methine proton resonances appeared as three singlets corresponding to two nonequivalent protons in the cis configuration plus one set of two equivalent protons in the trans configuration. The β-methine proton resonances of the uncyclized intermediates **3** leading to these complexes would be expected to have a similar appearance.

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Registry No. **3a**, 62081-93-0; **3b**, 96213-12-6; **3c**, 96213-14-8; **3d**, 96213-16-0; **3e**, 96213-18-2; **3f**, 96213-19-3; **13** (R = H), 62086-50-4; **13** (R = Me, R = H), 96213-21-7; **13** (R = Me), 96213-22-8; **13** (R = Me, R = Ph), 96213-23-9; *o*-phenylenediamine, 95-54-5; 1,1,3,3-tetramethoxypropane, 102-52-3; 4,4-dimethoxy-2-butanone, 5436-21-5; 2,4-pentanedione, 123-54-6; 4-methyl-*o*-phenylenediamine, 496-72-0; 4,5-dimethyl-*o*-phenylenediamine, 3171-45-7; benzoylacetone, 93-91-4; 1-phenyl-3-[(*o*-aminophenyl)imino]-1-butanone, 96213-24-0.

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

Synthesis and Characterization of NF_4CrF_6 and Reaction Chemistry of CrF_5

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NF_4CrF_6, a new stable NF_4^+ salt containing an energetic counterion, was prepared by treatment of CrF_5 with an excess of NF_4HF_2 in HF solution. The composition and ionic nature of NF_4CrF_6 was established by elemental analysis, vibrational and ^{19}F NMR spectroscopy, and its X-ray powder pattern. Reactions of CrF_5 with H_2O in HF, ClF_3, FNO, Cl_2, $CFCl_3$, and KrF_2 were studied to determine its acidity and oxidizing power. With FNO, a stable 1:1 adduct is formed, which on the basis of its vibrational spectra has the ionic structure $NO^+CrF_6^-$. The reaction of $NOCrF_6$ with NO produced $(NO^+)_2CrF_6^{2-}$, which by controlled pyrolysis was converted to $NO^+CrF_5^-$. With stoichiometric amounts of H_2O in HF, CrF_5 did not form a stable $OH_3^+CrF_6^-$ salt but the reaction resulted in hydrolysis to CrF_3O. The influence of the strong Lewis acids AsF_5 and SbF_5 on the oxidizing power of CrF_5 was also investigated. On the basis of the fact that CrF_5–SbF_5 mixtures can oxidize O_2 (IP = 12.06 eV) but not NF_3 (IP = 13.00 eV), the following qualitative oxidizer strength scale is proposed: $KrF^+ > PtF_6 > SbF_5 + F_2 +$ activation energy $> CrF_5$–SbF_5. The results of a normal-coordinate analysis of CrF_6^- and CrF_6^{2-} show the expected decrease in force constants with increasing negative charge.

Introduction

Chromium pentafluoride is a known, powerful oxidizer capable of fluorinating, for example, Xe to XeF_2 and XeF_4.[2,3] Furthermore, it is known that the oxidizing power of CrF_5 can be enhanced by the addition of a strong Lewis acid, such as SbF_5.[4] Thus, these CrF_5–Lewis acid mixtures can oxidize O_2 to O_2^+ and therefore are assigned an electron affinity comparable to that of PtF_6.[4] In view of this demonstrated high oxidizing power of CrF_5, the known existence of the CrF_6^- anion,[4] and the exceptional stability of NF_4^+ salts,[5,6] the synthesis of the new oxidizer $NF_4^+CrF_6^-$ appeared feasible.

Experimental Section

Apparatus. Volatile materials were manipulated in stainless-steel vacuum lines equipped with Teflon–FEP U-traps, 316 stainless-steel bellows-seal valves, and a Heise Bourdon tube-type pressure gauge.[7] Either quartz or sapphire tubes or Teflon–FEP ampules, equipped with stainless-steel valves, were used as reaction vessels. The lines and other hardware used were passivated with ClF_3 and, if HF was to be used, with HF. Nonvolatile or marginally volatile materials, such as SbF_5 and CrF_5, were handled in the dry N_2 atmosphere of a glovebox. Antimony pentafluoride was added to the reactors with a Teflon-needle syringe, and CrF_5, due to its tackiness at ambient temperature, was preferably handled after it had been cooled by liquid nitrogen. Metathetical reaction and solvolysis studies were carried out in HF solution by using an apparatus consisting of two Teflon–FEP U-traps interconnected through a coupling containing a porous Teflon filter.[8]

High-pressure, high-temperature reactions were carried out in 95- or 1000-cm^3 Monel cylinders equipped with Monel valves. The loaded cylinders were placed into an oven set at the desired reaction temperature. Decomposition studies were carried out in a sapphire reactor (Tyco Co.). The reactor was connected to a stainless-steel valve by a Swagelok compression fitting using Teflon ferrules. The reactor was heated by immersion into a stirred oil bath.

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer Model 283 spectrophotometer. Spectra of solids were obtained by using dry powders pressed between AgCl or AgBr windows in an Econo press (Barnes Engineering Co.). Spectra of gases were obtained by using a Teflon cell of 5-cm path length equipped with AgCl windows. Raman spectra were recorded on either a Cary Model 83 or a Spex Model 1403 spectrophotometer using the 488-nm exciting line of an Ar ion laser or the 647.1-nm exciting line of a Kr ion laser, respectively. Sealed quartz, Teflon–FEP, or sapphire tubes were used as sample containers in the transverse-viewing–transverse-excitation mode. A previously described[9] device was used for recording the low-temperature spectra. The ^{19}F NMR spectra of the samples contained in sealed, 5-mm-o.d. Teflon–FEP tubes (Wilmad Glass Co.) were recorded at 84.6 MHz on a Varian Model EM390 spectrometer equipped with a variable-temperature probe. X-ray diffraction patterns of the powdered samples in sealed 0.5-mm quartz capillaries were obtained by using a General Electric Model XRD-6 diffractometer, Ni-filtered Cu Kα radiation, and a 114.6-mm-diameter Philips camera.

Elemental analyses were performed by Mikroanalytische Laboratorien, Elbach, West Germany.

