low. The pseudo-first-order rate constants, k_{obsd}, were obtained from slopes of plots of ln $(A - A_\infty)$ vs. time. Such plots were linear to at least 70% completion of the reaction.

In the absence of ligand, $(H_3C)_6C_6Cr(CO)_2(C_6H_5C\equiv CC_6H_5)$ decomposed at a rate which was approximately 45% of that of the substitution reaction. This decomposition was accompanied by the formation of a green precipitate. In the presence of ligand, however, no precipitate formed and both the ultraviolet–visible and the infrared spectra indicated that $(H_3C)_6C_6Cr(CO)_2(L)$ was the only product.

From the values of k_{obsd} at six different temperatures (Table III) were calculated the enthalpy and entropy of activation together with their standard deviations.[4]

Results and Discussion

Infrared Spectra of $(H_3C)_6C_6Cr(CO)_2(olefin)$ Complexes.—The C–O stretching frequencies of these complexes are given in Table I. The frequencies significantly increase with the nature of the olefin: hydrocarbon olefin < acid-bearing olefin < anhydride-bearing olefin. This trend suggests an increase in Cr to olefin π bonding in the same order. The stability of these complexes toward decomposition in air also follows the same order. That π bonding from Cr to the olefin is of importance is supported by the decrease in the >C=O stretching frequencies of the anhydride group upon coordination to the metal. For example, these absorptions of maleic anhydride (1850 and 1777 cm^{-1}) shift to 1810 and 1743 cm^{-1} in $(H_3C)_6C_6Cr(CO)_2$-(maleic anhydride). The same is true for citraconic anhydride whose >C=O bands shift from 1830 and 1760 to 1803 and 1734 cm^{-1} upon complexation. The weakening of these >C=O bonds is consistent with significant π bonding from the Cr into the olefin π system. Endic anhydride behaves, as expected, like a simple hydrocarbon olefin since the anhydride group is removed from the olefinic bond by a saturated carbon atom.

It should be mentioned that all of these metal–carbonyl stretching frequencies are higher than those of analogous complexes with amine or phosphine donors. The C–O absorptions of $(H_3C)_6C_6Cr(CO)_2$-$P(C_6H_5)_3$, for example, occur at 1873 and 1810 cm^{-1}.[5]

Kinetics of Reaction 1.—The k_{obsd} values given in Table II clearly indicate that the rate of reaction 1 is independent of the nature and concentration of L and obeys the rate law

$$\text{rate} = k[(H_3C)_6C_6Cr(CO)_2(C_6H_5C\equiv CC_6H_5)]$$

Such a rate law suggests an SN1 mechanism in which the rate of $C_6H_5C\equiv CC_6H_5$ dissociation is rate determining. The positive value of the entropy of activation (+12.5 eu) supports this mechanism (Table III). The enthalpy of activation (27.9 kcal/mol) is somewhat lower than obtained for olefin dissociation from most of the $C_5H_5Mn(CO)_2(olefin)$ complexes.[1]

Attempts to study the analogous reaction of $1,3,5$-$(H_3C)_3H_3C_6Cr(CO)_2(C_6H_5C\equiv CC_6H_5)$ were frustrated by the instability of solutions of the complex. At the other extreme, $(H_3C)_6C_6Cr(CO)_2(maleic\ anhy$-

TABLE II
RATE OF REACTION 1 IN BENZENE AT 40.0°

L	[L], M	$10^4 k_{obsd}$, sec^{-1}
$P(C_6H_5)$	0.005	1.20
	0.010	1.19
	0.020	1.11
	0.025	1.12
	0.040	1.22
	0.050	1.06
$As(C_6H_5)_3$	0.005	1.06
	0.025	1.20
	0.050	1.23
$P(n\text{-}C_4H_9)_3$	0.005	1.14
	0.025	1.22
	0.050	1.17
$P(OC_6H_5)_3$	0.005	1.42
	0.050	1.19

TABLE III
RATE CONSTANTS FOR REACTION 1^a IN BENZENE

Temp, °C	$10^4 k$, sec^{-1}
40.0	1.15
45.0	2.37
50.0	4.78
52.5	6.72
55.0	9.41
60.0	18.2

^{a} $\Delta H^* = 27.9 \pm 0.7$ kcal/mol; $\Delta S^* = 12.5 \pm 2.0$ eu. Limits of error are one standard deviation.

dride) and $(H_3C)_6C_6Cr(CO)_2$(citraconic anhydride) do not react with $P(C_6H_5)_3$ or $P(n\text{-}C_4H_9)_3$ even in boiling benzene.

