TABLE III
FORCE CONSTANTS[a] FOR SOME XF_5 MOIETIES COMPUTED FOR BrF_5–SeF_5^- AND IF_5–TeF_5^- FORCING TRANSFERABILITY OF INTERACTION TERMS AND FOR ClF_5 AND SF_5^- BY REQUIRING A PERFECT FIT

	ClF_5	SF_5^- [b]	BrF_5	SeF_5^-	IF_5	TeF_5^-
f_R	3.47	4.12	4.03	3.82	4.82	3.56
f_r	2.67	2.06	3.24	2.41	3.82	2.27
f_β	2.86	2.26	2.23	1.95	2.10	1.86
f_α	1.14	0.86	0.82	0.63	0.72	0.54
$f_{rr'}$	0.24	0.52	0.27		0.36	
$f_{\beta\beta'}$	0.75	0.55	0.32		0.43	
$f_{\alpha\alpha'}$	0.01	0.11	0.04		0.04	
f_{rr}	0.16	0.23	0.15		0.06	
$f_{R\beta}$	0.4	0.25				
$f_{r\beta}$	0.15	0.15				
$f_{r\beta''}$	−0.15	−0.15				
f_r/f_R	0.77	0.50	0.82	0.63	0.79	0.64

[a] Stretching constants in mdyn/Å, deformation constants in mdyn/Å radian², and stretch–bend interaction constants in mdyn/Å radian. [b] For SF_5^-, $f_{\beta\beta}$ was also computed and has a value of 0.20 mdyn/Å radian².

The values reported for $f_{R\beta}$, $f_{r\beta}$, and $f_{r\beta''}$ for the pair ClF_5–SF_5^- can be accounted for by orbital-following arguments. Numerical experiments indicated no need to assume other interaction constants and convincingly showed that the observed frequencies could not be fitted unless values were accepted near those shown.

Comparison of the general trends within XF_5 and XF_5^- series shows a remarkable difference. Whereas the deformation force constants in each series have comparable values and follow the same trends, the valence force constants f_R and f_r show reverse trends. Thus, for the XF_5 group, the lightest member, ClF_5, shows the lowest stretching force constant values, but for XF_5^- the heaviest member, TeF_5^-, exhibits the lowest f_R value. However, a closer inspection of the trends of the valence force constants of fluorides throughout the periodic system[20] reveals a general reversal of the direction of that trend either within or close to the sixth main group. Furthermore, increasing stretching force constant values from chlorine to the corresponding bromine fluorides were also found for the ClF_3 and BrF_3 molecules[21] and the ClF_4^- and BrF_4^- anions.[22,23]

The usefulness of stretching force constants for the distinction between mainly covalent and semiionic three-center four-electron (3c-4e) bonds has previously been demonstrated for numerous halogen fluorides.[23,24] The square-pyramidal pentafluorides of the present study contain two types (*i.e.*, axial and equatorial) of fluorine ligands and a comparison of their stretching force constants should permit some conclusions concerning the nature of their bonds. Since ionic bonds do not contribute to the stretching force constants, semiionic bonds ideally should exhibit values half as large as those of covalent bonds. As can be seen from Table III, the f_r/f_R ratios of the pentafluorochalcogenate anions range from 0.50 for SF_5^- to 0.64 for TeF_5^-. This indicates strong contributions from semiionic 3c-4e p-pσ bonds[25–28] to the bonding of the four equatorial fluorine ligands and mainly covalent character for the single axial fluorine bond. This finding agrees with a model involving an sp hybrid of the central atom for the sterically active, free-electron pair and the single, axial fluorine atom while two p electrons of the central atom form two semiionic 3c-4e bond pairs with the remaining four equatorial fluorine atoms.

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(20) W. Sawodny, Habilitation Thesis, Technical University, Stuttgart, Germany, 1969.

(21) K. O. Christe, E. C. Curtis, and D. Pilipovich, *Spectrochim. Acta, Part A*, **27**, 931 (1971).

