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Coordination Complexes of Niobium and Tantalum. V. Eight-Coordinated Di- and Triperoxoniobates(V) and -tantalates(V) with Some Nitrogen and Oxygen Bidentate Ligands[1]

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Received April 1, 1968

Preparations of stable, crystalline peroxoniobates(V) and -tantalates(V) of the types $K_3[M(O_2)_2(C_2O_4)_2]H_2O$, $K[M(O_2)_3dipy]$, and $K[M(O_2)_3$-*o*-phen] (M = Nb, Ta) are described. Niobium and tantalum derivatives of the same type are isomorphous. $Nb(O_2)_2(OH)(H_2O)$dipy was prepared by hydrolysis of tetraperoxoniobate(V), but the attempted formation of the analogous pure tantalum derivative was not successful. Diperoxobis(oxalato), triperoxodipyridyl, and triperoxo-*o*-phenanthroline metalates were separated from hydrogen peroxide solutions of potassium niobate and tantalate, respectively, containing the corresponding ligand. The conductivity of potassium salts in aqueous solution shows the presence of 3 : 1 and 1 : 1 electrolytes, respectively. According to the chemical and infrared spectral evidence, the peroxo groups in all of the complexes are coordinated on the metal as bidentate ligands. Free oxalate, dipyridyl, and *o*-phenanthroline cannot be detected in aqueous solutions. Infrared spectra indicate normal bidentate coordination of the nitrogen ligands, indicating that niobium and tantalum are surrounded in these asymmetrical ligand fields by eight donor atoms.

Introduction

Tetraperoxoniobate(V) and -tantalate(V) are well-known species, and their potassium salts are isomorphous[2] with the dodecahedral $K_3Cr(O_2)_4$. Therefore, these ions are probably isostructural. In tetraperoxochromate(V) two peroxo ligands can be substituted by NH_3, CN^-, py, dipy, *o*-phen, etc. The resulting diperoxochromates contain then Cr(IV) and Cr(VI), in a trigonal-bipyramidal and a pentagonal-bipyramidal arrangement, respectively.[3] It is of interest to investigate in this respect the behavior of niobium and tantalum. Monoperoxofluoro-, -chloro-, and -oxalatoniobates and -tantalates were studied recently.[4,5] They appear to be seven-coordinate, if it is assumed that the peroxide group functions as a bidentate ligand. Ir evidence on the coordinated peroxo group was collected for a number of transition metal peroxy complexes.[6,7] The only reported case of a diperoxo complex of niobium are some niobates[8] containing probably the $Nb(O_2)_2(OH)_2^-$ species.[4] Triperoxo complexes of niobium and tantalum have not been reported in the literature so far.

Experimental Section

Reagents.—All of the reactants were analytical grade obtained commercially. For the synthesis of peroxo compounds potassium niobate(V) and tantalate(V) were prepared by fusing the metal pentoxides with potassium hydroxide. Analytical grade ethanol and acetone were used, and ether was purified by $FeSO_4$ and distillation. Anhydrous $K_3M(O_2)_4$ compounds (M = Nb, Ta) were prepared according to the literature.[9]

Preparation of the Compounds.—All of the potassium complex salts described were prepared by the following method. The hydrogen peroxide solution of potassium niobate or tantalate was treated with the corresponding ligand and the compounds were precipitated with ethanol or acetone. However, in order to obtain the compounds pure, the procedure described below has to be followed, because all of the substances cannot be successfully recrystallized.

$K_3[M(O_2)_2(C_2O_4)_2]H_2O$.—Potassium niobate (1 g) or tantalate (1.5 g) was dissolved in 30% hydrogen peroxide (20 and 25 ml, respectively). To this solution oxalic acid (0.8 g) was added in portions, with stirring. To the clear solution, obtained after the reaction was finished, ethanol was added with stirring, in small portions. Colorless small crystals were obtained, which were filtered off, washed with ethanol and ether, and dried at 10^{-3} mm; yield, about 50%. By further drying at 65° at 10^{-3} mm, over P_2O_5, for several days, the compounds did not lose the water molecule. The tantalum derivative was more stable than the niobium and could be recrystallized from aqueous solutions. Both complexes could be recrystallized from hydrogen peroxide without decomposition.