Materials. Literature methods were used for the syntheses of NF_4SbF_6,[10] KrF_2,[11] $KrFSbF_6$,[12] and FNO[13] and for the drying of HF.[14]

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Nitrogen trifluoride (Rocketdyne), F_2 (Air Products), NO, O_2, ClF_3, Cl_2 (Matheson), CrF_3, SbF_5, AsF_5 (Ozark Mahoning), $CrF_3{\cdot}3H_2O$ (Baker and Adamson), and Cr powder (Sargent, 100 mesh) were commercially available. Anhydrous CrF_3 was also obtained by dehydrating the hydrate at 200 °C. The purity of the volatile compounds was checked by vibrational spectroscopy prior to use and, where necessary, improved by fractional condensation. The $CFCl_3$ (Du Pont) was dried by storage over P_2O_5 and transferred by distillation without further purification.

Synthesis of CrF_5. It was found that the synthesis of CrF_5 can be carried out under reaction conditions milder than those previously reported.[15] In a typical preparation, CrF_3 (91.75 mmol) was loaded in the drybox into a prepassivated 1-L Monel high-pressure reactor. The reactor was connected to the vacuum line, and F_2 (947.66 mmol) was added at −196 °C. After 65 h at 260 °C, the remaining F_2 was removed at −196 °C, and CrF_5 (84.88 mmol, 92.5% yield based on CrF_3) was pumped off at 60–100 °C and trapped in a U-tube maintained at −78 °C.

Attempts to fluorinate Cr powder with ClF_3 in HF solution at room temperature for 16 h were unsuccessful, even in the presence of 2 atm of F_2, and the Cr powder was quantitatively recovered.

Preparation of NF_4CrF_6. A mixture of CsF (10.11 mmol) and NF_4SbF_6 (10.15 mmol) was loaded in the drybox into half of a prepassivated Teflon double-U metathesis apparatus.[8] Dry HF (~8 mL) was added on the vaccum line to the half containing NF_4SbF_6–CsF, and the resulting mixture was stirred for 30 min at 25 °C. After this mixture and the filter were cooled to −78 °C, the metathesis apparatus was inverted and the resulting solution of NF_4HF_2 in HF was filtered into the other half of the apparatus. Part of the HF solvent was pumped off during warm-up toward 0 °C until the first signs of decomposition of NF_4HF_2 were noted. The apparatus was then cooled to −196 °C and taken into the drybox and CrF_5 (5.34 mmol) added to it. The apparatus was reattached to the vacuum line and warmed to room temperature. The HF solvent and the excess of NF_4HF_2 were pumped off successively for 2 h at 25 °C and 45 min at 40 °C. Since the weight and the infrared spectrum of the solid residue still indicated the presence of bifluoride species, the solid was transferred to a sapphire tube and heated in a dynamic vacuum for 2 h at 95 °C. The resulting deep red, solid residue (1.5 g, corresponding to a quantitative yield based on CrF_5) was shown by vibrational spectroscopy to consist mainly of NF_4CrF_6 with small amounts of SbF_6^- as the only detectable impurity. On the basis of its elemental analysis, the product had the following composition (mol %): NF_4CrF_6, 96.3; $CsSbF_6$, 3.7. Anal. Calcd for the NF_4CrF_6 (96.3%)–$CsSbF_6$ (3.7%) mixture: Cr, 19.25; F, 71.96; Cs, 1.88; Sb, 1.73. Found: Cr, 19.69; F, 70.15; Cs, 1.90; Sb, 1.79.

The filter cake from the metathetical preparation of the NF_4HF_2 solution consisted of 3.6806 g of $CsSbF_6$ (weight calculated for 10.113 mmol of $CsSbF_6$ 3.7281 g), identified by its Raman and infrared spectra.

Decomposition Study of NF_4CrF_6. The compound was heated stepwise from 75 to 145 °C in a sapphire tube in a dynamic vacuum. Traps kept at −78 and −210 °C were used for collecting CrF_5 and NF_3, respectively. A pyrolysis temperature of 125 °C was required for the slow evolution of CrF_5 and NF_3. The vibrational spectra of the solid residue at the end of the incomplete pyrolysis showed no significant changes, indicating that NF_4CrF_6 does not undergo a stepwise decomposition to salts containing polyanions.

Reaction of NF_3 and F_2 with CrF_3 or CrF_5. CrF_3, when heated in a high-pressure Monel cylinder with a twofold excess of NF_3 and a threefold excess of F_2 at an autogenous pressure of 100 atm to 260 °C for 45 h, was converted to CrF_5 in high yield without any NF_3 uptake. Heating of the resulting CrF_5 with a fivefold excess each of NF_3 and F_2 for 140 °C for 6 days and subsequently to 125 °C for 41 days did not produce any detectable amounts of NF_4CrF_6.

Synthesis of $NOCrF_6$. CrF_5 (2.06 mmol) was loaded into a Teflon–FEP ampule in the drybox. The ampule was connected to the vacuum line, and anhydrous HF (1.8 mL, liquid) was added at −196 °C. The CrF_5 only partially dissolved in the HF at room temperature, resulting in a light red-brown solution. FNO (2.21 mmol) was added to the ampule at −196 °C, and the mixture was slowly warmed to room temperature, resulting in a dark purple solution. All volatile material was pumped off at room temperature, leaving behind a dark red-brown solid (0.399 g; weight calculated for 2.06 mmol of $NOCrF_6$ 0.404 g), which was identified by vibrational spectroscopy and elemental analysis as $NOCrF_6$. Anal. Calcd for $NOCrF_6$: N, 7.15; Cr, 26.53; F, 58.16; O, 8.16. Found: N, 6.90; Cr, 26.30; F, 58.10; O (by difference), 8.70.

Synthesis of $(NO)_2CrF_6$. In a Teflon–FEP ampule $NOCrF_6$ (2.03 mmol) was dissolved in anhydrous HF (96.5 mmol), and NO (2.03 mmol) was added at −196 °C. The mixture was warmed to room temperature for several hours. All material that was volatile at room temperature was pumped off until the solid, yellow-brown (pink when finely ground) residue showed a constant weight (0.456 g; weight calculated for 2.03 mmol of $(NO)_2CrF_6$ 0.459 g). The material was identified as $(NO^+)_2CrF_6^{2-}$ by vibrational spectroscopy. Anal. Calcd for $(NO)_2CrF_6$: Cr, 23.01; F, 50.44. Found: Cr, 22.8; F, 50.2.

Synthesis of $NOCrF_5$. A sample of $(NO)_2CrF_6$ (0.885 mmol) was heated in a sapphire tube to 130 °C in a dynamic vaccum until a constant weight (0.157 g; weight calculated for 0.885 mmol of $NOCrF_5$ 0.157 g) was obtained. The volatile material consisted of FNO, and the solid, brown residue was identified by vibrational spectroscopy as $NO^+CrF_5^-$. Attempts to convert $NOCrF_5$ to CrF_4 by vacuum pyrolysis at higher temperatures resulted in sublimation of the $NOCrF_5$ without decomposition.