(22) K. O. Christe and W. Sawodny, *Z. Anorg. Allg. Chem.*, **374**, 306 (1970).

(23) K. O. Christe and C. J. Schack, *Inorg. Chem.*, **9**, 1852 (1970).

(24) K. O. Christe, W. Sawodny, and J. P. Guertin, *ibid.*, **6**, 1159 (1967).

(25) G. C. Pimentel, *J. Chem. Phys.*, **19**, 446 (1951).

(26) R. J. Hach and R. E. Rundle, *J. Amer. Chem. Soc.*, **73**, 4321 (1951).

(27) R. E. Rundle, *ibid.*, **85**, 112 (1963).

(28) E. H. Wiebenga, E. E. Hawinga, and K. H. Boswijk, *Advan. Inorg. Chem. Radiochem.*, **3**, 158 (1961).

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Iodine Tris(perchlorate) and Cesium Tetrakis(perchlorato)iodate(III)

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The syntheses and some properties of the novel iodine perchlorates $I(OClO_3)_3$ and $Cs^+I(OClO_3)_4^-$ are reported. Their vibrational spectra were recorded and confirm their formulation as covalent perchlorates. A square-planar configuration is proposed for the $I(OClO_3)_4^-$ anion, whereas $I(OClO_3)_3$ appears to be polymeric.

Introduction

The preparation of iodine tris(perchlorate) from iodine, ozone, and anhydrous $HClO_4$ is described in ref 1. However, a cross-check with the original publication,[2] from which the preparation was abstracted, reveals that the original paper deals only with a compound having the empirical composition $I(ClO_4)_3 \cdot 2H_2O$. Numerous attempts have been reported to prepare iodine perchlorates in organic solvents from I_2 and $AgClO_4$. Whereas the experimental data were consistent with the formation of iodine perchlorates as unstable intermediates, all attempts to isolate and characterize these compounds were unsuccessful, owing

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(1) M. Schmeisser in "Handbook of Preparative Inorganic Chemistry," Vol. 1, G. Brauer, Ed., Academic Press, New York, N. Y., 1963, p 330.

(2) F. Fichter and H. Kappeler, *Z. Anorg. Allg. Chem.*, **91**, 134 (1915).

to their incompatibility with the solvent. In this paper, we report the successful preparation and isolation of $I(OClO_3)_3$ and $Cs^+I(OClO_3)_4^-$.

Experimental Section

Materials and Apparatus.—Volatile materials used in this work were manipulated in a well-passivated (with ClF_3) stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves (Hoke, Inc., 425 1F4Y). Pressures were measured with a Heise Bourdon tube-type gauge (0–1500 mm ± 0.1%). Iodine (reagent grade, Mallinckrodt) was resublimed before use. Anhydrous CsI (ROC/RIC, 99.9% minimum purity) was used without further purification. Chlorine perchlorate and $CsIBr_2$ were prepared and purified by the methods of Schack and Pilipovich[3] and Cremer and Duncan,[4] respectively. The purity of the volatile starting materials was determined by measurements of their vapor pressures and infrared spectra. Solid products were handled in the dry nitrogen atmosphere of a glove box.

The infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer in the range 4000–250 cm^{-1}. The spectra of gases were obtained using 304 stainless steel cells of 5-cm path length fitted with AgCl windows. Screw-cap metal cells with AgCl, AgBr, or BaF_2 windows and Teflon FEP gaskets were used for obtaining the spectra of solids as dry powders at ambient temperature. The quality of the infrared spectra could be somewhat improved by pressing two small single-crystal platelets of either AgCl or AgBr to a disk in a pellet press. The powdered sample was placed between the platelets before starting the pressing operation.

