vs. $\delta(^{13}C)$) gives an analogy between cyano and carbonyl ligands, the second one (d(Cu–C) vs. $\delta(^{13}C)$) shows clearly a difference between these two ligands.

Registry No. KCN, 151-50-8; NaCN, 143-33-9; $K_3Cu(CN)_4$, 14263-73-1; CuCN, 544-92-3; CN^-, 57-12-5; $Cu(CN)_4^{3-}$, 19441-11-3; $Cu(CN)_3^{2-}$, 16593-63-8; $Cu(CN)_2^-$, 18973-62-1.

References and Notes

(1) C. Kappenstein and R. P. Hugel, *Inorg. Chem.*, **17**, 1945 (1978).

(2) C. Kappenstein, R. P. Hugel, A. J. P. Alix, and J. L. Beaudoin, *J. Chim. Phys.*, **75**, 427 (1978).

(3) C. Kappenstein and R. P. Hugel, *Inorg. Chem.*, **16**, 250 (1977).

(4) Originally all chemical shifts were calculated vs. CN^- as standard, that is vs. the resonance frequency of cyanide solution. Later dioxane was used as standard (5%) for three solutions and we have checked the consistency of the results with the first ones. Chemical shift of dioxane vs. Me_4Si is 67.4 ppm.

(5) C. Kappenstein and R. Hugel, *J. Inorg. Nucl. Chem.*, **36**, 1821 (1974); *Rev. Chim. Miner.*, **6**, 1107 (1969).

(6) M. Hirota, Y. Koike, H. Ishizuka, A. Yamasaki, and S. Fujiwara, *Chem. Lett.*, 853 (1973).

(7) That is for example for the first domain: $\delta(\text{ppm}) = \delta(\text{Cu(CN)}_4)(x) + \delta(\text{CN})(1 - x)$ with $x = 4[\text{Cu(CN)}_4]/([\text{CN}] + 4[\text{Cu(CN)}_4])$.

(8) G. M. Bodner and L. J. Todd, *Inorg. Chem.*, **13**, 1335 (1974).

(9) G. M. Bodner, *Inorg. Chem.*, **13**, 2563 (1974); **14**, 1932 (1975); **14**, 2694 (1975).

(10) O. A. Gansow, D. A. Schexnayder, and B. Y. Kimura, *J. Am. Chem. Soc.*, **94**, 3406 (1972).

(11) O. A. Gansow, A. R. Burke, R. B. King, and M. S. Saran, *Inorg. Nucl. Chem. Lett.*, **10**, 291 (1974).

(12) The variations are +4 cm^{-1} ppm^{-1} for the first correlation (ν(CN)) and −0.009 Å ppm^{-1} for the second one (d(Cu–C)), to compare to the values taken from Bodner and Todd[8] for different metal carbonyls: +6 to +12 cm^{-1} ppm^{-1} and +0.006 Å ppm^{-1}. The Cu–C bond length for $Cu(CN)_2^-$ is taken as 1.88 ± 0.02 Å.

Contribution from the Department of Chemistry,
Auburn University, Auburn, Alabama 36830

Hydrolysis-Assisted Formation of a Mononuclear, Five-Coordinate Dihydroxotriiodocobaltate(II) Ion

W. L. Darby and L. M. Vallarino*

Received January 26, 1979

Crystalline hydroxo complexes of the transition-metal ions are extremely scarce, and the few known examples usually have dimeric or oligomeric structures in which the OH groups act as bridging ligands.[1] Accordingly, there is an almost complete lack of data regarding the characteristic ligating features of the OH^- anion toward transition-metal ions. In this note, we report the preparation and characterization of a crystalline compound which represents an unusual example of a mononuclear hydroxo complex of a first-row transition-metal ion, as well as a unique five-coordinate Co(II) species containing only simple negative ligands.

