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) oxotris(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.

Acknowledgment.—We thank the Solid State Department, Institute "Rudjer Bošković," for X-ray powder photographs.

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[6] T. F. Limar, J. G. Slatinskaja, and O. P. Sikora, *Zh. Neorgan. Khim.*, **9**, 2381 (1964); A. V. Vinogradov and I. B. Pavlova, *ibid.*, **10**, 2807 (1965).

Contribution from the Metals and
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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

Received May 1, 1968

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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[1] Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

[2] G. P. Smith and C. R. Boston, *J. Chem. Phys.*, **43**, 4051 (1965); **46**, 412 (1967).

[3] J. Brynestad, C. R. Boston, and G. P. Smith, *ibid.*, **47**, 3179 (1967

[4] C. H. Liu and L. R. Lieto, submitted for publication.

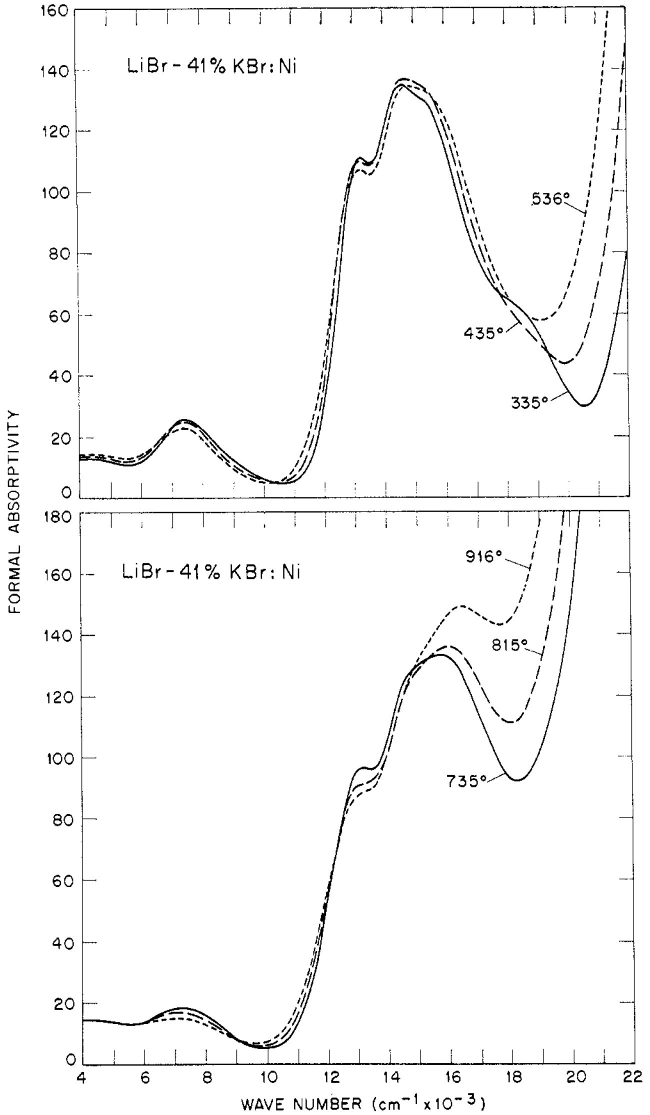

Figure 1.—Effect of temperature on the spectrum of Ni(II) in molten LiBr–41 mol % KBr. Each spectrum is labeled with the temperature at which it was measured.

to bromide ions,[2,5] but there is a shoulder near 19,000 cm^{-1} that belongs to entities with a different geometry. Thus at 335° there appears to be a distribution of nickel between two coordination geometries with most of the nickel ions having tetrahedral coordination and the rest having a different geometry. When the temperature is raised above 335°, the intensity over the 19,000-cm^{-1} shoulder at first drops and then, when the shoulder is gone, increases. In contrast, the intensity elsewhere above 16,000 cm^{-1} steadily increases with increasing temperature due largely to increasing overlap by the edge of the ultraviolet charge-transfer band. This behavior signifies a decrease in concentration with increasing temperature of the entities that give rise to the 19,000-cm^{-1} shoulder and, presumably, a corresponding increase in the concentration of nickel ions with tetrahedral coordination.

