the drying was completed by heating the compound *in vacuo* at 70 °C. All the preparative manipulations were carried out in vacuum line or dry-box.

Preparation of the Compounds.—*Dithiocyanatotrismethoxo-2,2′-bipyridylniobium*(V). $NbCl_5$ (1·45 g) was evacuated in a vacuum line and cooled. Methanol (*ca.* 5 ml) was distilled into the reaction vessel. The hydrochloride formed was removed by heating; evacuation was continued until the crystalline solid $NbCl_2(OMe)_3$ was obtained. It was dissolved in methanol (10 ml) filtered onto dry 2,2′-bipyridyl (1·8 g). The reaction mixture was heated to *ca.* 40 °C. A solution of potassium thiocyanate (1·20 g) in methanol (8 ml) was then added with stirring. After *ca.* 20 min at 50 °C the solution was filtered whilst hot and was then cooled to room temperature. Although a small amount of the compound was so obtained, the bulk crystallized out by further cooling to *ca.* 5 °C. Crystals were filtered off, washed twice with cold methanol, and dried *in vacuo*; yield 50%. When set aside in air the compound became yellow and later red. It melted at 86 °C (probably with dec.); a yellow melt resulted.

Dithiocyanatotrisethoxo-2,2′-bipyridylniobium(V).— $NbCl_5$ (1·20 g) was dissolved in ethanol (10 ml) in a vacuum line; it was then evacuated and redissolved; a solution of potassium thiocyanate (0·90 g) in ethanol (10 ml) was added with stirring. The cold reaction mixture was stirred for *ca.* 1 h; potassium chloride formed in the pale yellow solution was filtered off and the filtrate collected in a vessel containing dry bipyridyl (1 g). A crystalline precipitate soon formed and the mixture was cooled to 5 °C. The cold mixture was stirred for *ca.* 30 min and then filtered; the precipitate was washed twice with cold ethanol and dried *in vacuo*. The compound melted with decomposition at 81 °C; in air it became yellow after 5—10 min.

Dithiocyanatotrisethoxo-2,2′-bipyridyltantalum(V).— This compound was prepared from $NbCl_5$ (2·2 g) and $TaCl_2(OEt)_3$ dissolved in ethanol (6—8 ml) as described previously. A solution of potassium thiocyanate (1·40 g) in ethanol (10 ml) was then added to the reaction mixture which was stirred for 1 h at 60—65 °C. It was then cooled to 10 °C and filtered; the filtrate was collected in the vessel containing dry bipyridyl (1·30 g). After a few minutes of stirring, small crystals formed; the reaction mixture was then cooled. The product was filtered off and washed twice with 5 ml of cold ethanol; yield 50%. The compound had m.p. 75 °C. The compound was fairly stable and became yellow only after exposure to air for 2—3 days.

Dithiocyanatotrismethoxo-2,2′-bipyridyltantalum(V).— The compound could not be prepared as for the corresponding niobium derivative above. Instead, it was obtained from $[Ta(NCS)_2(OEt)_3(bipy)]$ by exchange with methanol. The ethoxo-complex (2·0 g) was dissolved in benzene (5 ml) and methanol (2—3 ml) was added to the solution; solvents were removed *in vacuo*. Methanol addition and evacuation was repeated. The residue was finally dissolved in 7—8 ml of methanol and gently heated to 30—40 °C. Crystals were obtained from the cool mixture and these were filtered off and dried *in vacuo*; the compound had m.p. 66 °C. The colourless crystals became yellow after exposure to air for 5—6 h.

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Analytical Procedures.—Niobium and tantalum were determined directly by ignition of the compounds in a platinum crucible and weighing of the residue as M_2O_5. Thus, the compound (50—100 mg) was dissolved in ethanol (*ca.* 0·5 ml); thiocyanates were oxidized with a few drops of hydrogen peroxide, and metal hydroxides were precipitated with a few drops of conc. ammonia. The mixture was carefully evaporated to dryness and the organic material was ignited; heating was completed at 950 °C. Carbon, hydrogen, nitrogen, and sulphur analyses were obtained from the Central Microanalytical Laboratory, Institute ' Rudjer Bošković ' (see Table).

Physical Measurements.—Conductivities were measured at 25 °C using a 1000 Hz conductivity bridge and a cell with the constant of $4{\cdot}04 \times 10^{-2}$ cm^{-1}. The concentration range was 10^{-2}—10^{-4}M.

Molecular weights were determined in benzene (at 37 °C), using Osmometer model 310 Mechrolab Inc., in the concn. range 1—5 × 10^{-2}M. Benzene was calibrated with bipyridyl and biphenyl at 37 °C in the argon atmosphere.

I.r. spectra were recorded on a Perkin-Elmer 221 in the range 4000—400 cm^{-1}, as Nujol and hexachlorobutadiene mulls.

X-Ray powder photographs were obtained in 0·3 mm capillaries with a Philips 57·54 and 114·6 mm camera and exposure times of 1·5 and 3 h, respectively, with Cu-K_α radiation.

The n.m.r. measurements were on Varian A-60A instrument.

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