TABLE VI

FORCE CONSTANTS OF THE POLYHALOGENS

Species	Assigned structure	Force constants, mdyn/Å	Ref
A and B	$\mathrm{Cl\overset{r}{—}Br\overset{r}{—}Cl}$ $\vert r'$ Cl	$k_r - k_{rr} \cong 1.16$ $k_{r'} \cong 1.90$	*a*
D	$\mathrm{Cl\overset{r}{—}Br\overset{r}{—}Cl}$ $\vert r'$ Br	$k_r - k_{rr} \cong 1.16$	*a*
$BrCl_2^-$	$\mathrm{Cl—Br—Cl^-}$	$k_r - k_{rr} = 0.55$	*b*
E	$\mathrm{Cl\overset{r}{—}Br\overset{r''}{—}Br}$ $\vert r'$ Br	$k_r \cong 1.25$ (assuming $k_{r''} \cong 1.0$ and $k_{rr''} \cong 0.30$) $k_{r'} \cong 1.88$	*a*
Br_2Cl^-	$\mathrm{Cl\overset{r}{—}Br\overset{r''}{—}Br^-}$	$k_r = 1.0$, $k_{r''} = 0.90$, $k_{rr''} = 0.4$	*c*
Cl_3	$\mathrm{Cl—Cl—Cl}$	$k_r - k_{rr} = 0.97$	*d*
Cl_3^-	$\mathrm{Cl—Cl—Cl^-}$	$k_r - k_{rr} = 0.41$	*e*
ClF_3	$\mathrm{F\overset{r}{—}Cl\overset{r}{—}F}$ $\vert r'$ F	$k_r \cong 2.90$, $k_{rr} \cong 0.23$, $k_{r'} \cong 3.52$	*f*
ClF_2^-	$\mathrm{F—Cl—F^-}$	$k_r = 2.35$ $k_{rr} = 0.17$	*g*

[a] Present work. [b] Reference 1. [c] Reference 3. [d] Reference 4. [e] J. C. Evans and G. Y-S. Lo, *J. Chem. Phys.*, **44,** 3638 (1966). [f] H. H. Claassen, B. Weinstock, and J. G. Malm, *ibid.*, **28,** 285 (1958); H. H. Claassen, G. L. Goodman, J. G. Malm, and F. Schreiner, *ibid.*, **42,** 1229 (1965). [g] K. O. Christe, W. Sawodny, and J. P. Guertin, *Inorg. Chem.*, **6,** 1159 (1967).

observed for the triatomic part of ClF_3 compared to ClF, $(k_r - k_{rr})/k_{\mathrm{ClF}} \cong 0.6$.[6,7]

Perhaps more interesting is the comparison to the $ClBrCl^-$ ion. Analogous to those of Cl_3 radical and the Cl_3^- ion, the force constant of ClBrCl ($f_r - f_{rr} = 1.16$ mdyn/Å) is higher than that of $ClBrCl^-$ ($f_r - f_{rr} = 0.55$ mdyn/Å). Considering the ClF_2^- ion and the ClF_3 molecule, we now have three opportunities for comparison of a linear trihalogen unit in a neutral and in an ionic molecule. These are also compiled in Table VI and they show that the negative charge on the trihalide ions weakens the bond somewhat, as discussed in ref 4.

Conclusions

Owing to the large number of possible bromine–halogen compounds, the molecular identifications proposed are not certain. The identification of the ClBrCl unit, either in the ClBrCl radical or a T-shaped molecule, is quite definite. Despite the tentativity in the other assignments, they are reasonable and they provide the first information about the possible existence of these polyhalogens. The evidence obtained indicates their structures and potential functions may prove to be consistent with those of the already known analogs. In particular, the bonding in an X_1–X_2–X_3 radical or in the linear three-center portion of a corresponding T-shaped molecule may be stronger than that of the analogous negatively charged ion X_1–X_2–X_3^-.

Acknowledgments.—We gratefully acknowledge research support from the Office of Naval Research.

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[6] H. H. Claassen, B. Weinstock, and J. G. Malm, *J. Chem. Phys.*, **28**, 285 (1958).

[7] H. H. Claassen, G. L. Goodman, J. G. Malm, and F. Schreiner, *ibid.*, **42**, 1229 (1965).

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An Infrared and Raman Spectral Study of Aqueous Mercury(II) Nitrate Solutions[1]

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Infrared and Raman spectroscopy have been used to study aqueous solutions of mercury(II) nitrate as well as a mixture of $Hg(NO_3)_2 \cdot H_2O$ and KNO_3. An intensity analysis of the *ca.* 720- and 740-cm^{-1} bands is consistent with the presence of $HgNO_3^+$ and $Hg(NO_3)_2$. The polarization of the 1284-cm^{-1} Raman band is presented as evidence that the nitrate ion is acting as a monodentate ligand. A vibrational assignment for the dinitratomercury(II) species, in terms of the D_{2h} point group, is described.