Experimental Section

Synthesis of $(LH)_2[Co(OH)_2I_3]I$, Where LH is $(H)(CH_3)N^+(CH_2CH_2)_2N^+(CH_3)_2$. A mixture of the green $[CoI_3L]$ complex[2] (600 mg, 1 mmol) and of the colorless trimethylpiperazinium iodide (260 mg, 1 mmol) was suspended in anhydrous ethanol (10 mL) and heated with stirring until the trimethylpiperazinium iodide was dissolved. The hot stirred suspension was treated with 2 drops (0.4 mL) of water; the green solution thereby turned almost colorless, and some of the green solid dissolved. As the mixture cooled down to room temperature, the suspended solid changed to small dark blue crystals. Additional dark blue crystals separated after 1 mL of triethyl orthoformate was added, with swirling, to the cooled suspension. The crystals were filtered, washed with a small volume of chilled anhydrous ethanol, and dried in vacuo; yield 490 mg (56%).

Deuterated $(LD)_2[Co(OD)_2I_3]I$ was prepared similarly to the hydrogen analogue, by using deuterioethanol as the solvent and deuterium oxide as the reagent. From the infrared spectrum the extent of deuteration was estimated to be 70–80%. Little or no hydrogen–deuterium exchange occurred when the crystalline hydrogen complex was exposed to D_2O vapor or suspended in deuterioethanol containing a small amount of D_2O.

Characterization of $(LH)_2[Co(OH)_2I_3]I$. Anal. Calcd for $C_{14}H_{38}N_4O_2I_4Co$: Co, 6.85; I, 58.96. Found: Co, 6.9; I, 59.2. The compound is paramagnetic, with $\mu_{\text{eff}} = 4.45\ \mu_B$ (measured at room temperature with a Gouy balance by using $Hg[Co(NCS)_4]$ as the standard). The infrared spectrum (4000–180 cm^{-1}) was obtained with a Perkin-Elmer Model 580 spectrophotometer by using Nujol and hexachlorobutadiene mulls between cesium iodide and polyethylene plates. (Polystyrene served as the calibration standard.) Characteristic stretching absorptions (cm^{-1}): ν(OH) 3260–3225 (vs, br), $\nu(N^+H)$ 2600 (vs, vbr), ν(Co–OH) 470 (m), ν(Co–I) 208 (vs). The hydrogen-sensitive stretching modes shifted upon deuteration: ν(OD) 2420, $\nu(N^+D)$ 1900, ν(Co–OD) 460 cm^{-1}. The remaining pattern (1500–180 cm^{-1}) closely resembled that of the trimethylpiperazinium cation in the iodide and perchlorate salts. The diffuse reflectance electronic (d–d) spectrum was obtained with a Cary Model 17 spectrophotometer by using magnesium carbonate as the reference. Observed absorptions (10^3 cm^{-1}): 7.0, 13.6, 16.6 (midpoint of a broad asymmetric band), 22.3 (vw), 24.7 (vw).

Thermal Behavior of $(LH)_2[Co(OH)_2I_3]I$. Crystalline $(LH)_2[Co(OH)_2I_3]I$, when heated to about 120 °C, changed to a heterogeneous mixture of green CoI_3L and colorless L^+I^-, identified from their infrared and electronic spectra. The color change was accompanied by a mass loss, and the thermogram (obtained with a Du Pont Model 950 thermal analyzer in the TGA mode) had a single-step shape. The vapor evolved, collected in a cold trap at −80 °C, was identified as pure water from its NMR spectrum. Mass loss: calcd for 2 H_2O, 4.18%; found, 4.0%. With the Du Pont thermal analyzer in the DTA mode, the sharply endothermic "water-loss reaction" was found to take place within a 5 °C interval, centered at 121 °C for the freshly prepared crystalline compound.

