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Coordination Complexes of Niobium and Tantalum. VII. Preparation and Infrared Spectra of Oxygen-18-Labeled Terminal and Bridging Monoxoniobium(V) Complexes and the Course of Coordinated Alkoxo Group Hydrolysis in Mixed-Ligand Niobium Complexes[1]

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Oxygen-18-labeled $NbOCl_3$, $NbOCl_3$dipy, and $NbOCl_2(OR)$dipy ($R = C_2H_5$, $n\text{-}C_3H_7$) were prepared, using $H_2{}^{18}O$ in correspondingly modified synthetic procedures. Isotopic shifts observed have confirmed the previous assignments of the niobium–oxygen stretching frequencies in the ir. Very good agreement between the observed and calculated frequencies has been found for the terminal monoxoniobium bond stretching modes. An estimate of the metal–oxygen bond force constant for these compounds is given. The values are in agreement with the expected bond order, as derived from the experimentally observed bond lengths, which are known for two of the four complexes. Hydrolysis of the coordinated alkoxo group involved in the preparation of oxodichloroalkoxodipyridylniobium(V) complexes occurs *via* water molecule coordination followed by formation of alcohol by reaction of the protons of the coordinated water molecule with the alkoxo group.

Introduction

The presence of a metal–oxygen double bond in transition metal complexes has long been correlated with a stretching band in the infrared spectrum[2] in the range between 1100 and 900 cm^{-1}. A number of authors have since used this assignment for several transition metal compounds and experimental data collected seem to be in accordance with this generalization.[3] However, these assignments have never been confirmed by isotopic substitution. Extensive studies of oxovanadium[4] and oxomolybdenum[5] compounds have been undertaken, with the molybdenum–oxygen bonding receiving the most attention. A simplified normal-coordinate treatment[6] and successful correlation of the stretching frequencies with bond length and bond order have been reported in the case of polyoxo tetrahedral and octahedral molybdenum compounds.[6,7] Bridging binuclear metal complexes have also been discussed.[8,9] Some of the proposed assignments and structural deductions seem to be rather ambitious due to the gross assumptions introduced and the small number of molybdenum complexes studied[9] No isotopic substitution studies were done to confirm any of these assignments.

The presence of a terminal or bridging monoxo group in relatively simple niobium and tantalum complexes can be detected without difficulty from the infrared spectral evidence. Experience with several derivatives of this type has shown that broad, strong bands in the region between 850 and 770 cm^{-1} signify the presence of a polymeric structure with an infinite chain of Nb–O–Nb bridges.[10] Sharp, intense bands between 890 and 950 cm^{-1} indicate a terminal niobium–oxygen bond, corresponding to a bond order approaching 2. Qualitatively, this pronounced dissimilarity in infrared spectra is obvious and can be used with confidence in simple octahedral and seven-coordinated complexes.[1,11] The problem, however, is much more involved in the derivatives comprising asymmetric mixed-ligand spheres,[12] containing ligands that absorb in the region between 950 and 850 cm^{-1}. Isotopic substitution is the only reliable solution under such circumstances, since an exact theoretical treatment of the asymmetric mixed-ligand fields is not possible, and since approximation methods involve ambiguous assumptions.

To check our empirical assignments in a series of niobium compounds containing the monoxo group, we have prepared four ^{18}O-labeled complexes. X-Ray structures are known for two of these: $NbOCl_3$[13] and $NbOCl_2(OC_2H_5)$dipy.[14]

Experimental Section

Chemicals and Materials.—Solvents and chemicals used were Analar grade. Ethanol and 1-propanol used were first dried over magnesium by standard procedure and then by passing the alcohol through a column (dimensions of 5 ft × 0.5 in.) packed with molecular sieves 3A. Alcohols containing $5 \times 10^{-4}\%$ water were obtained in this way, as determined by Karl Fischer analysis. Oxygen-18 was purchased from "Tehsnabeksport," Moscow, USSR, as $H_2{}^{18}O$, containing 60% $H_2{}^{18}O$. Benzene was dried with sodium and finally with $NbCl_5$ in the vacuum line. Experimental work was done at the Institute "Rudjer Bosković," Zagreb.

Preparation of the Labeled Compounds.—All the preparative work was done in a vacuum line and/or in the oxygen-free drybox.

$Nb^{18}OCl_3$.—This compound was prepared from $NbCl_5$ and

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[1] Part VI: N. Brničević and C. Djordjević, *Inorg. Chem.*, **7**, 1936 (1968).

[2] C. G. Barraclough, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 3552 (1959).

