peak in the 3350 to 3600 cm.$^{-1}$ region, which is assigned to the OH stretching frequency of coördinated water. This observation and the analytical data indicate that these complexes are dihydrates with the exception of the Cu(II) complex, which is a monohydrate. Attempts to dehydrate the Fe(II), Ni(II), Zn(II), Co(II), and Mn(II) complexes by sublimation were unsuccessful. The most intense band in the 1600 cm.$^{-1}$ region has been assigned to the carbonyl stretching frequency.[7] When the position of this band is compared for the different metal complexes, an interesting correlation is observed.

Sievers and Bailar[8] have shown for metal polyaminocarboxylate chelates that the position of the carbonyl stretching frequency is influenced by the charge to radius ratio q/r of the metal ion. It was found that the carbonyl stretching frequency of the carboxyl groups bonded to metals with q/r ratios of more than 3.6 occurred between 1625 and 1650 cm.$^{-1}$, and for those less than 3.6, at 1590 to 1615 cm.$^{-1}$.

In hexafluoroacetylacetonato complexes, in contrast with the complexes of carboxylic acids, coördination occurs through the oxygen of the carbonyl group, and the position of the carbonyl stretching frequency is shifted in opposite directions for these two classes of compounds. In metal–HFA complexes, it is expected that the band position of carbonyl groups attached to metals of high q/r ratios will be lower than those bonded to metals of low q/r ratios. The metals with high q/r ratios bond more strongly with the oxygen, thus reducing the double bond character of the carbon–oxygen bond.

Table I shows that the carbonyl stretching frequencies of the divalent metal ions and Nd(III), which have q/r values ranging from 2.2 to 2.6, appear at approximately 1650 cm.$^{-1}$; those of the trivalent metal ions Rh, Cr, and Fe, which have q/r values from 4.4 to 4.6, appear at 1610, 1612, and 1613 cm.$^{-1}$. If the charge to size ratio criteria is used, it is found that only for Al(III) and Zr(IV), whose q/r ratios are high, are results found contrary to those predicted.

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CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
UNIVERSITY OF KANSAS CITY,
KANSAS CITY, MISSOURI

Chloride and Bromide Complexes of Nickel(II) in Aqueous Solution[1]

BY D. A. NETZEL AND H. A. DROLL

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We wish to report on the small but significant changes in the visible absorption spectra of $Ni(ClO_4)_2$ solutions that contain relatively large concentrations of either chloride or bromide ions. Ion-exchange[2-4] and spectrophotometric studies indicate the presence of only either $NiCl^+$ or $NiBr^+$ in highly concentrated hydrohalic acid solutions of nickel(II). Recently, Lister and co-workers[5,6] failed to observe any spectral change in the range 240–900 mμ for chloride- and bromide-containing solutions of $Ni(ClO_4)_2$ at halide concentrations up to 0.12 *M*. However, we have observed changes of up to 18% in the optical density of 0.0447 *M* $Ni(ClO_4)_2$ solutions whose halide concentrations exceed 0.12 *M* (Table I). Unfortunately, these spectral changes occur in only an extremely narrow range of wave lengths near the maximum absorption at 400 mμ. We assume that a 1:1 complex is present which is responsible for the absorption shift. Since the absorption shift is small, the molar extinction coefficients ϵ_0 and ϵ_1 for $Ni(aq)^{2+}$ and NiX^+ (X = Cl, Br), respectively, are nearly equal. The equation

$$\bar{\epsilon}[X^-]/(\bar{\epsilon} - \epsilon_0) = \epsilon_1[X^-]/(\bar{\epsilon} - \epsilon_0) - 1/K$$

which relates the average molar extinction per nickel (optical density/total nickel concentration) to the stability constant, *K*, for the 1:1 complex, is derived from Beer's law, the stability constant expression for NiX^+, and the assumption that the equilibrium halide concentration equals the total halide ion concentration. This equation is the slope–intercept form of a straight line whose slope is the molar extinction coefficient for NiX^+ (ϵ_1) and whose intercept is the reciprocal of the stability constant. Table I includes values of the functions $\bar{\epsilon}[X^-]/(\bar{\epsilon} - \epsilon_0)$ and $[X^-]/(\bar{\epsilon} - \epsilon_0)$ calculated from the optical density values. An implied accuracy of 2% in the optical density measurements leads to an approximate accuracy of about 20% for these functions. These functions when plotted yield a straight line.