In general the set of spectra for 335, 435, and 536° is like the high-temperature spectra of nickel(II) ions in LiCl–41 mol % KCl (curves C, D, and E of Figure 4 in ref 3) where there is known to be a conformal equilibrium between nickel in approximately tetrahedral and approximately octahedral coordinations. Furthermore, the 19,000-cm^{-1} band in the bromide melt is in a reasonable position to be the $^3A_2(F) \rightarrow {}^3T_1(P)$ absorption of an octahedral nickel(II) bromide entity, and this absorption is expected to be the most intense band in the ligand field part of the octahedral spectrum.[6] We conclude that in the bromide melt at low temperatures (as in the corresponding chloride melt) there is a conformal equilibrium between nickel in approximately tetrahedral and approximately octahedral coordinations that shifts toward tetrahedral with increasing temperature. However, at a given temperature the equilibrium lies much further toward tetrahedral in a bromide melt than it is in the corresponding chloride melt.

With respect to many details the bromide spectrum responds to temperature change in the same way as the chloride spectrum. For example, it was found that when one kind of nickel coordination alone is present in the LiCl–KCl system at high temperatures, the spectra are internally linear[7] except at high wave numbers where the charge-transfer absorption edge comes in. That is, all trios of spectra are interrelated *via* $\epsilon_3(\lambda) = x\epsilon_1(\lambda) + (1 - x)\epsilon_2(\lambda)$, where $\epsilon_i(\lambda)$ is the formal absorptivity at the ith temperature and x is a number that depends on the three temperatures but not wavelength. This relation holds for the bromide spectra at 735, 815, and 916° (Figure 1) from 4000 to about 14,000 cm^{-1}. At higher wave numbers charge-transfer absorption becomes important and internal linearity breaks down. At these high temperatures the effect of increasing the temperature is primarily one of band broadening in both the bromide and the chloride systems. At lower temperatures, where the conformal equilibrium is observed, there is no internal linearity because of the effect on intensity of simultaneous band broadening and changes in concentration of the two species.

The chloride study[2,3] showed that at high temperatures changes both in temperature and solvent composition affect the three components of the intense band group in a particular way. [These bands are components of what would be the $^3T_1(F) \rightarrow {}^3T_1(P)$ transition in a rigorously tetrahedral species.] With increasing temperature or with increasing Li:K ratio, the highest energy component shifts toward higher wave numbers and increases in intensity relative to the other two components. Both of these effects are found in the bromide system. The effect of solvent composition may be seen by comparing the spectra for pure KBr and LiBr as solvents at 810° (Figure 2, in ref 2) with that for LiBr–41 mol % KBr as solvent at 815°. The origin of these effects has been discussed.[3]

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(5) G. P. Smith, C. H. Liu, and T. R. Griffiths, *J. Am. Chem. Soc.*, **86**, 4796 (1964).

(6) For example, compare the position of the $^3T_1(F) \rightarrow {}^3T_1(P)$ transition in crystalline Cs_3NiCl_5, where nickel is tetrahedrally coordinated, with the position of the $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transition in crystalline $CsNiCl_3$, where nickel is octahedrally coordinated, as given by C. R. Boston, J. Brynestad, and G. P. Smith, *J. Chem. Phys.*, **47**, 3193 (1967).

(7) For a discussion of internally linear spectra, see J. Brynestad and G. P. Smith, *J. Phys. Chem.*, **72**, 296 (1968).

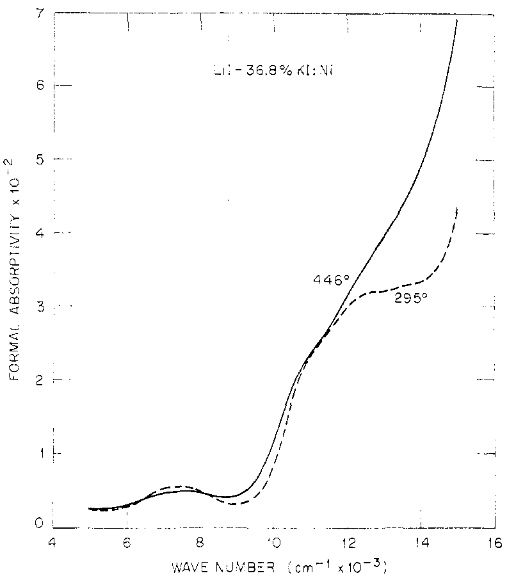

Figure 2.—Effect of temperature on the spectrum of Ni(II) in molten LiI–36.8 mol % KI. Each spectrum is labeled with the temperature at which it was measured.