[3] D. M. Adams, "Metal-Ligand and Related Vibrations," St. Martin's Press, New York, N. Y., 1968.

[4] J. Selbin, L. H. Holmes, and S. P. McGlynn, *J. Inorg. Nucl. Chem.*, **25**, 1359 (1963).

[5] M. L. Larson and F. W. Moore, *Inorg. Chem.*, **5**, 801 (1966).

[6] F. A. Cotton and R. M. Wing, *ibid.*, **4**, 867 (1965).

[7] D. Grandjean and R. Weiss, *Bull. Soc. Chim. Fr.*, 3058 (1967).

[8] D. J. Hewkin and W. P. Griffith, *J. Chem. Soc., A*, 472 (1966).

[9] R. M. Wing and K. P. Callahan, *Inorg. Chem.*, **8**, 871 (1969).

[10] C. Djordjević and V. Katović, *J. Inorg. Nucl. Chem.*, **25**, 1099 (1963).

[11] N. Brničević and C. Djordjević, *J. Less-Common Metals*, **13**, 470 (1967).

[12] C. Djordjević and V. Katović, *Chem. Commun.*, 224 (1966).

[13] D. E. Sands, A. Zalkin, and R. E. Elson, *Acta Crystallogr.*, **12**, 21 (1959).

[14] B. Kamenar and C. K. Prout, Sastanak kemičara Hrvatske, Zagreb, A-2/9 (1969).

$H_2{}^{18}O$ in the vacuum line. In an oxygen-free drybox a few drops of $H_2{}^{18}O$ were put in the reaction vessel under a layer of glass wool, and 2 g of $NbCl_5$ was put over it. The vessel was connected to the vacuum line by a mercury valve, cooled with liquid air, and evacuated to 10^{-5} mm. Liquid air was then removed and the reaction vessel was left at room temperature for a few days. The mercury valve allows the removal of the gaseous HCl formed by the reaction. $Nb^{18}OCl_3$ prepared in this way was purified by sublimation *in vacuo* from the same vessel. *Anal.* Calcd for $NbOCl_3$: Cl, 49.5. Found: Cl, 49.2.

$Nb^{18}OCl_3$dipy.—$Nb^{18}OCl_3$ (0.3 g) was suspended in 20 ml of carefully dried benzene. The reaction mixture was heated to boiling and 2,2′-dipyridyl (0.5 g) was added with stirring. The reaction mixture was refluxed for 4 hr and the white precipitate obtained was filtered in a drybox, washed with benzene, and dried *in vacuo*. *Anal.* Calcd for $C_{10}H_8N_2OCl_3Nb$: C, 32.4; H, 2.2; Cl, 27.0. Found: C, 32.7; H, 2.1; Cl, 27.0.

$Nb^{18}OCl_2(OR)$dipy ($R = C_2H_5$, n-C_3H_7).—These compounds were prepared in the following two ways.

A. $NbCl_5$ (1 g) was dissolved in 5 ml of the corresponding alcohol to which a few drops of $H_2{}^{18}O$ had been added. The reaction mixture was heated to 60° and evaporated *in vacuo* (5×10^{-2} mm). The viscous yellow liquid remaining was dissolved in 2 ml of alcohol, which contained $H_2{}^{18}O$, and then 2,2′-dipyridyl (0.6 g) dissolved in 1 ml of alcohol was added. The white crystals which appeared after 10 min were filtered in a drybox, washed with the corresponding alcohol, and dried *in vacuo*.

B. $NbCl_5$ (1.0 g) was dissolved in 5 ml of the corresponding alcohol (dried over molecular sieves). The reaction mixture was evacuated as above and the remaining oil was dissolved in 2 ml of dry alcohol ($5 \times 10^{-4}\%$ H_2O). 2,2′-Dipyridyl (0.6 g) dissolved in 1 ml of alcohol was added. When the alcohol was properly dried, no crystals were formed. However, when 2–3 drops of $H_2{}^{18}O$ were added to the clear solution, white crystals of the desired compound appeared. The compounds were identified by powder photographs.

Physical Measurements.—Ir spectra were recorded on a Perkin-Elmer spectrograph, Model 221, equipped with grating and KBr prism. The Nujol mulls were prepared in a drybox.

X-Ray powder photographs were obtained in 0.3-mm capillaries with a Philips 57.54-mm camera, using nickel-filtered Cu Kα radiation.

