between HF and strong Lewis acids, such as AsF_5

$$2HF + AsF_5 \longrightarrow H_2F^+AsF_6^-$$

In both cases, the electron-deficient cation (Cl^+ and H^+, respectively) is stabilized by adding one molecule of ClF or HF, respectively, to form a bent triatomic cation having fluorine as the central atom.

The FCl_2^+ cation is unusual for two reasons. (i) It is the first known interhalogen compound in which the most electronegative atom is the central atom. In all previously known interhalogen compounds the atom having the lowest electronegativity had always been the central atom. (ii) It is the first known example of a polymeric interhalogen cation.[44] It should be possible to prepare a whole new class of similar interhalogen cations (such as $Y\text{–}Y\text{–}Y^+$, $Y\text{–}Y\text{–}Z^+$, and $Y\text{–}X\text{–}Z^+$), by reaction of halogen fluorides with strong Lewis acids in the presence of halogen or interhalogen molecules suitable for stabilization of the halogen cation formed as an intermediate. Certain analogies exist between these hypothetical cations and the known $Y\text{–}Y\text{–}Y^-$, $Y\text{–}Y\text{–}X^-$, and $Y\text{–}X\text{–}Z^-$ interhalogen anions in which the Y^-, X^-, or Z^- anion is stabilized by the addition of a halogen (Y_2) or interhalogen (Y–X) molecule, respectively. For example, the I_3^-, I_2Br^-, and $BrICl^-$ anions have recently[45] been characterized by vibrational spectroscopy. In both, the triatomic polyhalogen anions and cations, the original monatomic ion is located in a terminal position. The basic difference between these cations and the anions is that the X^+ cation combines with the more electronegative part of the halogen or interhalogen molecule to form a bent cation. In the resulting triatomic cation the central atom has an electron octet (considering only the valence electrons) and a formal oxidation number of -1. In contrast, the X^- anion will combine with the more electropositive part of the halogen or interhalogen molecule to form a linear anion. In the resulting triatomic anion the central atom has an electron decet and a formal oxidation number of $+1$.

Acknowledgment.—This research was supported by the Office of Naval Research, Power Branch. The authors wish to express their gratitude to Dr. D. Pilipovich for his help in this work and to Professor Dr. J. Goubeau for stimulating discussions.

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[44] The possible existence of I_2Cl^+ and I_2Br^+ was suggested by R. A. Garrett, R. J. Gillispie, and J. B. Senior, *Inorg. Chem.*, **4**, 563 (1965), in an attempt to rationalize results from conductivity measurements on the $I_2\text{–}HIO_3\text{–}H_2SO_4\text{–}ICl$ and $I_2\text{–}HIO_3\text{–}H_2SO_4\text{–}IBr$ systems, respectively. However, these authors speculated that the ICl_2^+ cation would have the asymmetric, bent structure with iodine as the central atom, $[I\text{–}I\text{–}Cl]^+$.

[45] A. G. Maki and R. Forneris, *Spectrochim. Acta*, **23A**, 867 (1967).

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Infrared and Raman Studies of Nitrate Impurity in Nitrite Complexes

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Infrared and Raman analyses are proposed for the determination of nitrate impurity in hexanitronickelate(II) complexes. Vibrational bands characteristic of the NO_3^- impurity in the complexes can be assigned. The infrared spectra of the complexes $K_4Ni(NO_2)_6$, $K_4Ni(NO_2)_6 \cdot H_2O$, and $K_2BaNi(NO_2)_6$ and spectral changes observed on heating the hydrate are discussed. High-quality infrared spectra were obtained using multiple attenuated total reflectance techiques (MATR).

