Experimental and Theoretical Characterization of the Oxygen-Coordinated Donor−Acceptor Adducts of $COCl_2$, COClF, and COF_2 with AsF_5 and SbF_5

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When reacted with an excess of the corresponding carbonyl halides, AsF_5 and SbF_5 form the following 1:1 adducts: $COCl_2 \cdot AsF_5$, $COCl_2 \cdot SbF_5$, $COClF \cdot AsF_5$, $COClF \cdot SbF_5$, $COF_2 \cdot AsF_5$, and $COF_2 \cdot SbF_5$. All adducts are unstable at ambient temperature, and their dissociation enthalpies were determined from the dissociation pressure curves. Vibrational and multinuclear NMR spectra and theoretical calculations show that all compounds are oxygen-coordinated donor−acceptor adducts, and that the strengths of the oxygen bridges increase from COF_2 to $COCl_2$ and from AsF_5 to SbF_5. Full normal coordinate analyses of the adducts demonstrate that the bridging modes occur below 100 cm^{-1}, justifying the frequently used approximation of analyzing similar weak adducts in terms of their separate donor and acceptor molecules.

Introduction

In the course of an investigation of halocarbonyl cations,[1] it became necessary to study the competing Lewis base−Lewis acid interactions of the dihalocarbonyl compounds, $COCl_2$, COClF, and COF_2, with AsF_5 and SbF_5. Although the individual dihalocarbonyl and Lewis acid molecules are well characterized, little is known about their interactions.[2]

For $COCl_2$, no reports on the $AsF_5/COCl_2$ system were found, and the only report on the $SbF_5/COCl_2$ system consists of a brief comment[3] that with a 5-fold excess of SbF_5 in SO_2ClF solution at −78 °C a new signal was observed in the ^{13}C NMR spectrum, which was correctly attributed to the $COCl^+$ cation.[1] Other Lewis acids, which were studied in connection with $COCl_2$, include BF_3, BCl_3, $AlCl_3$, $AlBr_3$, $GaCl_3$, $SnCl_4$, $SbCl_5$, $MoCl_6$, WCl_6, and $PtCl_4$,[2] but only for $AlCl_3$ [4,5] and possibly $SbCl_5$ [4,6] was evidence presented for the existence of oxygen-coordinated 1:1 donor−acceptor adducts.

For COClF, the only reports on an interaction with Lewis acids are two NMR studies[3,7] with SbF_5 in SO_2ClF solution. The results from these studies indicate the presence of an oxygen-coordinated donor−acceptor adduct at low temperatures and halogen exchange at higher temperatures.

For COF_2, the presence of thermally unstable, oxygen-coordinated donor−acceptor complexes with SbF_5 and AsF_5 were first demonstrated by low-temperature ^{19}F NMR measurements,[7] and subsequently confirmed by low-temperature Raman spectroscopy.[8] However, no physical properties were reported for these adducts, and no reports could be found on other $COF_2 \cdot$ Lewis acid adducts.

Experimental Section

Materials and Methods. Carbonyl chloride (Matheson), COF_2 (PCR Research Chemicals), and AsF_5 (Ozark Mahoning) were used as received. Antimony pentafluoride (Ozark Mahoning) was distilled prior to use. The COClF was prepared by a literature method.[11]

The volatile materials were handled in a stainless steel vacuum line equipped with Teflon-FEP U-traps, 316 stainless steel bellows seal valves, and a Heise pressure gauge.[9] Nonvolatile materials were handled in the dry nitrogen atmophere of a glovebox. Raman spectra were recorded on a Cary model 83 GT using 1.5 W of the 488 nm exciting line of an Ar ion laser and flame-sealed Pyrex tubes as sample containers. A previously described[10] device was used for the recording of the low-temperature spectra. Infrared spectra were recorded on a Midac M FTIR spectrometer. NMR spectra were measured on a Varian Unity 300 MHz NMR spectrometer equipped with a 5 mm variable-temperature broad band probe. Sealed capillaries, which were filled with acetone-d_6 as lock substance, TMS as ^{13}C reference, and $CFCl_3$ or $C_6H_5CF_3$ as ^{19}F reference, were placed inside the NMR tubes with the listed ^{19}F shifts referenced to $CFCl_3$. For the NMR measurements, the corresponding adducts were prepared in 0.5" o.d. Teflon ampule using an excess of carbonyl halide, followed by removal of the excess at low temperature, transfer of the solid at −196 °C into an NMR tube in the dry box and addition of the solvent on the vacuum line.