We conclude that nickel entities in the LiBr–KBr system are quite similar to those in the LiCl–KCl system. The principal difference is a displacement of the conformal equilibrium more strongly toward tetrahedral geometry in the bromide system as compared with the chloride system.

Figure 2 shows the experimental results for the iodide melt. These spectra correspond to essentially tetrahedral coordination.[5] There are no bands that cannot be accounted for in terms of this geometry but the charge-transfer absorption is so strong in the region where the strongest octahedral band is expected that we cannot exclude the possibility of a small amount of nickel in octahedral coordination. Nevertheless, the results are in line with the supposition that at a given temperature, nickel(II) in LiX–KX (X = Cl, Br, or I) with about 40 mol % KX occurs in a tetrahedral–octahedral conformal equilibrium that is shifted increasingly toward tetrahedral in going from chloride through bromide to iodide. This effect is plausibly attributed to the increasing size of the halide ion, which would tend to destabilize octahedral geometry owing to crowding of adjacent halides.

Further evidence for the importance of this steric effect comes from a recent potentiometric study[8] of the over-all formation constants of the tetrahalonickel(II) ions in molten dimethyl sulfone at 125°. The stability was found to follow the order Br > Cl > I, whereas the normal order for metal halide complexes with dπ bonding is I > Br > Cl. This reversal in stability is reasonably attributed to the large size of the iodide ions packed around the relatively small nickel(II) ion. In dimethyl sulfone there is no evidence, either potentiometric[8] or spectrophotometric,[5] for nickel halide species with a coordination number greater than 4, and in molten halide salts with large organic cations, the tetrahedral NiX_4^{2-} complexes are the only appreciable species even at comparatively low temperatures.[5] The presence of octahedral coordination at low temperatures in LiCl–KCl mixtures as solvents has been accounted for in terms of the polarization of halide ions by outer-shell lithium ions,[3] and Mg^{2+} has been shown to play a similar role in $MgCl_2$–KCl mixtures as solvents.[9] Although the order of polarizability is $I^- > Br^- > Cl^-$, the present results show that the effectiveness of outer-shell Li^+ in inducing octahedral coordination of nickel(II) is greatest for molten chlorides and least for molten iodides. We conclude that the steric effect is of overriding importance in producing this reversal.

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(8) C. H. Liu, L. Newman, and J. Hasson, *Inorg. Chem.*, **7**, 1868 (1968).

(9) J. Brynestad and G. P. Smith, *J. Chem. Phys.*, **47**, 3190 (1967).

CONTRIBUTION FROM MIDWEST RESEARCH INSTITUTE,
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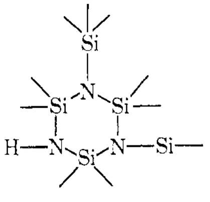
Anionic Rearrangement of a Cyclotrisilazane to a Cyclodisilazane

BY L. W. BREED

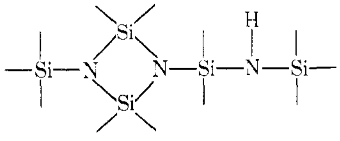
Received April 9, 1968

We published a method for preparing N-trimethylsilylhexamethylcyclotrisilazane (I) by the condensation of N-sodiohexamethylcyclotrisilazane with chlorotrimethylsilane[1] after Fink had reported that N,N′-bis(trimethylsilyl)hexamethylcyclotrisilazane (II) could be prepared in high yield from N,N′-dilithiohexamethylcyclotrisilazane and chlorotrimethylsilane at 160°, but that I, prepared from N-lithiohexamethylcyclotrisilazane and chlorotrimethylsilane, disproportionated to II and hexamethylcyclotrisilazane (III) at 160°.[2,3] We cited data and questioned the structural assignment of II by Fink on the basis of boiling points, refractive indices, the densities of the series III, I, II, and an inconsistent proton magnetic spectrum of II.[1]

We now wish to report that the compound originally assigned structure II can be unequivocally identified as N-trimethylsilyl-N′-1-(1,1,3,3-pentamethyldisilazanyl)-tetramethylcyclodisilazane (IV). (All unfilled valences are methyl groups here and throughout the rest of the paper.) The formation of structure IV under the conditions of the experiment can be explained on the basis of an anionic rearrangement accompanied by ring contraction



II



IV

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(1) L. W. Breed and R. L. Elliott, *Inorg. Chem.*, **2**, 1069 (1963).

(2) W. Fink, *Helv. Chim. Acta*, **45**, 1081 (1962).

(3) German Patent 1,187,615 (Feb 25, 1965).