of an incomplete theoretical treatment and are dependent upon spectral assignments which must be considered tentative until more is known about second row transition metal spectra. The assumption that the ΔE ($b_2 \rightarrow e$) transition is of high enough energy to lie in the near-infrared region is supported by the room temperature e.s.r. spectrum for this complex, which is easily observed. The existence of an e.s.r. spectrum at room temperature implies a long relaxation time and a substantial separation of the ground and first excited electronic levels.

Acknowledgments.—The authors are grateful to R. A. D. Wentworth for optical spectra and several helpful discussions. We also thank A. J. Freeman and R. E. Watson for an unpublished result and B. R. McGarvey for helpful discussions.

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Tetrahedral Bromide Complexes of Nickel(II) in Organic Solvents

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Received August 7, 1964

A spectrophotometric study of complexes of nickel(II) with bromide in acetone solution has shown that two tetrahedral complexes are formed. One complex is known to be $NiBr_4^{-2}$, and the other is shown to be a solvated complex of the type $Ni(solv)Br_3^-$. The same complexes are formed in tetrahydrofuran, dimethylacetamide, methyl ethyl ketone, acetonitrile, and nitromethane.

Introduction

In recent years, much attention has been directed to the use of organic solvents as convenient media for the production of halide complexes of the transition metals. In the case of nickel(II), where no definite evidence for complexes other than the monohalo has been found for aqueous solution,[1] complexes with up to four coordinated halides can be formed in organic solvents. Chloride complexes of nickel(II) have been studied in nitromethane,[2-4] acetonitrile,[4-7] dimethylformamide,[3,7-9] dimethylacetamide,[7] ethanol,[3] and trimethyl phosphate.[5] Bromide complexes have been studied in nitromethane,[2-4] acetonitrile,[4] dimethylformamide,[3] and acetone.[10,11] The investigators, using spectrophotometric, conductometric, and magnetic techniques, have shown that the highest halide complex produced in these solvents is tetrahedral NiX_4^{-2}, and that various other complexes can be formed, the higher complexes being tetrahedral and the lower complexes octahedral. We have investigated the behavior of the nickel(II)–bromide system in various organic solvents with the view of obtaining more definite information as to the structure and absorption spectra of the different species produced in these solvents. The present paper deals with the higher, tetrahedral complexes.

The spectrum of the tetrahedral tetrabromo nickelate ion is now well known, both in the solid state and in solution.[2-4] Goodgame, Goodgame, and Cotton observed the solvolysis of $NiBr_4^{-2}$ to a lower tetrahedral complex in acetonitrile and nitromethane and postulated the lower complex to be $NiBr_3(solv)^-$, where "solv" represents a coordinated solvent molecule. Šramko has observed the formation of a species with similar spectral characteristics as one of the steps in the production of $NiBr_4^{-2}$ by the addition of bromide to acetone solutions of nickelous perchlorate[11] and has also assigned the species the formula $NiBr_3^-$. This assignment is reasonable, but a more conclusive demonstration of the nature of the species and a more precise picture of its absorption spectrum seems desirable. In the present investigation, acetone was employed as a solvent for a detailed study of the higher complexes. The results obtained for acetone solution were used to interpret observations in other solvents.

Experimental

Materials.—Nickelous perchlorate hexahydrate was recrystallized G. F. Smith Co. $Ni(ClO_4)_2 \cdot 6H_2O$. The nickel content of the salt was checked by gravimetric analysis with dimethylglyoxime. Anhydrous nickelous bromide was prepared by treating nickelous carbonate with hydrobromic acid and evaporating to dryness. The composition was checked by bromide analysis. Tetraethylammonium tetrabromonickelate was prepared according to Gill and Nyholm.[2] Lithium bromide was Mallinckrodt N.F. VIII, recrystallized from water and ethanol, dried at 110°, and stored in a vacuum desiccator. Tetraethylammonium bromide was recrystallized Eastman salt. Lithium perchlorate was G. F. Smith Co. $LiClO_4$.

All solvents were Spectro grade. Acetone, acetonitrile, and tetrahydrofuran were dried over magnesium sulfate and redistilled, then passed through an alumina column. Nitromethane was purified according to Larson and Iwamoto.[12]

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[1] R. H. Herber and J. W. Irvine, *J. Am. Chem. Soc.*, **76**, 987 (1954); D. A. Netzel and H. A. Droll, *Inorg. Chem.*, **2**, 412 (1963).