CONTRIBUTION FROM THE INSTITUTE "RUDJER BOŠKOVIĆ" AND LABORATORY OF ANALYTICAL CHEMISTRY, FACULTY OF SCIENCE, THE UNIVERSITY, ZAGREB, YUGOSLAVIA

Coordination Complexes of Niobium and Tantalum. VI. Seven-Coordinated Oxalatoniobates(V) and -tantalates(V)[1]

BY NEVENKA BRNIČEVIĆ AND CIRILA DJORDJEVIĆ[2]

Oxalato derivatives of niobium and tantalum have been investigated only a few times previously.[3] These species are of interest, since they represent one of the few types of complexes of these metals which are stable in aqueous solution and because oxalic acid is one of the most common agents for dissolving niobium and tantalum pentoxides. The chemistry of these solutions, however, is vague and confused. It is obvious that several complex oxalatometal species exist in solution. Their presence and concentration are

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(2) Inquiries should be addressed to this author at: Laboratory of Analytical Chemistry, Faculty of Science, The University, Zagreb, Yugoslavia.
(3) (a) F. Russ, *Z. Anorg. Chem.*, **41**, 42 (1902); (b) F. Fairbrother and J. B. Taylor, *J. Chem. Soc.*, 4946 (1956).

(4) R. H. Moore, based on a report from Los Alamos Scientific Laboratory, LA 2367 plus addenda.
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TABLE I

MOLAR CONDUCTIVITY AND ANALYSIS OF THE COMPOUNDS

Complex	Mp, °C	Molar conductivity,[a] ohm^{-1} cm^2	Calcd C	H	M	P or As	C$_2$O$_4$	Found C	H	M	P or As	C$_2$O$_4$
[(C$_6$H$_5$)$_4$P]$_3$NbO(C$_2$O$_4$)$_3$	143	235	67.3	4.4	6.7	6.7	19.0	63.9	4.5	6.3	6.1	19.3
[(C$_6$H$_5$)$_4$As]$_3$NbO(C$_2$O$_4$)$_3$	140	235	61.5	4.0	6.1	14.8	17.3	59.8	4.7	6.6	14.2	17.7
[(C$_6$H$_5$)$_4$P]$_2$TaOH(C$_2$O$_4$)$_3$	214	160	56.8	3.6	15.9	5.4	23.1	56.5	4.1	16.4	5.2	22.8
[(C$_6$H$_5$)$_4$As]$_2$TaOH(C$_2$O$_4$)$_3$	206	163	52.8	3.4	14.7	12.2	21.5	52.7	3.7	15.2	11.8	20.8

[a] 10^{-3} M in nitromethane at 25°.

governed by complex equilibria which are dependent upon pH and the concentrations of oxalate and metal. Higher coordination numbers are expected but have not been confirmed, even by chemical evidence.

We have attempted to separate from aqueous oxalatometal solutions anionic complex forms by precipitation with different heavy cations. In this way we have prepared several types of hydrated complex oxalatoniobates and -tantalates,[4] but the anhydrous compounds have been obtained only with tetraphenylphosphonium and -arsonium cations. In Table I these complexes are given. They are crystalline substances, which are soluble in polar organic solvents and can be recrystallized from alcohol.

Tetraphenylphosphonium and -arsonium oxotris-(oxalato)niobates are colorless, crystalline, isomorphous compounds. Molar conductivity values in nitromethane solutions agree well with that for a 3:1 electrolyte. Infrared spectra do not show absorption in the region 3500–3000 cm^{-1}, indicating the absence of any OH group. Strong bands in the region 1720–1240 cm^{-1} indicate the presence of coordinated oxalate,[5] the other frequencies belonging to oxalates and tetraphenyl onium cations. In addition, a strong band is clearly resolved at 925 cm^{-1}, assigned to the Nb=O stretching.