The Raman spectra were recorded using a Coherent Radiation Laboratories Model 52 Ar laser as a source of 1.3 W of exciting light at 5145 Å. The scattered light was analyzed with a Spex Model 1400 double monochromator, a photomultiplier cooled to $\sim -25°$, and a dc ammeter. Glass melting point or Kel-F capillaries were used as sample containers in the transverse viewing–transverse excitation technique. The low-temperature spectra were recorded by the method of Miller and Harney.[5]

Preparation of $I(OClO_3)_3$.—Iodine (0.915 mmol) was loaded into a 10-ml prepassivated Teflon FEP ampoule closed off by a Hoke 316 stainless steel valve (425 1F4Y). Chlorine perchlorate (8.18 mmol) was added at −196°. The ampoule was kept at −50° for 70 hr. At this point, the dark iodine color had disappeared and a pale yellow (due to the presence of Cl_2) solid had formed. Upon cooling to −196°, the ampoule did not contain any noncondensable reaction products. The ampoule was slowly warmed to −45°. The volatile products were separated by fractional condensation and identified by infrared spectroscopy and their vapor pressure. They consisted of Cl_2 (2.70 mmol) and $ClOClO_3$ (2.74 mmol). The white, solid residue weighed 776 mg, in excellent agreement with the weight (777 mg) calculated for a complete conversion to $I(OClO_3)_3$.

A sample of $I(OClO_3)_3$ (775 mg, 1.82 mmol) was allowed to warm up from −45 to 23°. Close to 23°, it formed a brownish paste. Recooling of the sample to −196° showed no noncondensables. The sample was warmed up again to 23° and kept at this temperature for 12 hr while the volatile products were pumped off and separated by fractional condensation. The volatile material consisted of Cl_2O_7 (1.9 mmol) and smaller amounts of Cl_2O_6 and lower chlorine oxides. The pale yellow, nonvolatile residue had the following composition: ClO_4^-, 21.7%; total iodine, 61.0%; iodometric titration assuming an oxidation state of +5, I = 62.0%. The infrared spectrum of the solid showed the presence of the ClO_4^- anion. Additional Cl_2O_7 could be removed from the solid by heating it for several hours to 60° *in vacuo*. The infrared spectrum still showed the presence of ClO_4^-. The weight of the solid had decreased to 366 mg.

Attempted Preparation of $IOClO_3$.—Iodine (1.25 mmol) and $ClOClO_3$ (2.50 mmol) were allowed to react as described for $I(OClO_3)_3$. The iodine color had completely disappeared; however, no products volatile at −45° had formed. The nonvolatile residue was a white solid showing orange and gray-green spots. Upon slight warm-up, the sample turned black and decomposed.

Preparation of $Cs^+I(OClO_3)_4^-$.—A 10-ml prepassivated stainless steel cylinder was loaded with powdered CsI (1.15 mmol), followed by $ClOClO_3$ (6.10 mmol) at −196°. The reaction was allowed to proceed by warming the cylinder to −45°, where it was maintained for 5 weeks. On recooling to −196°, no noncondensable gases were observed. Volatile products were pumped from the reactor for several hours while and after it had warmed to ambient temperature. Separation of these species was effected by fractional condensation and identification by infrared and vapor pressure measurements. They consisted of Cl_2 (2.34 mmol) and unreacted $ClOClO_3$ (1.45 mmol). The solid product was pale yellow and weighed 749 mg, indicating a 99% conversion of the CsI to $Cs^+I(OClO_3)_4^-$ had occurred.

Attempted Preparation of $Cs^+I(OClO_3)_2^-$.—Chlorine perchlorate (6.27 mmol) was allowed to react with $CsIBr_2$ (2.76 mmol) at −45°. No unreacted $ClOClO_3$ was recovered and the volatile products consisted of Cl_2, Br_2, and BrCl only. The solid reaction product was inhomogeneous. The infrared spectra of the upper layers showed the presence of perchlorato groups, whereas for the lower layers these were absent.

Elemental Analysis.—Weighed samples were hydrolyzed in water. The amounts of total iodine and perchlorate were determined by X-ray fluoresecence spectroscopy and by a specific ion electrode (Orion Model 92-17), respectively. The oxidation state of iodine was found by iodometric titration.