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

[3] C. Furlani and G. Morpurgo, *Z. physik. Chem.*, **28**, 93 (1961).

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

[5] M. Baaz, V. Gutmann, G. Hampel, and J. R. Masaguer, *Monatsh. Chem.*, **93**, 1416 (1962).

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[10] S. A. Shchukarev and O. A. Lobaneva, *Dokl. Akad. Nauk SSSR*, **105**, 741 (1955).

[11] T. Šramko, *Chem. Zvesti*, **17**, 725 (1963).

[12] R. C. Larson and R. T. Iwamoto, *Inorg. Chem.*, **1**, 317 (1962).

Measurements.—All absorption spectra were measured on a Cary Model 14 recording spectrophotometer, Serial 244. The cell compartment was thermostated to 25.0 ± 0.2°. Matched quartz cells of path lengths ranging from 0.3 to 5 cm. were employed.

Solutions for spectrophotometric measurement were prepared in volumetric flasks. Stock solutions of nickel salt in the particular solvent were mixed with stock solutions of bromide salt in the same solvent, and the resulting solution was diluted to the mark with solvent.

Results

Acetone Solution.—Solutions of nickelous perchlorate hexahydrate, and also of anhydrous nickelous bromide, with varying amounts of lithium bromide added, were examined in the visible and near-infrared regions. The spectral changes produced in the visible region upon addition of lithium bromide to solutions of nickelous perchlorate hexahydrate in acetone have been described by Šramko.[11] They indicate the initial formation of one or more complexes which are octahedral followed by the formation of higher complexes which are tetrahedral. Visibly, successive color changes from pale green to yellow-green to emerald-green to blue-green to deep blue to pale blue occur as bromide is added. The visible bands are analogous to bands reported for nickel(II)-chloride solutions in various organic solvents.[2-9] Considerable overlap of complex formation occurs at lower bromide to nickel ratios, making spectral analysis difficult. At ratios >10, however, for solutions *ca.* 10^{-3} *M* in nickel, the spectra of the blue solutions indicate a two-species equilibrium. Isosbestic points occur at ~660, 817, and 1380 mμ. The final spectrum, produced at the highest bromide concentrations, is unmistakably that of tetrahedral $NiBr_4^{-2}$. Efforts were directed toward the identification of the lower tetrahedral complex involved in the two-species equilibrium.

The methods used to identify the complex make use of the spectra of solutions having constant nickel concentrations and varying bromide concentrations. In the first series of solutions investigated, nickel concentration was held constant at five different concentrations ranging from 4.14×10^{-4} to 2.00×10^{-2} *M*. For each nickel concentration, lithium bromide was added so that the ratio of bromide to nickel varied from 0.25 to 10. It was found that if the absorbance at a given wave length is plotted against the ratio of bromide to nickel, a change of slope occurs at a ratio of bromide to nickel of 3:1. The curves rise or fall asymptotically beyond this point. Some typical curves are shown in Figure 1. This is an indication that the lower tetrahedral complex involved in the two-species equilibrium occurring at higher Br/Ni ratios is a tribromo complex. A spectrum of the pure species can be obtained by extrapolating the linear portions of the curves to the ratio Br/Ni = 3 and taking the extrapolated absorbances as the absorbances of the pure complex.[13] This was done for the wave lengths at 10-mμ intervals between 800 and 550 mμ, which is the region in which the principal spectral features of the tetrahedral complexes occur. The spectrum derived by this procedure is shown in Figure 2, along with the spectrum of $NiBr_4^{-2}$ in acetone. The derived spectrum passes through an isosbestic point at 658 mμ and shows maxima at 643 and 707 mμ with molar extinction coefficients of 203 and 114, respectively. The same procedure was employed in the region 1100–1600 mμ, plots being made for every 20 mμ. The band obtained for this region is also shown in Figure 2; the band shows a maximum at 1360 mμ, with a molar extinction coefficient of 30.