Attempted Preparation of Pure $(LH)_2[Co(OH)_2I_3](ClO_4)$. The green CoI_3L (300 mg, 0.5 mmol) and trimethylpiperazinium perchlorate (115 mg, 0.5 mmol) were suspended in ethanol (7 mL) and the mixture was warmed gently until the white needles of the perchlorate were partly dissolved. A drop of water was added, and within minutes the suspended green solid changed to dark blue, while some of the white crystals changed in appearance. (Under a microscope, long needles as well as platelets were detected.) It was not possible to completely separate the blue from the white crystals owing to their similar solubilities. However, in repeated experiments, the cobalt-to-iodine mole ratio of this mixed product was found to be approximately 1 to 3.5, indicating that substitution of the "ionic" iodide by ClO_4^- had occurred, although not completely. From the infrared spectrum, the white crystals were identified as the starting material, $L^+ClO_4^-$ (needles), mixed with a small amount of the perchlorate of the protonated trimethylpiperazinium (platelets).

Results and Discussion

The monopositive trimethylpiperazinium cation L—a weak base of $pK_a = 4.3$—is known to act as a ligand toward transition-metal ions. Specifically, L coordinates to cobalt(II) halides forming crystalline, zwitterionic complexes of the general formula CoX_3L,[2] which have a pseudotetrahedral geometry with C_{3v} symmetry.[3] While not particularly sensitive to atmospheric moisture, these CoX_3L complexes readily dissolve in water, undergoing complete decomposition. For the iodo complex, however, reaction with a limited amount of water under controlled conditions results in the formation of a new complex, isolated as dark blue crystals of empirical formula $L_2 \cdot CoI_4 \cdot 2H_2O$.

For assignment of the coordination formula of this new complex, the following experimental evidence is especially relevant.

(1) The infrared spectrum shows no absorption in the 1600–1650 cm^{-1} region, where the deformation vibration of coordinated water commonly appears as a strong band. However, the spectrum shows two major hydrogen-sensitive absorptions in the higher energy region: One absorption appears as a strong band centered at 3240 cm^{-1} (2420 cm^{-1} in the deuterated species), characteristic of the OH stretching of metal hydroxides.[4] The other absorption appears as a very

0020-1669/79/1318-2617$01.00/0

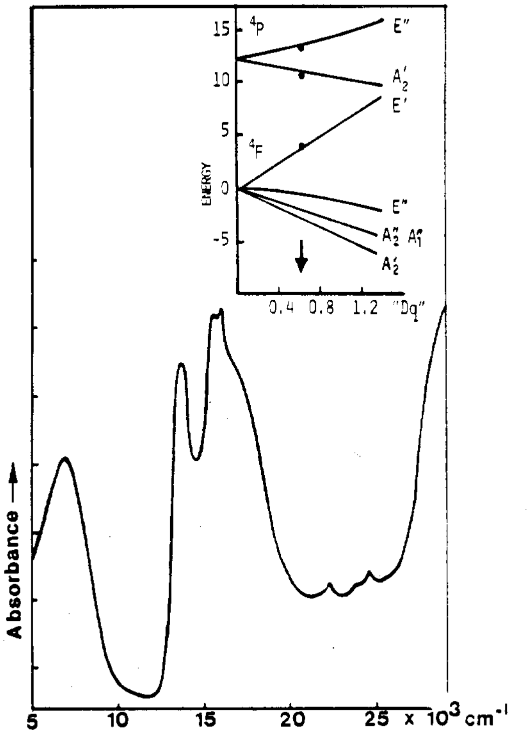

Figure 1. d–d electronic spectrum (reflectance) of $(LH)_2[Co(OH)_2I_3]I$ and energy-level diagram for Co(II) in a trigonal-bipyramidal field (after Ciampolini[6]). The black dots indicate the positions of the band maxima in the energy diagram.

broad, structured band, centered at approximately 2600 cm^{-1} (1900 cm^{-1} in the deuterated species), similar to the N^+H stretching mode observed in the hydrogen-bonded salts of protonated tertiary amines.[5] Thus the infrared spectral data indicate that the two "water molecules" of the empirical formula are actually present in the compound as their hydrolysis products—OH^- ions (bound to the cobalt(II) ion) and H^+ ions (bound to the tertiary nitrogen of the trimethylpiperazinium cation).