Introduction

The Raman spectrum of saturated mercury(II) nitrate has been observed to be more complex than that of the alkali metal nitrates.[2] Although the increased complexity suggests that the nitrate ion is considerably perturbed by the mercury(II) ion, the absence of an Hg–O stretch vibration supports the conclusion that there is little or no covalent interaction between the ions.

Formation constants for the species $HgNO_3^+$ and $Hg(NO_3)_2$ have been calculated from emf measurements.[3,4] For nitrate ion–mercury ion concentration ratios much higher than any used in this work the existence of a very weak complex ion, $Hg(NO_3)_4^{2-}$, was

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[1] Presented in part at the Seventh National Meeting, Society for Applied Spectroscopy, Chicago, Ill., May 13–17, 1968.

[2] R. E. Hester and R. A. Plane, *Inorg. Chem.*, **3**, 769 (1964).

[3] L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964 p 174.

[4] G. Infeldt and L. G. Sillén, *Svensk Kem. Tidskr.*, **58**, 104 (1946).

inferred from a solvent extraction investigation.[5] Under similar conditions an ion-exchange study has revealed the species $Hg(NO_3)_3^-$ and $Hg(NO_3)_4^{2-}$ adsorbed on the resin.[6]

The addition of potassium nitrate to some metal nitrate hydrates results in the formation of mixtures which are liquid at about room temperature.[7] Presumably there is considerable metal–nitrate interaction in these systems of low water content. Vibrational spectra of the mercury(II) nitrate monohydrate plus potassium nitrate mixture and of mercury(II) nitrate solutions have been studied to determine the identity and structure of the species predominating in the mercury(II) ion–nitrate ion–water system. Knowledge of the vibrational frequencies and intensities of many metal–nitrate ion–water systems is essential to further our understanding of the behavior of the nitrate ion in aqueous electrolyte solutions; this report is one of a series devoted to a systematic investigation of metal–nitrate–solvent interactions.[8–12]

Experimental Section

The Raman data reported in this paper were obtained with a Cary Model 81 spectrophotometer equipped with a thermostated cell. The temperature was controlled at 25 ± 0.2°. Integrated Raman intensities were measured relative to the 458-cm^{-1} band of carbon tetrachloride. Overlapping bands were resolved and areas of component bands were measured by means of a hybrid analog–digital computer routine.[10,11] Infrared spectra were recorded with a Beckman IR-9 spectrophotometer; samples were contained in cells equipped with silver chloride windows.

A stock solution of 7.0 *M* sodium nitrate (BDH Analar reagent) was prepared by dissolution of the dried and weighed salt in water. A solution of mercury(II) perchlorate (*ca.* 4.6 *M*) was prepared by dissolving mercury(II) oxide (Fisher Certified reagent) in 30% perchloric acid (Baker and Adamson reagent grade). The undissolved oxide was removed by filtration through a fine-porosity glass filter. The mercury content of the solution was determined by a gravimetric method, the mercury being precipitated as $Hg_5(IO_6)_2$.[13]

Solutions for the molar ratio method of analysis[14] were prepared from stock solutions; the mercury(II) ion concentration was 1.10 *M* and the nitrate ion concentration varied from 1.12 to 5.04 *M*. Perchloric acid was added to the solutions to prevent hydrolysis of the mercury(II) ion.

Solutions for the Job method of analysis[14] were prepared from the stock solutions by standard techniques. Concentrations were adjusted so that the total concentration of mercury(II) ion plus nitrate ion was equal to 4.0 *M*. Perchloric acid was added to prevent hydrolysis of the mercury(II) ion. Solutions used for Raman studies were filtered through a fine-porosity glass filter prior to recording their spectra.

The solution formed from mercury(II) nitrate monohydrate and potassium nitrate was prepared by grinding together, with slight warming, the mercury salt (Fisher Certified reagent) with a small arbitrary amount of the potassium salt (BDH Analar reagent). The resulting solution was too viscous to filter through a glass frit. Suspended material was easily removed from the solution by centrifugation (10,000 rpm for 10 min).

Results

Raman and infrared spectra of the mercury(II) nitrate monohydrate plus potassium nitrate mixture are shown in Figure 1 and recorded in Table I. The infrared and Raman spectra of saturated mercury(II) nitrate are also recorded in Table I. The relative integrated intensities of the bands at *ca.* 720 and 740 cm^{-1} were measured. The manner in which the intensity of the 740-cm^{-1} band changes with changing solution composition is illustrated in Figure 2 (Job method of analysis) and Figure 3 (molar ratio method of analysis). The 720-cm^{-1} band intensities were converted to unbound nitrate concentrations as described below. These are also shown in Figures 2 and 3.

