Co-ordination Complexes of Niobium and Tantalum. Part XV.[1] Sulphoxide Complexes of Oxobis(oxalato)niobates(v)

By **Nevenka Brničević** and **Cirila Djordjević,*** Institute ' Rudjer Bošković ', Zagreb, Yugoslavia, and College of William and Mary, Williamsburg, Virginia 23185, U.S.A.

The preparation and properties of crystalline colourless complexes of the composition $\text{M}^{\text{I}}[\text{NbO}(\text{C}_2\text{O}_4)_2(\text{dmso})_2]$ ($\text{M} = \text{NH}_4$, K, Rb, or Cs; dmso = dimethyl sulphoxide), and $\text{M}^{\text{I}}[\text{NbO}(\text{C}_2\text{O}_4)_2(\text{tmso})_2]$ ($\text{M} = \text{NH}_4$, K, Rb; tmso = tetramethylene sulphoxide) are described. The complexes were prepared by dissolving the corresponding M^{I} salts of oxobis(oxalato)aquoniobates in dmso and tmso, respectively. Stability trends and i.r. spectra of these oxobis(oxalato)bis(sulphoxide)niobate(v) series of complexes are discussed. According to chemical and i.r. evidence the complexes contain two oxygen-bonded sulphoxide ligands and the presence of seven-co-ordinate niobium(v) in these complexes is assumed.

INTERACTION of dimethyl sulphoxide with various metal ions has been extensively studied during the last decade, because it has been found that the molecule is a suitable solvent, useful reagent, and interesting ligand. In addition, some promising biological applications have been discovered. These investigations were recently summarized in a review.[2] The ambidentate character of sulphoxides is of a particular interest. The co-ordination *via* oxygen and sulphur, respectively, can be relatively simply distinguished in the vibrational spectra by locating the stretching frequency of the S=O bond. In derivatives in which the oxygen is co-ordinated to the metal ν(S=O) modes have been found to occur at lower frequency than in the free molecule, whereas the complexes with co-ordinated sulphur show an increase in the energy of this vibrational mode.[2] Recently the presence of both oxygen and sulphur co-ordinated dmso ligands, has been detected in some transition metal complexes.[3] The vibrational spectrum of free DMSO[4] and the spectra of complexes containing co-ordinated dmso ligand[3-10] have been reported. Methyl ^{1}H resonance and chemical shifts in various ligand environments have been studied.[11] Tetramethylene sulphoxide is supposed to behave very similarly.[12]

Reactions of niobium pentahalides with DMSO † have been investigated. Niobium pentachloride and pentabromide have been found to exchange two halogens with an oxygen to form oxotrihalogenobis(dimethyl sulphoxide)niobium(v) complexes.[13] On the other hand, the pentafluorides of Nb^{V} and Ta^{V} simply add two dmso ligands into the co-ordination sphere,[14] raising the co-ordination number of the metal. It has also been found recently that, on treatment with DMSO, the cluster $\text{Nb}_6\text{Cl}_{12}{}^{2+}$ remains untouched[15] and the sulphoxide molecules remain as lattice components in the resulting compound of the formula $[\text{Nb}_6\text{Cl}_{12}]\text{Cl}_2(\text{DMSO})_4$.

Studies described here were undertaken in order to help elucidate the structure of the oxobis(oxalato)aquoniobate(v) salts,[16] which were prepared in our laboratory several years ago. DMSO And TMSO have been found to be suitable solvents in which the oxobisoxalatoniobate moiety is retained, and only the two co-ordinated water molecules, and no other ligands, exchange with the sulphoxide ligands. The characterization of the oxobisoxalatobis(sulphoxide)niobate(v) series obtained has been found to be much simpler than the characterization of the parent aquo-complexes. The reason for it is a

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† When dimethyl sulphoxide is acting as a ligand it is, in this paper, abbreviated to dmso; in all other states it is represented by DMSO (likewise TMSO, tmso).

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much easier distinction between the co-ordinated sulphoxide ligand and a free sulphoxide molecule in the vibrational spectra, than the differentiation between the co-ordinated water molecule and a lattice water molecule, respectively. The latter has finally been revealed by the *X*-ray structure analysis.[17] The results are in agreement with the chemical and spectral evidence reported here. They indicate the presence of two co-ordinated water molecules, which, exchanged with sulphoxide ligands, result in the seven-co-ordinate Nb^V, found in the oxobis(oxalato)bis(aquo)niobate ion by structural studies.