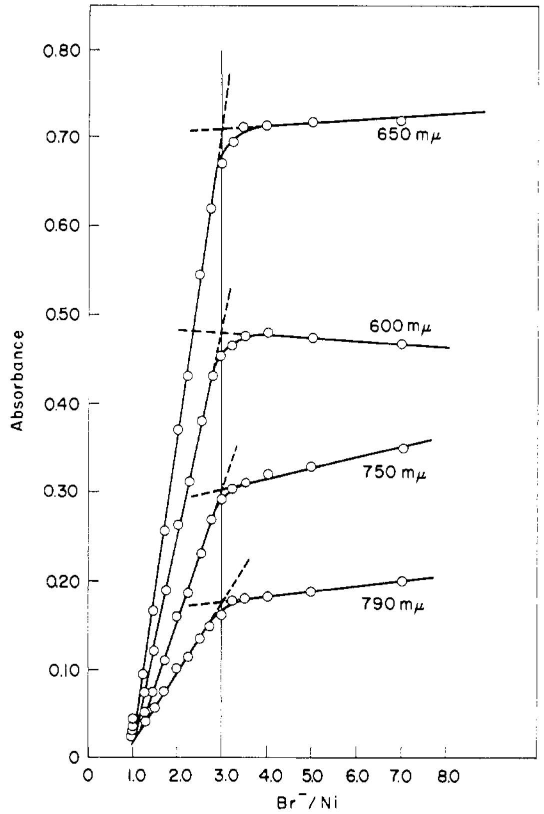

Figure 1.—Examples of plots of absorbance *vs.* molar ratio of bromide to nickel; solutions of nickelous perchlorate + bromide in acetone, Ni = 7.15×10^{-4} *M*.

A second series of solutions was investigated in order to verify the nature of the lower tetrahedral complex and to derive a spectrum for it. Lithium bromide was added to acetone solutions of nickelous perchlorate or nickelous bromide in sufficient quantities to produce a family of spectra passing through the isosbestic point at 658 mμ. Figure 3 shows a typical family. These spectra were treated by a method outlined by Rossotti and Rossotti.[14] In the present case, let us assume that the lower complex in the two-species equilibrium is a tribromo complex, $NiBr_3^-$; the higher complex is known to be $NiBr_4^{-2}$. We will represent the molar extinction coefficients of the two species by ϵ_3 and ϵ_4, and the difference in absorbance between a solution consisting entirely of $NiBr_4^{-2}$ and a solution containing a mixture of the species by ΔA. It can be shown that if the law of mass action holds

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[13] A. S. Meyers and G. H. Ayres, *J. Am. Chem. Soc.*, **79**, 49 (1957).

[14] F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Co., New York, N. Y., 1961, p. 276.

