caused by the nitrate ion, using molar absorptivities of 80.9 and 19.2 reported by Bjerrum and Rasmussen for the pure *cis* and *trans* isomers. Comparison of samples 2 and 4 yields (80.4 − 77.0)100/(80.9 − 19.2) or 5.5 mol % more *trans* ion in the nitrate solution than in the perchlorate. The other three pairs of samples—6 and 8, 10 and 12, and 14 and 16—yield, respectively, 4.7, 3.4, and 4.9 more mol %.

Integration of the methylene proton peak areas in the pmr spectra[6] of the equilibrium mixtures indicated 4 ± 2 mol % *trans* ion in 2 *M* perchloric acid. In 3 *M* nitric acid, the *trans* ion could not be detected. Both *cis* and *trans* salts gave the same equilibrium results.

Nitric acid causes a significant rearrangement of the amino proton peaks from their positions in perchloric acid solution; the peak representing the amino groups *trans* to each other divides with half of it moving downfield 0.6 ppm while the entire peak representing the amino groups *trans* to aquo groups moves downfield 0.3 ppm. Sulfuric and hydrobromic acids produce similar changes of less magnitude, the positions varying with acid concentration as reported by Fung.[10]

The deshielding of amino proton peaks in such complex ions by anions has been recently interpreted by Millen and Watts[11] to indicate ion association, possibly through proton bridges which lock the amino protons into axial and equatorial positions. The perchlorate ion reportedly does not engage in hydrogen bonding[12] and consequently only one peak, however broad, is evident for the amino protons *trans* to each other in perchlorate solution.

Acknowledgment.—This research was supported by a grant through the Mankato State College Faculty Research Council.

---

(10) B. M. Fung, *J. Am. Chem. Soc.*, **89**, 5788 (1967).
(11) W. A. Millen and D. W. Watts, *ibid.*, **89**, 6858 (1967).
(12) D. W. Watts, *et al.*, *Australian J. Chem.*, **19**, 43, 51 (1966).

CONTRIBUTION FROM ROCKETDYNE, A DIVISION OF
NORTH AMERICAN ROCKWELL CORPORATION,
CANOGA PARK, CALIFORNIA 91304

On the Complex Formation of Chlorine Pentafluoride with Lewis Acids and Bases

BY KARL O. CHRISTE AND DONALD PILIPOVICH

Received September 12, 1968

Chlorine mono-, tri-, and pentafluorides are known to exist. Of these the first two compounds show amphoteric character and form ionic complexes with strong Lewis acids and bases. Thus, ClF forms with strong Lewis acids the FCl_2^+ cation[1] and with strong Lewis bases the ClF_2^- anion.[2–4] Similarly, the ClF_2^+ cation[5–12] and ClF_4^- anion[13–18] have been prepared from ClF_3. In spite of the fact that the existence of ClF_5 was published[19] 5 years ago, no data have been published on its complex formation with Lewis acids and bases. In this paper we wish to report on the preparation and some properties of adducts derived from ClF_5.

Experimental Section

Materials and Apparatus.—The materials used in this work were manipulated in a well-seasoned 304 stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves (Hoke Inc., 4251F4Y). Chlorine pentafluoride (prepared in this laboratory[20]) was purified by fractional condensation and stored in a stainless steel cylinder over dry CsF. Prior to use, the ClF_5 was purified once more by fractional condensation. Nitrosyl fluoride was prepared from NO and F_2 at −196° and purified by fractional condensation. Arsenic pentafluoride (from Ozark-Mahoning Co.) and BF_3 (from The Matheson Co., Inc.) were purified by several low-temperature vacuum distillations. Antimony pentafluoride (from Ozark-Mahoning Co.) was purified by vacuum distillation at ambient temperature. Hydrogen fluoride (from The Matheson Co., Inc.) was purified by removing all volatiles at −196°, exposing the residue at ambient temperature for 12 hr to a fluorine pressure of 2 atm followed by removal of all volatiles at −196° *in vacuo*. Cesium fluoride (from K & K Laboratories) was dried by fusion in a platinum crucible. The purity of the volatile starting materials was determined by measurements of their vapor pressures and infrared spectra. Because of their hygroscopic nature, materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glove box.