$Nb(O_2)_2(OH)(H_2O)$dipy.—To the aqueous solution (40 ml) of $K_3Nb(O_2)_4$ (2 g), dipyridyl (0.92 g) was added. To the suspension obtained 1 *N* H_2SO_4 was added dropwise, with stirring, until a pH of not less than 5.5 was reached. The mixture was stirred for 10 min. The yellow precipitate formed was filtered off, washed with water and ethanol, and dried at 5×10^{-3} mm; yield, about 40%. Attempts to prepare the corresponding tantalum deivative under analogous conditions were not successful, the product obtained being contaminated with $K_3Ta(O_2)_4$.

$K[Nb(O_2)_3dipy]$.—Potassium niobate (0.6 g) was slowly added to an ice-cooled solution of 30% hydrogen peroxide (10 ml). To the clear, cooled solution, dipyridyl (0.8 g), dissolved in ethanol (4 ml), was added dropwise. If at this step some precipitate appeared, it was rejected. The clear solution was treated with ethanol, and after being permitted to stand for about 0.5 hr, the peroxo compound was obtained. Very small, colorless crystals were filtered off, washed by ethanol and ether, and dried at 10^{-3} mm; yield, about 60%. The compound obtained in this way contained two water molecules. The anhydrous complex could be obtained only after drying for a few days over P_2O_5 at 10^{-3} mm. This procedure did not decompose the complex. X-Ray powder photographs of the hydrated and anhydrous derivatives were identical, indicating the identical structural arrangement.

$K[Ta(O_2)_3dipy]$.—A 30% hydrogen peroxide solution (15 ml), potassium tantalate (1 g), and dipyridyl (0.8 g) were brought

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(1) Part IV: N. Brničević and C. Djordjević, *J. Less-Common Metals*, **13**, 470 (1967).

(2) R. Stomberg, *Acta Chem. Scand.*, **17**, 1563 (1963).

(3) R. Stomberg, *Arkiv Kemi*, **24**, 111 (1965), and references therein.

(4) W. P. Griffith, *J. Chem. Soc.*, 5248 (1964).

(5) J. Dehand, J. E. Guerchais, and R. Rohmer, *Bull. Soc. Chim. France*, 346 (1966), and refereces therein.

(6) E. Wendling and R. Rohmer, *ibid.*, 8 (1967); E. Wendling, *ibid.*, 16 (1967).

(7) W. P. Griffith and T. D. Wickins, *J. Chem. Soc., A*, 590 (1967); 397 (1968).

(8) I. K. Grigoreva, K. I. Selenzneva, and V. M. Duganova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 937 (1962).

(9) A. Sieverts and E. L. Müller, *Z. Anorg. Allgem. Chem.*, **173**, 297 (1928).

TABLE I

ANALYTICAL DATA

Compound	% calcd C	H	N	K	M	O_2^{2-}	C_2O_4	% found C	H	N	K	M	O_2^{2-}	C_2O_4
$Nb(O_2)_2(OH)(H_2O)$dipy	34.5	3.2	8.1	...	26.7	18.1	...	34.8	3.5	8.1	...	26.2	17.9	...
$K_3M(O_2)_2(C_2O_4)_2H_2O$														
M = Nb	10.3	0.4	...	25.1	19.8	13.7	37.6	10.7	0.4	...	25.3	20.0	14.0	38.6
M = Ta	8.6	0.4	...	21.1	32.5	11.5	31.6	8.2	0.5	...	21.4	32.9	11.4	32.0
$KM(O_2)_3$dipy														
M = Nb	31.3	2.1	7.3	10.2	24.2	25.0		31.0	2.4	7.4	10.3	24.3	24.6	
M = Ta	25.4	1.7	5.9	8.3	38.3	20.3		25.1	2.3	5.8	8.3	37.5	20.4	
$KM(O_2)_3$-*o*-phen														
M = Nb	35.4	2.0	6.9	9.6	22.7	23.5		35.8	2.4	6.7	9.7	23.2	22.8	
M = Ta	29.1	1.6	5.7	7.9	36.4	19.3		28.9	1.7	5.7	7.9	36.8	19.2	

together as described above for the niobium compound. To complete the reaction, the mixture was kept for 0.5 hr at a temperature between 0 and 5°, and then ethanol was added slowly. The precipitate formed first was contaminated with $K_3Ta(O_2)_4$ and rejected. To the clear solution more ethanol was added and pure, fine, white crystals of the desired compound were obtained. They were filtered, washed with ethanol and ether, and dried at 10^{-3} mm for 5–6 hr; yield, about 50%. According to the analysis and ir spectrum the substance contained two molecules of water, which could be removed by further drying *in vacuo*, as described above for niobium.