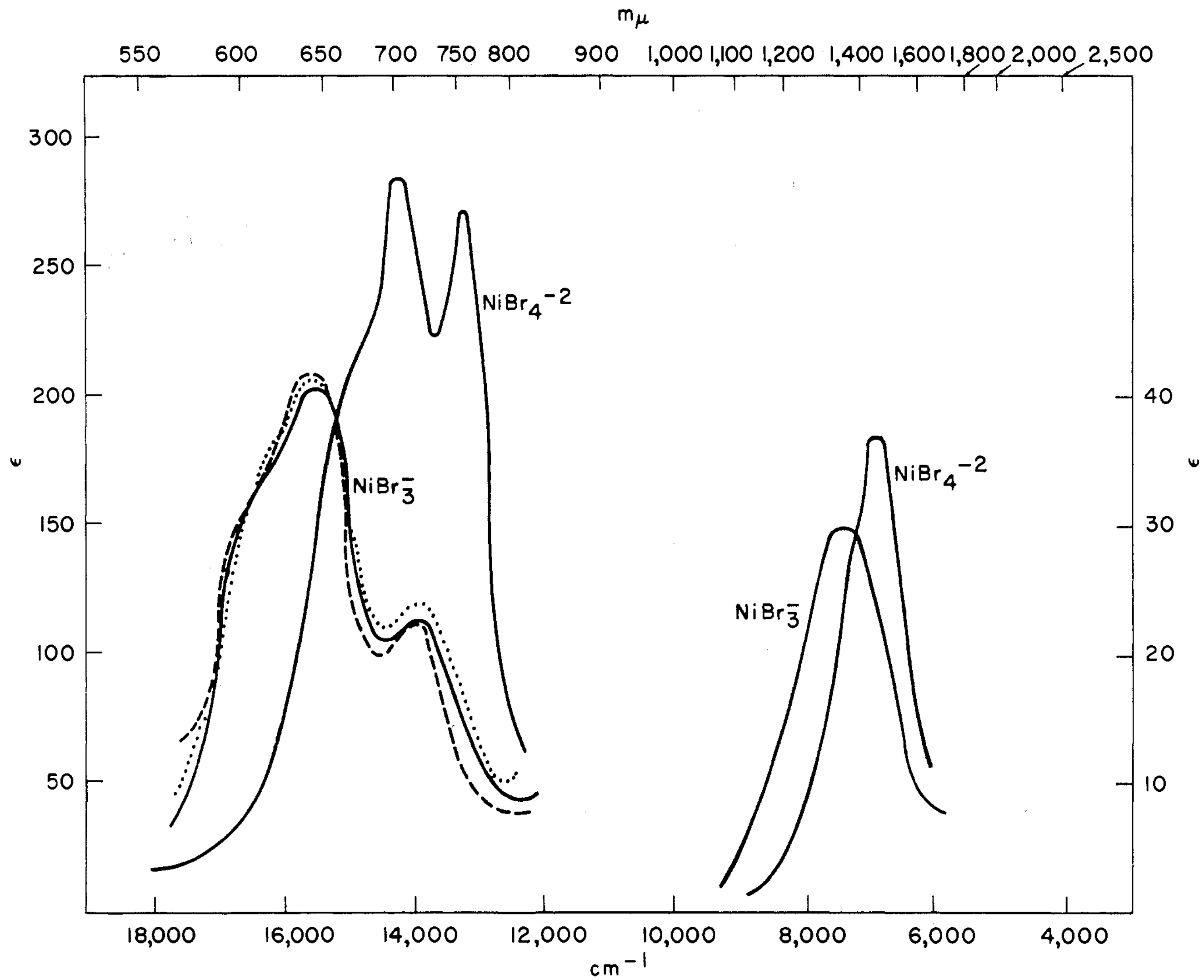

Figure 2.—Absorption spectra of tetrahedral bromide complexes of nickel(II) in acetone. For visible spectrum of $NiBr_3^-$, dotted line shows spectrum obtained from plots of absorbance *vs.* molar ratio of Br/Ni ,dashed line shows spectrum obtained from plots of $l\Sigma Ni/\Delta A$ *vs.* (Br^-), and solid line shows spectrum obtained by extrapolation of spectrum observed at Br/Ni ratios of 1–3.

$$\frac{l\Sigma Ni}{\Delta A} = \frac{1}{\Delta\epsilon} + \frac{K_{34}(Br^-)}{\Delta\epsilon} \qquad (1)$$

where l is the length of the absorption cell, ΣNi is the total nickel concentration, K_{34} is the equilibrium constant between the two species, and $\Delta\epsilon = \epsilon_4 - \epsilon_3$. Hence, if the equilibrium is between the species $NiBr^{-2}$ and $NiBr_3^-$, a plot of $l\Sigma Ni/\Delta A$ *vs.* (Br^-) should yield a straight line with an intercept equal to $1/\Delta\epsilon$ and a slope equal to $K_{34}/\Delta\epsilon$. The problem now is to calculate the free bromide concentration, (Br^-). The concentration of bromide not bound to nickel is equal to $\Sigma Br^- - 4(NiBr_4^{-2}) - 3(NiBr_3^-) = \Sigma Br^- - 4\Sigma Ni + (NiBr_3^-)$, where ΣBr^- stands for total bromide concentration. Lithium bromide is known to be largely ion-paired in acetone solution[15]; hence the concentration of free bromide is equal to $\Sigma Br^- - 4\Sigma Ni + (NiBr_3^-) - (LiBr)$, where (LiBr) represents the concentration of undissociated lithium bromide. When $(NiBr_3^-) << \Sigma Br^-$, as is true in the curves examined, we have

$$(Br^-) \cong \Sigma Br^- - 4\Sigma Ni - (LiBr) \qquad (2)$$

If the fraction of LiBr dissociated into Li^+ and Br^- is represented by α, we then have

$$(Br^-) = \alpha(\Sigma Br^- - 4\Sigma Ni) \qquad (3)$$

Hence, if α is known, the value of (Br^-) for a given total nickel and bromide concentration can be calculated from eq. 3, and a plot can then be made of $l\Sigma Ni/\Delta A$ *vs.* (Br^-).

Data obtained for four different sets of solutions were treated by this method; the nickel concentration in these solutions ranged from 3.45×10^{-4} to 1.98×10^{-3} *M*. In calculating the free bromide concentration, values of α were estimated from the data of Evans and Sugden.[15] The plots of $l\Sigma Ni/\Delta A$ *vs.* (Br^-) were indeed linear. Values of $\Delta\epsilon$ were obtained from the intercepts and ϵ_3 was then calculated from $\Delta\epsilon$; the extinction coefficients of solutions concentrated in bromide to such an extent that no further change in spectrum occurred upon further addition of bromide were taken as ϵ_4. Absorbances for wave lengths at 10-mμ

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(15) C. C. Evans and S. Sugden, *J. Chem. Soc.*, 270 (1949).