(2) When heated to approximately 120 °C, the dark blue complex sharply loses two molecules of water, forming an equimolar mixture of the crystalline CoI_3L complexes and L^+I^-. The TGA and DTA curves show that the "dehydration process" occurs in a single step, indicating the equivalence of the two water molecules released, and hence the equivalence of their OH^- and H^+ constituents in the original compound.

(3) The electronic d–d spectrum of the dark blue complex is not compatible with either a tetrahedral or an octahedral environment for the Co(II) ion. Rather, the general pattern of the spectrum (Figure 1) is typical of high-spin, five-coordinate cobalt(II) and indicates a crystal field of D_{3h} symmetry. The low value of "*Dq*" obtained by fitting the energies of the observed absorptions to Ciampolini's energy level diagram[6] is consistent with an environment of three (equatorial) iodo and two (axial) hydroxo ligands. On the basis of the available information, the dark blue complex of empirical formula $L_2{\cdot}CoI_4{\cdot}2H_2O$ can, therefore, be formulated as a "double salt" containing protonated piperazinium cations, trigonal-bipyramidal $[Co(OH)_2I_3]^{3-}$ complex anions, and "free" iodide ions. Strong and equivalent hydrogen bonding between each OH^- ligand of the complex anion and an N^+H group of a neighboring cation is suggested by the relatively low-frequency, narrow, unsplit contour of the OH stretching band, by the low frequency of the N^+H stretching band, and also by the ease of the one-step "dehydration" reaction. Undoubtedly hydrogen bonding plays a determining role in the overall stabilization of this double salt and particularly of the unusual five-coordinate Co(II) complex anion.

Five-coordinate complexes of Co(II) are fairly common but usually contain uncharged, sterically hindered organic ligands, often with a polychelate structure.[7] In contrast, the complexes of Co(II) with simple "inorganic" anions are usually four-coordinate and tetrahedral. For the $[Co(OH)_2I_3]^{3-}$ ion, therefore, considerable interligand repulsion would be expected and evidence for it can be found in the spectral data. In fact, the electronic spectrum shows that the crystal field acting on the Co(II) ion is by far the weakest observed for any five-coordinate Co(II) complex, with a *Dq* between 0.60×10^3 and 0.65×10^3 cm^{-1}. This value is appreciably lower than that calculated for the CoO_2I_3 chromophore on the assumption of an average environment and with a value of 0.90×10^3 cm^{-1} for the *Dq* of O donor ligands (from the spectrum of square-pyramidal $[Co(ClO_4)(OAsPh_2Me)_4]^+$)[8] and a value of 0.27×10^3 cm^{-1} for the *Dq* of the I^- ligands (from the spectrum of the tetrahedral $[CoI_4]^{2-}$).[9] This low crystal field environment may be considered to reflect a strong repulsion exerted by the bulky (equatorial) iodo ligands on the (axial) hydroxo ligands. In agreement with this conclusion, the Co–OH stretching vibration (470 cm^{-1}) occurs some 30 cm^{-1} below the lower limit of other known hydroxo complexes,[10] whereas the Co–I stretching mode (208–204 cm^{-1}) occurs in the usual range.[11]