$K[Nb(O_2)_3$-*o*-phen].—Potassium niobate (0.6 g) was slowly added to an ice-cooled 30% hydrogen peroxide solution (10 ml). Phenanthroline (1 g) was then added to the clear solution and the reaction mixture was stirred for 1 hr. By the first ethanol precipitation the product obtained was contaminated with potassium niobate and was rejected. The clear filtrate was treated with more ethanol, yielding then a crop of finely crystalline, pure complex. The crystals were washed with ethanol and ether and dried at 10^{-3} mm for 5–6 hr; yield, about 60%. The compound obtained in this way contained about three molecules of water, which could be removed by drying over P_2O_5 at 10^{-3} mm for a few days.

$K[Ta(O_2)_3$-*o*-phen].—Potassium tantalate (0.8 g), dissolved in 30% hydrogen peroxide (15 ml), was treated with *o*-phenanthroline (1 g) as described for the niobium derivative. After 1 hr of standing, the solution was treated four or five times with ethanol (20 ml) and the precipitate formed was rejected. Finally, acetone was added to the clear filtrate and the crystalline, pure complex was obtained. It was filtered, washed with ethanol and ether, and dried at 10^{-3} mm for 5–6 hr; yield, about 40%. The compound obtained in this way contained about three molecules of water, which could be removed without decomposition as described for the niobium derivative.

Physical Measurements.—The magnetic susceptibilities of the solid complexes were obtained at room temperature by the Gouy method. All of the compounds showed a slight paramagnetism with a magnetic moment between 0.4 and 0.6 BM (corrected for diamagnetism).

Conductances were measured using a 1000-c conductivity bridge and a cell with a cell constant of 0.2 cm^{-1}. Molar conductances were determined at 25°, at concentrations of 10^{-3} *M*. The specific conductance of the water used was no greater than 2.24×10^{-6} ohm^{-1} cm^2.

X-Ray powder photographs were obtained in 0.3-mm capillaries with a Phillips 57, 54-mm camera and exposure time of 1.5 hr.

Ir spectra were recorded in Nujol and hexachlorobutadiene mulls, using a Perkin-Elmer Model 221 spectrophotometer in the region between 4000 and 650 cm^{-1}.

Methods of Analysis.—Niobium was determined in the diperoxohydroxoaquodipyridyl complex directly: by destroying the compound in a platinum crucible with concentrated ammonium hydroxide (0.5 ml), gentle heating of the reaction mixture, and evaporating to dryness. The residue was carefully burned and then heated at 950° for 20 min. In the other compounds containing potassium, niobium and tantalum were separated as hydroxides and determined by the tannin method.[10]

Potassium was determined gravimetrically as sulfate in filtrates from which niobium and tantalum were removed as hydroxides. The organic matter was destroyed by several evaporations with concentrated sulfuric and nitric acid. Alternatively, potassium was determined by flame photometry in solutions obtained directly, by dissolving complexes in water, or in filtrates left after niobium and tantalum removal.

Peroxides were determined by titration with cerium(IV) sulfate and by iodometry. In the oxalato derivatives the sum of peroxide and oxalate was obtained by cerium(IV) titration and peroxide was determined by iodometry.

Carbon, hydrogen, and nitrogen were determined by standard microanalytical methods.

Analytical data are collected in the Table I.

Results

Potassium niobate(V) and tantalate(V) react in hydrogen peroxide solutions with oxalates, dipyridyl, and *o*-phenanthroline to form stable, crystalline di- and triperoxo complexes, in which simultaneous coordination of peroxo and the corresponding bidentate ligand occurs. Hydrolysis of tetraperoxoniobate in the presence of dipyridyl has led to the formation of a diperoxohydroxoaquodipyridyl niobium(V) species. The compounds shown in Table II represent new types of niobium and tantalum peroxo derivatives.