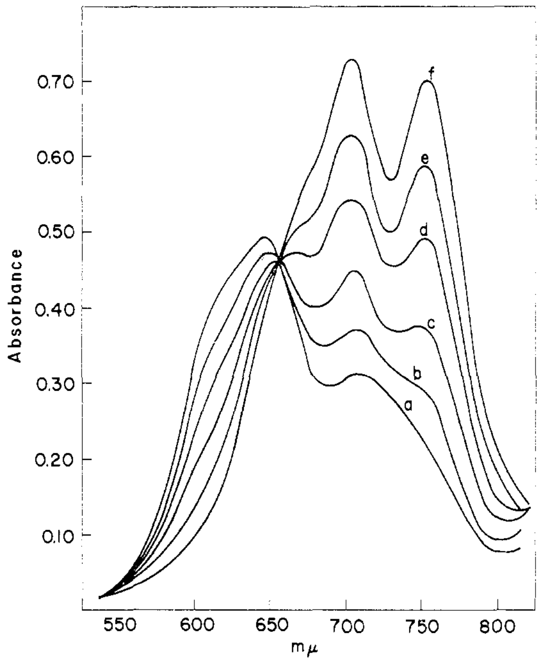

Figure 3.—Absorption spectra of solutions of nickelous perchlorate + lithium bromide in acetone, Ni = 2.50×10^{-3} *M*. Molar ratios of bromide to nickel: a, 4.3; b, 6.6; c, 10.8; d, 21.0; e, 40.3; f, 112.5.

intervals between 800 and 570 mμ were treated in this manner. Examples of $\Delta\epsilon$ and K_{34} values obtained from the plots are shown in Table I. The calculated spectrum for $NiBr_3^-$ is shown in Figure 2. This spectrum agrees well with spectrum obtained by the mole-ratio plots. Thus both methods indicate that the species is a tribromo complex and yield a spectrum which indicates, by intensity and band positions,[16] that the species is tetrahedral. The most likely formula for the species is $Ni(solv)Br_3^-$, where "solv" stands for a coordinated solvent (in this case acetone) molecule, as postulated by Goodgame, Goodgame, and Cotton[4] and by Šramko.[11]

TABLE I

EXAMPLES OF $\Delta\epsilon$ AND K_{34} VALUES OBTAINED FROM PLOTS OF $l\Sigma Ni/\Delta A$ *vs.* (Br^-)

		λ, mμ			
		770	740	700	630
$\Delta\epsilon$	I[a]	182	157	186	95
	II	176	160	182	108
	III	175	156	183	103
	IV	183	159	186	118
$K_{34} \times 10^{-2}$	I	0.98	1.0	1.1	1.1
	II	0.89	1.1	0.97	1.2
	III	0.87	0.88	0.91	1.0
	IV	0.96	1.0	0.88	1.3

[a] ΣNi: I, 3.45×10^{-4}; II, 7.28×10^{-4}; III, 1.46×10^{-3}; IV, 1.98×10^{-3}.

A third approximation to a spectrum for the pure tribromo complex was obtained by use of the spectrum observed at Br/Ni ratios of 1–3, for nickel concentrations between 10^{-4} and 10^{-3} *M*. In this range, the spectrum has the characteristics of the spectrum derived by the above methods and shows no alteration in shape with increasing concentration of bromide, but increases uniformly in intensity. This is due to the fact that under these conditions the tribromo tetrahedral complex is in equilibrium with lower, octahedral complexes whose absorbance is effectively zero at the nickel concentrations employed. Hence the spectrum produced under these conditions may be regarded as an "observed" spectrum for the tribromo complex; multiplication of the measured extinction coefficients by a factor which enables the spectrum to pass through the isosbestic point at 658 mμ yields approximate extinction coefficients for the pure $NiBr_3^-$ species. Spectra obtained for five different solutions were treated in this manner and the results averaged. The spectrum thus obtained is shown in Figure 2; this "observed" spectrum agrees well with the spectra derived indirectly.