The ClF_3–CrF_5 System. In a flamed-out quartz tube ClF_3 (12.22 mmol) was condensed at −196 °C onto CrF_5 (2.04 mmol). A deep red-brown solution was formed on warming the reaction mixture to 25 °C. The tube was cooled to −78 °C and material volatile at −78 °C was pumped off for 7 h. On the basis of the weight increase of the tube, the CrF_5 had retained 0.195 mmol of ClF_3. The Raman spectrum of this mixture, recorded at −130 °C, showed only bands due to solid ClF_3 and solid CrF_5.

The Cl_2–CrF_5 System. A mixture of CrF_5 (5.44 mmol) and Cl_2 (2.68 mmol) was heated in a sapphire tube to 127 °C for 57 h. On the basis of the observed material balance and infrared spectra of the solid residue, only 49% of the CrF_5 was reduced to CrF_4. Heating to higher temperatures resulted in a complete reduction of CrF_5 but also in the formation of some CrF_3 as a byproduct. Thus, heating of CrF_5 (4.71 mmol) and Cl_2 (2.44 mmol) to 185 °C for 20 h produced 0.6034 g of a brown solid (weight calculated for 4.71 mmol of CrF_4 0.6031 g) and ClF (3.99 mmol) and ClF_3 (about 0.3 mmol). Although the Cr analysis of the solid product was close to that expected for CrF_4 (calcd 40.62; found 40.42), its X-ray powder pattern and infrared spectrum showed the presence of some CrF_3.

The $KrFSbF_6$–CrF_5 and $KrFSbF_6$–CrF_5–HF Systems. In a sapphire tube a mixture of $KrFSbF_6$ (1.09 mmol) and CrF_5 (1.96 mmol) was warmed to the melting point of CrF_5 (34 °C), at which point gas evolution started. On the basis of the observed material balance and vibrational spectra, all $KrFSbF_6$ had decomposed to Kr, F_2, and SbF_5 but no oxidation of CrF_5 to CrF_6 had occurred. Similar results were obtained when this reaction was repeated in HF solution.

The CrF_5–H_2O–HF System. A Teflon–FEP ampule containing a Teflon-coated magnetic stirring bar was loaded in the drybox with CrF_5 (2.58 mmol), and HF (2.19 mmol) was added on the vacuum line. The ampule was taken to the drybox and cooled to −196 °C, and a preweighed amount of H_2O (2.58 mmol), sealed in a Teflon tube, was added by cooling the tube to −196 °C, cutting it open, and placing it inside the ampule. The ampule was closed, evacuated at −196 °C, and kept at 25 °C for 20 h with stirring. A pink solid and an orange-pink solution were formed. Removal of all volatile material at 25 °C in a dynamic vacuum resulted in the formation of a brownish solid residue, which was identified as CrF_3O by its vibrational spectrum, elemental analysis, and X-ray powder diffraction pattern.[16]

Reaction of CrF_5–SbF_5 with O_2. The reaction between $CrF_5{\cdot}nSbF_5$ and O_2 was conducted in a manner similar to that reported by Gard et al.,[4] except that it was carried out in a 45-mL Teflon–FEP ampule. A mixture of CrF_5 (2.37 mmol) and SbF_5 (6.54 mmol) was dynamically pumped at room temperature in an attempt to reach the previously reported[4] $CrF_5{\cdot}2SbF_5$ composition. The pumping had to be stopped before reaching this composition since CrF_5 was removed together with SbF_5. At this stage with the assumption that only minor amounts of CrF_5 had been removed, the molar ration of SbF_5:CrF_5 approximated 2.47:1. Oxygen (4.736 mmol) was then admitted into the ampule at −196 °C. When the mixture was warmed to room temperature, a pale yellow-green solid was formed. On the basis of the observed O_2 material balance, about 1 mol of O_2 was taken up per 1 mol of CrF_5. No significant loss of mass was observed by dynamic pumping on the solid at room temperature for 1 h. The presence of $O_2^+Sb_2F_{11}^-$ in the solid product was established by Raman spectroscopy and its X-ray powder diffraction pattern.[17]

Reaction of CrF_5–SbF_5 with NF_3. Chromium pentafluoride (29.30 mmol) was combined in a Teflon–FEP ampule with SbF_5 (59.05 mmol). The mixture was outgassed by repeated pumping at −78 °C, followed by

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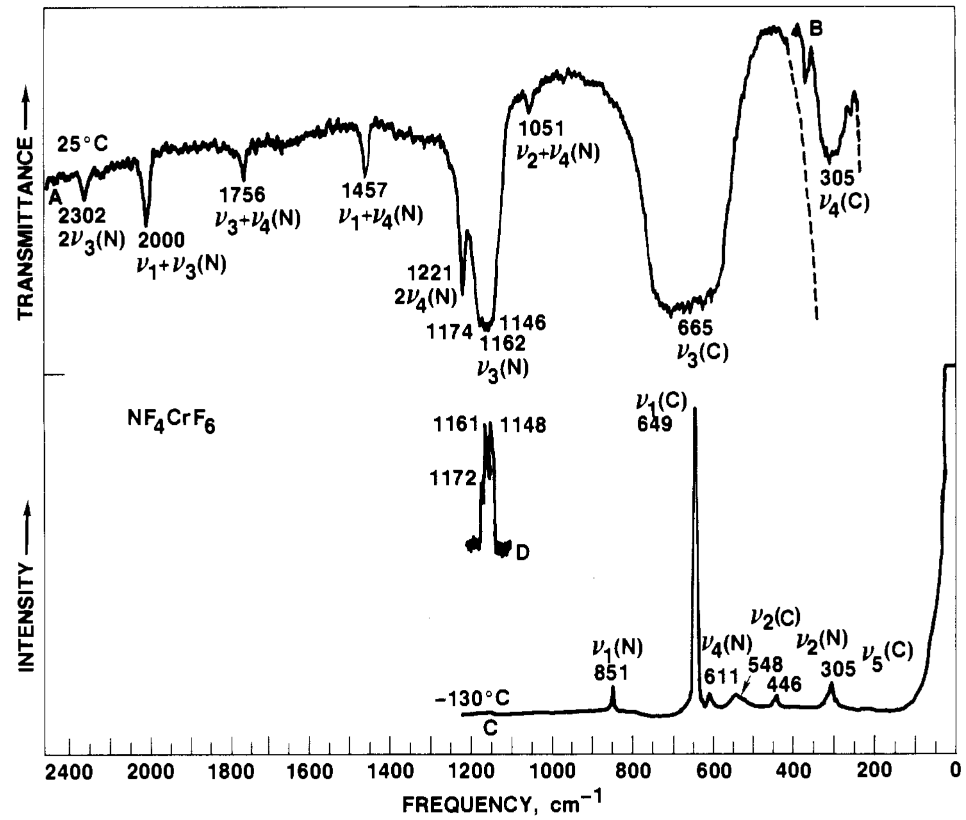