Introduction

In a recent publication[1] we have shown that the relatively high absorptivities of the $\nu_2(A'')$ and $\nu_3(E')$ modes of the NO_3^- ion in infrared spectra, *ca.* 827 and 1387 cm^{-1}, respectively, permit detection and analysis of NO_3^- in the presence of NO_2^- for NO_3^- to NO_2^- ion ratios as low as 0.002. Vibrational bands attributed to various nitro and nitrito transition metal complexes are often reported in this spectral region. The possibility that vibrational bands due to NO_3^- may contribute to the observed spectrum of the complexed nitrite has generally been neglected. One might suspect NO_3^- to interfere for several reasons: (a) KNO_2 is often used as a starting material in the preparation of nitrite complexes but the so-called reagent grade KNO_2 commercially available has been reported to contain 0.3–10% NO_3^- and is very difficult to purify,[2,3] (b) nitrite complexes are usually made in slightly acidic aqueous solutions[4,5] but the NO_2^- ion is unstable with respect to NO_3^- in acid solution,[6] (c) NO_3^- and NO_2^- ions have the same charge and similar size so NO_3^- might easily copre-

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[1] M. H. Brooker and D. E. Irish, *Can. J. Chem.*, **46**, 229 (1968).

[2] E. Rapoport, *J. Chem. Phys.*, **45**, 2721 (1966).

[3] J. D. Ray, *J. Inorg. Nucl. Chem.*, **15**, 290 (1960).

[4] D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, **6**, 813 (1967).

[5] H. Elliot, B. J. Hathaway, and R. C. Slade, *ibid.*, **5**, 669 (1966).

[6] M. J. N. Pourbaix, "Atlas of Electrochemical Equilibria in Aqueous Solutions," Pergamon Press, New York, N. Y., 1966, p 501.

cipitate (KNO_2 and KNO_3 are known to form a solid solution[7]), and (d) no suitable analysis for small amounts of NO_3^- in nitrite complexes has previously existed.

The infrared and Raman techniques previously reported[1] for determination of NO_3^- impurity in KNO_2 have been modified to permit the analysis of NO_3^- in some hexanitronickelate(II) complexes. From the results of the analyses the intensities of NO_3^- frequencies have been estimated and used to assign bands due to NO_3^- impurity in the complexes. A broad band, *ca.* 1400 cm^{-1}, has now been assigned to NO_3^- impurity in each of the three complexes studied: $K_4Ni(NO_2)_6$, $K_4Ni(NO_2)_6 \cdot H_2O$, and $K_2BaNi(NO_2)_6$. The increased clarity of the infrared spectra obtained by multiple attenuated total reflectance (MATR) sampling techniques reveals several interesting differences between the observed spectra and those previously reported.

Experimental Section

The preparation and properties of $K_4Ni(NO_2)_6$ and $K_4Ni(NO_2)_6 \cdot H_2O$ have been described previously.[4] $K_2BaNi(NO_2)_6$ was prepared as reported[8] except $NiBr_2$ was used instead of $NiCl_2$. The formation of the complexes was always accompanied by the faint odor of nitrous acid. $K_4Ni(NO_2)_6$ was kept in a dry atmosphere to prevent conversion to the hydrate.

$NiBr_2$ was prepared by treating 49% HBr with excess $Ni(OH)_2$. The saturated $NiBr_2$ solution had a pH of ~6. HBr was Fisher Certified reagent grade. $Ni(OH)_2$ (97–99%) was supplied by Alfa Chemicals. KNO_2 was Baker and Adamson reagent grade of 95% minimum nitrite assay. A 0.30 wt % NO_3^- impurity was determined by the Raman method.[1] Reagent Grade BDH KNO_2 (89% minimum nitrite) was analyzed by the same method and found to have a 4.4 wt % NO_3^- impurity. In neither case was the NO_3^- impurity listed by the manufacturer. Baker and Adamson KNO_2 was used without further purification. Analar KNO_3 99% and Anachemia carbonate-free[9] KOH were used as purchased.