TABLE II

DECOMPOSITION, MOLAR CONDUCTIVITY, AND PEROXO BANDS IN THE INFRARED OF DI- AND TRIPEROXO COMPLEXES

Compound	Dec pt, °C	Molar conductivity in water, ohm^{-1} cm^2	Peroxo bands in the infrared spectrum[a]
$Nb(O_2)_2(OH)(H_2O)$dipy	120	...	860 s, 845 s
$K_3Nb(O_2)_2(C_2O_4)_2H_2O$	>300	436	870 s, 845 s
$K_3Ta(O_2)_2(C_2O_4)_2H_2O$	>300	442	865 s, 835 s
$KNb(O_2)_3$dipy	110	148	870 s, 820 s 800 s
$KTa(O_2)_3$dipy	150	142	865 sh, 805 sh 840 s, 795 s
$KNb(O_2)_3$-*o*-phen	130	152	865 s, 815 sh 800 s
$KTa(O_2)_3$-*o*-phen	160	139	865 s, 805 sh 795 s

[a] Values in cm^{-1}; s, strong; sh, shoulder.

It has been known for a long time that dodecahedral $M(O_2)_4^{3-}$ (M = Nb, Ta) ions exist in hydrogen per-

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(10) I. M. Kolthoff and P. J. Elving, "Treatise on Analytical Chemistry," Vol. 6, Interscience Publishers, Inc., New York, N. Y., 1964, Part II, p 284.

oxide solution and can be separated as salts in the solid state. By dissolving potassium niobate and tantalate in hydrogen peroxide in the presence of oxalates, two peroxo ligands are substituted and diperoxobis(oxalato) species are formed. With dipyridyl and *o*-phenanthroline, however, only one peroxo group is being replaced and triperoxo species with bidentate nitrogen ligands are obtained. Coordination number 8 is retained in anhydrous triperoxodipyridyl and *o*-phenanthroline derivatives.

All of these potassium salts are soluble in water and hydrogen peroxide and insoluble in the organic solvents. The complexes do not melt but decompose and by heating evolve oxygen. They are slightly paramagnetic, the magnetic moments of 0.4–0.6 BM indicating the absence of a spin component. The magnetic susceptibility observed is probably originated in the temperature-independent paramagnetism of niobium(V) and tantalum(V). Compared with different peroxo derivatives of other transition metals, these compounds are remarkably stable and can be kept for weeks in dark, dry atmosphere. By standing in air, at room temperature, they slowly release oxygen, this decomposition being probably catalyzed by traces of impurities, moisture, and light. The compounds were characterized by X-ray powder photographs, and it was found that the niobium and tantalum derivatives with the same bidentate ligand are isomorphous.

According to the chemical evidence all of the peroxo groups present are coordinated to the metal ion. The aqueous solutions of the compounds do not evolve oxygen but iodine, from buffered potassium iodide solutions. The same behavior is observed for $K_3M(O_2)_4$, where M = Cr, Nb, Ta. In addition, H_2O_2 cannot be extracted in ether, showing that no free hydrogen peroxide is present in the crystal lattice. On drying *in vacuo* the complexes do not release oxygen, which is a further indication of the absence of the loosely bound H_2O_2 molecules. The aqueous solutions of potassium salts were treated with barium(II) and iron(III), chosen as sensitive tests for oxalate and dipyridyl and *o*-phenanthroline, respectively, formed by eventual dissociation of the complexes. All of these tests were negative, showing that in the aqueous solution the hydrolysis and dissociation of the complex anions are negligible. Conductivities in aqueous solutions agree well with the expected values for 3:1 and 1:1 electrolytes, respectively. The particular stability of diperoxobis(oxalato)metalates has to be pointed out. It is possible to recrystallize the tantalum compound from aqueous solutions and the complex anions are destroyed only with strong acid. In addition, decomposition above 300° reflects a remarkable stability in comparison with the rest of the transition metal peroxides.

Ir spectra show a number of characteristic strong bands in the region of 870–800 cm^{-1} originated in the coordinated peroxo group vibrations (Table II). The spectra of all of these derivatives show no bands which can be assigned to M=O or M—O—M stretching modes, which can be unambiguously distinguished in niobium and tantalum complexes.[1]

Infrared spectra of $K_3M(O_2)_2(C_2O_4)_2H_2O$ (M = Nb, Ta) suggest that the oxalate ligands are bidentate, by comparison with the results of ir studies on a wide range of transition metal oxalato complexes,[11] as well as on monoperoxooxalatoniobates and -tantalates, reported so far.[7] The OH stretchings from the water molecule occur in the range 3400–3200 cm^{-1}, indicating, in agreement with the chemical evidence, that this water molecule is firmly bound in the structure.