Figure 1. Vibrational spectra of solid NF_4CrF_6: traces A and B, infrared spectra of the powder at 25 °C pressed between AgCl and AgBr disks, respectively; traces C and D, Raman spectra of the solid recorded at -130 °C with 647.1-nm excitation at two different sensitivity levels, respectively. The listed assignments are based on space group T_d for NF_4^+ (N) and O_h for CrF_6^- (C).

warming to 25 °C. The solution was then magnetically stirred and pressurized with about 2 atm of NF_3 gas. No significant NF_3 uptake was noticed after 1 h at room temperature and 1 hour at 60 °C. All other attempts to react CrF_5–SbF_5 with NF_3, such as those using longer reaction times, increased NF_3 pressures, and liquid HF as a solvent, were equally unsuccessful.

Reaction of CrF_5–SbF_5 with $CFCl_3$. $CFCl_3$ (10.21 mmol) was condensed at -196 °C onto a mixture of CrF_5 (1.45 mmol) and SbF_5 (1.56 mmol) in a Teflon–FEP ampule. When the mixture was warmed to 25 °C, a brown precipitate was formed, together with chlorine as evidenced by the yellow color of the $CFCl_3$ solution. An amorphous, yellow-green, solid residue was obtained after pumping off the volatile material at 25 °C. The ^{19}F NMR spectrum of the volatiles showed that part of the $CFCl_3$ had been fluorinated to CF_2Cl_2, CF_3Cl, and CF_4.

When this reaction was repeated in the absence of SbF_5 with a 20-fold excess of $CFCl_3$, the main products were Cl_2, CCl_4, or CF_2Cl_2, and CF_3Cl. An amorphous, brownish, solid residue was obtained whose Cr analysis corresponded closely to the value expected for CrF_4. Anal. Calcd for CrF_4: Cr, 40.62. Found: Cr, 40.55.

Reaction of CrF_5–AsF_5 with O_2. Equimolar amounts of AsF_5 and CrF_5, when combined in a Teflon–FEP ampule, formed a deep red solution at -78 °C and did not undergo a visible reaction on warm-up to 25 °C. Upon addition of a threefold excess of O_2 at -196 °C and subsequent repeated temperature cycling between -78 and +25 °C, a rust-colored solid formed that, on the basis of its infrared spectrum and X-ray powder diffraction pattern, contained $O_2^+AsF_6^-$[18] in addition to some unidentified material.

Results and Discussion

Synthesis and Characterization of NF_4CrF_6. Since CrF_5 is a relatively strong and volatile Lewis acid, the direct synthesis[19] of NF_4CrF_6 from NF_3, F_2, and CrF_5 at elevated temperature and pressure seemed feasible. However, our attempts using conditions (125 °C, 100 atm, 41 days) similar to those[20] that previously had been successful for NF_4AsF_6 failed. Since NF_4CrF_6 is marginally stable at 125 °C (see below), the failure of the high-temperature–high-pressure method appears not to be caused by insufficient thermal stability of the NF_4CrF_6 final product. On the basis of similar experiences with other relatively stable NF_4^+ salts, such as NF_4BF_4 or NF_4PF_6, the failure of the direct thermal synthesis methods for these compounds might be attributed to the inability of the corresponding Lewis acids to stabilize, under the given reaction conditions, the required NF_3^+ radical cation intermediate.[12]

Since NF_4CrF_6 could not be obtained by direct thermal synthesis, indirect methods[19] were investigated. It was found that the reaction of NF_4HF_2[6] with CrF_5 in HF solution affords NF_4CrF_6 in essentially quantitative yield:

$$NF_4HF_2 + CrF_5 \xrightarrow{HF} NF_4CrF_6 + HF \qquad (1)$$

The use of an excess of NF_4HF_2 in this reaction is advantageous to ensure complete conversion of the CrF_5. Since NF_4HF_2 is thermally unstable, decomposing above room temperature to gaseous NF_3, F_2, and HF,[6] its excess can easily be removed from the solid NF_4CrF_6 product by pumping at 25–100 °C.

The NF_4CrF_6 salt is a deep red, crystallinic solid, stable in a dynamic vacuum to about 120 °C. It starts to decompose slowly at 125 °C to NF_3, F_2, and CrF_5. No species such as $NF_4Cr_2F_{11}$, $(NF_4)_2CrF_6$, or CrF_6 was observed when the compound was gradually pyrolyzed under pumping at temperatures ranging from 125 to 145 °C. In HF at 23 °C the NF_4CrF_6 salt is highly soluble at a rate of 6.39 g of NF_4CrF_6/g of HF.

The ionic nature of NF_4CrF_6, both in the solid state and in HF solution, was verified by vibrational and ^{19}F NMR spectroscopy. The Raman and infrared spectra of the solid, together with the observed frequencies and assignments for tetrahedral NF_4^+ (T_d)[21] and octahedral CrF_6^- (O_h), are shown in Figure 1. The splittings into the three degenerate components observed for $\nu_3(F_2)$ of NF_4^+

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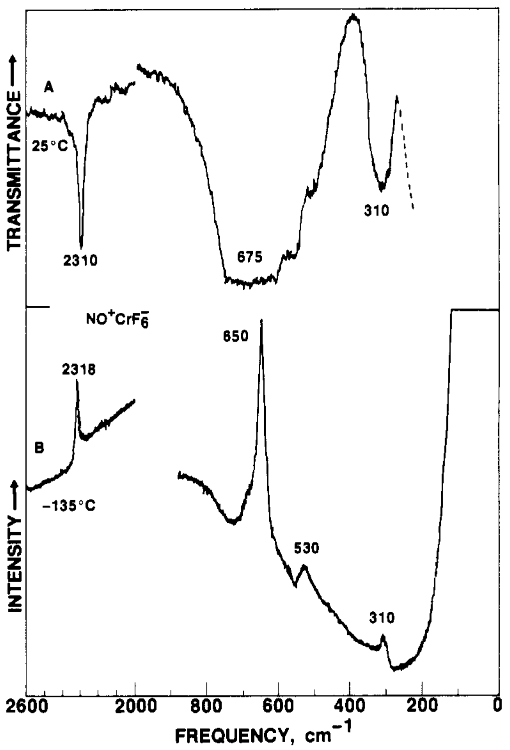