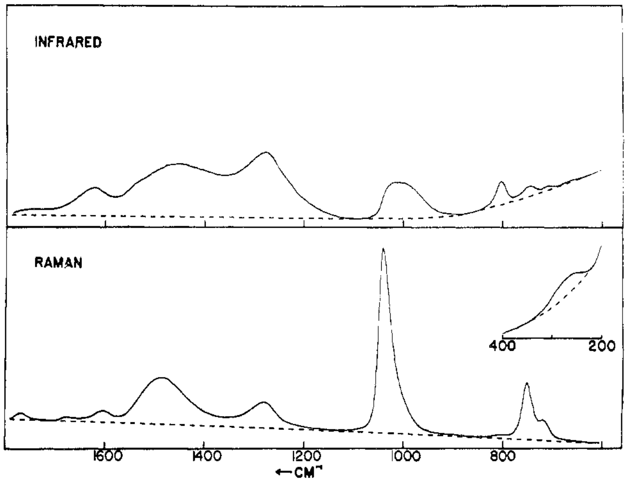

Figure 1.—The infrared and Raman spectra of the mercury(II) nitrate monohydrate plus potassium nitrate mixture.

Table I

Vibrational Frequencies of Some Mercury(II)–Nitrate Systems (cm^{-1})[a]

$Hg(NO_3)_2 \cdot H_2O$–KNO_3 mixture Raman	$Hg(NO_3)_2 \cdot H_2O$–KNO_3 mixture Ir	CH_3HgNO_3[b] (4.3 *M* aq)	Satd aq mercury(II) nitrate Raman	Satd aq mercury(II) nitrate Ir
266 wb, P		292	326 m, b, P	
	708 w, b			
718 m			716 m	
	745 m, b			
750 m, P		750	740 m, P	740 w
	803 m, sp			
810 w			810 w	810 m, sp
	986 m, b			826 w, sh
1010 w, b, P, sh		1000		998 w, sh
	1023 m, b		~1010 w, b, P, sh	
1040 s, P				1028 m
	1276 s, b		1043 s, P	
1284 m, P		1282		
			1296 m, P	1296 s
1345 w	1345 w			
			1345 w	1344 w
1400 w	1400 w			
	1460 s, b		1400 w	1400 w
1486 m, b		1502		1446 s
			1457 m	

[a] Abbreviations: P, polarized line; s, strong intensity; m, medium intensity; w, feeble intensity; b, broad line; sp, sharp; sh, shoulder. [b] P. L. Goggin and L. A. Woodward, *Trans. Faraday Soc.*, **58**, 1495 (1962).

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(5) S. S. Choi and D. G. Tuck, *Inorg. Chem.*, **2**, 780 (1963).

(6) H. Waki, *Bull. Chem. Soc. Japan*, **34**, 829 (1961).

(7) C. A. Angell, *J. Electrochem. Soc.*, **112**, 1224 (1965).

(8) D. E. Irish and G. E. Walrafen, *J. Chem. Phys.*, **46**, 378 (1967).

(9) J. T. Miller and D. E. Irish, *Can. J. Chem.*, **45**, 147 (1967).

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(12) D. L. Nelson and D. E. Irish, unpublished work.

(13) A. I. Vogel, "Textbook of Quantitative Inorganic Analysis," 2nd ed, Longmans, Green and Co., Ltd., London, 1951, p 423.

(14) M. M. Jones, "Elementary Coordination Chemistry," Prentice-Hall Inc., Englewood Cliffs, N. J., 1964.

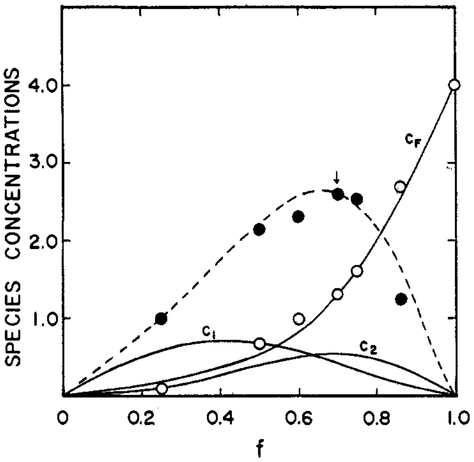

Figure 2.—Species concentrations *vs.* the Job ratio, *f*: solid lines, computed concentrations of $HgNO_3^+$ (C_1), $Hg(NO_3)_2$ (C_2), and NO_3^- (C_F); dashed curve, $C_1 + 4C_2$; ○, measured NO_3^- concentrations from I_{720}; ●, I_{740} data normalized to fit the curve at $f = 0.7$.