Infrared spectra of $K[M(O_2)_3dipy]$ (M = Nb, Ta) indicate the presence of coordinated dipyridyl. The shift of characteristic dipyridyl frequencies containing C=N stretchings and CH deformation modes in the range of 1600, 1420, and 750 cm^{-1} is observed, in agreement with previous studies on dipyridyl coordination.[12] Important information from these spectra is the absence of NH stretchings, which would occur around 2400 cm^{-1} on dipyridinium cation formation. The infrared spectra of the analogous *o*-phenanthroline complexes show the characteristics of coordinated *o*-phenanthroline and the absence of any phenanthrolinium cation formation.

The infrared spectrum of $Nb(O_2)_2(OH)(H_2O)dipy$ reveals the presence of coordinated dipyridyl and the absence of dipyridinium cation. Bands arising from a niobium–oxygen double bond or niobium–oxygen bridging vibrational modes are not present in the spectrum. OH stretchings appear in the region of 3300 cm^{-1} as a broad absorption, indicating some hydrogen bonding. The compound gives a clear X-ray powder photograph. The water molecule cannot be removed on prolonged heating over P_2O_5 *in vacuo*. The compound is not soluble in water or organic solvents.

Discussion

The evidence suggests that the stable transition metal peroxo species do not exist only with electronegative ligands, as supposed before,[7] but with polarizable ligands such as dipyridyl or *o*-phenanthroline as well.

It has been observed in general that transition metal peroxo complexes are most readily formed by the elements of the chromium, vanadium, and titanium group. Our results show that with niobium and tantalum the most stable species of this type do not necessarily involve electronegative ligands such as oxide, hydroxide, fluoride, sulfate, or oxalate. Polarizable ligands such as dipyridyl or *o*-phenanthroline, moreover, seem to stabilize the triperoxoniobate and -tantalate species. The stabilization is probably achieved by a favorable equilibration of the charge on the central metal ion, as the different ligands may be expected to take advantage of possible alteration of bond lengths, without loss of symmetry.

[11] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963.

[12] D. H. Busch and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **78**, 1137 (1956); S. P. Sinha, *Spectrochim. Acta*, **20**, 879 (1964); W. M. Carmichael, D. A. Edwards, and R. A. Walton, *J. Chem. Soc., A*, 97 (1966).

The di- and triperoxo species described are soluble in water, where they are stable enough to allow the reproducible conductivity measurement. An appreciable dissociation of complex anions in aqueous solution does not occur because free bidentate ligands cannot be detected by the usual chemical tests. Reactions described here may prove useful as a preparative method for mixed peroxo transition metal complexes, with the limitation that the ligands involved must not be sensitive to hydrogen peroxide oxidation.

Apart from the chemical evidence, infrared spectra confirm the presence of a coordinated peroxo group. Group vibrational bands appearing in the region between 870 and 800 cm^{-1} show a more complex absorption than in the tetraperoxo and monoperoxo species. The number and position of these bands, which are given in the Table II, depend obviously upon the over-all symmetry of the molecule, as well as upon the local symmetry, the nature, and the number of the coordinated peroxo groups. Strong, sharp bands are observed, their position and intensity being sensitive to the rest of the ligand field. Monoperoxo chromates show a single strong infrared absorption between 890 and 870 cm^{-1}, and this band is found at a lower frequency for salts of group V metals. For tetraperoxoniobate and -tantalate, probably owing to lack of coupling between peroxo group stretchings in a symmetrical field, only a single strong, broad band is observed at 813 and 807 cm^{-1}, respectively. The asymmetrical fields in di- and triperoxoniobium and -tantalum complexes invoke a more complicated coupling of oxygen–oxygen stretchings and M–O modes, resulting in the appearance of two or more strong, resolved frequencies. The metal sensitivity of these frequencies implies the complex nature of the vibration and O–O stretching couplings with M–O modes.

$\text{Nb(O}_2\text{)}_2\text{(OH)(H}_2\text{O)dipy}$ is an interesting compound. A "perniobium acid" $\text{H[Nb(O}_2\text{)O}_2\text{]}\cdot n\text{H}_2\text{O}$, probably polymeric, was previously prepared in a similar way.[13] The dipyridylniobium peroxide, however, according to the spectral evidence, seems to be built of discrete units, which may be bound to some extent by hydrogen bonding. Two strong, well-resolved bands (see Table II), assigned to O–O stretchings, imply the presence of bidentate peroxo groups and do not indicate a bridging position. The complex absorption, however, occurring around 3300 cm^{-1}, originated in OH stretchings, is not indicative enough to allow the distinction between the formulation give above and an acid of the type $\text{H[Nb(O}_2\text{)}_2\text{(OH)}_2\text{dipy]}$. The extent of proton dissociation is in any case not sufficient to induce a corresponding solubility. Chemical evidence, combined with the infrared spectral evidence, indicates therefore that in this compound with or without eventual proton dissociation, eight-coordination is achieved.