Figure 2. Vibrational spectra of solid $NOCrF_6$: trace A, infrared spectrum of the powder pressed between AgBr disks; trace B, low-temperature Raman spectrum.

in the Raman spectrum are due to solid-state effects and are frequently observed for NF_4^+ salts.[21] For CrF_6^-, only the two infrared-active modes, $\nu_3(F_{1u})$ and $\nu_4(F_{1u})$, have previously been reported for their Cs^+ and NO_2^+ salts.[4] In spite of the broadness of the observed bands and the associated difficulty in choosing their band centers, the previously reported frequencies ($CsCrF_6$ $\nu_3 = 600$, $\nu_4 = 295$ cm^{-1}; NO_2CrF_6 $\nu_3 = 600$, $\nu_4 = 275$ cm^{-1})[4] are in poor agreement with our values for NF_4CrF_6 and $NOCrF_6$ (see Figures 1 and 2). The results of a normal-coordinate analysis for CrF_6^- are given below.

The Raman spectrum of NF_4CrF_6 in HF solution at ambient temperature showed only minor shifts from the spectrum of the solid for the bands due to NF_4^+ ($\nu_1 = 854$, $\nu_4 = 612$, $\nu_2 = 446$ cm^{-1}) but showed shifts to significantly higher frequencies for the bands due to CrF_6^- ($\nu_1 = 649 \rightarrow 678$, $\nu_5 = 305 \rightarrow 348$ cm^{-1}). These shifts, together with the surprisingly high solubility of NF_4CrF_6 in HF (see above) and the ^{19}F NMR observations (see below), suggest strong interaction between CrF_6^- and the HF solvent.

The ^{19}F NMR spectrum of NF_4CrF_6 in HF solution at 29 °C showed a triplet of equal intensity at $\phi = 215.2$ with $J_{^{14}N^{19}F} = 118$ Hz, characteristic[20,22] for NF_4^+. A very broad line centered at $\phi = -136$ was assigned to the HF solvent in exchange with CrF_6^-, which contains a paramagnetic Cr(V) central atom.

The X-ray powder diffraction pattern of NF_4CrF_6 was recorded and is given as supplementary material. The observed pattern is very complex and could not be indexed, suggesting that NF_4CrF_6 is not isotypic with the previously known tetragonal NF_4MF_6-type (M = P, As, Sb, Bi) salts.[23]

Synthesis and Characterization of $NOCrF_6$, $(NO)_2CrF_6$, and $NOCrF_5$. Before this study, only two CrF_6^- salts had been known, i.e. $CsCrF_6$ and NO_2CrF_6.[4] It was now found that, in addition to NF_4CrF_6 (see above), CrF_5 also forms a stable 1:1 adduct with FNO. When stoichiometric amounts of CrF_5 and FNO are combined in HF solution, the compound $NOCrF_6$ is formed:

$$FNO + CrF_5 \xrightarrow{HF} NOCrF_6 \qquad (2)$$

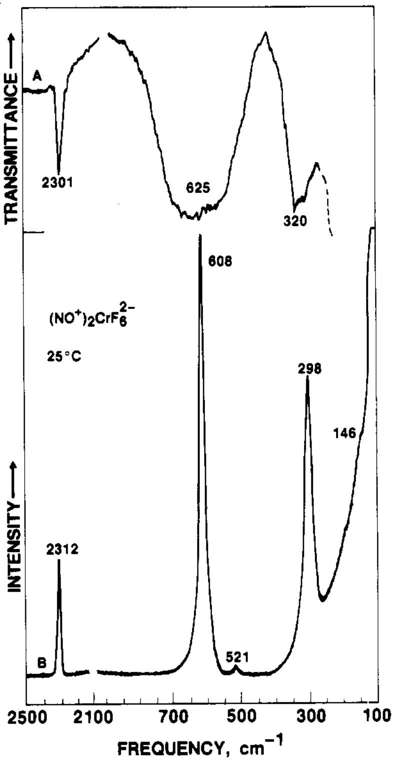

Figure 3. Vibrational spectra of solid $(NO)_2CrF_6$: trace A, infrared spectrum; trace B, Raman spectrum.

The deep red solid is stable at room temperature and sublimes at higher temperatures. Its X-ray powder diffraction pattern (given as supplementary material) is too complex for indexing and strongly differs from that of cubic $NO^+AsF_6^-$.[18] This is a further confirmation that CrF_6^- salts appear not to be isotypic with their corresponding main group metal(V) salts.

The ionic nature of solid $NOCrF_6$ was established by vibrational spectroscopy (see Figure 2). The infrared and Raman spectra clearly show a band at about 2310 cm^{-1} characteristic for the NO stretching mode of the NO^+ cation,[18,24] in addition to the bands characteristic for the CrF_6^- anion (see above).

When an HF solution of $NOCrF_6$ was treated with a stoichiometric amount of NO, the $Cr^VF_6^-$ anion was reduced to $Cr^{IV}F_6^{2-}$, resulting in the formation of the new $(NO)_2CrF_6$ salt:

$$NOCrF_6 + NO \xrightarrow{HF} (NO)_2CrF_6 \qquad (3)$$

This salt is a yellow-brown (pink when finely ground), crystallinic solid that is stable at room temperature but decomposes in a dynamic vacuum at 130 °C. Its X-ray powder diffraction pattern is given as supplementary material. The ionic nature of $(NO)_2CrF_6$ was established by vibrational spectroscopy (see Figure 3). The NO^+ stretching mode is again observed around 2300 cm^{-1}, with the slightly lower frequency, when compared to that of $NOCrF_6$, being due to the presence of a doubly charged counterion. The bands due to CrF_6^{2-} are similar to those of CrF_6^- but are shifted to slightly lower frequencies. This frequency shift is caused by the increased negative charge of the anion (see the normal-coordinate analysis). On the basis of the number of bands and their relative intensities, it appears safe to conclude that CrF_6^{2-} is also octahedral. The results of a normal-coordinate analysis for CrF_6^{2-} are given below.