The analysis for NO_3^- in $K_4Ni(NO_2)_6$ was performed as follows. Accurately weighed aliquots (4.427 g or 9 mmol) of $K_4Ni(NO_2)_6$ were added to solutions consisting of 400 ml[10] of distilled water and 2 ml of 1 *N* KOH. Increasing amounts (0–4 mmol) of KNO_3 were added to each solution. Additional KOH was added immediately from a buret until the solution had a pH of ~10. An excess of KOH is not desirable.[9] When the $Ni(OH)_2$ had settled, it was removed by filtration through fine-sintered glass. The $Ni(OH)_2$ precipitate was washed several times with distilled water.[10] The filtrate was evaporated to a volume of about 10 ml, treated with activated charcoal, filtered through paper, and filtered again through sintered glass. Although faintly yellow, the solutions were free of turbidity. Raman spectra for the KNO_3–KNO_2 solutions were recorded as previously reported.[1] Solid solutions of the KNO_3–KNO_2 for the infrared analysis[1] were made by crystallizing the aqueous solutions. For infrared spectra the solid solutions were pressed against a KRS-5 prism cut at 60° and placed in the Wilk's model 9 MATR attachment.

In order to determine the effect of KNO_2 purity on the purity of the resulting complex a series of $K_4Ni(NO_2)_6$ samples was prepared with identical techniques but with KNO_2 solutions of different NO_3^- concentrations. The NO_3^- contamination in the complexes so formed was subsequently determined by the Raman method which proved to be more accurate than the infrared technique.

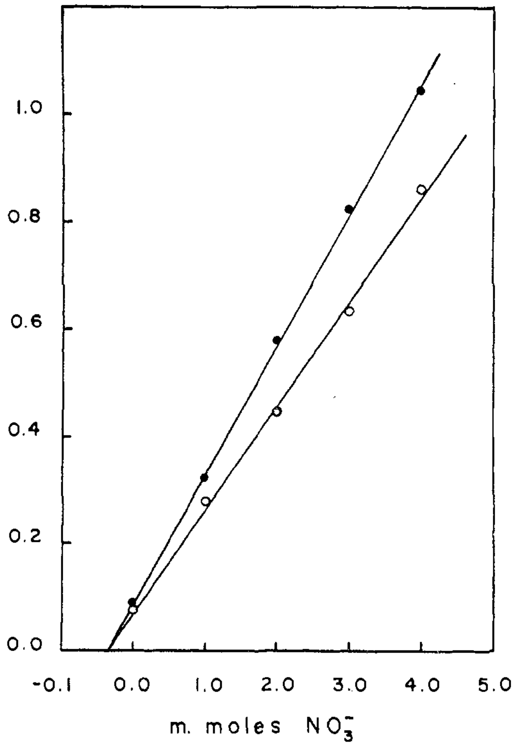

Figure 1.—Raman intensity ratio I_{1050}/I_{810} (●) and infrared absorbance ratio A_{837}/A_{806} (O) *vs.* millimoles of NO_3^- added to aliquots containing 9 mmol of $K_4Ni(NO_2)_6$.

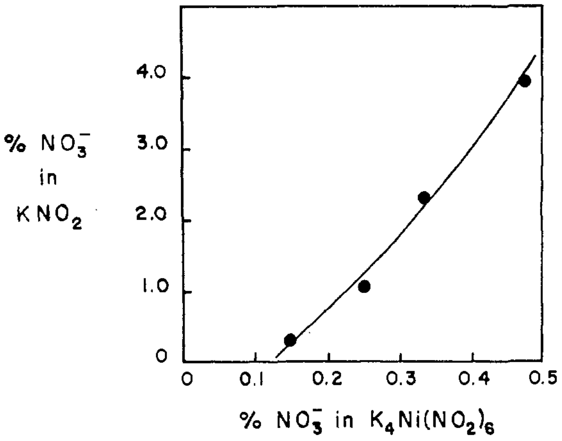

Figure 2.—The weight per cent of NO_3^- in KNO_2 starting material *vs.* weight per cent of NO_3^- in the $K_4Ni(NO_2)_6$ product.

Infrared spectra of the complexes were also recorded for powders pressed against a 60° KRS-5 prism. Spectra recorded in this manner were free of band distortion and of high resolution. The temperature at which the MATR spectra were recorded could be controlled by a Haake constant-temperature circulator. Temperatures of 95 ± 1° were easily maintained for the length of time required for conversion of $K_4Ni(NO_2)_6 \cdot H_2O$ to the anhydrous form.