Results and Discussion

Caution! Chlorine perchlorate is shock sensitive[3] and samples of both $I(OClO_3)_3$ and $Cs^+I(OClO_3)_4^-$ have exploded even at low temperature while recording their laser Raman spectra. Proper safety precautions must be taken when working with these compounds.

Syntheses and Properties.—The novel compound iodine tris(perchlorate) was prepared by the low-temperature reaction of iodine with an excess of $ClOClO_3$. Its composition was established by quantitative synthesis: $I_2 + 6ClOClO_3 \rightarrow 2I(OClO_3)_3 + 3Cl_2$, with the material balance for all components being 99+%. The compound is a white solid, stable at −45°. During its synthesis, no explosions were encountered; however, when exposed to a laser beam, explosive decomposition occurred even at low temperatures. It decomposes upon warming to ambient temperature. Depending upon the warm-up conditions (*i.e.*, warm-up rate and pressure) differences in the decomposition behavior were observed. Thus, the melting to a brownish paste was not observed in all cases, and in some instances, the appearance of orange and brown colors was observed, which might be ascribed to the formation of ClO_2 and lower chlorine oxides, respectively. The following observations were made for the decomposition process: (1) the volatile decomposition products consisted mainly of Cl_2O_7 but also contained smaller amounts of Cl_2O_6 and lower chlorine oxides; (2) the solid residue contained only iodine in the +5 oxidation state and its infrared spectrum showed the presence of the ClO_4^- anion;[6] (3) upon pyrolysis or longer exposure to the laser beam, the Raman spectrum of the solid is identical with that previously reported[7] for I_2O_5 (see Figure 1, trace B); (4) the elemental analysis and material balance of the solid are in fair agreement with those calculated for a mixture of 62.4 mol % IO_2ClO_4 and 37.6 mol % I_2O_5. Upon extended pyrolysis, the percentage of I_2O_5 increases. These observations are best interpreted in terms of an initial Cl_2O_7 elimination, $I(OClO_3)_3 \rightarrow [OIOClO_3] + Cl_2O_7$, followed by an internal redox reaction yielding

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[3] C. J. Schack and D. Pilipovich, *Inorg. Chem.*, **9**, 1387 (1970).

[4] H. W. Cremer and D. R. Duncan, *J. Chem. Soc.*, 1860 (1931).

[5] F. A. Miller and B. M. Harney, private communication.

[6] J. W. Nebgen, A. D. McElroy, and H. F. Klodowski, *Inorg. Chem.*, **4**, 1796 (1965).

[7] P. M. A. Sherwood and J. J. Turner, *Spectrochim. Acta, Part A*, **26**, 1975 (1970).

+5 iodine, lower chlorine oxides, IO_2ClO_4, and I_2O_5. It is not surprising that mainly Cl_2O_7 and some chlorine oxides of low oxidation state were observed and not Cl_2O_6 as might be expected according to $I(OClO_3)_3 \rightarrow IO_2ClO_4 + Cl_2O_6$. It is well known that the perchlorate ion does not oxidize CsI whereas ClO_3^- or ClO_2^- does. Hence, Cl_2O_7 might also be a less effective oxidizing agent than Cl_2O_6 or the lower chlorine oxides.

Attempts to prepare iodine monoperchlorate from stoichiometric amounts of iodine and $ClOClO_3$ failed. Apparently, $ClOClO_3$ oxidizes iodine rapidly to oxidation states higher than +1. The resulting mixed iodine chloride perchlorate with a formal oxidation state of +2 would be expected to be highly unstable and susceptible to disproportionation and decomposition.