Preparation of $ClF_5 \cdot AsF_5$.—In a typical experiment, ClF_5 (51.65 mmol) and AsF_5 (43.27 mmol) were combined at −196° in a U trap. The mixture was allowed to warm up slowly until melting and reaction occurred. When the pressure inside the trap reached 760 mm, the mixture was cooled again to −196°. This procedure was repeated several times until the reaction was complete. Unreacted ClF_5 (8.61 mmol) was recovered by distillation at −78°. Therefore, AsF_5 (43.27 mmol) had reacted with ClF_5 (43.04 mmol) in a mole ratio of 1:0.995, producing the complex $ClF_5 \cdot AsF_5$.

Preparation of $ClF_5 \cdot SbF_5$.—Antimony pentafluoride (104

---

(1) K. O. Christe and W. Sawodny, *Inorg. Chem.*, **8**, 212 (1969).
(2) K. O. Christe and J. P. Guertin, *ibid.*, **4**, 905 (1965).
(3) K. O. Christe and J. P. Guertin, *ibid.*, **4**, 1785 (1965).
(4) K. O. Christe, W. Sawodny, and J. P. Guertin, *ibid.*, **6**, 1159 (1967).
(5) J. W. Dale and D. A. MacLeod, private communication.
(6) A. E. Pavlath, Dissertation, Hungarian Academy of Science, Budapest, Hungary, 1954.
(7) F. Seel and O. Detmer, *Angew. Chem.*, **70**, 163 (1958); *Z. Anorg. Allgem. Chem.*, **301**, 113 (1959).
(8) N. Bartlett and D. H. Lohmann, *J. Chem. Soc.*, 5253 (1962).
(9) H. Selig and J. Shamir, *Inorg. Chem.*, **3**, 294 (1964).
(10) K. O. Christe and A. E. Pavlath, *Z. Anorg. Allgem. Chem.*, **335**, 210 (1965).
(11) F. P. Gortsema and R. H. Toeniskoetter, *Inorg. Chem.*, **5**, 1925 (1966).
(12) K. O. Christe and W. Sawodny, *ibid.*, **6**, 313 (1967).
(13) L. B. Asprey, J. L. Margrave, and M. E. Silverthorn, *J. Am. Chem. Soc.*, **83**, 2955 (1961).
(14) B. H. Kelly, B. Post, and R. W. Mason, *ibid.*, **85**, 307 (1963).
(15) E. Whitney, R. MacLaren, C. Fogle, and T. Hurley, *ibid.*, **86**, 2583 (1964).
(16) E. Whitney, R. MacLaren, T. Hurley, and C. Fogle, *ibid.*, **86**, 4340 (1964).
(17) K. O. Christe and J. P. Guertin, *Inorg. Chem.*, **5**, 473 (1966).
(18) K. O. Christe and W. Sawodny, *Z. Anorg. Allgem. Chem.*, **357**, 125 (1968).
(19) D. F. Smith, *Science*, **140**, 899 (1963).
(20) D. Pilipovich, W. Maya, E. A. Lawton, H. F. Bauer, D. F. Sheehan, N. N. Ogimachi, R. D. Wilson, F. C. Gunderloy, and V. E. Bedwell, *Inorg. Chem.*, **6**, 1918 (1967).

mmol) was transferred in the glove box to a Kel-F trap containing a Teflon-coated, magnetic stirring bar. The trap was connected to the vacuum line and 30 ml of liquid HF was condensed into the trap at −196°. The contents of the trap were warmed to ambient temperature and stirred until all SbF$_5$ had dissolved in the HF. This trap was connected to a second trap by means of flexible Teflon tubing. The second trap contained liquid ClF$_5$ (201 mmol) at −78°. The trap containing the SbF$_5$–HF solution was inverted and the SbF$_5$–HF solution was slowly added to the liquid ClF$_5$ at −78° with shaking. The mixture was kept at −78° for 24 hr. Subsequently, the HF solvent and excess ClF$_5$ were removed by vacuum distillation at −20°. Weighing of the trap, empty, with SbF$_5$, and after complex formation, indicated a ClF$_5$ to SbF$_5$ combining ratio of 1:1.08. Similarly, the 1:1 adduct was also obtained when SbF$_5$ was combined with a large excess of ClF$_5$ at −196° in a Monel cylinder. The cylinder was allowed to warm to ambient temperature and was placed on a shaker for 60 hr. Excess ClF$_5$ was removed by vacuum distillation at ambient temperature.