RESULTS AND DISCUSSION

Two novel series of complexes have been prepared and are listed in the Table. They were obtained by recrystallizing the parent oxobis(oxalato)(aquo)niobate salts[16,17] of the formula $M^I[NbO(C_2O_4)_2(H_2O)_2],xH_2O$, from the appropriate sulphoxide solvent. The solvated derivatives containing three sulphoxide molecules are generally obtained by this procedure. However, one of the three solvent molecules can be removed by heating. Complexes containing three and two sulph-

Analytical data, decomposition point, pertinent i.r. bands/cm^{-1}

Complex	Decomp. (t/°C)	ν(S=O) and ν(Nb=O)	Δν(S=O)[a]	Analysis (%) Found					Calc.				
				C	H	S	X[b]	Nb	C	H	S	X[b]	Nb
$NH_4[NbO(C_2O_4)_2(dmso)_2]$,DMSO	113	1050s 980s 950s 922sh 910vs	70	22·0	4·2	17·6	2·5	17·3	22·3	4·1	17·9	2·6	17·3
$NH_4[NbO(C_2O_4)_2(dmso)_2]$	176	980s 950s 925sh 951vs	70	20·9	3·5	13·3	2·8	20·0	20·9	3·5	13·9	3·0	20·2
$K[NbO(C_2O_4)_2(dmso)_2]$,DMSO	112	1050s 965s 933s 915vs	85	21·5	3·3	16·5	6·8	16·7	21·5	3·2	17·2	7·0	16·6
$K[NbO(C_2O_4)_2(dmso)_2]$	182	970s 935sh 918vs	80	20·3	2·7	13·0	7·5	18·8	20·0	2·5	13·3	8·1	19·3
$Rb[NbO(C_2O_4)_2(dmso)_2$,DMSO	123	1050s 985s 950m 935sh 915vs	65	20·0	3·2	16·0	14·0	15·4	19·8	3·0	15·9	14·1	15·4
$Rb[NbO(C_2O_4)_2(dmso)_2]$	177	980s 945s 925sh 915vs	70	18·4	2·4	11·6	15·7	17·0	18·2	2·3	12·2	16·2	17·6
$Cs[NbO(C_2O_4)_2(dmso)_2]$	173	980s 950s 925sh 915vs	70	17·2	2·2	10·4	22·6	15·6	16·7	2·1	11·2	23·1	16·2
$NH_4[NbO(C_2O_4)_2(tmso)_2]$,TMSO	121	1020sh 1005vs 990sh 975sh 930s 910s	47	31·7	5·1	15·8	2·3	14·5	31·2	4·6	15·6	2·3	15·1
$NH_4[NbO(C_2O_4)_2(tmso)_2]$	196	975s 940sh 910vs	47	27·2	4·6	11·8	2·3	18·6	28·2	3·9	12·5	2·7	18·1
$K[NbO(C_2O_4)_2(tmso)_2]$,TMSO	128	1020s 1010sh 970s 935sh 920vs 908vs	52	29·1	3·8	14·7	5·9	14·2	30·2	3·8	15·1	6·1	14·6
$K[NbO(C_2O_4)_2(tmso)_2]$	230	975s 940sh 915vs 900sh	47	26·0	3·4	11·4	6·8	17·7	27·1	3·0	12·0	7·3	17·4
$Rn[NbO(C_2O_4)_2(tmso)_2]$,TMSO	134	1020s 970s 936m 918vs 906vs	52	27·7	3·4	13·2	13·4	14·2	28·1	3·5	14·1	12·5	13·6

[a] Difference between the (S=O) stretching frequency found in the free sulphoxide molecule[6,21] and the highest (S=O) band found in the complex containing the corresponding sulphoxide ligand. [b] Alkali metal or nitrogen as appropriate.

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oxide molecules respectively, are both colourless, crystalline solids. The two kinds of sulphoxide molecules present can be clearly distinguished by t.g.a. Nevertheless, the lattice-held third molecule cannot be separated merely by prolonged pumping *in vacuo*, as has been observed for some other solvated sulphoxide complexes.[6,9]