The Beckman IR-9 spectrophotometer was calibrated using the 431.2-cm^{-1} line of water vapor as well as the usual polystyrene frequencies. All recorded frequencies are expected to be ac-

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[7] J. Bureau, *Ann. Chim.* (Paris), [11] **8**, 5 (1937).

[8] D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, **3**, 1389 (1964).

[9] Precautions were taken to prevent contamination by CO_3^{2-} since a Raman vibrational band at *ca.* 1065 cm^{-1} for this ion could interfere with the 1050-cm^{-1} NO_3^- band used in the analysis.

[10] Large volumes of solution and thorough washing of the $Ni(OH)_2$ kept the NO_2^- from coprecipitating with the $Ni(OH)_2$.

TABLE I

COMPARISON OF INFRARED VIBRATIONAL SPECTRA FOR SOME HEXANITRONICKELATE(II) COMPLEXES

$K_4Ni(NO_2)_6$		$K_4Ni(NO_2)_6 \cdot H_2O$		$K_2BaNi(NO_2)_6$			
a	*b*	*a*	*b*	*a*	*c*	*d*	Assignments
					291		Ni–N asym str
420 m	414 m						$\rho_{wag}(NO_2)$
425 m	423 w	433 m	427 m	436 m	433	435 w	
		515 s	510 br	500 br			H_2O libration
813 m	813 m	811 s	810 s	813 s	813	810 m, sp	$\delta(NO_2)$
826 m	826 m	830 m	833 m	837 m	838	836 w	
845 vw	846 vw						$\delta(ONO)$
866 m	867 m						
1222 s	1206 s						$\nu_{sym\ str}(ONO)$
1245 sh		1260 sh		1240 sh			ν_3(free NO_2^-)
1306 s				1308 vs	1306		$\nu_{sym}(NO_2)$
1330 s	1325 vs	1318 vs	1319 vs			1341 vs	
1345 vvw	1347 w	1345 sh	1346 w	1345 sh	1343	1348 s	$\nu_{asym}(NO_2)$
1388 m, s	1387 m						$\nu_{asym}(ONO)$
1395 m, br		1395 m, br		1405 w, br		1405 m, sh	$\nu_3(NO_3^-$ impurity)
		1627 br	1621 m	1645 w		1640 vw	$\nu_2(H_2O)$ + overtones

[a] MATR (this work). [b] Mull.[4] [c] Mull.[14] [d] KBr disk.[15]