The average value of the equilibrium quotient K_{34} in eq. 1 was found, from the plots of $l\Sigma Ni/\Delta A$ *vs.* (Br^-), to be $(1.0 \pm 0.3) \times 10^2$ in the concentration range studied. Because of the approximations and assumptions involved in the method, this value must be regarded as only a rough estimate of the true equilibrium constant. Attempts to refine the value of K_{34} by keeping ionic strength constant were unsuccessful, as it was found that the addition of neutral salts such as $LiClO_4$ and $Mg(ClO_4)_2$ shifted the equilibrium toward lower, octahedral complexes; a two-species equilibrium was no longer present over a sufficient range of bromide concentration to permit the evaluation of K_{34}. Although spectral evidence for the formation of the tribromo species was found at Br/Ni ratios of less than 0.5, no evidence for the presence of the tetrabromo complex was found at ratios lower than 3. This is an indication that the formation constant for the tribromo complex is close to the formation constants for the lower complexes, but much larger than the formation constant for the tetrabromo complex.

Other Solvents.—Comparison of the spectra obtained for the tri- and tetrabromo complexes in acetone with spectra of solutions of nickel(II) in certain other solvents sufficiently concentrated in bromide leaves little doubt that the same species are formed in these solvents. Spectra for acetonitrile and nitromethane solutions have been published.[2–4] We have observed similar spectra at 25° for solutions in tetrahydrofuran, dimethylacetamide, and methyl ethyl ketone. Furlani and Morpurgo found that these spectral characteristics can be produced in dimethylformamide, but elevated temperature is required[3]; this is in marked contrast to the behavior of nickel(II) + chloride in this solvent, where tetrahedral chloro complexes are readily formed at room temperature.[3,8,9]

In tetrahydrofuran and dimethylacetamide, the tribromo complex appears to predominate even at high bromide concentrations, and formation of the tetrabromo species is incomplete at 25°. In tetrahydrofuran, furthermore, a definite two-species equilibrium between $NiBr_3^-$ and $NiBr_4^{-2}$ does not seem to be established at 25°; a portion of the nickel remains octahedrally coordinated even at high bromide concentrations.

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(16) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.*, **6**, 134 (1959).

Both tetrahedral complexes are readily formed at 25° in acetonitrile, acetone, and methyl ethyl ketone, although a large excess of bromide is needed to produce complete conversion to $NiBr_4^{-2}$. In nitromethane, it is necessary to use tetrabromo nickelate and bromide salts of large organic cations as the sources of nickel and bromide.[2-4] We have found that tetraethylammonium tetrabromonickelate in carefully purified nitromethane is less than 50% solvolyzed to $NiBr_3^-$.

When tetraethylammonium tetrabromonickelate is dissolved in acetonitrile or dimethylacetamide, the spectrum obtained is the same spectrum produced upon addition of 4 equivalents of lithium bromide to an equimolar solution of nickelous perchlorate in the same solvent. This production of the same species by solvolysis of $NiBr_4^{-2}$ as is produced by addition of bromide to Ni^{+2} provides a further indication that the lower tetrahedral complex is a tribromo, monomeric complex. Similarly, solutions of anhydrous $NiBr_2$ in dimethylacetamide, acetonitrile, and acetone show the same spectra as solutions of nickelous perchlorate + 2 equivalents of lithium bromide in these solvents. These spectra show the peaks of the tribromo complex, suggesting the disproportionation of nickel(II) dibromide in these solvents. Nickel(II) dichloride has been shown to exhibit the same behavior in dimethylformamide.[8,9]

The spectral characteristics of the tribromo and tetrabromo complexes in the different solvents at 25° are summarized in Table II. The extinction coefficients for $NiBr_3^-$ in acetone are the average values obtained by the methods described in the previous section. Approximate extinction coefficients for $NiBr_3^-$ in the other solvents were obtained by the third method employed for acetone solutions, *i.e.*, by extrapolation of the spectrum observed at Br/Ni ratios of 1–3 and nickel concentrations between 10^{-4} and 10^{-3} *M*. For each solvent, at least two different nickel concentrations and at least three different bromide concentrations for each nickel concentration were employed. The observed extinction coefficients were multiplied by a factor which enabled the observed spectrum to pass through the isosbestic point produced at higher bromide concentrations. Both the visible and near-infrared bands were treated in this manner. Spectra produced in acetone, acetonitrile, methyl ethyl ketone, and nitromethane solutions concentrated in bromide to such an extent that no further alteration in spectrum occurred upon further additions of bromide were taken to be the spectra of $NiBr_4^{-2}$ in these solvents. In the case of nitromethane and acetonitrile, agreement with the values of Furlani and Morpurgo for $NiBr_4^{-2}$ is quite good.[3]