Crystalline complexes containing two sulphoxide units involve oxobis(oxalato)bis(sulphoxide)niobate(V), with seven-co-ordinate niobium(V). Although derived from the parent hydrated oxobis(oxalato)bisaquoniobates(V) they do not retain any water molecules, and are, when compared with several other mixed-ligand[16] complexes of Nb^V, relatively stable towards hydrolysis. This lack of hydration has been noticed before.[18] Dimethyl sulphoxide derivatives are slightly sensitive to moisture, and tetramethylene sulphoxide complexes are even more stable towards hydrolysis, decomposing only partially in hot water. The complexes are also fairly stable to heat, as evident from the decomposition temperatures (derived from t.g.a.) of oxobisoxalatobis(sulphoxide)niobate salts (Table). As expected, complexes with co-ordinated sulphoxide molecules alone decompose at higher temperature than the complexes containing an additional lattice sulphoxide molecule. Further, it is of interest that the decomposition temperatures of the solvated and nonsolvated complexes, respectively, of identical formula type, containing water,[16] DMSO, and TMSO, respectively, increase from the aquo- to sulphoxide complexes, and the TMSO complexes have been found to decompose at higher temperatures than the corresponding DMSO derivatives. According to *X*-ray powder patterns the salts listed in the Table do not form an isomorphous series. The compounds are soluble in water and parent sulphoxide, and only slightly soluble in methanol and dimethylformamide. From hot aqueous solutions the parent aquo-complexes can be recovered, demonstrating the retention and thus stability of the oxobisoxalatoniobate moiety in solutions. The conductivity measurements of 10^{-3}M-solutions in methanol at 25 °C indicate the presence of 1 : 1 electrolytes, since reproducible values of the molar conductivity obtained for all the reported complexes fell between 83 and 97 Ω^{-1} cm^2 mol^{-1}.

I.r. spectra are in agreement with the thermal analysis. They indicate the presence of two types of sulphoxide in the complexes containing three sulphoxide molecules, and the presence of co-ordinated sulphoxides alone in the spectra of the complexes with two dimethyl sulphoxide and tetramethylene sulphoxide units, respectively. In addition, the i.r. spectra proved to be helpful in assessing the type of sulphoxide bonding, as well as the presence of a terminal oxo- and two co-ordinated oxalato-ligands. All these vibrational modes make the i.r. spectra complex, yet it is possible to detect clearly the main characteristic group frequencies, which happen to occur in different spectral ranges, and therefore do not overlap to a great extent.

The strong absorption *ca.* 1700 cm^{-1} originates in the co-ordinated oxalates.[19] Compared to the spectra of parent oxobisoxalatobisaquoniobate complexes, the oxalato bands are found at approximately the same frequency. They are also similar in intensity and multiplicity, implying analogous symmetry of the oxalato-ligands in these two series of mixed-ligand oxodioxalatoniobates. The Nb–O(oxalato) stretching frequency occurs at *ca.* 540 cm^{-1}, at almost the same position for all the complexes reported here.

The region between 1200 and 900 cm^{-1} is of particular importance, because it includes Nb=O and S=O stretching bands. Methyl group vibrations also appear near and are coupled with the S=O modes.[4] Spectra of all the complexes show several strong bands in this region. In order to eliminate the CH_3 rocking bands from the spectra, caesium and ammonium salts of oxobis(oxalato)-bis(sulphoxide)niobate complexes containing [$^2H_6$]dmso were prepared. For both these [$^2H_6$]dmso complexes two strong bands appearing at 1005 and 970 cm^{-1} have been found to disappear on comparison with the spectra of the dimethyl sulphoxide complexes. Additional bands are found in the spectra of the deuteriated derivatives at 1020, 840, 830 (doublet), and 765 cm^{-1}. The methyl deformation and rocking bands, respectively, were found to shift on deuteriation by about 200 cm^{-1}, as previously observed.[9] The other bands, left unchanged, originate in the S=O and Nb=O stretchings and are listed in the Table.

Spectra of all the complexes do not show any bands in the region between 1200 and 1100 cm^{-1}, where the S=O stretch is reported to occur when dimethyl sulphoxide is co-ordinated *via* the sulphur atom. It therefore seems certain that the dimethyl sulphoxide present as ligand in these complexes is bonded to niobium through the oxygen atom. The complexes comprising a lattice-held DMSO molecule exhibit a strong band at 1050 cm^{-1}, and this band is not present in the spectra of complexes containing only two dmso ligands. This band occurs at a frequency expected for the free molecule,[3-10] and is therefore assigned to the S=O stretching of the non-co-ordinated DMSO molecule. Strong bands between 1000 and 900 cm^{-1} given in the Table belong therefore to S=O stretchings of co-ordinated sulphoxides and Nb=O stretching. It is, of course, not possible to propose an assignment for any of these two stretchings in particular, without an ^{18}O spectral study. In the parent aquo-complexes the Nb=O stretching appears as a single band at 945 cm^{-1}. However, due to different ligand sphere properties in analogous sulphoxide complexes this frequency is probably shifted, as observed before in the spectra of various oxoniobium(V) complexes.[20] Based on previous assignments generally applied in the dmso

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complexes,[4-10] all the bands in this region apart from one which is due to Nb=O stretchings originate in S=O stretching modes. In the free dimethyl sulphoxide ν(S=O) appears at *ca.* 1050 cm^{-1}, and in the Table the shifts of this band are given, calculated with respect to the first strong band observed in this region. The magnitude of this shift (85—65 cm^{-1}) is of the order expected, and found previously in various metal complexes.[3-10] In agreement with previous assignments [7,8] well resolved bands found in the spectra of these complexes at *ca.* 435 cm^{-1} have been assigned to Nb–O(dmso) stretchings.