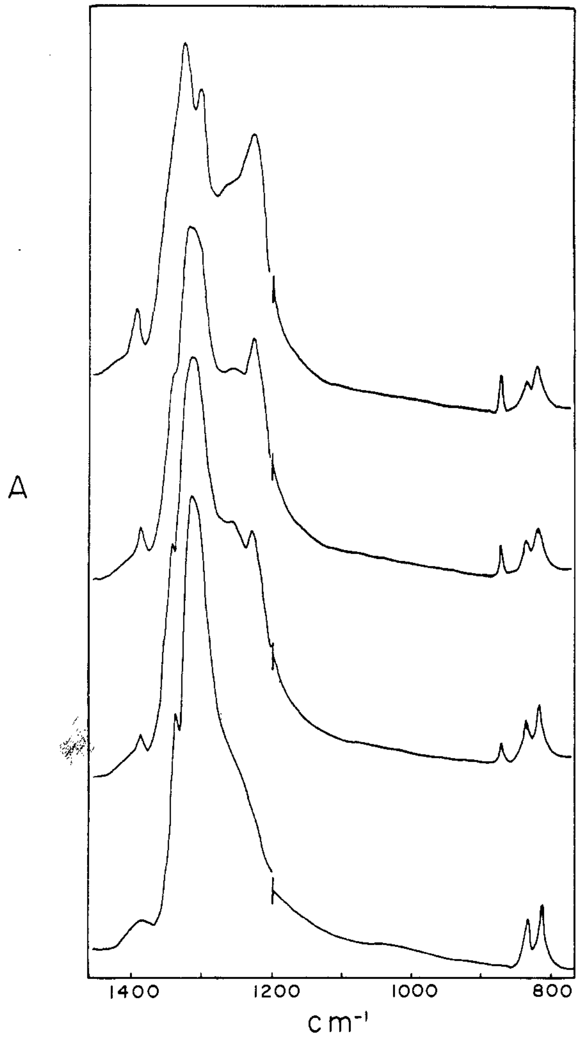

Figure 3.—A portion of some MATR infrared spectra obtained during dehydration of $K_4Ni(NO_2)_6 \cdot H_2O$: lower trace, $K_4Ni(NO_2)_6 \cdot H_2O$; intermediate traces, partially dehydrated sample; top trace, $K_4Ni(NO_2)_6$.

curate to ±1 cm^{-1}. The order break at 1200 cm^{-1} contributes a small discontinuity to the spectra.

Results

Figure 1 shows the results of the infrared and Raman analyses for a particular sample of $K_4Ni(NO_2)_6$. The NO_3^- impurity in this compound, obtained by extrapolation, is 0.036 ± 0.002 and 0.004 mmol from the Raman and infrared methods, respectively, per 9 mmol of sample. This corresponds to about 0.51 wt % NO_3^- impurity in this sample. Identical results were obtained for several aliquots of the same sample. Variations in pH or temperature of the solution in which the complex was dissolved did not affect the results unless the pH was less than 6.

The amount of nitrate impurity in other samples of $K_4Ni(NO_2)_6$ was found to vary from 0.15 to 0.6% NO_3^-. The length of time the complex remained in the mother liquor seemed to increase the NO_3^- impurity since the mixture was not stable. Figure 2 indicates how the purity of the $K_4Ni(NO_2)_6$ depends on the purity of the KNO_2 used in the preparation of the complex for samples prepared in a minimum constant time (1 min between combination of reagents and isolation of dry product). A sample of $K_2BaNi(NO_2)_6$ was found to have 0.33% NO_3^- as impurity.

Table I lists the observed vibrational frequencies for the three hexanitronickelate(II) complexes and recently reported frequencies for comparison. Probable assignments for the observed frequencies are also indicated.

Goodgame and Hitchman[4] recently reported that the orange $K_4Ni(NO_2)_6 \cdot H_2O$ could readily be dehydrated at 100° to give the red $K_4Ni(NO_2)_6$. For the latter compound these authors assigned bands at 1388 and 1205 cm^{-1} to nitrito stretching frequencies. To investigate these assignments a sample of $K_4Ni(NO_2)_6 \cdot H_2O$ was dehydrated at 95° in the MATR cell. Figure 3 shows the infrared spectra obtained at various stages of dehydration. Bands at 845, 866, 1222, 1306, and 1388 cm^{-1} increase together and are maximal for the dehydrated $K_4Ni(NO_2)_6$. On cooling, the process