Discussion

Tetrahedrally coordinated Ni(II) has been treated theoretically by Liehr and Ballhausen.[16] The intense band in the visible region is the ν_3 band due to the transition $^3T_1(F) \rightarrow {}^3T_1(P)$; the near-infrared band is the ν_2 band corresponding to $^3T_1(F) \rightarrow {}^3A_2(F)$. The weak bands occurring in the vicinity of 20,000 and 10,000 cm.$^{-1}$ have been assigned to spin-forbidden transitions from $^3T_1(F)$ to $^1T_2(G)$ and $^1T_2(D)$, respectively.[3,4] The bands of the tetrabromo complex show almost no variation in position in the different solvents. Their energies correspond to a value of ~3400 for the ligand field parameter Δ. The spectrum of the tribromo complex would be expected to show effects due to low-symmetry components; however, no effects definitely ascribable to such components occur. Cotton, Faut, and Goodgame observed a splitting of the ν_2 band for the ion $Ni(C_6H_5)_3PBr_3^-$[17]; this splitting was not observed for the tribromo complexes $Ni(solv)Br_3^-$ studied here. The complex apparently does not deviate very strongly from a tetrahedral arrangement of the ligands. The principal effect of the substitution of a solvent molecule for a halide ion is to shift the band toward higher energies; this effect is in line with predictions from the spectrochemical series.[18] The series predicts a larger shift in the case of acetonitrile than for the other solvents, as acetonitrile would coordinate through a nitrogen atom whereas all of the other solvents investigated would coordinate through an oxygen atom. Table I shows that the ν_3 bands of $NiBr_3^-$ in the different solvents exhibit little difference in energy, but the ν_2 band for acetonitrile occurs at a significantly higher energy than the ν_2 bands for the other solvents.

TABLE II

ABSORPTION SPECTRA OF $NiBr_3^-$ AND $NiBr_4^{-2}$ IN ORGANIC SOLVENTS AT 25°

	$NiBr_3^-$		$NiBr_4^{-2}$	
Solvent	λ, mμ	ϵ_{max},[a] moles^{-1} l. cm.$^{-1}$	λ, mμ	ϵ_{max},[a] moles^{-1} l. cm.$^{-1}$
Acetone	1360	30	1450	38
	707	114	754	272
	643	203	704	284
	610	sh	670	sh
	493	19		
CH_3CN	1240	33	1430	33
	700	sh	754	279
	647	206	706	274
	610	sh	670	sh
	493	15		
$CH_3COC_2H_5$	1370	31	1450	40
	715	110	753	240
	647	188	700	247
	610	sh	660	sh
	493	15		
CH_3NO_2	*b*		1420	30
			755	260
			707	269
			660	sh
DMA	1370	30		
	705	sh		*b*
	656	202		
	620	sh		
	490	15		
THF	1380	32		
	705	sh		
	645	~200		*b*
	610	sh		
	492	~18		

[a] sh, shoulder. [b] Formation incomplete at 25°.

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(17) F. A. Cotton, O. D. Faut, and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 344 (1961).

(18) L. E. Orgel, *J. Chem. Phys.*, **23**, 1004 (1955).

This is in agreement with the Liehr–Ballhausen diagram, which shows that the energy of ν_2 is much more sensitive to changes in Δ in the region under consideration than is the energy of ν_3.[16] This shift of the ν_2 band also provides evidence that, in the cases where $Ni(ClO_4)_2 \cdot 6H_2O$ was used as the source of nickel for the acetonitrile solutions, the solvent molecule coordinated in the tribromo complex is acetonitrile rather than water.

The tri- and tetrabromo complexes are apparently the only tetrahedral species present at appreciable concentrations in the solvents investigated. The absorption bands of tetrahedral nickel(II) complexes are characterized by being about 100 times more intense than those of the octahedral complexes,[4] and only the two species characterized here are needed to explain the intense bands observed in nickel(II)–bromide solutions in the different solvents. Numerous solid tetrahedral dibromo complexes of the type NiL_2Br_2 have been prepared and their solid and solution spectra have been measured[4,17,19]; no corresponding spectra were observed for the nickel(II)–bromide solutions investigated here. This does not completely rule out the presence of a tetrahedral dibromo complex, but does indicate that if such a complex exists it incorporates such a small fraction of the total nickel that its absorption bands are completely obscured by those of the tri- and tetrabromo complexes. The tetrahedral structure apparently does not become the favored structure until the coordination of the third bromide. Similar behavior has been observed for the nickel(II)–chloride[9] and the copper(II)–chloride and bromide systems.[20] The cobalt(II)–chloride system shows similar behavior in dimethylformamide,[21] but in other solvents such as alcohols and acetone the tetrahedral structure is stabilized upon coordination of the second halide.[22]