The BF$_3$–ClF$_5$ System.—Chlorine pentafluoride (14.41 mmol) and BF$_3$ (11.62 mmol) were combined at −196° in a U trap. The mixture was allowed to warm up until the pressure inside the trap reached 900 mm. Then the trap was cooled again to −196°. This procedure was repeated several times. The contents of the trap were warmed to −111.6° and a constant pressure of 94 mm was observed. Increasing the temperature of the mixture to −95.1° resulted in a water-clear liquid having a constant vapor pressure of 590 mm. All BF$_3$ together with some ClF$_5$ could be removed from the trap by vacuum distillation at −95.1°. The residue was identified by its infrared spectrum and consisted of pure ClF$_5$.

The NOF–ClF$_5$ System.—Chlorine pentafluoride (39.4 mmol) and NOF (39.4 mmol) were combined at −196° in a Teflon FEP U trap. The mixture was allowed to warm to −78.8° and was kept at this temperature for 24 hr. It remained at all times a water-clear liquid and no sign of solid formation could be observed. The vapor pressure above the liquid amounted to 116 mm shortly after reaching −78.8° and decreased to a constant value of 92 mm in the course of the following 24 hr. Subsequently, the contents of the trap were examined at ambient temperature in the gas phase by infrared spectroscopy. Only ClF$_5$ and NOF could be detected.

Dissociation Pressure Measurements.—The ClF$_5$·AsF$_5$ complex was prepared in a Teflon FEP U trap directly connected to a Heise, Bourdon tube-type gauge (0–1500 mm (±0.1%)) and the temperature of the cooling bath was determined with a copper–constantan thermocouple. To be certain that an equilibrium existed at each temperature reading, a sample of the gas above the solid complex was pumped off and a constant pressure was reestablished. True equilibrium existed at a given temperature if the pressures, before and after the pumping off procedure, were identical. Equilibrium pressures were always approached from below a given temperature. The following temperature (°C)–vapor pressure (mm) relations were observed: −31.20, 6.0; −25.33, 11.2; −0.18, 123; 5.18, 187; 9.69, 226.

X-Ray Powder Data.—Debye–Scherrer powder patterns were taken using a Philips Norelco instrument, Type No. 12046, with copper Kα radiation and a nickel filter. Samples were sealed in Lindemann glass tubes (∼0.3- and ∼0.5-mm o.d.).

Infrared Spectra.—The infrared spectra were recorded on a Beckman Model IR-7 with CsI interchange and a Perkin-Elmer Model 337 spectrophotometer in the ranges 700–200 and 4000–400 cm^{-1}, respectively. 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 plates or polyethylene disks and Teflon FEP gaskets were used for obtaining the spectra of solids as dry powders. The polyethylene disks were protected against interaction with the sample by a very thin Teflon sheet. Compensation for bands due to the window material was achieved by placing an empty cell in the reference beam.

Results

Synthesis.—Chlorine pentafluoride and AsF$_5$, when mixed at −78°, produced the 1:1 complex ClF$_5$·AsF$_5$, a white, crystalline solid. The 1:1 combining ratio was established by quantitative synthesis and infrared measurements of the gas phase above the solid complex. The latter measurements show that the complex is completely dissociated in the gas phase at 25°. Similarly, ClF$_5$ and SbF$_5$, when combined either under pressure or in HF solution, formed the 1:1 adduct ClF$_5$·SbF$_5$. It was found advantageous to add the HF–SbF$_5$ solution slowly to excess ClF$_5$ with stirring. When the ClF$_5$ was added to the HF–SbF$_5$ solution, the ClF$_5$ to SbF$_5$ combining ratio increased to about 1:1.36. The resulting compound had a wet appearance and a low melting point of about 35°. Its infrared spectrum indicated the presence of polymeric anions of the type SbF$_6^-$·xSbF$_5$. (Attempts to increase the melting point of this product by treating it with a tenfold excess of ClF$_5$ for 2 days at 50° under autogenous pressure and shaking were unsuccessful. No ClF$_5$ was consumed and the appearance and melting point of the product had changed only slightly.) Both adducts ClF$_5$·AsF$_5$ and ClF$_5$·SbF$_5$ react violently with water or organic materials. No evidence was found for complex formation between ClF$_5$ and BF$_3$. Strong Lewis bases, such as CsF or NOF, did not produce complexes with ClF$_5$.