Application of the method of average points enables us to estimate values for the stability constants, valid at an ionic strength of 5.7 *M*: $K = 0.3 \pm 0.1$ for $Ni^{2+} + Cl^- \rightleftarrows NiCl^+$ and $K = 0.5 \pm 0.2$ for $Ni^{2+} + Br^- \rightleftarrows NiBr^+$. Similarly, the molar extinction coefficients for $NiCl^+$ and $NiBr^+$ for both wave lengths given in Table I are evaluated to be 6 ± 1 l. mole^{-1} cm.$^{-1}$. The molar extinction coefficients for $Ni(aq)^{2+}$ at 395 and 400 μ are 5.0 ± 0.1 and 4.7 ± 0.1 l. mole^{-1} cm.$^{-1}$, respectively.

Experimental

Reagents.—Reagent grade $Ni(ClO_4)_2 \cdot 6H_2O$ (G. Frederick Smith Co., Columbus, Ohio) was used without further purification to make the standard nickel solution about 0.5 *M* in nickel(II) and 1 *M* in perchloric acid. Aliquot samples were taken and the amount of nickel was determined by precipitation with dimethylglyoxime. The final nickel solution contained 0.491 *M* Ni^{2+} and 1.987 *M* ClO_4^-.

A series of mixed 6 *M* HX–6 *M* $HClO_4$ solutions was obtained

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(1) Abstracted in part from the M.S. thesis of D. A. Netzel.

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(6) M. W. Lister and D. W. Wilson, *ibid.*, **39**, 2606 (1961).

TABLE I

$Ni^{2+} + Cl^- \rightleftarrows NiCl^+$ Total Ni concn. = 0.0447 *M*

	395 mμ			400 mμ		
$[Cl^-]$, *M*	Optical density	$\frac{\bar{\epsilon}[Cl^-]}{(\bar{\epsilon} - \epsilon_0)}$	$\frac{[Cl^-]}{(\bar{\epsilon} - \epsilon_0)}$	Optical density	$\frac{\bar{\epsilon}[Cl^-]}{(\bar{\epsilon} - \epsilon_0)}$	$\frac{[Cl^-]}{(\bar{\epsilon} - \epsilon_0)}$
0.000	0.223	..	...	0.212	..	...
0.545	.231	14	2.7	.226	9	1.7
1.089	.233	23	4.4	.231	13	2.6
2.178	.240	29	5.4	.241	18	3.4
3.267	.244	36	6.6	.247	23	4.2
4.356	.247	43	7.8	.251	28	5.0
5.446	.246	56	10.0	.251	35	6.2

$Ni^{2+} + Br^- \rightleftarrows NiBr^+$ Total Ni concn. = 0.0447 *M*

	395 mμ			400 mμ		
$[Br^-]$, *M*	Optical density	$\frac{\bar{\epsilon}[Br^-]}{(\bar{\epsilon} - \epsilon_0)}$	$\frac{[Br^-]}{(\bar{\epsilon} - \epsilon_0)}$	Optical density	$\frac{\bar{\epsilon}[Br^-]}{(\bar{\epsilon} - \epsilon_0)}$	$\frac{[Br^-]}{(\bar{\epsilon} - \epsilon_0)}$
0.000	0.223	..	...	0.212	..	...
0.544	.227	25	4.9	.219	17	3.5
1.088	.233	23	4.4	.226	18	3.5
2.176	.239	31	5.7	.234	23	4.4
3.264	.242	39	7.3	.240	28	5.2
4.352	.243	50	9.3	.241	36	6.7
5.440	.246	56	10.0	.245	40	7.4