Although the synthesis of K_2CrF_6 has been reported as early as 1950,[25] very little is known about the CrF_6^{2-} anion.[26,27] Furthermore, the reported syntheses involving the fluorination of

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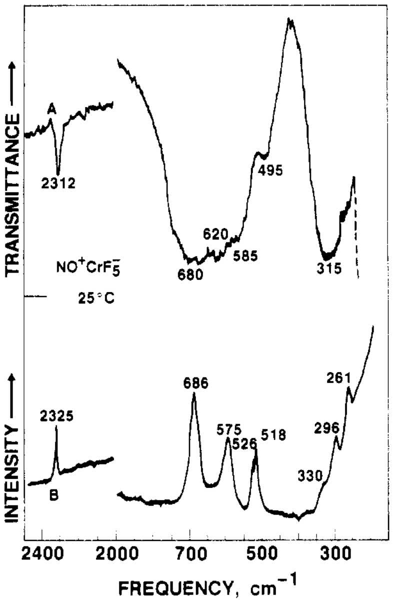

Figure 4. Vibrational spectra of solid $NOCrF_5$: trace A, infrared spectrum; trace B, Raman spectrum.

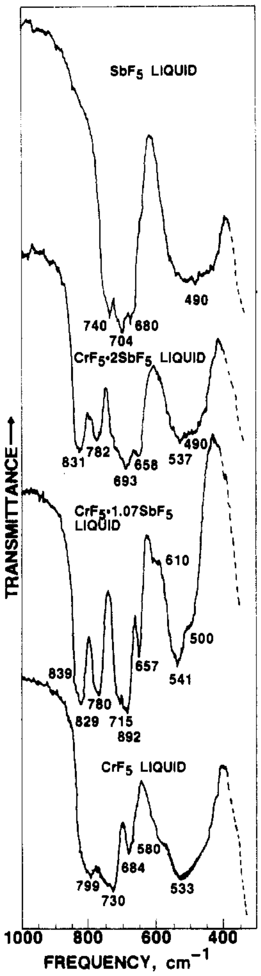

Figure 5. Infrared spectra of liquid SbF_5, CrF_5, and their mixtures at 35 °C between AgCl disks.

either a mixture of KCl + $CrCl_3$ with F_2 or a mixture of KCl + CrF_4 with BrF_3 yielded products that varied in composition.[25,27] Therefore, the above described synthesis, based on the readily accessible and purifiable CrF_5, FNO, and NO, offers a superior route to CrF_6^{2-} salts of excellent purity, as shown by the Raman spectrum of $(NO)_2CrF_6$ in Figure 3.

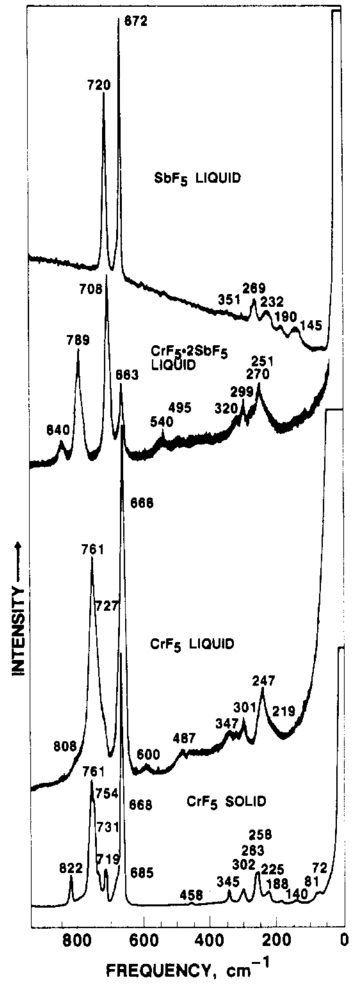

Figure 6. Raman spectra of liquid SbF_5, $CrF_5 \cdot 2SbF_5$, and CrF_5 (at 35 °C) and of solid CrF_5 (at −130 °C).

When a sample of $(NO)_2CrF_6$ was subjected to vacuum pyrolysis at 130 °C, the following stepwise decomposition occurred resulting in the formation of $NOCrF_5$, another new compound:

$$(NO)_2CrF_6 \xrightarrow{130\ ^\circ C} NOCrF_5 + FNO \qquad (4)$$

This salt is a brown, crystallinic solid that sublimes above 130 °C without further decomposition, thus preempting the use of its pyrolysis as a method for the preparation of CrF_4. The X-ray powder diffraction pattern of $NOCrF_5$ is given as supplementary material. The ionic nature of $NOCrF_5$ was established by vibrational spectroscopy (see Figure 4), which showed the presence of the NO^+ cation (ν_{NO} at about 2320 cm^{-1}). On the basis of the general similarity of the CrF_5^- bands to those observed for several GeF_5^- salts,[28,29] a polymeric cis-fluorine-bridged structure appears most likely for CrF_5^-.

Lewis Acid Strength of CrF_5. On the basis of a previous report, CrF_5 is amphoteric, forming adducts with the Lewis bases CsF and FNO_2 and the Lewis acid SbF_5.[4] The Lewis acid character of CrF_5 was confirmed by the results of this study, which showed that CrF_5 forms stable $NO^+CrF_6^-$ and $NF_4^+CrF_6^-$ salts. Therefore, CrF_5 must be considered a relatively strong Lewis acid. However, it is significantly weaker than AsF_5, as shown by the fact that, even at −78 °C, CrF_5 does not form a stable adduct with ClF_3, while $ClF_2^+AsF_6^-$ is marginally stable at ambient temperature.[30] Similarly, attempts failed to prepare a $KrF^+CrF_6^-$

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Table I. Vibrational Frequencies and Modified Valence Force Fields[a] of CrF_6^- and CrF_6^{2-}

assign in point group O_h			freq, cm^{-1}				force const, mdyn/Å		
			CrF_6^-			CrF_6^{2-}			
			$NOCrF_6$	NF_4CrF_6	av	$(NO)_2CrF_6$		CrF_6^-	CrF_6^{2-}
A_{1g}	ν_1	ν_{sym} in phase	650	649	649	608	$F_{11} = f_r + 4f_{rr} + f_{rr'}$	4.714	4.137
E_g	ν_2	ν_{sym} out of phase	530	548	537	521	$F_{22} = f_r - 2f_{rr} + f_{rr'}$	3.227	3.038
F_{1u}	ν_3	ν_{asym}	675	665	670	625	$F_{33} = f_r - f_{rr'}$	3.103	2.748
	ν_4	δ_{asym}	310	305	308	320	$F_{44} = f_\alpha + 2f_{\alpha\alpha} - 2f_{\alpha\alpha''} - f_{\alpha\alpha'''}$	0.2878	0.3107
							$F_{34} = 2(f_{r\alpha} - f_{r\alpha''})$	0.2430	0.2623
F_{2g}	ν_5	δ_{sym}	310	305	308	298	$F_{55} = f_\alpha - 2f_{\alpha\alpha'} + f_{\alpha\alpha'''}$	0.2654	0.2485
							f_r	3.416	3.077
							f_{rr}	0.248	0.183
							$f_{rr'}$	0.308	0.329