A non-co-ordinated tetramethylene sulphoxide molecule is detected in the spectra of the complexes given in the Table by the presence of strong bands at *ca.* 1020 and 1005 cm^{-1}. In the spectra of compounds containing only two tmso molecules these bands disappear, and only two strong bands are found at *ca.* 975 and 910 (with shoulders) cm^{-1}. The latter indicates that the tmso molecules are co-ordinated to niobium *via* oxygen atoms.[21] Bands arising from the oxalato-group occur at almost the same positions as in the spectra of the dmso complexes. The Nb–O(tmso) stretchings are found at *ca.* 438 cm^{-1}, as expected.[21]

The sulphoxide complexes described here represent a novel type of mixed-ligand complex. Chemical and spectral evidence indicate that these complexes are stereochemically similar to the parent oxobis(oxalato)-bis(aquo) complexes.[17] Accordingly, they are assumed to involve seven-co-ordinate niobium(V) in a pentagonal bipyramidal arrangement, with two bidentate oxalates in the plane and the oxo-group on an apical position. The two sulphoxide oxygens are expected to substitute the two co-ordinated water molecules, and occupy an apical and a planar position, respectively, resulting in a *cis*-arrangement of the sulphoxide ligands. Such asymmetrical location is most probably responsible for the multiple splitting of S=O stretchings, observed between 1000 and 900 cm^{-1}.

EXPERIMENTAL

Oxobis(oxalato)bis(aquo)niobates(V) were prepared as described previously,[16] and all the other chemicals were obtained commercially (B.D.H. and Merck, AnalaR grade).

Preparations.— *Oxobis(oxalato)bis(dimethylsulphoxide)-niobate*(V) *salts of ammonium, potassium, rubidium, and caesium.* The corresponding oxobis(oxalato)bis(aquo)-niobate(V) salt (*ca.* 2 g) was dissolved in dimethyl sulphoxide (20 ml) under stirring and heated to *ca.* 100 °C. The solution was kept at this temperature for *ca.* 10 min and then cooled to room temperature. If some precipitate was formed, the solution was left standing for the precipitate to settle down. The clear solution was decanted and evaporated under reduced pressure (5×10^{-3} mmHg) at 50 °C, until crystallization started. Reaction mixture was then left overnight. Colourless crystals were filtered off, washed with absolute ethanol, and dried *in vacuo.* For rubidium and caesium the evaporation was prolonged to increase the yield. Ammonium, potassium, and rubidium salts obtained in this way contained a DMSO molecule of crystallization, which was removed by heating the solvated complexes at 130 °C for 3 h. Caesium salt prepared from the solution was not solvated.

Ammonium and caesium salts containing [$^2H_6$]dmso were prepared analogously with [$^2H_5$]ethanol used for washings.

Tetramethylene sulphoxide complexes were prepared similarly, by dissolving the parent complexes at room temperature in TMSO, and leaving the clear solution overnight. Potassium and rubidium complexes were found to form very quickly.

Analyses.—Niobium was precipitated by the tannin method, and weight as Nb_2O_3. Alkali metals were determined as sulphates, after removing niobium and destroying the organic matter by repeated evaporations with concentrated sulphuric and nitric acids. Sulphur was determined as $BaSO_4$, after the combustion of the complex. Carbon, hydrogen, and nitrogen were determined by standard methods in the Central Microanalytical Laboratory of the Institute ' Rudjer Bošković.'

Physical Measurements.—I.r. spectra were recorded in Nujol and hexachlorobutadiene mulls on a Perkin-Elmer 221 spectrophotometer. *X*-Ray powder photographs were taken in 0·3 mm capillaries with a Philips 57·54 mm camera and exposure time of *ca.* 1·5 h. T.g.a. measurements were performed on the Cahn RG electro-micro-balance, with a heating rate of 2 °C min^{-1}, in a static air atmosphere. The d.t.a. apparatus used was a commercial unit (Gebruder-Netzsch, Germany) with the heating rate of 5 °C min^{-1}.

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