Tantalum pentoxide is less soluble in oxalic acid than niobium pentoxide, and an almost tenfold excess of the oxalates is needed to obtain clear solutions. By precipitation with tetraphenylphosphonium and -arsonium cations, as for niobium, colorless substances soluble in polar organic solvents were obtained. However, the compounds are not isomorphous with the niobium derivatives and their composition and conductivity in nitromethane correspond to 2:1 electrolytes. The phosphonium tantalate complex is crystalline, showing a clear X-ray powder diffraction pattern, but the arsonium derivative is poorly crystalline, giving a diffuse X-ray powder photograph. Infrared spectra of these tantalum compounds are similar to the spectra of niobium derivatives, showing the presence of coordinated oxalate and absence of a clearly resolved OH stretching. However, the strong band present in niobium spectra at 925 cm^{-1} is missing. The frequency at 890 cm^{-1}, containing O—C=O vibrational modes,[5] may perhaps overlap with the Ta=O stretching.

According to the band intensity, comparable with the other oxalatometal complexes, however, this does not seem to be probable. Analyses and conductivity results undoubtedly indicate the presence of a complex tantalate anion of charge −2, containing three oxalato ligands.

Experimental Section

Preparation of the Compounds. [(C$_6$H$_5$)$_4$P]$_3$[NbO(C$_2$O$_4$)$_3$] and [(C$_6$H$_5$)$_4$As]$_3$[NbO(C$_2$O$_4$)$_3$].—To an aqueous solution (25 ml) containing 0.36 × 10^{-2} M niobium and 0.85 × 10^{-2} M H$_2$C$_2$O$_4$, a saturated solution of 4 or 4.5 g of tetraphenylphosphonium or tetraphenylarsonium chloride, respectively, was added. The reaction mixture was left overnight in the cold. The crystalline precipitate formed was separated and recrystallized several times from 90% ethanol by precipitation with ether; yield, about 50%.

[(C$_6$H$_5$)$_4$P]$_2$[TaOH(C$_2$O$_4$)$_3$] and [(C$_6$H$_5$)$_4$As]$_2$[TaOH(C$_2$O$_4$)$_3$].—To an aqueous solution (25 ml) containing about 1.1 × 10^{-3} M tantalum and 1.0 × 10^{-2} M H$_2$C$_2$O$_4$, a saturated solution of 2.0 or 2.2 g of (C$_6$H$_5$)$_4$PCl or (C$_6$H$_5$)$_4$AsCl, respectively, was added. The reaction mixture was left in the cold overnight. The precipitate formed was separated and recrystallized from 90% alcohol by precipitation with ether; yield, about 60%.

During the several recrystallizations, niobium and tantalum derivatives partially decomposed, which was reflected primarily in lower carbon analyses.

Physical Measurements.—Conductivity was measured at 25°, using a 1000-c conductivity bridge and a cell with a cell constant of 0.2 cm^{-1}. Molar conductances were determined for concentrations of 10^{-3} M in nitromethane of a specific conductivity not greater than 6.3 × 10^{-6} ohm^{-1} cm^2.

Infrared spectra were recorded on a Perkin-Elmer spectrophotometer, Model 221, in the region 4000–600 cm^{-1}. The samples were prepared as Nujol and hexachlorobutadiene mulls.

X-Ray powder photographs were taken in 0.3-mm capillaries with a Philips 114.6-mm camera and Cu Kα radiation. Exposure time was 3 hr.

Method of Analyses.—Niobium and tantalum were determined in complexes not containing phosphorus by careful ignition of the substance in a platinum crucible and by weighing the residue as M$_2$O$_5$. Compounds with phosphorus were decomposed by several evaporations with concentrated H$_2$SO$_4$ and HNO$_3$, and subsequently the metals were precipitated as hydroxides, filtered, dried, heated at 950°, and weighed as M$_2$O$_5$.

Phosphorus was determined by microanalytical decomposition and precipitation in the form of phosphomolybdate. Arsenic was determined after decomposition of the compounds by titration with 10^{-2} N Na$_2$S$_2$O$_3$. Oxalates were determined by titration with 10^{-2} N KMnO$_4$.

Carbon and hydrogen were determined microanalytically.

Discussion

It has to be pointed out that, under very similar conditions, niobium and tantalum do not precipitate identical complex salts. According to the analyses and molar conductivity, the complex niobates bear the

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(5) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963.

charge −3, but tantalates of charge −2 are formed. The metal:oxalate ratio has been found to be the same for both. The difference is thus expected to arise from the oxalato oxygen atoms, which may be coordinated as $HC_2O_4^-$ without loss of the proton, or from the oxo group, which may be replaced by a hydroxo group.

