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The Complex Salts: $(CH_3)_4NI(NO_3)_4$, $(CH_3)_4NI(NO_3)_2$ and $(CH_3)_4NBr(NO_3)_2$

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Received July 13, 1966

The preparations of tetramethylammonium tetrakis(nitrato)iodate(III), $(CH_3)_4NI(NO_3)_4$, tetramethylammonium bis(nitrato)-iodate(I), $(CH_3)_4NI(NO_3)_2$, and tetramethylammonium bis(nitrato)bromate(I), $(CH_3)_4NBr(NO_3)_2$, are described, and some physical and chemical properties of these salts are given.

Introduction

Since halogen(I) and -(III) fluorosulfates[1] and nitrates[2] as well as complex O-fluorosulfatohalate(III) salts[3] have been prepared, it was of interest to investigate whether conditions could be found for the synthesis of complex halogen nitrato salts. Indeed, silver nitrate and/or chlorine nitrate were found to behave as nitrating agents toward the tetramethylammonium salts of the tetrachloroiodate(III), dichlorobromate(I), and dichloroiodate(I) anions.

Experimental Section

Reagents.—The $ClNO_3$[2] and the complex salts $(CH_3)_4NICl_4$ $(CH_3)_4NICl_2$, and $(CH_3)_4NBrCl_2$[4] were prepared by literature methods. The Spectro Grade acetonitrile and Freon 113 were stored in the presence of 5-A molecular sieves to ensure dryness.

Preparation of Tetramethylammonium Bis(nitrato)iodate(I).—In a typical preparation stoichiometric quantities of $AgNO_3$ (19.2940 mmoles) and $(CH_3)_4NICl_2$ (9.6360 mmoles) were used. The latter was weighed into a 100-ml round-bottom flask with a stopcock attachment. CH_3CN (25 ml) was then distilled into the bulb using a vacuum line. The bulb mixture was warmed to room temperature and stirred for 1 hr. Nearly all of the $(CH_3)_4NICl_2$ dissolved. The $AgNO_3$ was added to the bulb within a nitrogen drybox and a white precipitate of AgCl formed immediately. The mixture was stirred for 2 hr and then vacuum filtered twice. The filtrate was allowed to stand 2 hr longer and a small amount of solid separated. The liquid phase was carefully decanted in a drybox and then the liquid was removed by pumping *in vacuo*. The solid residue was washed with CH_2Cl_2 several times. The pale yellow crystalline solid was recovered in 95.2% yield (9.173 mmoles). *Anal.* Calcd for $C_4H_{12}IN_3O_6$: C, 14.78; H, 3.72; N, 12.93; I, 39.1; equiv wt, 162.5. Found: C, 14.85; H, 3.74; N, 13.21; I, 38.7; equiv wt, 167.0.

Preparation of Tetramethylammonium Bis(nitrato)bromate(I).—This compound was prepared by placing $(CH_3)_4NBrCl_2$ (0.6565 mmole) in a 75-ml thick-walled Pyrex bulb with a Fischer–Porter valve and then $ClNO_3$ (3.2825 mmoles) was vacuum distilled into the bulb at −196°. The bulb was allowed to warm slowly to room temperature over a 4-hr period. The yellow solid gradually turned white while it was being stirred and the bulb was allowed to stand at room temperature for 3 hr. Chlorine and the excess $ClNO_3$ were removed and the solid was pumped upon until it reached constant weight. The final weight corresponded to 100.6% yield (0.6602 mmole). *Anal.* Calcd for $C_4H_{12}BrN_3O_6$: N, 15.1; Br, 28.8; equiv wt, 139. Found: N, 14.7; Br, 28.6; equiv wt, 138.

Tetramethylammonium Tetrakis(nitrato)iodate(III).—Into a reaction vessel similar to that described above were placed $(CH_3)_4NICl_4$ (1.8478 mmoles) and 5.0 ml of Freon 113. Chlorine nitrate (10.0 mmoles) was then distilled into the reactor at −196°. The reactor was allowed to warm to 0° and was maintained there for 18 hr. After this time Cl_2, excess $ClNO_3$, and Freon 113 were removed by evacuation of the mixture at 0° until a constant weight was achieved. The residue, a white solid, consisting of 1.7757 mmoles of a substance having the formula $(CH_3)_4NI(NO_3)_4$ remained. This is equivalent to 96.2% yield. *Anal.* Calcd for $C_4H_{12}IN_5O_{12}$: I, 28.8; Cl, negative. Found: I, 27.8; Cl, negative.