Triperoxo derivatives with dipyridyl show more complex peroxo bands than the diperoxodipyridyl compound (see Table II). For tantalum, the shift of these bands toward lower wavelength causes partial overlap of the doublet with the near dipyridyl absorption, but the additional maxima are still clearly resolved. For the analogous *o*-phenanthroline complexes a similar absorption pattern of the peroxo group vibrational bands is observed, to some extent obscured by *o*-phenanthroline absorption in this region. Nevertheless, these frequencies are sufficiently well resolved to allow their assignment on comparison with the *o*-phenanthroline spectrum. The position of these bands, however, may well be perturbed to some extent by the presence of CH vibrational modes of the central ring, absorbing in the near vicinity. The triperoxoniobate and -tantalate with dipyridyl and *o*-phenanthroline are therefore to be regarded as being eight-coordinated, probably of a distorted dodecahedral geometry, owing to the asymmetrical fields consisting of three bidentate peroxide groups and one bidentate nitrogen group.

Potassium diperoxobis(oxalato)niobate and -tantalate show two sharp, strong peroxo bands. $\text{K}_3\text{[M(O}_2\text{)}_2\text{(C}_2\text{O}_4\text{)}_2\text{]H}_2\text{O}$ species are expected to have distorted dodecahedral structure if regarded as derivatives of $\text{M(O}_2\text{)}_4{}^{3-}$. However, the extra water molecule, which was not removed by prolonged vacuum drying over P_2O_5, may well be involved in the coordination sphere, increasing the coordination number to 9. On the other hand, the bulky oxalate groups in the crystal structure may offer a convenient cage where a water molecule could be kept strongly by hydrogen bonding.

Conductivity measurements have shown presence of the expected 3:1 and 1:1 electrolytes, respectively, in the diperoxo and triperoxo complexes. However, the coordination sphere of these chelated niobate and tantalate anions in the aqueous solution is possibly changed, since the reorganization energy in going from eight- to nine- or nine- to ten-coordinate structure is very small.[14] In the oxalatoperoxides a water molecule is indeed retained even in the solid state.

Dodecahedral geometry, established for the chelate structure in tetraperoxochromate, involves chromium–oxygen separations of $\text{Cr–O}_1 = 1.87 \pm 0.02$ Å and $\text{Cr–O}_2 = 1.97 \pm 0.02$ Å, the distances varying by 0.1 Å. The metal–oxygen distance depends, among other factors, upon the extent of electron transfer from the antibonding $2p\pi^*$ peroxo group orbital, which causes a corresponding shortening of the O–O bond, observed in the chromium peroxo complexes. In a ligand field formed by peroxo groups and polarizable bidentate nitrogen ligands, the stabilization can be achieved by various combinations of ligand electron delocalization, invoking, in consequence, differences in the metal–ligand bond lengths. It would be therefore of interest to know the crystal structure and bond distances in

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[13] P. Melikoff and L. Pissarjewsky, *Z. Anorg. Allgem. Chem.*, **20**, 340 (1899).

[14] E. L. Muetterties and C. M. Wright, *Quart. Rev.* (London), **21**, 109 (1967).

these asymmetrical niobium and tantalum mixed peroxides. This information can lead to a better understanding of the stabilization displayed by additional oxygen or nitrogen chelates, reflected in chemical properties of these complexes.

Acknowledgment.—We thank the Solid State Department, Institute "Rudjer Bošković," for X-ray powder photographs. One of us (N. V.) is indebted to the Institute of Soil Science, Sarajevo, for financial support.

Contribution from Brookhaven National Laboratory, Upton, New York, and the Polytechnic Institute of Brooklyn, Brooklyn, New York

Potentiometric Studies on Tetrahalonickelate(II) Ions in Molten Dimethyl Sulfone[1a,b]

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Received March 25, 1968

The 4:1 halide–nickel(II) ratio in and the mononuclear nature of the tetrahalonickelate(II) ions in dimethyl sulfone at 125° were demonstrated potentiometrically. Amalgamated and pure nickel coils served as the indicator electrodes while the silver(I)–silver system provided the reference potential. The formation constants of the chloride, bromide, and iodide complexes were measured; the stability followed the order $Br > Cl > I$. The application of the information obtained in this solvent to molten halide salt systems was discussed.