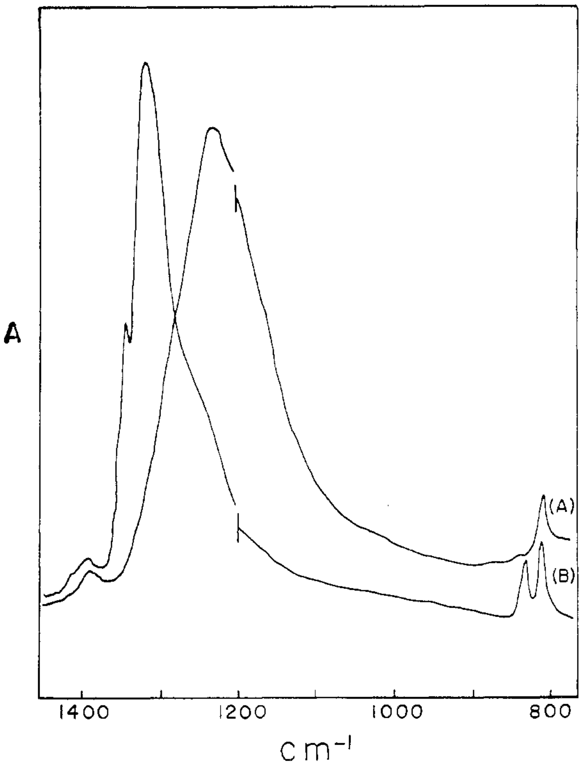

Figure 4.—A portion of the infrared spectra of (A) KNO_2 and (B) $K_4Ni(NO_2)_6 \cdot H_2O$. In both samples the $NO_3^-:NO_2^-$ ion ratio was approximately 1:200.

was found to be reversible and the spectrum reverted to that of the hydrate.

$K_4Ni(NO_2)_6 \cdot H_2O$ resembles $K_2BaNi(NO_2)_6$ both in physical appearance and in its infrared spectrum. $K_2BaNi(NO_2)_6$ does not appear to be a hydrate since prolonged drying at 100° left the complex unchanged.

Discussion

Since all of the complexes analyzed had an NO_3^-: NO_2^- ion ratio greater than 0.002, one would expect to be able to detect $\nu_1(NO_3^-)$ at *ca.* 1050 cm^{-1} in the Raman spectrum and $\nu_3(NO_3^-)$ at *ca.* 1400 cm^{-1} and perhaps $\nu_2(NO_3^-)$ at *ca.* 837 cm^{-1} in the infrared spectrum. The spectra of a KNO_3–KNO_2 mixture and $K_4Ni(NO_2)_6 \cdot H_2O$, each with an $NO_3^-:NO_2^-$ ion ratio of 0.005 are shown in Figure 4. In each spectrum the band at 1395 cm^{-1} is of similar shape and magnitude. This band is now assigned to NO_3^- present as an impurity. The band at 1395 cm^{-1} had not been observed before in $K_4Ni(NO_2)_6 \cdot H_2O$.[4,11–13] Either the workers had very pure complex or, more probably, the NO_3^- band was masked by the mulling agents used. From a comparison of the bands at *ca.* 830 cm^{-1} in the two spectra of Figure 4, it appears that the band at 830 cm^{-1} is correctly assigned to the complex and is not due to NO_3^- although NO_3^- may contribute to the intensity. Note that in trace A a weak 837-cm^{-1} band characteristic of the impurity is present but for the complex the band is much more intense despite the almost equal intensity at 1395 cm^{-1} in the two spectra.

By arguments analogous to those preceding, a weak band at 1405 cm^{-1} in the spectrum of $K_4BaNi(NO_2)_6$, previously assigned by Hathaway and Slade[5] to an asymmetric NO_2 stretch, has been reassigned to NO_3^- impurity.

In Figure 3 it can be seen that on dehydration of $K_4Ni(NO_2)_6 \cdot H_2O$ a new band at 1388 cm^{-1} is superimposed on the NO_3^- band at 1395 cm^{-1}. The bands observed at 1388, 1222, 866, and 845 cm^{-1}, which increase together as dehydration proceeds, are attributed to the ligand in a new orientation. These results are consistent with those of Goodgame and Hitchman,[4] who assigned these frequencies to nitrito vibrations and formulated the anhydrous compound as $K_4Ni(NO_2)_4(ONO)_2$. The band at 1306 cm^{-1} in $K_4Ni(NO_2)_6$ has not previously been reported. Differences in the frequencies between the observed and reported spectra of $K_4Ni(NO_2)_6$ in the 1200–1350-cm^{-1} region may be due to more complete dehydration.