Thermochemical Properties.—Based on the observed vapor pressure–temperature relations, a plot of log P_{mm} *vs.* T^{-1} (in °K) for the heterogeneous equilibrium

$$\mathrm{ClF_5\cdot AsF_5(s) = ClF_5(g) + AsF_5(g)}$$

is a straight line. The equation

$$\log P_{\mathrm{mm}} = 12.2008 - \frac{2763.6}{T}$$

represents these data in the temperature range −31.2–9.7°. By extrapolation, a dissociation pressure of 1 atm was obtained at 23.4°. At 25° the dissociation pressure amounts to 845 mm. From the slope of the log P_{mm} *vs.* T^{-1} curve, $\Delta H_{\mathrm{d}}^{\circ}$[21] = 25.23 kcal mol^{-1} was found. From $\Delta F^{\circ}_T = -RT \ln Kp_{\mathrm{atm}}$, a free energy change $\Delta F^{\circ}_{298} = 0.694$ kcal mol^{-1} and from $\Delta S^{\circ}_T = (\Delta H^{\circ} - \Delta F^{\circ}_T)T^{-1}$, an entropy change $\Delta S^{\circ}_{298} = 82.3$ cal deg^{-1} mol^{-1} were found for the dissociation process at 25°. A heat of formation of $\mathrm{ClF_4^+AsF_6^-}$(s), $\Delta H_{\mathrm{f}}^{\circ}{}_{298} = -376.8$ kcal mol^{-1}, was calculated based upon $\Delta H_{\mathrm{f}}^{\circ}{}_{298}[\mathrm{ClF_5(g)}]$[22] = −56.0 kcal mol^{-1} and $\Delta H_{\mathrm{f}}^{\circ}{}_{298}[\mathrm{AsF_5(g)}]$[23] = −295.6 kcal mol^{-1}.

The ClF$_5$·SbF complex, a white crystalline powder, is stable at room temperature. Its melting point

---

(21) It is not strictly correct to infer that the measured heat of reaction for the dissociation process equals the thermodynamic heat of dissociation. This would only be appropriate if the complex were in the gas phase or if the heat of sublimation of the complex were zero. However, for convenience, $\Delta H_{\mathrm{d}}^{\circ}$ will be used throughout the text to mean the heat of reaction of a complete dissociation process of the type: complex(s) = gas + gas.

(22) H. F. Bauer and D. F. Sheehan, *Inorg. Chem.*, **6**, 1736 (1967).

(23) P. A. G. O'Hare and W. N. Hubbard, *J. Phys. Chem.*, **69**, 4358 (1965).

(measured in a sealed off Teflon FEP tube) varied for different preparations from 35 to 88°. This variation could possibly be due to changes in the composition of the adduct.

X-Ray and Nmr Data.—Debye-Scherrer powder patterns were obtained for $ClF_5 \cdot SbF_5$. However, the pattern was too complex to allow determination of the crystal system and lattice parameters. Attempts to record the F^{19} nmr spectrum of the complex in HF solution failed owing to rapid exchange.

Vibrational Spectra.—The infrared spectra of solid ClF_5, $ClF_5 \cdot AsF_5$, and $ClF_5 \cdot SbF_5$ and the Raman spectrum of $ClF_5 \cdot SbF_5$ have been recorded. The spectra of the adducts are best interpreted in terms of ionic structures containing the ClF_4^+ cation. The latter most likely has symmetry C_{2v}. Detailed results on the vibrational spectra of ClF_4^+, BrF_4^+, and IF_4^+ will be published in a separate paper.[24]