Crystalline tetrahalonickelate(II) salts with large organic cations are well known.[2-4] The solution spectra of nickel(II) in some molten halides[5,6] and organic solvents with added alkali halides[3] were reported to be those of essentially tetrahedral complexes. In a recent publication,[7] the spectra of the halide complexes of nickel(II) in molten dimethyl sulfone at 125° were measured and shown to be virtually identical with those of nickel(II) in molten substituted ammonium, phosphonium, and arsonium halides. Ligand field interpretation of the spectra indicated that these complexes were tetrahedral in structure. Since the oxygen atoms of the solvent dimethyl sulfone molecules possess only weak coordinating capacity, they are easily and completely replaced from the coordination sphere of dissolved transition metal ions when an excess of alkali halides is added. Thus, dimethyl sulfone can be considered as "inert" diluent in these cases. Its use as solvent allows the study of the halide concentration dependence of the transition metal ion–halide interaction and should be of great value in clarifying the chemistry of these metal ions in molten halides. In the present work, the compositions and the over-all formation constants of the nickel(II)–halide complexes in molten dimethyl sulfone at 125° were determined potentiometrically. Lithium perchlorate at a concentration of 2 *M* was used as inert electrolyte. There was no detectable interaction between perchlorate and the solvated nickel(II) ion. A silver(I)–silver electrode furnished the reference potential, and amalgamated and pure nickel wires served as the indicator electrodes. These measurements represent the first quantitative evaluation of the stability of the tetrahalonickelate(II) ions.

Assuming that at sufficiently high halide concentrations a limiting complex, $\mathrm{Ni}_q\mathrm{X}_p{}^{2q-p}$, is the predominant species, it can be shown by appropriate substitutions into the Nernst equation that at 125°

$$E = E^\circ + \frac{0.07899}{2} \log C_{\mathrm{Ni}}{}^{1/q} - \frac{0.07899}{2} \log [\mathrm{X}^-]^{p/q} - \frac{0.07899}{2} \log (\beta^{1/q} q^{1/q})$$

where E is the electrode potential at the nickel indicator electrode in volts, E° is the formal potential of the nickel(II)–nickel system in volts relative to the same chosen reference electrode, C_{Ni} is the total nickel(II) concentration in moles per liter, $[\mathrm{X}^-]$ is the equilibrium concentration of the halide of interest in moles per liter, β is the over-all formation constant, and p and q are coefficients described in the equations

$$q\mathrm{Ni(II)} + p\mathrm{X}^- \rightleftarrows \mathrm{Ni}_q\mathrm{X}_p{}^{2q-p}$$

$$\beta = \frac{[\mathrm{Ni}_q\mathrm{X}_p{}^{2q-p}]}{[\mathrm{Ni(II)}]^q[\mathrm{X}^-]^p}$$

A plot of the potential of the nickel indicator electrode at a high constant halide concentration *vs.* the logarithm of the total nickel(II) concentration should be a straight line with a slope equal to $0.0395/q$. A plot of the potential of the nickel indicator electrode at a constant total nickel(II) concentration *vs.* the logarithm of the halide ion concentration should also be a straight line. The slope is equal to $-0.0395p/q$, and β can easily be calculated from the intercept.

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[1] (a) This work was done under the auspices of the United States Atomic Energy Commission; (b) parts of this paper are based upon the Ph.D. thesis of J. Hasson, Polytechnic Institute of Brooklyn, 1967; (c) Department of Chemistry, Arizona State University, Tempe, Ariz. (d) Brookhaven National Laboratory, Upton, N. Y.

[2] N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

[3] D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *J. Am. Chem. Soc.*, **83**, 4161 (1961).

[4] D. M. Adams, J. Chatt, J. M. Davidson, and J. Garrett, *J. Chem. Soc.*, 2189 (1963).

[5] D. M. Gruen and R. L. McBeth, *J. Phys. Chem.*, **63**, 393 (1959).

[6] C. R. Boston and G. P. Smith, *J. Am. Chem. Soc.*, **85**, 1006 (1963).

[7] G. P. Smith, C. H. Liu, and T. R. Griffiths, *ibid.*, **86**, 4796 (1964).