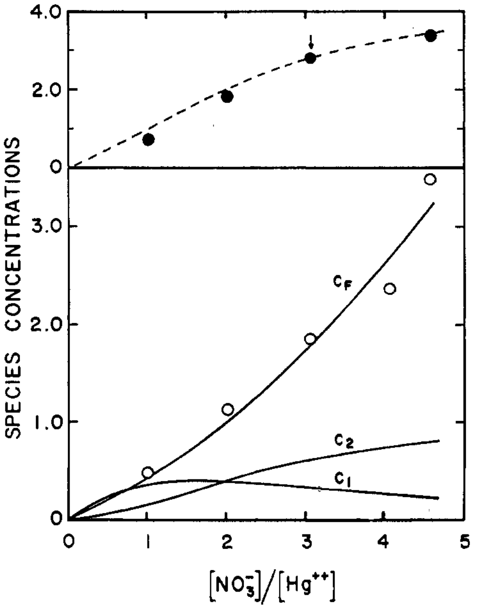

Figure 3.—Species concentrations *vs.* the nitrate:mercury concentration ratio ($[Hg^{2+}]$ is 1.10 *M*): solid lines, computed concentrations of $HgNO_3^+$ (C_1), $Hg(NO_3)_2$ (C_2), and NO_3^- (C_F); dashed curve, $C_1 + 4C_2$; ○, measured NO_3^- concentrations from I_{720}; ●, I_{740} data normalized to fit the curve at a ratio of 3.05.

Discussion

The Raman spectrum of the mixture of mercury(II) nitrate monohydrate plus potassium nitrate is qualitatively similar to that of a saturated solution of mercury(II) nitrate except for a broad polarized band at 266 cm^{-1} observed for the mixture. This observation is important insofar as a band previously observed in this region has been ascribed to an Hg–O stretch.[15–17] Although this band is not observed in the Raman spectra of aqueous solutions of mercury(II) nitrate, the fact that the other regions of the spectra, both for the mixture and for the solution, are qualitatively the same suggests the occurrence of complex nitratomercury(II) species in aqueous mercury(II) nitrate solutions.

Intensity Variations.—The solvated nitrate ion generates the following vibrational spectrum: 1404 cm^{-1} (Raman, ir), 1348 cm^{-1} (Raman, ir), 1049 cm^{-1} (Raman), 825 cm^{-1} (ir), and 719 cm^{-1} (Raman, ir).[10]

The coordination of the nitrate group to a metal ion leads to a lowering of the symmetry of the nitrate ion which may result in the removal of the degeneracy of certain vibrations and in the appearance of forbidden (on the basis of a D_{3h} point group) infrared or Raman bands. There is also the possibility of completely new bands appearing in the spectrum, indicative of the larger number of atoms in the species. A quantitative study of these new bands should lead to information about the new complex nitrato species occurring in solution. The identity of the predominant species in the solutions studied has been inferred from the intensities of the bands at *ca.* 720 and 740 cm^{-1}.

The stepwise formation constants reported by Infeldt and Sillén[4] are $K_1 = 1.3$ for $HgNO_3^+$ and $K_2 = 1.0$ for $Hg(NO_3)_2$ in solutions of ionic strength 3.0 and temperature 25°. These constants were used to calculate C_1, the concentration of $HgNO_3^+$, C_2, the concentration of $Hg(NO_3)_2$, and C_F, the concentration of unbound nitrate ion in each of the solutions studied (see Figures 2 and 3). The intensity of the 720-cm^{-1} line can be directly compared with C_F if it is assumed that this band originates essentially from unbound nitrate. To convert the intensities to concentrations, the relative integrated intensities of the 720-cm^{-1} band from solutions of $NaNO_3$ were measured. These intensities are not directly proportional to the concentration of $NaNO_3$; there is marked positive deviation from linearity similar to that reported for solutions of ammonium nitrate.[8] The intensities obtained from aqueous NH_4NO_3 solutions[8] lie on the curve with those from $NaNO_3$ solutions if the former are normalized at one concentration to the scale of the latter. This empirical curve provides the necessary relationship to convert the intensities of the 720-cm^{-1} band of the mercuric nitrate systems to concentrations of unbound nitrate. The open circles in Figures 3 and 4 are the concentrations of the unbound nitrate as calculated from the data. The close correspondence of the data and the computed concentrations, C_F, support the proposal that $HgNO_3^+$ and $Hg(NO_3)_2$ are the predominant species. The formation constants appear to be valid over a wider range of concentrations than might have been anticipated although they were measured for a high ionic strength. Nixon and Plane[18] also noted the relative constancy of concentration quotients with changing solution composition for a number of concentrated electrolyte systems.