The MATR spectrum for $K_2BaNi(NO_2)_6$ is in good agreement with the literature as seen in Table I. The NO_3^- band at 1405 cm^{-1} is not observed when the Nujol mull technique is used[14] but is observed by MATR or KBr pellet techniques.[5] The frequency of the NO_2^- symmetric stretch recorded for a KBr disk[5] is approximately 30 cm^{-1} higher than that given by MATR or mull methods but such shifts are common for spectra of inorganic salts in alkali halide lattices.[15]

There is disagreement in the literature on the location of ρ wag for coordinated nitro groups. Goodgame and Hitchman[4,8] assigned bands at *ca.* 430 cm^{-1} to ρ wag but Elliot, *et al.*,[5] assigned bands in this region to the M–N asymmetric stretch. Very recent far-infrared studies including normal-coordinate analysis for the complex $K_2BaNi(NO_2)_6$ by Nakagawa, *et al.*,[14] assigned the NO_2 wag at 433 cm^{-1} and the Ni–N asymmetric stretch at 291 cm^{-1}. A recent study[11] reported a Raman band at 221 cm^{-1} and an infrared band at 277 cm^{-1} consistent with the above assignment. We have therefore assigned bands at *ca.* 430 cm^{-1} to ρ wag. The assignment of the 515-cm^{-1} and the *ca.* 1627-cm^{-1} bands to H_2O in the $K_4Ni(NO_2)_6 \cdot H_2O$ spectrum is confirmed by the decrease in the intensity of these bands when the complex is dried at 100°. $K_2BaNi(NO_2)_6$ does not appear to have a hydrated form but weak bands at 500 and 1645 cm^{-1} are assigned to H_2O since their intensities decrease after drying at 100°.

The assignments of the infrared bands in the stretching region 1200–1400 cm^{-1} are based on the following. For coordinated nitro groups Le Postollec and Mathieu[16]

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(11) A. Garnier and R. Lucus, *Compt. Rend.*, **262B**, 1279 (1966).

(12) M. Le Postollec, *ibid.*, **254B**, 2988 (1962).

(13) J. Mathieu, "Theory and Structure of Complex Compounds," Papers Presented at Symposium, Wroclaw, Poland, June 1962, B. Jezowska-Trzebratowska, Ed., Pergamon Press, New York, N. Y., 1964, pp 55–61.

(14) I. Nakagawa, T. Shimanouchi, and K. Yamasaki, *Inorg. Chem.*, **7**, 1332 (1968).

(15) J. Ketelaar and J. Van Der Elsken, *J. Chem. Phys.*, **30**, 336 (1959).

(16) M. Le Postollec and J. P. Mathieu, *Compt. Rend.*, **254B**, 1800 (1962); *ibid.*, **265B**, 138 (1967).

proposed that $\nu_{asym} > \nu_{sym}$. This fact has been confirmed by recent Raman polarization studies[17] and normal-coordinate analysis.[14] For coordinated nitrito groups $\nu_{asym} > \nu_{sym}$.[8,18] Generally $\nu_{sym}(ONO) < \nu_{sym}(NO_2)$ and $\nu_{asym}(ONO) > \nu_{asym}(NO_2)$.[8,17] It should be noted that the converse applies to the free NO_2^- ion where $\nu_{sym} > \nu_{asym}$,[1,19] a fact that has often been misquoted.[8,20] The assignments given in Table I are consistent with normal-coordinate analysis[14] although that computation does not predict two intense bands at *ca.* 813 and 837 cm^{-1}.

It should be possible to use variations of the NO_3^- analysis to determine the purity of a wide variety of nitrite complexes. One may then assign bands to NO_3^- impurity if it occurs in nitrite complexes for $NO_3^-:NO_2^- > 0.002$. High-quality infrared spectra of inorganic compounds can be obtained by MATR techniques for which the inherent weaknesses of alkali halide pellets and organic mulls are not a problem.

Acknowledgments.—This work was supported by a grant from the National Research Council of Canada and by the Government of Ontario in the form of an Ontario Graduate Fellowship award to M. H. B.

[17] M. J. Cleare and W. P. Griffith, *J. Chem. Soc., A*, 1144 (1967).

[18] F. Basolo and G. S. Hammaker, *Inorg. Chem.*, **1**, 1 (1962).