Tetraphenylphosphonium and -arsonium oxotris(oxalato)niobates, according to the chemical and infrared spectral evidence, represent complexes of niobium(V) with the coordination number 7. The oxalatotantalates described allow the presence of one of the two anionic forms: $Ta(OH)(C_2O_4)_3^{2-}$ or $TaO(HC_2O_4)$-$(C_2O_4)_2^{2-}$. In both cases, however, the locations of the (probably strongly hydrogen-bonded) protons are almost identical, if an oxalate group is coordinated without loss of the proton. If, however, by some transfer mechanism, the terminal carbonyl group of an oxalato ligand bears the proton, strong intermolecular hydrogen bonding would occur and the Ta=O bond would be present in the complex anion.

Infrared spectra should give a straightforward answer to this problem, but for these tantalates the spectra are not explicit. The eventual Ta=O stretching, shifted toward lower wavelength, could be covered perhaps with the O—C=O vibrational mode absorption, occurring in the near vicinity. Infrared spectra suggest, however, that this is not probable. On the other hand, the $HC_2O_4^-$ vibrational modes should be different from the $C_2O_4^{2-}$ modes. In the spectra of these niobium and tantalum complexes oxalato bands differ slightly in the 1700–1500-cm^{-1} region, but the small differences may well be caused by the change of the over-all symmetry of the complexes, which are not isomorphous. Attempts to exchange the proton in the tantalate by deuterium have not been successful. No significant frequency shift was found. This can be explained by a small intensity of such an OH mode, probably involved in strong hydrogen bonding, which could be covered easily by strong cation and oxalato ligand absorption.

The experimental evidence on anhydrous tetraphenylphosphonium and -arsonium oxotris(oxalato)niobate-(V) given above shows that niobium has the coordination number 7. In the case of previously reported metal salts,[3a,6] one could not distinguish between 7 and higher coordination numbers, because of the water molecules present in the compounds. For the tantalates described here, the data for distinction between the two possible anionic forms given are lacking. However, in these anhydrous complexes the coordination number 7 remains for both alternatives. Tetraphenylphosphonium and -arsonium cations have therefore proved to be convenient for precipitation of the anhydrous seven-coordinated oxalatoniobates and -tantalates.

It is of interest to mention that according to the literature[3a,6] it is possible to prepare dihydrates of sodium, potassium, and hexaamminecobalt(III) oxo-

tris(oxalato)niobates. Their spectra show clearly resolved Nb=O stretching around 930 cm^{-1}, but the water molecules present may or may not be coordinated on the metal. From the chemical and spectral evidence only it is therefore not possible to deduce the niobium coordination number in these compounds. However, so far, we have not been able to prepare the pure tantalum salts of the same type. These studies thus show that in the oxalato solutions, under similar conditions, niobium(V) and tantalum(V) do not form identical complex species. As a consequence, the metal compounds separated from such systems are not of the same type, showing that niobium and tantalum chemistries are not all as similar as they might appear superficially.

Coordination of Nickel(II) in Molten Lithium Bromide–Potassium Bromide and Lithium Iodide–Potassium Iodide Mixtures[1]

BY CHARLES R. BOSTON, C. H. LIU, AND G. PEDRO SMITH

We report the effect which temperature changes have on the optical spectra of dilute solutions of Ni(II) in molten LiBr–41 mol % KBr and LiI–36.8 mol % KI. These spectra arise from d → d type of transitions centered on Ni(II) ions, and are quite sensitive to coordination geometry. By comparing these data with previous results for Ni(II) in molten LiBr, KBr, and LiCl–KCl mixtures,[2,3] we are able to determine the effect of the Li:K ratio on Ni(II) coordination in bromide melts, and the effect of changing from chloride to bromide to iodide in LiX–KX mixtures containing approximately 40 mol % KX (X = Cl, Br, or I).

Experimental procedures were like those in earlier studies.[2,3] Molar concentrations of nickel(II) were determined from the composition by weight of the mixtures and the densities of the solvents.[4]

Results and Discussion

Figure 1 shows the formal absorptivity (l./mol cm) of dilute solutions of $NiBr_2$ in molten LiBr–41 mol % KBr at temperatures from 335 to 916°. The spectrum at 335° is due largely to nickel tetrahedrally coordinated

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