The intensity of the 740-cm^{-1} band cannot easily be converted to species concentrations C_1 and C_2, particularly if it consists of contributions from more than one

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[15] R. R. Miano and R. A. Plane, *Inorg. Chem.*, **3**, 987 (1964).

[16] P. L. Goggin and L. A. Woodward, *Trans. Faraday Soc.*, **58**, 1495 (1962).

[17] J. H. R. Clarke and L. A. Woodward, *ibid.*, **61**, 207 (1965); **62**, 3022 (1966).

[18] J. Nixon and R. A. Plane, *J. Am. Chem. Soc.*, **84**, 4445 (1962).

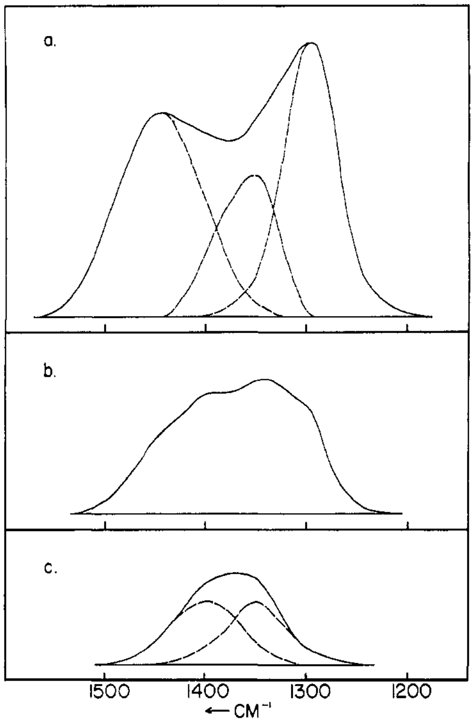

Figure 4.—Infrared spectrum of aqueous mercury(II) nitrate solutions (1200–1600 cm^{-1}): (a) 5.0 *M*; (b) 2.5 *M*; (c) 0.25 *M*.

species and if the specific molar intensities of these vary with concentration as did that of the 720-cm^{-1} band. However, a comparison can be made between the computed concentrations C_1 and C_2 and the intensity, I_{740}. A plot of I_{740} *vs.* f peaks near $f = 0.7$. C_1 and C_2 can be added to give a contour which peaks at 0.7 if they are weighted in the ratio 1:4 (see dashed line, Figure 2). If I_{740} is fitted to the contour at $f = 0.7$ the plot of the remaining intensity points conforms to the shape of the computed curve within experimental error (compare closed circles with the dashed curve, Figure 2). The weakness of the Job method is illustrated by Figure 2. When more than one species forms and contributes to the property being measured, the change of the property with composition may not reveal either the number of contributing species or their identity.[19] A similar comparison between I_{740} and $(C_1 + 4C_2)$ is shown in Figure 3 for the molar ratio study. A peak height analysis of the 740-cm^{-1} band contour at several frequencies suggests that the envelope contains a low-frequency component (*ca.* 735 cm^{-1}) arising from $HgNO_3^+$ and a higher frequency component (*ca.* 743 cm^{-1}) arising from $Hg(NO_3)_2$.

From the intensity analysis we conclude that the species $HgNO_3^+$ and $Hg(NO_3)_2$ are predominant in solutions with a nitrate ion to mercury ion concentration ratio less than 10. Calculation indicates that at high stoichiometric concentration $Hg(NO_3)_2$ is much in excess of $HgNO_3^+$. The vibrational spectra of the $Hg(NO_3)_2 \cdot H_2O$–KNO_3 mixture can be interpreted on the assumption that only $Hg(NO_3)_2$ and unbound NO_3^- are contributing. This analysis follows.

Band Assignments.—For an unequivocal band assignment the conclusions should be checked by isotope substitution and normal-coordinate analysis, neither of which has been undertaken in this work. Instead, provisional assignments have been made for the dinitratomercury(II) species which is considered to be the most important species occurring in the mercury(II) nitrate monohydrate–potassium nitrate mixture.

Several models may be proposed for the dinitratomercury(II) species. Two of the most probable are linear with the nitrate group acting as a monodentate or bidentate ligand. The observation of a polarized Raman band at 1284 cm^{-1} suggests that the nitrate ion is acting as a monodentate ligand. Vibrational analysis indicates that for bidentate coordination the polarized Raman band will be associated with the terminal NO stretch and will therefore occur to high frequency (*e.g.*, 1538 cm^{-1})[9] whereas for monodentate coordination the polarized Raman band will be associated with the terminal NO_2 symmetric stretch and will occur at lower frequencies.[20] A number of nitrato species have now been classified as monodentate or bidentate with the aid of this criterion.[9,21–23] It can be seen from an inspection of the Raman and infrared spectra of the system (Table I) that there are no frequency coincidences, although many of the infrared and Raman band positions are very similar. This suggests that the dinitratomercury(II) species has a center of symmetry and is inconsistent with a tetrahedral species such as $Hg(NO_3)_4^{2-}$.