in which the volume % of 6 *M* HX was varied from 0 to 100. The separate 6 *M* HX and 6 *M* $HClO_4$ solutions had been standardized previously by titration against 1 *N* NaOH. Just prior to a spectrophotometric measurement, each sample was made by adding 5.00 ml. of the standard nickel solution to 50.00 ml. of the appropriate HX–$HClO_4$ solution. The ionic strength of each sample was 5.7 *M*. The halide ion concentrations listed in Table I were calculated from the known molarities of the 6 *M* acids and on the assumption that no volume change attended either the preparation of the mixed HX–$HClO_4$ solutions or the addition of standard nickel solution to each of the mixed HX–$HClO_4$ solutions.

Measurements.—A Beckman Model DU spectrophotometer, fitted with a constant-temperature cell compartment, was used. Constant temperature was maintained at 25 ± 0.1° by circulating water through the cell compartment from a water bath which was maintained at 25 ± 0.01°. All data were obtained with matched 1-cm. cells. A blank was prepared for each sample. The blank solutions contained 5 ml. of 2 *M* $HClO_4$ added to 50 ml. of the same HX–$HClO_4$ solution as for the corresponding samples. The reproducibility of the measurements was determined by taking readings on two separate occasions for each sample. The reproducibility obtained was ± 0.75%.

CONTRIBUTION FROM THE
RESEARCH AND DEVELOPMENT LABORATORIES,
PENNSALT CHEMICALS CORP.,
WYNDMOOR, PENNSYLVANIA

Reaction of Chlorine Trifluoride with Ammonium Fluoride. Preparation of Chlorodifluoroamine

BY DAVID M. GARDNER, WILLIAM W. KNIPE,
AND CHARLES J. MACKLEY

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Prior studies at this Laboratory involving attempts to moderate the reaction of ClF_3 with NH_3 by dilution of the reactants with inert gas, high gas flow rates, and the use of a special jet reactor[1] resulted in complete oxidation of the NH_3 and often ignition as reported by Ruff and Krug.[2] The reaction is best represented by eq. 1.

$$2NH_3 + 2ClF_3 \longrightarrow N_2 + 6HF + Cl_2 \qquad (1)$$

During this work it was found that NH_3 in the form of the simple salts, NH_4F and NH_4HF_2, reacts under certain conditions with ClF_3 to yield chlorodifluoramine, NF_2Cl. This compound was first prepared by Petry[3] by the reaction of difluoramine with boron trichloride. Liquid ClF_3 reacts with NH_4F from −50 to about −5° to yield NF_2Cl; however, the reacting mixture nearly always explodes on warming to temperatures of −5 to 0°. Gaseous ClF_3 reacts smoothly with NH_4F and NH_4HF_2 under controlled temperature and flow conditions to yield NF_2Cl according to eq. 2 and 3.

$$3NH_4F + 5ClF_3 \longrightarrow 3NF_2Cl + 12HF + Cl_2 \qquad (2)$$

$$3NH_4HF_2 + 5ClF_3 \longrightarrow 3NF_2Cl + 15HF + Cl_2 \qquad (3)$$

The reaction expressed by either eq. 2 or 3 is always simultaneous with that given by eq. 4.

$$2NH_4F + 2ClF_3 \longrightarrow N_2 + 8HF + Cl_2 \qquad (4)$$

The latter reaction predominates whenever localized overheating of the reactants occurs. Consequently, the gaseous ClF_3 was diluted with N_2 and the flow rate of the gas mixture was regulated to eliminate hot spots in the solid ammonium fluoride reactant bed. It was later found that this is most easily accomplished by employing a suspension of solid ammonium fluoride in a fluorocarbon oil. The oil functions to dissipate localized heat and thus maintains a more uniform reaction temperature.

In contrast with the behavior of ClF_3, chlorine

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[3] R. C. Petry, *J. Am. Chem. Soc.*, **82**, 2400 (1960).