The salt $Cs^+I(OClO_3)_4^-$ was prepared according to $Cs^+I^- + 4ClOClO_3 \rightarrow Cs^+I(OClO_3)_4^- + 2Cl_2$. Its composition was again ascertained by quantitative synthesis. It is a pale yellow solid and is stable at ambient temperature. Its decomposition has been studied less extensively than that of $I(OClO_3)_3$. However, the Raman spectra (Figure 1, trace A, and Figure 2, traces B and C) demonstrate the formation of a common intermediate decomposition product which is not I_2O_5 and does not contain the ClO_4^- anion. The formation of this intermediate might be favored by the laser light.

Attempts to prepare $Cs^+I(OClO_3)_2^-$ according to $Cs^+IBr_2^- + 2ClOClO_3 \rightarrow Cs^+I(OClO_3)_2^- + 2BrCl$ were unsuccessful. Part of the product was converted to +3 iodine salts while some of the $Cs^+IBr_2^-$ starting material was recovered unchanged.

Considering the low thermal stability and high reactivity of $I(OClO_3)_3$, it is not surprising that previous attempts[8-11] had failed to prepare and isolate these compounds from organic solvents. From the properties of $I(OClO_3)_3$, it also appears unlikely that the product obtained[2] by Fichter and Kappeler was indeed a dihydrate of $I(OClO_3)_3$. Other possible structures such as $IO_2ClO_4 \cdot 2HOClO_3$ might be written for their product which approach the reported[2] composition.

Vibrational Spectra.—Figures 1 and 2 show the Raman spectra of $I(OClO_3)_3$ and $Cs^+I(OClO_3)_4^-$, respectively. The spectra of both compounds had to be recorded at low temperature to avoid (explosive) decomposition in the laser beam. For $Cs^+I(OClO_3)_4^-$, which is the more stable of the two compounds, a spectrum was obtained which was essentially free of decomposition product bands (trace A, Figure 2). Traces B and C show the same sample at various stages of decomposition and allow the identification of the bands belonging to the decomposition products. It was not possible to obtain a spectrum of $I(OClO_3)_3$ free of decomposition products. However, the decomposition product was identical with that observed for $Cs^+I(OClO_3)_4^-$ (trace C, Figure 2). Therefore, the bands due to $I(OClO_3)_3$ itself can be readily identified. The spectrum of the product obtained by vacuum pyrolysis of $I(OClO_3)_3$ at 60° is shown as trace B in Figure 1. It is distinct from that in the low-temperature decomposition and is identical with

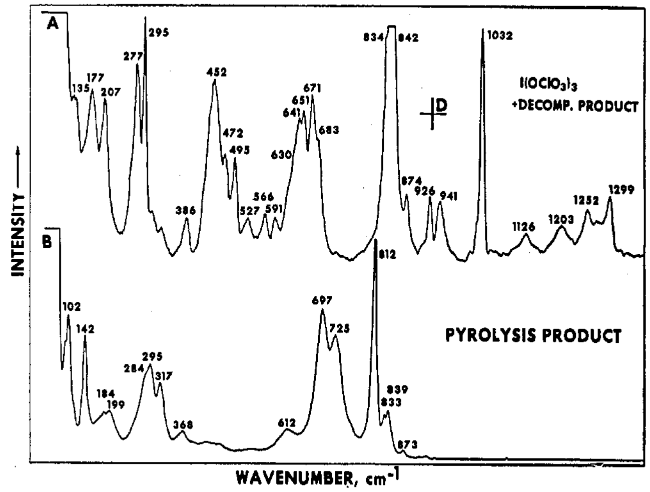

Figure 1.—Raman spectra of $I(OClO_3)_3$, recorded at −60° (trace A), and of its decomposition product (trace B) obtained by vacuum pyrolysis at 60°. D indicates spectral slit width.