These two observations, a polarized 1284-cm^{-1} Raman band and absence of coincidences, suggest that the species may be formulated $O_2NOHgONO_2$ and assigned D_{2h} symmetry. Consistent with this is the disappearance of the 362-cm^{-1} band and the appearance of the 266-cm^{-1} band. The former is attributed to a mercury ion–water interaction and the latter to the Hg–O stretch of the complex. A bent structure would probably contain water in the first coordination sphere; the absence of the 362-cm^{-1} line suggests this is not the case. The observation of the 266-cm^{-1} line is consistent with the proposal that linear Hg(II) species should show increased covalent binding. The linear species would have the following reduced representation of internal motion

$$\Gamma_{\text{vib}} = 4A_g(\text{Raman}) + A_u(\text{inactive}) + 4B_{1u}(\text{ir}) + 2B_{2g}(\text{Raman}) + 4B_{2u}(\text{ir}) + 3B_{3g}(\text{Raman}) + 3B_{3u}(\text{ir})$$

Four polarized (A_g) Raman bands, five unpolarized Raman bands ($2B_{2g}$, $3B_{3g}$), and eleven infrared bands ($4B_{1u}$, $4B_{2u}$, $3B_{3u}$) are predicted.

The assignment of frequencies to the normal modes of vibration of the dinitratomercry(II) species (Table II) is consistent with that generally accepted for the nitrate ligand.[24] Bands at 1290–1253 and 1531–1481 cm^{-1}

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(19) F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Co., Inc., New York, N. Y., 1961, p 50.

(20) H. Brintzinger and R. E. Hester, *Inorg. Chem.*, **5**, 980 (1966).

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(22) J. R. Ferraro, A. Walker, and C. Cristallini, *Inorg. Nucl. Chem. Letters*, **1**, 25 (1965).

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(24) C. C. Addison and N. Logan, *Advan. Inorg. Chem. Radiochem.*, **6**, 98 (1964).

have been ascribed to stretches of the NO_2 group.[24] The polarized Raman band at 1284 cm^{-1} may therefore be assigned to the NO_2 symmetric in-phase stretch and the infrared band at 1276 cm^{-1} to the out-of-phase stretch (Table II). (When two nitrate groups are linked to a common metal atom, it is possible for a vibration of one nitrate to be in or out of phase with the corresponding vibration of the other nitrate.) Similarly the bands at 1486 cm^{-1} (Raman) and 1460 cm^{-1} (infrared) may be assigned to the asymmetric out-of-phase and in-phase stretches.

TABLE II

THE ASSIGNMENT OF THE INFRARED AND RAMAN BANDS OBSERVED FOR THE MERCURY(II) NITRATE MONOHYDRATE PLUS POTASSIUM NITRATE MIXTURE

Raman, cm^{-1}	Infrared, cm^{-1}	ν	Species	Approximate vibration
1486		16	B_{3g}	NO_2 asym out-of-phase str
	1460	12	B_{2u}	NO_2 asym in-phase str
(1345–1400)	(1345–1400)	. . .	. . .	Characteristic of free nitrate
	1276	6	B_{1u}	NO_2 sym out-of-phase str
1284		1	A_g	NO_2 sym in-phase str
1040		. . .	. . .	Characteristic of free nitrate
1010		2	A_g	NO in-phase str
	1023	7	B_{1u}	NO out-of-phase str, combination $\nu_4 + \nu_8$ in Fermi resonance with ν_7
	986	4 + 8	B_{1u}	
810		10	B_{2g}	NO_2 out-of-plane out-of-phase bend
	803	19	B_{3u}	NO_2 out-of-plane in-phase bend
ia[a]	ia[a]	5	Au	NO_2 out-of-phase twist around molecular axis
750		3	A_g	NO_2 in-plane sym in-phase bend
	745	8	B_{1u}	NO_2 in-plane sym out-of-phase bend
718		17	B_{3g}	NO_2 in-plane asym out-of-phase bend
	708	13	B_{2u}	NO_2 in-plane asym in-phase bend
	. . .	14	B_{2u}	Hg–O–NO_2 in-plane in-phase bend
. . .		18	B_{3g}	Hg–O–NO_2 in-plane out-of-phase bend
	. . .	9	B_{1u}	Hg–O out-of-phase str
266		4	A_g	Hg–O in-phase str
	. . .	20	B_{3u}	Hg–O–NO_2 out-of-plane in-phase bend
. . .		11	B_{2g}	Hg–O–NO_2 out-of-plane out-of-phase bend
	. . .	21	B_{3u}	O–Hg–O out-of-plane bend
	. . .	15	B_{2u}	O–Hg–O in-plane bend

[a] Inactive.