Results and Discussion

Niobium ^{18}O-labeled complexes studied and reported here comprise octahedral $NbOCl_3$, which contains an infinite chain of bent Nb–O–Nb bridges; $NbOCl_3$dipy, of an unknown structure; and $NbOCl_2(OR)$dipy ($R = C_2H_5$, n-C_3H_7) complexes with terminal niobium–oxygen bonds in distorted octahedral mixed-ligand fields. Presence of the terminal niobium–oxygen bond in the last three complexes had been proposed earlier on the basis of infrared evidence.[12] X-Ray structure analysis[14] later confirmed this assignment for $NbOCl_2(OC_2H_5)$dipy. This molecule has a distorted octahedral arrangement with discrete octahedra having two chlorides on the apical positions and dipyridyl, alkoxo, and oxo groups in the plane. Niobium–oxygen distances are 1.72 and 1.87 Å for the oxo and alkoxo group, respectively. The analogous propoxo derivative probably has a similar structure. The symmetry of $NbOCl_3$dipy is not known. Crystals must comprise polyhedra of coordination number 6 or more, with respect to different possibilities of chloride bridging.

TABLE I

NIOBIUM–OXYGEN STRETCHING FREQUENCIES IN THE INFRARED SPECTRA (CM^{-1})

Compound	Nb–^{16}O	Nb–^{18}O	Isotopic shift ratio[a] $\nu Nb–^{18}O/\nu Nb–^{16}O$	Force constant,[b] mdynes/Å ^{16}O	^{18}O
$NbOCl_3$	770 br	750 br	0.9740	4.8	5.0
$NbOCl_3$dipy	934 920 sh	893 883 sh	0.9561	7.0	7.1
$NbOCl_2(OC_2H_5)$dipy	914 893 885 sh	863			6.6
$NbOCl_2(OC_3H_7)$dipy	912	869	0.9528	6.7	6.7

[a] Calculated ratio is 0.9512. [b] Estimated by the relationship $k = [5.89 \times 10^{-7}/(\mu_{Nb} + \mu_O)]\nu^2$ (mdyn/Å), where μ_{Nb} and μ_O are the reciprocals of the masses of niobium and oxygen, respectively, in amu.

The bands showing the ^{18}O isotopic shifts are given in Table I. The ^{16}O and ^{18}O ir spectra of $NbOCl_3$dipy and $NbOCl_2(OR)$dipy ($R = C_2H_5$, n-C_3H_7) are shown in Figures 1–3. The spectra of the labeled compounds show both Nb–^{16}O and Nb–^{18}O vibrational absorptions since the $H_2{}^{18}O$ used in the preparation of these compounds contained only 60% ^{18}O. The Nb–^{18}O vibration is clearly resolved as a sharp, strong additional band in each of the three mixed-ligand complexes (see Figures 1–3). Since the types of niobium–oxygen bonding, as well as the spectra, differ in the complexes studied, they will be discussed individually.

$NbOCl_3$ shows a strong, broad absorption with a maximum at 770 cm^{-1}. This band was assigned to Nb–O–Nb stretching modes. The crystal structure of $NbOCl_3$ has shown that planar Nb_2Cl_6 units are linked by oxygen atoms forming infinite chains of Nb–O–Nb bridges, with the Nb–O distance 1.99 ± 0.01 Å and an angle of about 168° on the oxygen.[13] In the spectrum of the labeled compound containing ^{16}O and ^{18}O, this broad band is not resolved, but the band maximum is shifted to lower energy, occurring at 750 cm^{-1}. An accurate analysis of the isotopic shift for this broad, unresolved band is of course not possible. Nevertheless, qualitatively, the sensitivity of this broad absorption to ^{18}O exchange can be described by the isotopic shift given in Table I.

$NbOCl_3$dipy shows in the region between 1000 and 800 cm^{-1} only one strong band at 934 cm^{-1} with a shoulder at 920 cm^{-1}, assigned to the Nb–O stretching mode. (See Figure 1.) In this region 2,2′-dipyridyl shows only very weak absorption. The Nb–^{18}O band appears in the spectrum of the labeled compound at 893 cm^{-1} with a shoulder at 883 cm^{-1}. No other ^{18}O-sensitive bands of a reasonable intensity were found in the spectrum in the region between 1800 and 400 cm^{-1}. Shoulders are observed on the niobium–oxygen stretching bands, which are not found in the spectra of alkoxo-2,2′-dipyridyl derivatives.

$NbOCl_2(OC_2H_5)$dipy has a more complex spectrum in the region of 1000–800 cm^{-1}. In addition to the expected Nb–O stretching frequencies, ethoxo modes assigned to C–O stretching vibrations appear[15] here. In

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(15) D. C. Bradley and A. H. Westlake, "Symposium on Coordination Chemistry, Tihany, 1964," p 671.