The ease of formation of the $[Co(OH)_2I_3]^{3-}$ ion and the thermal stability of its crystalline double salt $(LH)_2[Co(OH)_2I_3]I$ are quite remarkable in view of the scarcity of hydroxo complexes of the transition-metal ions. In general, this scarcity results from the extremely low solubility of the transition-metal hydroxides, so that even at a neutral pH most metal ions begin to precipitate as mixtures of hydroxo-bridged species with a composition approaching that of "basic salts". It may, therefore, be expected that discrete hydroxo complexes of the transition metals will be formed more readily when the concentration of OH^- ions present in solution is carefully controlled by some hydrolytic process. In our example this requirement is fulfilled by the N tertiary atom of the monoquaternized piperazine acting as a proton acceptor from a water molecule, and thereby releasing OH^- ions in just the stoichiometric ratio required for the formation of the $[Co(OH)_2I_3]^{3-}$ species. The flexible, protonated piperazinium cation can further provide effective stabilization of the $[Co(OH)_2I_3]^{3-}$ counterion through hydrogen bonding and appropriate conformational packing in the crystalline state. In this respect, the double salt $(LH)_2[Co(OH)_2I_3]I$ represents another example of the stabilization of unusual complex ions by specifically tailored counterions, previously reported by various authors.[12] In the present case, however, the hydrolytic formation of both the cation and the anion furnishes a novel route to the formation of the complex.

Registry No. $(LH)_2[Co(OH)_2I_3]I$, 70332-96-6; CoI_3L, 36391-09-0.

References and Notes

(1) J. R. Ferraro, R. Driver, W. R. Walker, and W. Woznicek, *Inorg. Chem.*, **6**, 1586 (1967); J. R. Ferraro and W. R. Walker, *ibid.*, **4**, 1382 (1965); W. R. McWhinnie, *J. Inorg. Nucl. Chem.*, **27**, 1063 (1965).
(2) A. S. N. Murthy, J. V. Quagliano, and L. M. Vallarino, *Inorg. Chim. Acta*, **6**, 49 (1972).
(3) B. B. Garrett, V. L. Goedken, and J. V. Quagliano, *J. Am. Chem. Soc.*, **92**, 489 (1970).
(4) W. P. Griffith, *J. Chem. Soc.*, 245 (1964); L. H. Jones, *J. Chem. Phys.*, **22**, 217 (1954); D. Scargill, *J. Chem. Soc.*, 4440 (1961); P. Tarte, *Spectrochim. Acta*, **13**, 107 (1958).
(5) J. V. Quagliano, A. K. Banerjee, V. L. Goedken, and L. M. Vallarino, *J. Am. Chem. Soc.*, **92**, 482 (1970); P. Sauvageau and C. Sandorfy, *Can. J. Chem.*, **38**, 1901 (1960).
(6) M. Ciampolini, *Struct. Bonding (Berlin)*, **6**, 52 (1969).
(7) L. Sacconi, *Pure Appl. Chem.*, **17**, 95 (1968).
(8) F. Lions, J. G. Dance, and J. Lewis, *J. Chem. Soc. A*, 565 (1967).
(9) A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, 1968, p 324, and references therein.

(10) J. R. Ferraro, "Low-Frequency Vibrations of Inorganic and Coordination Compounds", Plenum Press, New York, 1971, pp 75–6, and references therein; D. M. Adams, "Metal-Ligand and Related Vibrations", St. Martin's Press, New York, 1968, pp 251–3, and references therein.
(11) A. Sabatini and L. Sacconi, *J. Am. Chem. Soc.*, **86**, 17 (1964); D. H. Brown, K. P. Forest, R. H. Nuttall, and D. W. A. Sharp, *J. Chem. Soc. A*, 2146 (1968).
(12) F. Basolo, *Coord. Chem. Rev.*, **3**, 213 (1968), and references therein; V. L. Goedken, L. M. Vallarino, and J. V. Quagliano, *J. Am. Chem. Soc.*, **92**, 303 (1970).

Contribution from the Rocketdyne Division of Rockwell
International Corporation, Canoga Park, California 91304

Reactions of Fluorine Perchlorate with Fluorocarbons and the Polarity of the O–F Bond in Covalent Hypofluorites

Carl J. Schack* and Karl O. Christe

Received March 9, 1979

Although $FOClO_3$ has been known for decades,[1,2] its reaction chemistry has remained virtually unexplored and is limited to references to unpublished work, cited in a review.[3] This lack of data is attributed to the previous report[2] that $FOClO_3$ consistently exploded during attempted freezing. During a study[4] of NF_4ClO_4, it was found that very pure $FOClO_3$ could be obtained in high yield by the thermal decomposition of NF_4ClO_4. The $FOClO_3$, prepared in this manner, could be manipulated and repeatedly frozen without explosions, thus allowing us to study some of its properties[5] and reaction chemistry.