The NO stretch of complexed nitrate is reported[24] to occur in the region 1034–970 cm^{-1} and therefore the polarized Raman band at 1010 cm^{-1} may be assigned to the in-phase stretch and one of the infrared bands in the region 986–1023 cm^{-1} may be assigned to the out-of-phase NO stretch.

A polarized Raman band at 266 cm^{-1} is ascribed to the in-phase Hg–O stretch in accord with previous work.[15–17] As the infrared measurements only extend as low as 400 cm^{-1}, presumably the corresponding out-of-phase Hg–O stretch has not been observed although it is probably higher than 266 cm^{-1}.

Symmetric and asymmetric in-plane bends of the NO_2 group have been assigned to bands at approximately 740 and 713 cm^{-1}.[24] The polarized Raman band at 750 cm^{-1} may be assigned to the in-plane symmetric in-phase bend and the infrared band at 745 cm^{-1} to the out-of-phase motion. The asymmetric in-plane bending motions may be similarly assigned, the 708-cm^{-1} infrared band to the in-phase motion and the 718-cm^{-1} Raman band to the out-of-phase motion.

A band at 800–781 cm^{-1} has been assigned to the out-of-plane rocking motion of a complexed nitrate ion.[24] The NO_2 out-of-plane bend is a type of motion similar to the out-of-plane rock. Bands at 803 and 810 cm^{-1} may therefore be assigned to the NO out-of-plane in-phase and out-of-phase bends. It is probable that the bands characteristic of the O–Hg–O and Hg–O–NO_2 bends are of too low frequency to have been observed.[16]

This band characterization leaves unassigned the Raman bands at 1040, 1345, and 1400 cm^{-1} and the infrared bands at 986 or 1023, 1345, and 1400 cm^{-1}. It is probable that there is free nitrate ion present in the solutions studied. The assignment of the bands at 1345 and 1400 cm^{-1} to free nitrate ion is supported by the spectral results for the alkali metal nitrates where the splitting of the normally degenerate ν_3 (E′) mode has been attributed to water perturbation of the nitrate ion.[10]

The infrared spectrum of a dilute (0.25 *M*) solution of mercury(II) nitrate (Figure 4c) clearly shows the two bands at 1345 and 1400 cm^{-1} characteristic of the solvated nitrate ion. At higher concentrations (Figure 4a and b) the two bands at 1276 and 1460 cm^{-1}, characteristic of the complex nitrato species, can be seen to be gaining in prominence.

Free nitrate ion is also strongly active in the 1050-cm^{-1} region of the Raman spectrum and possibly also in the infrared spectrum. The Raman band at 1040 cm^{-1} is probably due to uncomplexed nitrate ion and the shoulder at 1010 cm^{-1} is due to the NO in-phase stretch of the complexed nitrate; therefore, the corresponding band due to the out-of-phase motion of the complex in the infrared spectrum should also be around 1010 cm^{-1}.

The mean of the two infrared bands in this region (986 and 1023 cm^{-1}) is 1004 cm^{-1}. It is possible that the fundamental NO out-of-phase stretch appears as a doublet because of Fermi resonance with another mode. Since the species of the NO out-of-phase stretch is B_{1u}, the mode in Fermi resonance with it must also be of B_{1u} species. A combination of the Hg–O in-phase vibration (266 cm^{-1}) and the NO_2 symmetric out-of-phase bend (745 cm^{-1}) gives a vibration frequency of 1011 cm^{-1} of the B_{1u} species. Fermi resonance between this combination band and the fundamental corresponding to the NO in-phase stretch could explain the two bands of comparable intensity at 986 and 1023 cm^{-1} in the infrared spectrum. An alternative, or perhaps additional, combination which could be in Fermi resonance with ν_7 (B_{1u}) is ν_3 (A_g) (750 cm^{-1}) + ν_9 (B_{1u}). This would require a value of 254 cm^{-1} for the unobserved Hg–O out-of-phase stretch. Because this value is lower than the 266-cm^{-1} Hg–O in-phase stretch and the out-of-phase stretch is expected to be at higher wave numbers, the former explanation is preferred.

Although no band is apparently observable in the infrared spectrum corresponding to the Raman band at 1040 cm^{-1}, characteristic of uncomplexed nitrate, the infrared spectrum of a dilute solution of mercury(II) nitrate has a band at 1032 cm^{-1} instead of the bands at 1023 and 986 cm^{-1} observed for the saturated solutions.

The assignments of the infrared and Raman bands observed for the mercury(II) nitrate monohydrate plus potassium nitrate mixture are summarized in Table II.