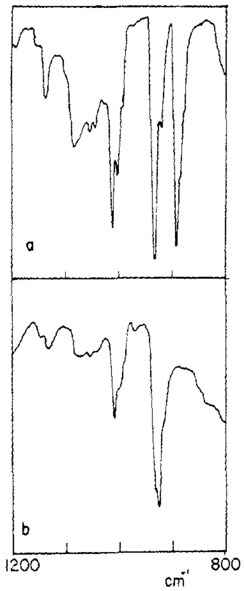

Figure 1.—Infrared spectra of $NbOCl_3$dipy: (a) ^{18}O labeled; (b) ^{16}O complex.

the methoxo- and propoxometal derivatives these C–O stretching modes do not occur below 1000 cm^{-1}, but in the $Nb(OC_2H_5)_5$ dimer[15] and $NbCl_2(OC_2H_5)_3$ dimer these modes absorb at 914, 880 and 920, 850 cm^{-1}, respectively. Ethanol itself, unlike other alcohols, shows a band at 928 cm^{-1}. $Nb^{16}OCl_2(OC_2H_5)$dipy shows a strong, well-resolved doublet with maxima at 913 and 893 cm^{-1} and a shoulder at 885 cm^{-1}. On ^{18}O isotopic substitution this doublet is reduced in intensity at the expense of the $Nb^{18}O$ stretching frequency band, which occurs at 863 cm^{-1} as a single sharp band. (See Figure 2.) Due to the complex absorption occurring in the ^{16}O derivative in the metal–oxygen stretching region, it is not possible to assign accurately a given frequency to the Nb–^{16}O stretching. For this reason the isotopic shift ratio and corresponding force constant are not given in Table I. The 914-cm^{-1} band cannot represent a pure Nb–^{16}O stretching, since the isotopic shift calculated with this frequency turns out to be larger than the theoretical isotopic shift ratio allows. The Nb–^{18}O stretching band does not show a shoulder and no other ^{18}O-sensitive bands were found in the spectrum between 1700 and 400 cm^{-1}.

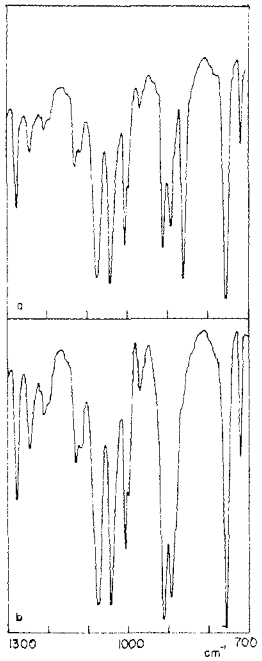

Figure 2.—Infrared spectra of $NbOCl_2(OC_2H_5)$dipy: (a) ^{18}O labeled; (b) ^{16}O complex.

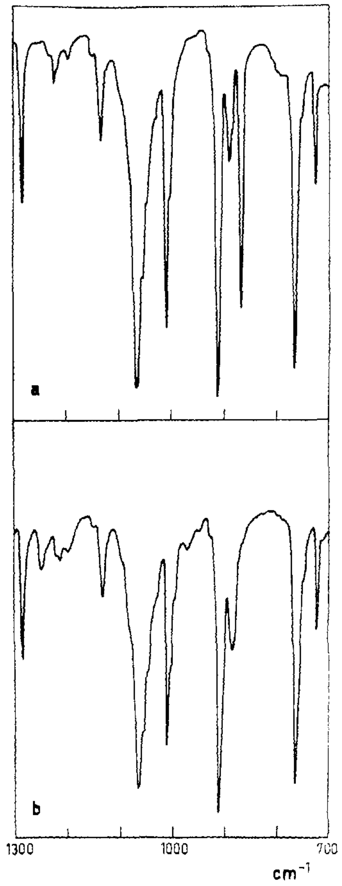

Figure 3.—Infrared spectra of $NbOCl_2(OC_3H_7)$dipy: (a) ^{18}O labeled; (b) ^{16}O complex.