Of particular interest to us were the reactions of $FOClO_3$ with fluorocarbons. Previous work[6] in our laboratory had demonstrated that $ClOClO_3$ and $BrOClO_3$ add readily to fluorocarbon double bonds, resulting in covalent fluorocarbon perchlorates. Consequently, one would expect fluorine perchlorate to undergo a similar reaction. However, a literature citation[3] suggested that $FOClO_3$ does not add across the double bond in $Cl_2C{=}CF_2$. Furthermore, reactions of covalent hypofluorites, such as CF_3OF, are commonly interpreted in terms of a highly unusual $CF_3O^{\delta-}{-}F^{\delta+}$ type polarization of the O–F bond ("positive fluorine"). If the O–F bond in CF_3OF is indeed polarized in this direction, the fluorine in $FOClO_3$ should be even more positive because of the higher electronegativity of the perchlorato group. Since the direction of the addition of a hypohalite across an unsymmetrical olefinic double bond strongly depends on the direction and the degree of polarization of the O–Hal bond,[7] a study of the $O_3ClOF/CF_3CF{=}CF_2$ reaction system offered an ideal opportunity to experimentally test the validity of the "positive fluorine" concept.

Experimental Section

Caution! Although no explosions were encountered in the present study, $FOClO_3$ must be considered a highly sensitive material and should be manipulated only in small quantities with appropriate safety precautions.

Apparatus and Materials. Volatile materials were manipulated in a well-passivated (with ClF_3) 304 stainless steel vacuum line equipped with Teflon-FEP U-traps and bellows-seal valves. Pressures were measured with a Heise Bourdon tube-type gage (0–1500 mm, ±0.1%). Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer. The ^{19}F NMR spectra were recorded on a Varian Model EM 390 spectrometer at 84.6 MHz using Teflon-FEP sample tubes (CS Laboratory Supplies) and $CFCl_3$ as an internal standard. Hexafluoropropylene and CF_3I were purchased while $CF_2{=}CF_2$ was prepared by pyrolyzing Teflon. Fluorine perchlorate was obtained from the decomposition of NF_4ClO_4.[4,5]

Reaction with Hexafluoropropylene. A 30-mL stainless steel cylinder was loaded at −196 °C with $FOClO_3$ (1.59 mmol) and C_3F_6 (2.05 mmol). The closed cylinder was warmed to −45 °C and kept at that temperature overnight. Separation of the products was achieved by vacuum fractionation in U-traps cooled at −78, −95, and −196 °C. The coldest trap contained unreacted C_3F_6 together with $FClO_3$, C_2F_5CFO, and a small amount of $(CF_3)_2CO$. In the other traps only the colorless liquid $C_3F_7OClO_3$ was found (1.18 mmol, 74% yield based on $FOClO_3$). The following temperature–vapor pressure data were measured (°C, mm): −46.6, 4; −22.7, 17; −9.3, 36; 0.0, 59; 10.6, 99; 22.0, 161. The vapor pressure–temperature relation is described by the equation $\log P = 7.5257 - (1571.94/T)$ (pressure in mmHg and temperature in K) with a calculated normal boiling point of 65.2 °C and a heat of vaporization of 7.19 kcal/mol. A vapor density of 265 g/mol was measured compared to a calculated value of 268.5 g/mol for $C_3F_7ClO_4$. Strong mass spectral peaks were found for the ions $C_2F_4ClO_4^+$, $C_3F_7^+$, $CF_2ClO_4^+$, $C_3F_5O^+$, $C_3F_5^+$, $C_2F_5^+$, $C_2F_4O^+$, $C_2F_4^+$, $C_2F_3O^+$, ClO_3^+, $C_2F_2O^+$, CF_3^+ (base peak), ClO_2^+, COF_2^+, ClO^+, CF_2^+, and COF^+. The following infrared bands were observed (cm^{-1}, intensity): 1340 (sh), 1325 (sh), 1290 (vs), 1250 (sh), 1235 (vs), 1200 (m), 1171 (w), 1153 (m), 1119 (ms), 1088 (m), 1026 (s), 988 (s), 968 (m–s), 784 (w), 746 (m), 723 (w), 676 (m), 641 (m–s), 614 (s), 530 (w).