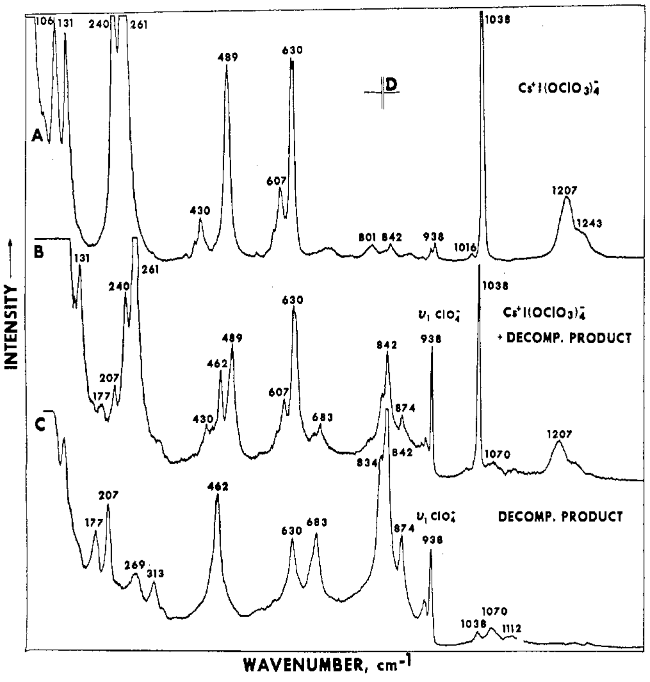

Figure 2.—Raman spectra of $Cs^+I(OClO_3)_4^-$, recorded at −70° (trace A), and of its decomposition products (traces B and C).

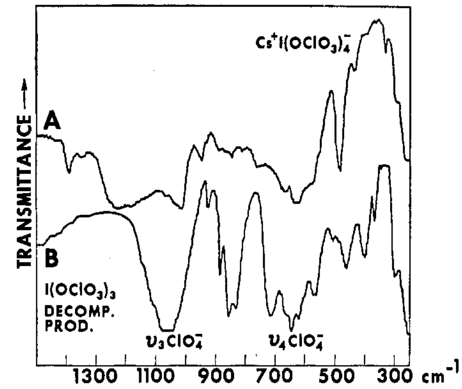

Figure 3.—Infrared spectra of $Cs^+I(OClO_3)_4^-$ (trace A) and of the $I(OClO_3)_3$ decomposition product (trace B) as AgBr disks.

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(8) M. Gomberg, *J. Amer. Chem. Soc.*, **45**, 398 (1923).

(9) L. Birckenbach and J. Goubeau, *Ber.*, **65**, 395 (1932).

(10) R. N. Haszeldine and A. G. Sharpe, *J. Chem. Soc.*, 993 (1952).

(11) N. W. Alcock and T. C. Waddington, *ibid.*, 2510 (1962).

TABLE I

VIBRATIONAL SPECTRUM OF $Cs^+I(OClO_3)_4^-$ COMPARED TO THOSE OF $ClOClO_3$ AND $BrOClO_3$

Obsd freq, cm^{-1}, and intens					
$ClOClO_3$[a]		$BrOClO_3$[a]	$Cs^+I(OClO_3)_4^-$		
Ir	Raman	Ir	Ir	Raman	Approx description of mode
1283 vs	1280 mw	1275 vs	1230 vs	1243 w, sh	Antisym ClO_3 str
				1207 mw	
1040 s	1036 vs	1039 s	1015 vs	1038 s	Sym ClO_3 str
				1016 vw	
646 vs	643 ms	648 s	630 vs	630 s	O–Cl str
580 sh	582 m		570–650 vs	607 mw	ClO_3 scissor, δ_{as} ClO_3
561 m	561 w	570 ms			
511 mw	516 s	509 m	485 s	489 s	δ umbrella ClO_3
			430 vw	430 mw	
				261 vs	ν sym in-phase IO_4
				240 s	ν sym out-of-phase IO_4
				131 ms	IOCl def
				106 ms	

[a] Reference 13.

that reported[7] for I_2O_5. Figure 3 shows the infrared spectrum of $Cs^+I(OClO_3)_4^-$ and that of the $I(OClO_3)_3$ decomposition product. The latter shows strong absorptions characteristic for the ClO_4^- ion.[6] Since covalent perchlorates generally attack silver halide windows with ClO_4^- formation, the spectrum was also recorded using BaF_2 windows. It was identical with that shown in Figure 3.