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New Ternary Oxides of Mercury with the Pyrochlore Structure

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Three new ternary oxides of mercury—$Hg_2Nb_2O_7$, $Hg_2Ta_2O_7$, and $Hg_2Sb_2O_7$—have been prepared and characterized. All three have the cubic pyrochlore structure with cell edges of 10.453, 10.452, and 10.349 Å, respectively. The structure of $Hg_2Nb_2O_7$ was refined by least-squares to an R of 0.027 using 26 reflections collected with a powder diffractometer. It is shown that the pyrochlore structure may be visualized as two interpenetrating networks, one network being identical with one of the two interpenetrating networks in Cu_2O.

Introduction

Very little is known about ternary oxides of mercury. A recent excellent review on mercury compounds by Aurivillius[1] discusses several oxyhalides of mercury; however, the only ternary oxides mentioned are of the type A_2HgO_2 where A is an alkali metal. One reason for the apparent lack of knowledge about ternary oxides of mercury is that the preparation by usual solid-state methods is hampered by the ease with which mercury is reduced to the metal.

In various mercury oxide compounds mercury has frequently been found[1] in essentially linear, twofold coordination. This paper describes the preparation and characterization of three new ternary oxides of mercury where mercury is again in essentially linear, twofold coordination.

Experimental Section

Reactants.—Niobium and tantalum pentoxide were prepared by oxidizing, at 600° in air, Specpure metals obtained from Johnson, Matthey & Co. Antimony sesquioxide was reagent grade, and Specpure mercuric oxide was obtained from Johnson, Matthey & Co.

Syntheses.—The reactants were intimately mixed in appropriate amounts by grinding together in an agate mortar and pestle. The preparation of $Hg_2Sb_2O_7$ was conveniently carried out by heating the reactants at 500° for 2 days in an open silica boat under about 1 atm of oxygen. When this method was attempted for $Hg_2Nb_2O_7$ and $Hg_2Ta_2O_7$, all of the mercuric oxide separated from the other oxide; consequently, a closed system was used. For $Hg_2Nb_2O_7$ and $Hg_2Ta_2O_7$, appropriate amounts of the mixed reactants were pelleted, sealed in evacuated silica tubes, and heated at 500° for 2 days.

In high-pressure experiments, the preformed compounds or reactant mixtures were sealed in pressure-collapsible gold containers. $Hg_2Nb_2O_7$ and $Hg_2Ta_2O_7$ were most conveniently prepared at 700° and 3 kbars. The apparatus used in the 60-kbar experiments has been previously described by Bither, *et al.*[2]

Analyses were carried out by standard techniques, and densities (d, g/cm^3) were determined using a pycnometer. *Anal.* Calcd for $Hg_2Nb_2O_7$: Hg, 57.4; Nb, 26.6; O, 16.0; d, 8.128. Found: Hg, 56.8; Nb, 26.8; O, 15.8; d, 8.10. Calcd for $Hg_2Ta_2O_7$: Hg, 45.8; Ta, 41.4; O, 12.8; d, 10.179. Found: Hg, 45.1; Ta, 42.1; O, 13.1; d, 10.13. Calcd for $Hg_2Sb_2O_7$: Hg, 53.0; Sb, 32.2; O, 14.8; d, 9.067. Found: Hg, 52.9; Sb, 32.0; O, 14.5; d, 9.02. Errors for the densities are considered to be about ±0.06 g/cm^3.

X-Ray Analyses.—Integrated X-ray powder data were gathered with a General Electric XRD-5 diffractometer using Cu Kα radiation, an Ni filter, a scintillation detector, and a pulse height analyzer. The intensity of each peak was determined by scanning at 0.2°/min and accumulating both time and counts. Background was determined before the first peak, between every two peaks, and after the last peak. The values obtained were plotted against 2θ, and a smooth curve was drawn through the points. The background function of 2θ was not monotonic; *e.g.*, there were minima at ~23 and 40° (2θ). The background corrections obtained from this curve are similar to but more reliable than those which would be obtained by assuming a strictly linear interpolation between backgrounds determined on the two sides of the peak.

The sample was prepared by grinding in a mechanical mortar and pestle for several hours and then passing it through a 400-mesh sieve. The powder was packed in a tray by several different methods and X-ray data were taken to determine if preferred orientation was a serious problem. Comparison of the several sets of data led to the conclusion that preferred orientation was not significant. This conclusion was further supported by the visual observation of no qualitative differences between the diffractometer and Debye–Scherrer patterns. The depth of the flat sample tray was about 1 mm, which effectively prohibits any X-rays from passing through the sample. The di-

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(1) K. Aurivillius, *Arkiv. Kemi*, **24**, 151 (1965).

(2) T. A. Bither, J. L. Gillson, and H. S. Young, *Inorg. Chem.*, **5**, 1559 (1966).