[19] R. E. Weston, Jr., and T. F. Brodasky, *J. Chem. Phys.*, **27**, 683 (1957).

[20] B. J. Hathaway an R. C. Slade, *J. Chem. Soc., A*, 1485 (1966).

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Perbromic Acid and Perbromates: Synthesis and Some Properties[1]

BY EVAN H. APPELMAN

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A new and more convenient synthesis of perbromates has been developed, consisting of oxidation of bromate with fluorine in alkaline solution. Perbromic acid is a strong monobasic acid. Its aqueous solutions are stable up to about 6 *M* (55% $HBrO_4$) but decompose at higher concentration. It is a sluggish oxidant, intermediate in apparent oxidizing power between perchlorate and periodate. Potassium perbromate analyzes as $KBrO_4$. It decomposes at 280° to the bromate. Spectral evidence indicates that the tetrahedral BrO_4^- ion is the principal perbromate species in solid $KBrO_4$ and in neutral and acid perbromate solutions. There is no rapid oxygen exchange between BrO_4^- and water.

Introduction

In a recent communication[2] this author has reported the synthesis of ponderable amounts of perbromates by oxidation of bromate either electrolytically or with xenon difluoride. Neither method lends itself readily to large-scale preparations, and we have now found a much more convenient synthesis to be the oxidation of bromate in alkaline solution by molecular fluorine. By means of this method we have prepared a solution containing 24 g of $HBrO_4$, which we have used to begin the investigation of perbromate chemistry.

Experimental Section

Synthesis of Perbromic Acid and Perbromates.—A 0.5-lb fluorine cylinder was equipped with a Monel pressure-reducing regulator incorporating a Kel-F diaphragm (Matheson Co.). A Teflon-packed Monel needle valve was attached to the regulator, and a length of copper tubing was connected to the needle valve. A length of platinum tubing was silver-soldered to the end of the copper tube, and a short piece of Teflon tubing was fitted over the platinum tube. The Teflon extended about 1 in. below the end of the platinum.[3] This Teflon-tipped platinum tube was placed in a Teflon bottle containing about 1200 ml of a solution *ca.* 5 *M* in NaOH and *ca.* 1 *M* in $NaBrO_3$.[4] The bottle was cooled in an ice bath, and fluorine was bubbled in slowly until the solution became acid.[5] The resulting solution was *ca.* 0.2 *M* in perbromate.

In the following purification procedure, all solutions containing substantial amounts of fluoride and/or alkali were handled in Teflon or polypropylene vessels.

The solution was concentrated by evaporation in a Teflon beaker under a heat lamp and was then chilled. The precipitated sodium fluoride and bromate were removed by centrifugation.

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] E. H. Appelman, *J. Am. Chem. Soc.*, **90**, 1900 (1968).

[3] The Teflon tip prevents clogging. It should have at least a $^3/_{16}$-in. i.d. More recent experiments indicate that platinum inhibits the formation of perbromate, and 50–100% higher yields may be obtained if only Teflon is in contact with the solution. A disadvantage of Teflon is that it sometimes catches fire in fluorine. Although the combustion stops at once when the fluorine supply is turned off, the Teflon may require replacement. TFE Teflon is preferable to the FEP type.

[4] The solution is made by adding 1 part of 50% NaOH solution to 3 parts of *ca.* 1.3 *M* $NaBrO_3$. It is supersaturated in sodium bromate, which slowly crystallizes out. The presence of solid sodium bromate in the reaction mixture improves the yield of perbromate with respect to fluorine consumed, probably by maintaining saturation as the reaction proceeds.

[5] Although most of the fluorine is absorbed by the base, enough escapes to make it imperative that the reaction be carried out in a well-ventilated fume hood. The reaction is not smooth, and small explosions may take place in the vapor above the solution. Under no circumstances should the apparatus be left to run unattended. Introduction of more fluorine after the base has been neutralized turns the solution yellow but does not appreciably increase the yield of perbromate.