Reaction with Tetrafluoroethylene. Fluorine perchlorate (0.61 mmol) and C_2F_4 (0.62 mmol) were combined at −196 °C in a 10-mL stainless steel cylinder. By evaporation of the liquid nitrogen from a liquid nitrogen–dry ice slush used to cool the reaction cylinder, the temperature was allowed to slowly rise to −78 °C and finally over several days by loss of solid CO_2 to about −45 °C. Fractional condensation of the products at −112 and −196 °C permitted the isolation of $C_2F_5OClO_3$ (0.42 mmol, 68% yield) which was identified by its known vibrational, NMR, and mass spectra.[8] Smaller amounts of CF_3CFO, C_2F_6, Cl_2, and O_2 were observed as byproducts.

Reaction with Trifluoromethyl Iodide. Into a cold (−196 °C) 30-mL stainless steel cylinder CF_3I (0.66 mmol) and then $FOClO_3$ (1.40 mmol) were condensed. Warm-up to about −45 °C was accomplished slowly as noted in the preceding example. After several days at −45 °C the reactor was recooled to −196 °C, and the presence of a considerable amount of noncondensable gas (oxygen) was noted. Fractionation of the condensable products showed a mixture of COF_2, CF_4, Cl_2, I_2, IF_5, and a solid iodine oxide to be the principal species present. However, a small amount of CF_3OClO_3 (0.05 mmol, 8% yield) was also found and identified by comparison with reported data.[8]

Results and Discussion

Under carefully controlled reaction conditions, similar to those previously used for the polar additions of $ClOClO_3$ and $BrOClO_3$,[6] fluorine perchlorate was found to add across olefinic double bonds in high yield. With tetrafluoroethylene the following reaction occurred:

$$CF_2{=}CF_2 + FOClO_3 \xrightarrow{-45\ ^\circ C} CF_3CF_2OClO_3$$

With the unsymmetrical olefin perfluoropropylene a mixture of two isomers was found

$$\begin{aligned} CF_3CF{=}CF_2 + FOClO_3 \xrightarrow{-45\ ^\circ C} \\ \underset{68\%}{CF_3CF_2CF_2OClO_3} + \underset{32\%}{CF_3CF(OClO_3)CF_3} \end{aligned}$$

These two perfluoropropyl perchlorates are novel compounds which were identified by vapor density measurements and spectroscopic data. The presence of the covalent $-OClO_3$ group was demonstrated by infrared spectroscopy which showed the intense bands typical of this group[8] at 1290 ($\nu_{as}(ClO_3)$), 1026 ($\nu_s(ClO_3)$), and 614 cm^{-1} (ν(Cl–O)). Additional support for the covalent perchlorate structure was obtained from the mass spectrum which showed strong peaks for the ions, ClO_3^+, ClO_2^+, and ClO^+ but not for ClO_4^+, as is generally the case for fluorocarbon perchlorates. A parent ion was not observed, and the highest m/e was $C_2F_4ClO_4^+$, i.e., the parent minus a CF_3 group.

Gas chromatography of the product revealed a slight asymmetry for the $C_3F_7ClO_4$ peak, thereby indicating the presence of isomers. This was confirmed by ^{19}F NMR spectroscopy, showing that both possible adducts were formed. The observed chemical shifts and coupling constants, together

0020-1669/79/1318-2619$01.00/0