Alternatively, this material can be prepared by mixing stoichiometric quantities of $AgNO_3$ (44.055 mmoles) and $(CH_3)_4NICl_4$ (11.020 mmoles) in the presence of CH_3CN (20 ml) at room temperature and allowing the reaction mixture to stand for 3 hr. Reaction occurred immediately. The mixture was vacuum filtered and the precipitated AgCl was repeatedly washed with CH_3CN to ensure the complete removal of the product from the precipitate. Methylene chloride was added to the filtrate until a cloudiness appeared. The solution was again vacuum filtered after being allowed to stand for 3 hr. Some of the desired product was lost in this step, but most of the complex salt remained in solution. The solvent was removed under vacuum and the solid residue was washed several times with cold CH_3CN which was removed by vacuum decantation. The white solid was thoroughly dried under vacuum. A yield greater than 80% was obtained using this procedure. *Anal.* Calcd for $C_4H_{12}IN_5O_{12}$: C, 10.69; H, 2.67; I, 28.3; N, 15.59. Found: C, 11.14; H, 2.95; I, 28.7; N, 15.61 (Dumas) and 14.8 (Kjeldahl). The infrared spectra of the two samples prepared by these methods were identical.

Infrared Spectra.—The infrared spectra of the complexes were taken using Nujol mulls with a Perkin-Elmer Model 21 spectrophotometer. The observed bands are tabulated in Table I. No differences in the spectra were observed when Kel-F oil was employed as a mulling agent, thus eliminating the possibility of reaction between the compounds and Nujol.

Conductivity Measurements.—The conductance measurements were performed at 24.0 ± 0.3° using the equipment previously described.[5] Acetonitrile, having a specific conductivity of 1.28×10^{-6} ohm^{-1}, was used as a solvent. The cell employed had a cell constant of 0.1669 cm^{-1}. The concentrations (*M*) and the observed equivalent conductances (cm^2 ohm equiv) in parentheses for $(CH_3)_4NBrCl_2$ are 8.630×10^{-3} (164.3), 4.315×10^{-3} (173.5), 2.157×10^{-3} (181.1), 1.079×10^{-3} (187.8) ($\Lambda_\infty = 199$); for $(CH_3)_4NBr(NO_3)_2$ these values are 6.597×10^{-3} (162.1), 3.298×10^{-3} (171.0), 1.649×10^{-3} (179.1), 8.245×10^{-4} (183.4) ($\Lambda_\infty = 195$); and for $(CH_3)_4NI(NO_3)_2$ they are 6.538×10^{-3} (157.6), 3.269×10^{-3} (166.3), 1.635×10^{-3} (171.8), and 8.175×10^{-4} (176.3) ($\Lambda_\infty = 186$).

Ultraviolet Spectra.—The ultraviolet spectra of these complexes were taken in acetonitrile solutions using a Beckman DK1 spectrophotometer. The spectrum of the complex $(CH_3)_4NI(NO_3)_4$ contained a maximum at 212 mμ (ε 21,500). The spectrum of the two halogen(I) complexes contained maxima at 214 mμ (ε 9010) and at approximately 210 mμ (ε 10,900) for $(CH_3)_4NBr(NO_3)_2$ and $(CH_3)_4NI(NO_3)_2$, respectively. Under the experimental conditions absorption maxima with extinction coefficients of less than 50 would not have been observed.

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(1) J. E. Roberts and G. H. Cady, *J. Am. Chem. Soc.*, **82**, 352 (1960).

(2) M. Schmeiser and K. Brändle, *Angew. Chem.*, **73**, 388 (1961).

(3) M. Lustig and G. H. Cady, *Inorg. Chem.*, **1**, 714 (1962).

(4) I. Popov and R. E. Buckles, *Inorg. Syn.*, **5**, 169 (1957).

(5) J. K. Ruff, *Inorg. Chem.*, **2**, 813 (1963).

TABLE I

Tentative assignment	$(CH_3)_4NI(NO_3)_4$, cm^{-1}	$(CH_3)_4NI(NO_3)_2$, cm^{-1}	$(CH_3)_4NBr(NO_3)_2$, cm^{-1}
CH str^a	3050 w	3050 w	3039 w
NO_2 antisym str (ν_4)^{b,c}	1499 s	1504 s	1515 vs
$(CH_3)_4N$ group	1404 w	1471 s	1480 s
CN str^a	1494 w	1404 w	1404 w
NO_2 sym str (ν_1)^{b,c}	1319 w	1316 sh	1329 sh
	1290 sh	1282 s, doublet	1269 s
	1252 vs	1245 s	1243 vs
NO str (ν_2)^{b,c}	971 ms	971 m	920 vs, br
$(CH_3)_4N$ group^d	998 vs, br	993 vs, br	945 vs
Out-of-plane rock (ν_6)^{b,c}	784 m	784 m	776 m
NO_2 sym bend (ν_3)^{b,c}	725 m	725 m	722 ms
NO_2 antisym bend (ν_5)^{b,c}	699 m	699 m	690 ms

[a] L. J. Bellamy, "Infrared Spectra of Complex Molecules," 2nd ed, Methuen and Co., Ltd., London, 1959. [b] C. C. Addison and N. Logan, *Advan. Inorg. Chem. Radiochem.*, **6,** 98 (1964). [c] B. O. Field and C. J. Hardy, *Quart. Rev.* (London), **18,** 385 (1964). [d] No specific assignments are made; however, tetramethylammonium compounds have bands at nearly the same frequencies; *e.g.*, $(CH_3)_4NBrCl_2$ has bands at 2077 (m), 1405 (m), 1474 (s) 1404 (m), 1271 (w), 944 (vs), and 913 (w) cm^{-1}, and both $(CH_3)_4NICl_2$ and $(CH_3)_4NICl_4$ also have bands at very nearly the same frequencies.