[a] Assuming $F_{34} \equiv$ minimum.

salt from KrF_2 and CrF_5 in either the presence or absence of HF as a solvent. For comparison, $KrF^+AsF_6^-$ is well-known and decomposes only slowly at room temperature.[31]

Although a distinct $CrF_5 \cdot 2SbF_5$ adduct, formulated as $CrF_4Sb_2F_{11}$, has previously been reported,[4] we could not verify the existence of such an adduct. Attempts to reach this composition through vaporization of SbF_5 from CrF_5 solutions in an excess of SbF_5, as well as vibrational spectra (see Figures 5 and 6), failed to give any evidence for a definite compound and resulted in the simultaneous removal of both components. In our opinion, the spectra of these CrF_5–SbF_5 mixtures are best interpreted in terms of intersolutions of the two compounds, with the observed changes in the spectra being due to different degrees of mixed fluorine bridging between the individual components. This view is also supported by the fact that the viscosity of SbF_5 is strongly decreased by the dissolution of the highly polymeric CrF_5. If a predominantly ionic $CrF_4Sb_2F_{11}$ adduct were formed, an increase in viscosity or formation of a solid would be expected. Liquid AsF_5 was found to be also an excellent solvent for CrF_5, resulting in dark brown solutions of low viscosity.

Oxidation Reactions with CrF_5. Oxidation reactions involving either neat CrF_5 or CrF_5–Lewis acid (SbF_5 or AsF_5) mixtures were carried out to determine its relative oxidative power. It was found that neat CrF_5 does not oxidize ClF_3 to ClF_5. Furthermore, even in the presence of F_2, it does not oxidize O_2 to O_2^+ at 30 °C and NF_3 to NF_4^+ at 125 °C. It is capable, however, of oxidizing Cl_2 to ClF at 120 °C and $CFCl_3$ to Cl_2 and a mixture of CF_2Cl_2, CF_3Cl, and CF_4 at room temperature. In both reactions, CrF_5 is reduced to lower valent chromium fluorides. Some brown solid, presumably CrF_4,[27,32] could be sublimed from the crude CrF_5 + Cl_2 reaction product in a static vacuum at 185 °C. The sublimation residue was shown by vibrational spectroscopy and X-ray powder diffraction data to contain also some CrF_3. The brown sublimate showed a broad, strong Raman line at 780 cm^{-1}, no detectable X-ray diffraction lines, and two broad infrared bands ranging from 830 to 740 and 640 to 490 cm^{-1}, respectively. The infrared spectrum is quite distinct from that of CrF_3, which does not exhibit a band in the 800-cm^{-1} region. The brown color observed for our sample of CrF_4 is in good agreement with Wartenberg's original report[32] and does not confirm a subsequent report stating that CrF_4 is dark green and that the brown color is due to an oxide layer generated by exposure to air.[27]

The oxidizing power of CrF_5 is significantly enhanced by strong Lewis acids, such as SbF_5 and AsF_5. This is not surprising and is generally the case for many oxidizers. Thus, $CrF_5 \cdot 2SbF_5$ has been reported to oxidize O_2 to O_2^+ at room temperature, and the solid reaction product has been formulated as $O_2(CrF_4Sb_2F_{11})$.[4] We have confirmed this reaction and its approximate 1:1 stoichiometry and have identified the solid reaction product as a mixture of $O_2^+Sb_2F_{11}^-$ and lower valent chromium fluorides:

$$O_2 + CrF_5 \cdot 2SbF_5 \rightarrow O_2^+Sb_2F_{11}^- + [CrF_4] \qquad (5)$$

Extraction of $O_2^+SbF_6^-$ from the product was possible by treatment with liquid HF.

The oxidation of O_2 to O_2^+ can also be achieved with CrF_5–AsF_5 mixtures at or below room temperature. By analogy with the corresponding SbF_5 system, the solid reaction product contained $O_2^+AsF_6^-$.

Attempts were unsuccessful to oxidize NF_3 to NF_4^+ using similar conditions, i.e. pressurizing liquid $CrF_5 \cdot 2SbF_5$ with several atmospheres of NF_3 at room temperature. On the basis of the facts that CrF_5–Lewis acid mixtures are capable of oxidizing O_2 and Xe,[4] which have ionization potentials of 12.06 and 12.13 eV, respectively, but cannot oxidize NF_3 with an IP of 13.00 eV, their electron affinity or oxidizing power can be limited to the relatively narrow range of 12.13–13.00 eV. Since PtF_6, KrF^+ salts, and F_2–Lewis acid mixtures activated by a suitable activation energy source are all capable of oxidizing NF_3 to NF_4^+ under comparable conditions,[12] CrF_5–Lewis acid mixtures are a weaker oxidizer than any one of these systems. On the basis of the above and previous[12] results, the following order of decreasing oxidizer strength can be proposed for these systems: KrF^+ salts > PtF_6 > Lewis acid + F_2 + activation energy > CrF_5–Lewis acid.

Reactions of CrF_5 with either KrF_2 or KrF^+ salts were carried out in attempts to produce CrF_6, but so far all attempts in this direction have been unsuccessful.

Synthesis and Properties of CrF_3O. Our attempts to isolate a stable oxonium salt of CrF_6^- according to

$$CrF_5 + H_2O + HF \xrightarrow{HF} [OH_3^+CrF_6^-] \qquad (6)$$

were unsuccessful but resulted in the formation of CrF_3O after removal of the HF solvent:[16]

$$[OH_3^+CrF_6^-] \xrightarrow{-HF} CrF_3O + 3HF \qquad (7)$$

The intermediate formation of OH_3CrF_6 was not unequivocally established but appears very likely from the observation of a pink solid and stable pink HF solution. This reaction produces CrF_3O in quantitative yield and is superior to the previously reported[16] synthesis, which involves the reaction of CrO_3 with ClF, followed by multiple treatments with F_2 at 120 °C. The properties observed for CrF_3O were in good agreement with those previously reported.[16] The observed X-ray powder diffraction pattern is given as supplementary material.