The spectrum of $Cs^+I(OClO_3)_4^-$ will be discussed first due to its simplicity. Comparison with the known spectrum of other covalent halogen perchlorates[8,12,13] reveals that the compound contains exclusively covalent, monodentate perchlorato groups. A listing of the observed frequencies together with a tentative assignment is given in Table I. The slight frequency decrease of some of the perchlorato bands on going from halogen mono(perchlorates) to the tetrakis(perchlorato)iodate(III) anion may be explained by the formal negative charge in the latter. A similar decrease has also been observed for the corresponding halogen fluorosulfates.[14-16] The vibrational spectrum of $I(OClO_3)_4^-$ is analogous to that[15] of $I(OSO_2F)_4^-$ and suggests a similar structure for both anions. In agreement with Carter, Jones, and Aubke,[15] we suggest a square-planar configuration for the IO_4 skeleton by analogy with that found for the corresponding tetrafluorohalogenate(III) anions, ClF_4^- and BrF_4^-.[17,18] For the IO_4 skeletal stretching modes, we propose an assignment different from that made previously[15] for $I(OSO_2F)_4^-$. The two symmetric IO_4 stretching modes should both be of very high intensity in the Raman spectrum and be separated by less than 100 cm^{-1}.[17,18] Furthermore, they should be observed for both ions, $I(OClO_3)_4^-$ and $I(OSO_2F)_4^-$. Therefore, the assignment of the bands at 261 and 240 cm^{-1} to the symmetric in-phase and symmetric out-of-phase IO_4 stretching modes, respectively, appears more plausible than that previously suggested.[15] On the basis of the available data, it cannot be decided whether or not the chlorine atoms are coplanar with the IO_4 group.

For $I(OClO_3)_3$, the Raman spectrum (Figure 1, trace A) is rather complex in the 1100–1300-cm^{-1} region. By analogy with the halogen trifluorides and halogen tris(fluorosulfates),[15] these features might be explained in terms of two nonequivalent types of perchlorato groups. The substantial shift to lower frequencies of two of these bands (1203 and 1126 cm^{-1}) indicates strong bridging as expected for a polymeric structure. The bands occurring in the following regions are tentatively assigned to the following type of vibrations: 1100–1300 cm^{-1}, antisymmetric ClO_3 stretch; 920–1040 cm^{-1}, symmetric ClO_3 stretch; 600–690 cm^{-1}, scissoring deformation of ClO_3; 440–500 cm^{-1}, umbrella deformation of ClO_3 and IO stretch; 270–300 cm^{-1}, IO_2 stretching modes; 100–200 cm^{-1}, I–O–Cl bending modes. Again, the bands assigned to the IO_x stretching modes have almost identical counterparts in the $I(OSO_2F)_3$ spectrum,[15] indicating the close structural relationship between these halogen perchlorates and the corresponding fluorosulfates.

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(12) C. J. Schack, K. O. Christe, D. Pilipovich, and R. D. Wilson, *Inorg. Chem.*, **10**, 1078 (1971).

(13) K. O. Christe, C. J. Schack, and E. C. Curtis, *ibid.*, **10**, 1589 (1971).

(14) K. O. Christe, C. J. Schack, and E. C. Curtis, *Spectrochim. Acta, Part A*, **26**, 2367 (1970).

(15) H. A. Carter, S. P. L. Jones, and F. Aubke, *Inorg. Chem.*, **9**, 2485 (1970).

(16) A. M. Qureshi, L. E. Levchuk, and F. Aubke, *Can. J. Chem.*, **49**, 2544 (1971).

(17) K. O. Christe and W. Sawodny, *Z. Anorg. Allg. Chem.*, **374**, 306 (1970).

(18) K. O. Christe and C. J. Schack, *Inorg. Chem.*, **9**, 1852 (1970).