$NbOCl_2(OC_3H_7)$dipy has proved to be much more suitable for the isotopic shift analysis than the ethoxo derivative, because, as for $NbOCl_3$dipy, there are no other bands in the examined region but the metal–oxygen stretching modes. As shown in Figure 3, the Nb–^{16}O stretching band occurs at 912 cm^{-1}. The ^{18}O-labeled compound shows a decrease in intensity of this band and an additional band at 869 cm^{-1}, due to the Nb–^{18}O stretching mode. Neither the Nb–^{16}O nor the Nb–^{18}O bands have shoulders and no other ^{18}O-sensitive bands appear in the region between 1700 and 400 cm^{-1}. Niobium–oxygen alkoxo group stretching vibrations occurring between 600 and 550 cm^{-1} are thus not affected by the ^{18}O presence in the "niobyl" group. Therefore, according to the ir evidence, there is no ^{18}O enrichment of the alkoxo group due to $H_2{}^{18}O$ hydrolysis occurring during the preparation of the labeled complexes. Ligand ^{18}O enrichment due to $H_2{}^{18}O$ hydrolysis has been noted for certain niobium–tropolone complexes.[16]

Some general conclusions can be derived from these results. Isotopic exchange studies show that previously used empirical assignments of bridging and terminal Nb–O bonds in Nb(V) complexes, based on ir evidence, are correct. The two types of bonding can be safely distinguished. The terminal Nb–O stretching modes occur as a strong, well-resolved band between 950 and 890 cm^{-1}. The exact position of this frequency depends upon the nature of the heteroligands present in the coordination sphere. In the polymeric type of complexes, the characteristic broad absorption between 850 and 770 cm^{-1} comprises Nb–O–Nb stretching modes. The position and the shape of this band obviously depend on the bond angle, as well as on the nature of other ligands in the molecule.[11] This type of chain bridging is different from that discussed in the dimer compounds[8,9] of molybdenum and accounts for the different position of the M–O–M stretching frequency in these two types of complexes. The observed ratio $\nu_{^{18}O}/\nu_{^{16}O}$ given in Table I is remarkably similar for $NbOCl_3$dipy and $NbOCl_2(OC_3H_7)$dipy, indicating that interaction between the two niobium–oxygen bonds existing in the latter derivative is negligible. It has been observed that, similar to other oxygenyl derivatives of transition metals, the Nb–O stretching frequencies in six- and seven-coordinated mixed-ligand "niobyl" complexes are sensitive to the nature of the other ligands, indicating that the niobium-to-oxygen bond cannot be treated independently of the bonding of niobium to other ligands present.

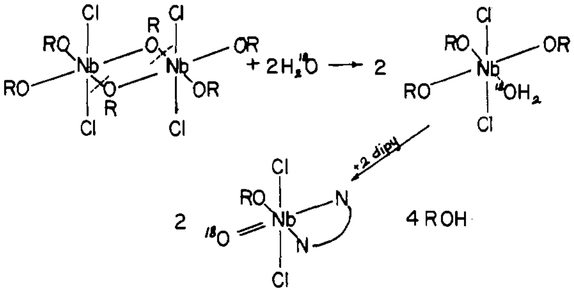

Figure 4.—Hydrolysis of $[NbCl_2(OR)_3]_2$ and formation of $NbOCl_2(OR)$dipy.

During the course of these studies we have observed another interesting experimental fact that deserves attention. The preparation of $NbOCl_2(OR)$dipy complexes was achieved in two ways, described as A and B in the Experimental Section. In procedure B $H_2{}^{18}O$ was introduced at the final step by addition into the alcohol solution, where in ethoxo preparation $NbCl_2(OC_2H_5)_3$ dimers[17] are present. The mixed complex, containing the Nb–^{18}O group, is thus formed through water molecule oxygen coordination as shown below (see also Figure 4)

$$H_2{}^{18}O + NbCl_2(OR)_3 + \text{dipy} \longrightarrow Nb^{18}OCl_2(OR)\text{dipy} + 2ROH$$

$NbCl_2(OR)_3$ dimers, present in the alcohol solutions, are split in the presence of water and 2,2′-dipyridyl. The water molecule occupies the vacant position on the metal ion and subsequently two alcohol molecules are released, formed from the coordinated vicinal alkoxo groups and from the protons of the coordinated water molecule. The process of compound formation therefore involves cleavage of the niobium–oxygen (alkoxide) bond, followed by oxo–niobium bond formation and 2,2′-dipyridyl coordination. This process is very sensitive to the amount of water present in the alcohol and requires the presence of 2,2′-dipyridyl. In these mixed niobium(V) alkoxide complexes the initial hydrolytic step therefore involves coordination of water to the metal, as previously suggested by Bradley.[18] Further hydrolysis is prevented by 2,2′-dipyridyl coordination.

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[16] E. L. Muetterties and C. M. Wright, *J. Amer. Chem. Soc.*, **87**, 4706, (1965).

[17] L. Kolditz and M. Schoenherr, *Z. Chem.*, **5**, 349 (1965).

[18] D. C. Bradley, *Progr. Inorg. Chem.*, **2**, 303 (1960).