[19] F. A. Cotton and D. M. L. Goodgame, *J. Am. Chem. Soc.*, **82**, 5771 (1960); D. M. L. Goodgame and F. A. Cotton, *ibid.*, **82**, 5774 (1960); D. M. L. Goodgame and M. Goodgame, *J. Chem. Soc.*, 207 (1963); S. Buffagni, L. M. Vallarino, and J. V. Quagliano, *Inorg. Chem.*, **3**, 480 (1964), and references therein.

[20] W. Schneider and A. v. Zelewsky, *Helv. Chim. Acta*, **46**, 1848 (1963).

[21] S. Buffagni and T. M. Dunn, *J. Chem. Soc.*, 5105 (1961).

[22] L. I. Katzin and E. Gebert, *J. Am. Chem. Soc.*, **72**, 5464 (1950); D. A. Fine, *ibid.*, **84**, 1139 (1962).

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The Far-Infrared Spectra of Metal–Halide Complexes of Pyridine and Related Ligands

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Received August 24, 1964

Metal–halide complexes of pyridine and certain other nitrogen-donor ligands have been extensively investigated in the 200–700 cm.$^{-1}$ region and assignments of metal–halogen ν(M–X) and metal–ligand ν(M–L) stretching vibrations are made. The relationship of the numbers of ν(M–X) and ν(M–L) vibrations and their frequencies to the stereochemistries of the complexes (MX_mL_n) is outlined. In particular, it is shown that complexes with tetrahedral and octahedral stereochemistries may be clearly distinguished by their infrared patterns. Nujol mull spectra and solution spectra are essentially the same.

Introduction

Relatively few systematic studies of the far-infrared spectra of metal–halide complexes have been carried out. However, with the appearance of commercial double-beam spectrometers capable of reaching down to at least 200 cm.$^{-1}$, data are beginning to accumulate on metal–chlorine ν(M–Cl), metal–bromine ν(M–Br), and in some cases on metal–iodine ν(M–I) stretching vibrations. The assignments were placed on a firm basis by the initial studies on the t_2 stretching vibrations of the MX_4^{n-} series of anions (M = Mn, Fe, Co, Ni, Cu, Zn) by Clark and Dunn,[1] Adams, *et al.*,[2] and later by Sabatini and Sacconi.[3]

As a natural extension to this work, we have for several years been studying the far-infrared spectra of complexes of the type MX_mL_n, where L is a neutral electron-donor ligand. Metal–pyridine complexes are among the most extensive series known, and furthermore they include examples of complexes with the following stereochemistries: tetrahedral ($MX_2 \cdot 2py$) octahedral ($MX_2 \cdot 4py$, $MX_3 \cdot 3py$, and $MX_4 \cdot 2py$, for all of which *cis* and *trans* isomers are known), polymeric octahedral and distorted polymeric octahedral ($MX_2 \cdot 2py$, both of which contain halogen bridges), and *cis*- and *trans*-planar ($MX_2 \cdot 2py$). A summary of the relevant X-ray information on metal–pyridine complexes is given in Table I.

All the above types of complexes have been included in the present study, and the relationship between ν(M–X) vibrations and stereochemistry is outlined and shown to have potential application to the diagnosis of the stereochemistry and coordination number of new metal–halide complexes. This will be particularly important where the metal atom has a closed shell of valence electrons and hence the techniques of electronic absorption spectroscopy and magnetism may yield no unambiguous information on stereochemistry.[4]

The new stretching vibrations expected in complexes of the type MX_mL_n over those found in MX_4^{n-} anions

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[1] R. J. H. Clark and T. M. Dunn, *J. Chem. Soc.*, 1198 (1963).

[2] D. M. Adams, J. Chatt, J. M. Davidson, and J. Gerratt, *ibid.*, 2189 (1963).

[3] A. Sabatini and L. Sacconi, *J. Am. Chem. Soc.*, **86**, 17 (1964).

[4] N. S. Gill, R. S. Nyholm, G. A. Barclay, T. I. Christie, and P. J. Pauling, *J. Inorg. Nucl. Chem.*, **18**, 88 (1961).