Results and Discussion

The salts prepared in this work are the first examples of compounds containing nitrato groups complexed with a halogen, although some of the analogous O-fluorosulfato complex anions have been described.[3] Numerous examples of transition metal nitrate complex anions are known and more recently the nontransition metal complex $(CH_3)_4NB(NO_3)_4$ has been prepared.[6] In general, either N_2O_4 or N_2O_5 has been used in the preparation of these metal complexes. Two alternative preparative methods were employed in this study. Both methods produced $(CH_3)_4NI(NO_3)_4$.

$$(CH_3)_4NICl_4 + 4AgNO_3 \xrightarrow{CH_3CN} (CH_3)_4NI(NO_3)_4 + 4AgCl$$

$$(CH_3)_4NICl_4 + 4ClNO_3 \xrightarrow{\text{Freon 113}} (CH_3)_4NI(NO_3)_4 + 4Cl_2$$

However, only the first method was used to form the iodate(I) complex in order to avoid oxidation to iodate(III). The second method had to be used to form the bis(nitrato)bromate(I) anion. No evidence was found for any bromate(III) complexes in this reaction even when a large excess of $ClNO_3$ was employed.

The salts are yellow to white hygroscopic solids which react with water and oxidize KI in aqueous acid solutions. Both the iodate(I) and iodate(III) complexes appear to decompose slowly at room temperature to form NO_2, NO, N_2, and oxygen. Some iodine is also obtained when the decomposition is carried out at elevated temperatures. The bromate(I) salt is more stable than the iodate salts but also decomposes in a similar manner. All the salts are more stable than the corresponding uncomplexed halogen nitrates.[2] Although the iodate(I) and -(III) complex nitrate salts are prepared using CH_3CN as a solvent, once these salts are removed from this solvent, they redissolve in it only with difficulty. The bromate(I) derivative is also reluctant to dissolve in CH_3CN. This may entail a reorganization in the structure of these materials but further investigation will be necessary to ascertain this.

The infrared spectra of the three salts $(CH_3)_4NI(NO_3)_4$, $(CH_3)_4NI(NO_3)_2$, and $(CH_3)_4NBr(NO_3)_2$ are consistent with the presence of covalent nitrato groups having the symmetry of either the C_{2v} point group or the C_s point group. Ionic nitrate absorptions, in the region of 1330 cm^{-1} for $(CH_3)_4NNO_3$, are absent in the spectra. Bands which can be assigned to all six of the fundamental modes for a unidentate nitrato group are observed.[7] The positions of the ν_4 and ν_1 modes and their separation (approximately 250 cm^{-1} for all three complexes) are in the range attributable to unidentate nitrato groups.[8] However, the complex nitrate $(C_6H_5)_3AsCH_3Co(NO_3)_4$ which has recently been shown to contain only bidentate nitrato groups[9] has two strong bands which lie in the region of the ν_4 and ν_1 modes for a unidentate nitrato group.[10] Furthermore the value obtained for the difference ($\nu_4 - \nu_1$) for this cobalt complex is less than that observed in this study. The value of this difference is expected to increase in changing from unidentate to bidentate bonding for both the nitrato group[8] and the isoelectronic carbonato group.[11] Therefore it is impossible to eliminate conclusively the presence of bidentate nitrato groups in these materials from infrared studies alone. If they were present the iodine (bromine) would have a coordination number of 4 to 8 depending on the oxidation state.

The ultraviolet spectra of the salts show maxima in the 2100-A region. The position of the λ_{max} observed in this work compares with those found for simple nitrates.[12]

The conductance of the two complexes $(CH_3)NBr(NO_3)_2$ and $(CH_3)_4NI(NO_3)_2$ shows that they behave as 1:1 electrolytes in acetonitrile. The value of the equivalent conductance at infinite dilution found for the bromate(I) and iodate(I) complexes was 195 and 186 ohm^{-1} cm^{-2}, respectively. A value of 199 ohm^{-1}

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(6) C. R. Guibert and M. D. Marshall, *J. Am. Chem. Soc.*, **88,** 189 (1966).

(7) See footnote *b*, Table I.

(8) See footnote *c*, Table I.

(9) J. G. Bergman, Jr., and F. A. Cotton, *Inorg. Chem.*, **5,** 1208 (1966).

(10) D. K. Straub, R. S. Drago, and J. T. Donoghue, *ibid.*, **1,** 848 (1962).

(11) K. Nakamoto, "Infrared Spectra of Inorganic and Co-ordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 160.

(12) E. Rabinawitch, *Rev. Mod. Phys.*, **14,** 112 (1942).