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ACCEPTOR PROPERTIES OF IODINE HEPTAFLUORIDE: OCTAFLUOROPERIODATES(VII)

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May 1974 LBL-3704

ACCEPTOR PROPERTIES OF IODINE HEPTAFLUORIDE: OCTAFLUOROPERIODATES(VII).

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Iodine heptafluoride is a donor of fluoride ion, and salts of the octahedral IF_6^+ cation are well-known (1). By contrast, IF_7 does not react directly at room temperature with alkali metal fluorides (2), although the formation of a solid derivative with NOF has been reported but not investigated in detail (3). Described in this paper are the synthesis and characterization of two octafluoroperiodate(VII) salts, $CsIF_8$ and $[NO^+][IF_8^-]$.

IF_7 and NOF indeed react below room temperature in a Kel-F trap to give a white solid which has a vapour pressure ca. 300 mm at 25°C, and which is slightly volatile at -78°C. Quantitative experiments established that the compounds combine in equimolar proportions, the solid thus having the stoicheiometry $NOF.IF_7$; the infrared spectrum of the vapour above the solid shows absorptions due to IF_7 and NOF, together with products of the decomposition of the latter on the cell walls. The evidence given below indicates that the solid is the salt $[NO^+][IF_8^-]$.

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$NOF.IF_7$ reacts quantitatively with BF_3 to give $[NO^+][BF_4^-]$, IF_7 being displaced. The Raman spectrum of the solid, recorded for a sample at -100°C sealed in a Teflon-FEP tube, is enumerated in Table 1. Shown therein are none of the Raman lines of the parent compounds, but there is a feature at 2242 cm^{-1} attributable to the fundamental of the NO^+ cation, which is commonly encountered in the range 2150-2400 cm^{-1} (4). The remaining Raman lines, all lying below 700 cm^{-1}, are not characteristic of any known fluoroiodine anion [e.g. IF_4^-, IF_6^{3-} (5); IF_6^-, "$I_3F_{16}^-$" (6)] or cation [e.g. IF_4^+ (7), IF_6^+ (8)]; the absence of lines in the region 750-1000 cm^{-1} indicates the absence of species containing I=O bonds. The Raman lines below 700 cm^{-1} are therefore attributed to the IF_8^- anion; by analogy with IF_7 (9), fundamentals in I-F stretching modes are assigned above 500 cm^{-1}, and F-I-F deformations below 500 cm^{-1}.

TABLE 1

Raman Spectra of $CsIF_8$ and $[NO^+][IF_8^-]$

$CsIF_8$		$[NO^+][IF_8^-]$		Assignment
cm^{-1}	Int.	cm^{-1}	Int.	
		2242	w	ν (NO^+)
655	mw	650	vvw	
594	vs	594	vs	ν (I-F)
539	m	550 527	vw vw	
461	m	467	m	
415 403	mw mw	418	m	
375	vw	339	m,b	δ (F-I-F)
270	vw	246	m,b	
200	vw,b			

Attempts to induce reaction between CsF and IF_7 by heating them to 150°C in a Monel bomb gave a mixture of $CsIF_6$ and Cs_2NiF_6. However, CsF and IF_7 combine if NOF (b.pt. -56°C) is used as solvent. In a typical experiment, finely powdered caesium fluoride (0.213 g, 1.37 mmol) and IF_7 (1.6 mmol) were left in a tared Kel-F tube (fitted with a Kel-F valve) at -45°C for 48 hours with ca. 2 ml liquid NOF; during this time the tube was occasionally shaken. Volatiles (NOF, IF_7) were removed at -45°C, and the tube was found to contain a white solid (0.52 g, corresponding to 90% conversion to $CsIF_8$) which gave a characteristic Raman spectrum (Table 1) and X-ray powder pattern (Table 2). Complete reaction was not obtained in any experiment, and the product invariably displayed very weak features due to unreacted CsF and to $CsIF_6$ (6) in its X-ray powder pattern and (for the latter impurity) its Raman spectrum; lines arising from these impurities have not been included in the tables.

The similarity of the Raman spectra of $[NO^+][IF_8^-]$ and $CsIF_8$ in the I-F stretching region indicates that a common anion is present; differences in the deformation region are typical of the variations encountered in the frequencies of polarizable anions with changes in the counterion. Satisfactory infrared spectra of the octafluoroperiodates could not be obtained because of reaction with window materials, and conclusions about the structure of the IF_8^- anion cannot be drawn from the data at present available. However, the X-ray powder pattern of $CsIF_8$ is easily indexed for a tetragonal unit cell, $\underline{a}$ = 7.785(10) Å, $\underline{c}$ = 5.18(1) Å, V = 313.9 Å^3; following Zachariason's rule (10), the packing is chiefly determined by fluoride ions (volume 18 ± 1 Å^3) and caesium ions (volume ca. 20 Å^3), and there are thus two formula units in each unit cell.

TABLE 2

Partial X-Ray Powder Data for $CsIF_8$.

$10^4 \cdot 1/d^2$ obs.	$10^4 \cdot 1/d^2$ calc.[a]	hkl	I/I_0	$10^4 \cdot 1/d^2$ obs.	$10^4 \cdot 1/d^2$ calc.[a]	hkl	I/I_0
-	0165	100	-	-	1650	310	-
-	0330	110	-	1668	1657	102	vvw,b
-	0373	001	-	-	1693	221	-
0544	0538	101	w	1828	1822	112	vvw
0666	0660	200	ms	-	1858	301	-
0712	0703	111	s	2024	2023	311	s
-	0825	210	-	-	2145	320	-
1052	1033	201	vvw	2156	2152	202	mw
1199	1198	211	vvw	2321	2317	212	mw
1322	1320	220	vw	2527	2518	321	w
-	1485	300	-	2639	2640	400	w
1494	1492	003	vvw	2807	{2805 2812	410 222	vw

a) Calculated for tetragonal cell, a = 7.785(10) Å, c = 5.18(1) Å.

$[NO^+][IF_8^-]$ is reasonably stable in fluorocarbon apparatus, but in the presence of metal rapidly decomposes to a mixture of NO_2, NO_2F, NOF, IF_5, and IF_7. $CsIF_8$ is a strong oxidizing agent: it liberates oxygen from water, and decomposes to $CsIF_6$ on storage in Kel-F at room temperature. While the failure of IF_7 and CsF to react directly at 25°C reflects the poor solvent ability of IF_7, the heptafluoride is clearly only a weak Lewis acid. Formation of molecular donor-acceptor complexes with bases may also be thwarted by its fluorinating properties; thus IF_7 and NMe_3 were found to react with uncontrollable violence, producing a black intractable solid.

Experimental

Manipulations were carried out either in the dry nitrogen atmosphere of a VAC Dri-Lab, or with a prefluorinated Monel and Kel-F vacuum system. NOF, prepared from NO and fluorine, was subsequently purified and transferred in a line composed entirely of Kel-F; IF_7 was made by fluorinating IF_5 at 1200 p.s.i. and 250°C (9); caesium fluoride (Alfa) showed in its powder pattern no lines due to $CsHF_2$. X-ray powder photographs and Raman spectra of $CsIF_8$ were obtained from the same sample, sealed in a narrow quartz capillary.

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