Normal-Coordinate Analyses of CrF_6^- and CrF_6^{2-}. Since for CrF_6^{2-} no vibrational spectra at all and for CrF_6^- only incomplete data[4] had previously been reported, normal-coordinate analyses were carried out for these two anions. Modified valence force fields were computed, assuming $F_{34} \equiv$ minimum, due to the underdetermined nature of the F_{1u} block. On the basis of a previous study[33] and experience with similar octahedral ions,[34] this condition is expected to be a good approximation to a general valence force field. The observed frequencies, their assignments in point group O_h, and the computed force constants are summarized in Table

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I. As expected, the Cr–F stretching force constant f_r decreases from CrF_6^- to CrF_6^{2-} due to a bond weakening caused by the increased $Cr^{\delta+}$–$F^{\delta-}$ polarity of the bonds in CrF_6^{2-}.

Conclusion. Chromium pentafluoride is a moderately strong Lewis acid capable of forming stable CrF_6^- salts with NF_4^+ and NO^+. The NF_4^+ salt is of particular interest as an oxidizer because in it an oxidizing anion is combined with a strongly oxidizing cation. Contrary to previous reports,[4] no evidence was found for CrF_5 forming a distinct, predominantly ionic $CrF_4Sb_2F_{11}$ adduct with SbF_5. The oxidizing power of CrF_5 is greatly enhanced by strong Lewis acids but does not match that of PtF_6. Chromium(V) salts can selectively be reduced to Cr(IV) salts with NO. In this manner the new Cr(IV) salts $(NO)_2CrF_6$ and $NOCrF_5$ can be prepared. Similarly, CrF_5 can be reduced to mainly CrF_4 with either Cl_2 or $CFCl_3$. Reaction of CrF_5 with stoichiometric amounts of H_2O in HF produces an unstable oxonium salt that decomposes on HF removal to CrF_3O, thus providing a convenient new synthesis for this compound.

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Supplementary Material Available: A table of X-ray powder diffraction patterns for some Cr-containing compounds (1 page). Ordering information is given on any current masthead page.

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Kinetics and Mechanism for Oxidation of Tetracyanoplatinate(II) by Chlorine and Hypochlorous Acid and for Hydrolysis of Chlorine in Aqueous Solution[†]

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Oxidation of $Pt(CN)_4^{2-}$ in aqueous solutions of chlorine has been followed by stopped-flow spectrophotometry. For pH <~7, the reaction takes place by two parallel paths with Cl_2 and HOCl as oxidants according to the rate law rate = $(k_{Cl_2}[Cl_2] + k_{HOCl}[HOCl])[Pt(CN)_4^{2-}]$. In unbuffered solutions of chlorine in aqueous $NaClO_4$, the slow HOCl path is predominant, whereas in weakly acidic solutions buffered with HCl, oxidation takes place via the 10^5 times faster Cl_2 path. For certain conditions, the displacement of the hydrolysis equilibrium of chlorine

$$Cl_2 + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HOCl + Cl^- + H^+$$

becomes rate-determining for the oxidation of $Pt(CN)_4^{2-}$ by Cl_2, which then appears to be zero order in complex. Such experiments give k_1 and k_{-1}. Rate constants at 25 °C for a 1.00 M perchlorate medium are $k_{Cl_2} = (1.08 \pm 0.10) \times 10^7\ M^{-1}\ s^{-1}$, $k_{HOCl} = 97.9 \pm 1.1\ M^{-1}\ s^{-1}$, $k_1 = 8.7 \pm 0.2\ s^{-1}$, and $k_{-1} = (2.66 \pm 0.03) \times 10^4\ M^{-2}\ s^{-1}$. The equilibrium constant for the chlorine hydrolysis is obtained from the kinetics as $(3.27 \pm 0.11) \times 10^{-4}\ M^2$. The primary reaction product for oxidation of $Pt(CN)_4^{2-}$ by an excess of Cl_2 in acidic solution is *trans*-$Pt(CN)_4Cl(H_2O)^-$, which slowly reacts with a second chloride to give *trans*-$Pt(CN)_4Cl_2^{2-}$. Oxidation by HOCl gives primarily *trans*-$Pt(CN)_4(OH)_2^{2-}$, which rapidly reacts with a second molecule of HOCl to form a stable hypochlorite complex, *trans*-$Pt(CN)_4(OCl)(OH)^{2-}$. In weakly alkaline solution (pH 11), oxidation of $Pt(CN)_4^{2-}$ with ClO^- gives *trans*-$Pt(CN)_4(OH)_2^{2-}$ as the reaction product. Oxidation with HOCl and ClO^- is an inner-sphere two-electron transfer with the oxygen of the hypochlorite as the bridging atom. Chloride anation of *trans*-$Pt(CN)_4(OCl)(H_2O)^-$ is a rapid second-order reaction with rate constant $26.5 \pm 0.2\ M^{-1}\ s^{-1}$.

Introduction

Oxidation of square-planar complexes of platinum(II) by chlorine or bromine in aqueous solution gives a *trans*-dihalo complex of platinum(IV) as the final reaction product. This is a classical method to prepare such platinum(IV) complexes.[1] It was shown already in 1954, in a study of the chlorination of $PtCl_4^{2-}$, that aqua complexes appear as intermediates in this reaction.[2] The two-step mechanism of eq 1 has been suggested[2-7]

$$PtL_4 + X_2 \xrightarrow{\text{fast}} X\text{–}PtL_4\text{–}OH_2 \xrightarrow{+X^-} X\text{–}PtL_4\text{–}X \qquad (1)$$

(X = halide). The first and very rapid reaction has been described as an oxidative addition of dihalogen to the platinum(II) complex.[3-7] This reaction is very fast in most cases, and there are very few reports on its kinetics so far. From stopped-flow measurements of the oxidation of $PtCl_4^{2-}$ by chlorine, it was concluded that the rate was independent of the concentration of one or both reactants.[5] That conclusion was later rebutted, and the oxidation was shown to be first order in both chlorine and complex.[7] Such a rate law was also found for the oxidation of $PdCl_4^{2-}$ by chlorine.[8] Oxidation of $Pt(CN)_4^{2-}$ by iodine has been studied by use of stopped-flow spectrophotometry, and those results are also compatible with a mechanism involving reaction between an iodine molecule and the complex.[7]

The subsequent reaction of eq 1 is much slower, and it has been the subject of several kinetic studies. It is a substitution of the water ligand of the intermediate aqua complex by halide. This reaction is accelerated by platinum(II) complexes[5-7] and by free halide.[3,4,7,9]

Aqueous solutions of chlorine contain Cl_2 and HOCl in equilibrium with each other according to eq 2.[10] Both these molecules

$$Cl_2 + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HOCl + H^+ + Cl^- \qquad (2)$$

oxidize platinum(II) complexes quantitatively.[11] The possibility

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[†] This work is part of a Ph.D. thesis by L.D., Lund University, 1985.

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