Discussion

The synthesis of a well-defined 1:1 adduct between ClF_5 and AsF_5 presents no difficulties. In the case of SbF_5 the reaction conditions must be controlled more carefully owing to the absence of a common liquid range between ClF_5[20] (bp −14° (760 mm)) and SbF_5 (mp 7°) at ambient pressure. Hence, either a common solvent, such as HF, or increased pressure should be used in the synthesis of $ClF_5 \cdot SbF_5$. The formation of polymeric anions of the type $SbF_6^- \cdot xSbF_5$ is not unexpected and has been observed in similar systems.[25,26] It can be essentially avoided by adding the SbF_5-containing solution slowly to excess ClF_5 or by carrying out the synthesis under elevated pressure using again a large excess of ClF_5. Boron trifluoride appears to be too weak a Lewis acid for forming a complex with ClF_5. The vapor pressure of 590 mm measured above the liquid BF_3–ClF_5 system at −95.1° is only slightly lower than that of 594 mm calculated[27] for two ideal liquids according to Raoult's law. Since ClF_5 had been used in excess (55 mol %) and has a negligible vapor pressure[20] at −95°, it can be concluded that there is practically no positive interaction between BF_3 and ClF_5 at temperatures as low as −95°. The tendency to form adducts with ClF_5 decreases in the order $SbF_5 > AsF_5 > BF_3$ and is the same as that observed for other halogen fluorides such as ClF_3,[10] ClF,[1] or IF_5.[28,29] The heat of dissociation,[21] 25.23 kcal mol^{-1}, obtained for $ClF_5 \cdot AsF_5$ is of the same order of magnitude as the values obtained for similar ionic complexes such as $ClF_2^+BF_4^-$ [9] (23.6 kcal mol^{-1}) and $NO^+ClF_4^-$ [16] (15.8 kcal mol^{-1}).

The failure to observe complex formation between ClF_5 and Lewis bases is not surprising since the preparation of ClF_5 by fluorination of $Cs^+ClF_4^-$ [20] had indicated no interaction between CsF and ClF_5. Vapor pressure measurements on the liquid ClF_5–NOF system (in a 1:1 mole ratio) at −78.8° showed only a small negative deviation from the value (116 mm) calculated[20,30] for an ideal mixture according to Raoult's law. An infrared spectrum of the mixture after being kept at −78° for 24 hr showed that no chemical reaction, such as oxidation of NOF, had occurred.

The fact that ClF_5 (having one free localized electron pair) is capable of forming adducts with strong Lewis acids but not with Lewis bases suggests that in chlorine fluorides the highest possible coordination number of pentavalent chlorine toward fluorine (or localized free electron pairs) is 6. The conclusion that ClF_5 is saturated with respect to coordination number and hence also little associated in the liquid phase is further supported by spectroscopic evidence[31] and the low boiling point and Trouton constant[20] reported for ClF_5. Based on these data, the preparation of a stable, mainly covalent chlorine heptafluoride would be quite surprising.

Acknowledgment.—The authors are pleased to acknowledge support for this work by the Office of Naval Research, Power Branch.

---

[24] K. O. Christe and W. Sawodny, to be submitted for publication.

[25] J. K. Ruff, *Inorg. Chem.*, **5**, 1791 (1966).

[26] J. Weidlein and K. Dehnicke, *Z. Anorg. Allgem. Chem.*, **348**, 278 (1966).

[27] K. K. Kelley, U. S. Bureau of Mines Bulletin 383, U. S. Government Printing Office, Washington, D. C., 1935.

[28] A. A. Woolf, *J. Chem. Soc.*, 3678 (1950).

[29] K. O. Christe and W. Sawodny, submitted for publication.

[30] O. Ruff, W. Menzel, and W. Neumann, *Z. Anorg. Allgem. Chem.*, **208**, 293 (1932).

[31] G. M. Begun, W. H. Fletcher, and D. F. Smith, *J. Chem. Phys.*, **42**, 2236 (1965).

Contribution from the Department of Chemistry,
The University, Sheffield, England

Transition Metal Dithiolene Complexes. V.[1] Ligand-Exchange Reactions in Nitrosyl Iron Bis-1,2-dithiolenes

By E. J. Wharton,[2] C. J. Winscom,[2]
and J. A. McCleverty

Received September 9, 1968

The assumption that transition metal dithiolene complexes do not undergo ligand-exchange reactions has been shown to be incorrect.[3] Using polarography, it has been possible to show that ligand exchange does occur between planar nickel bisdithiolenes in solution. We have subsequently found that similar exchange reactions occur between nitrosyliron bisdithiolene complexes.

---

(1) Part IV: J. A. McCleverty, J. Locke, E. J. Wharton, and M. Gerloch, *J. Chem. Soc., A*, 816 (1968).

(2) Supported by the Science Research Council of Great Britain.

(3) A. Davison, J. A. McCleverty, E. T. Shawl, and E. J. Wharton, *J. Am. Chem. Soc.*, **89**, 830 (1967).