For the dissociation pressure measurements, the 1:1 adducts of AsF_5 and SbF_5 with the carbonyl halides were preformed in a Teflon-FEP ampule, which was directly connected to a Heise pressure gauge. The

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equilibrium dissociation pressures were established for each temperature, approaching the equilibria from both sides, i.e., higher pressures and lower pressures. The thermochemical properties were derived in the same manner as previously described.[12] The method used for the tensiometric titration (vapor pressure−composition isotherm) of the AsF_5−COF_2 system has previously been described.[4]

Preparation of COF_2·AsF_5. Arsenic pentafluoride (3.75 mmol) and COF_2 (40.0 mmol) were combined in a 3/4″ o.d. Teflon-FEP ampule at −196 °C. The mixture was stirred at −78 °C for 1 h with a magnetic stirring bar, resulting in a suspension of a white solid in liquid COF_2. The excess of COF_2 was pumped off at −126 °C, leaving behind the white, solid COF_2·AsF_5 adduct in quantitative yield. The adduct melts in the range of −45 to −42 °C. Dissociation pressure (temperature [°C], pressure [mm]): (−100, 2), (−95, 4), (−90, 7), (−85, 13), (−81, 20), (−75, 38), (−71, 58), (−70, 66), (−66, 98), (−65, 108), (−64, 119), (−63, 131), (−62, 140), (−60, 168), (−57, 211), (−55, 253). NMR (SO_2ClF, −60 °C) for COF_2·AsF_5: $\delta(^{13}C)$ 137.8 ppm; $^1J(^{13}C-^{19}F)$ 330 Hz; $\delta(^{19}F)$ 16 ppm. For COF_2: $\delta(^{13}C)$ 130.0 ppm; $^1J(^{13}C-^{19}F)$ 313 Hz; $\delta(^{19}F)$ 23 ppm.

Preparation of COF_2·SbF_5. A mixture of SbF_5 (16.8 mmol) and COF_2 (40.0 mmol) was reacted, and the resulting white, solid 1:1 adduct isolated as described for COF_2·AsF_5. The yield of COF_2·SbF_5 was quantitative.

Preparation of COClF·AsF_5. A mixture of AsF_5 (1.7 mmol) and COClF (30.2 mmol) was stirred at −78 °C for 1 h. The excess of COClF was pumped off at −110 °C, leaving behind COClF·AsF_5 (1.7 mmol) as a white, solid powder melting in the range −42 to −39 °C. Dissociation pressure (temperature [°C], pressure [mm]): (−87, 3), (−84, 4), (−82, 5), (−80, 6), (−79, 7), (−78, 8), (−77, 9), (−76, 10), (−75, 11), (−74, 14), (−73, 16), (−72, 18), (−71, 20), (−70, 22), (−69, 25), (−68, 28), (−67, 32), (−66, 35), (−65, 39), (−64, 44), (−63, 50), (−62, 56), (−61, 62), (−60, 68), (−59, 76), (−58, 85), (−57, 94), (−56, 104), (−55, 117), (−54, 128), (−53, 140), (−52, 157), (−51, 170), (−50, 192), (−49, 224), (−48, 247), (−47, 275), (−46, 298), (−45, 320), (−44, 342), (−43, 363), (−42, 380).

Preparation of COClF·SbF_5. A mixture of SbF_5 (2.3 mmol) and COClF (15.6 mmol) was reacted as described for COClF·AsF_5, resulting in the quantitative formation of the white, solid COClF·SbF_5 adduct. NMR (SO_2ClF, −60 °C) for COClF·SbF_5: $\delta(^{13}C)$ 163.8 ppm; $^1J(^{13}C-^{19}F)$ 383 Hz; $\delta(^{19}F)$ 73.9 ppm. For COFCl: $\delta(^{13}C)$ 142.0 ppm; $^1J(^{13}C-^{19}F)$ 368 Hz; $\delta(^{19}F)$ 59.7 ppm. Dissociation pressure (temperature [°C] pressure [mm]): (−43, 3), (−40, 9), (−38, 11), (−36, 14), (−34, 19), (−29, 35), (−25, 54), (−23, 70), (−20, 96), (−16, 139), (−15, 152), (−13, 173), (−12, 187), (−11, 194), (−10, 200).

Preparation of $COCl_2$·AsF_5. A mixture of AsF_5 (12.0 mmol) and $COCl_2$ (30.0 mmol) was stirred at −78 °C for 1 h. The excess of $COCl_2$ was pumped off at −85 °C, leaving behind 3.2 g of a white solid (weight calcd for 12.0 mmol of $COCl_2$·AsF_5 = 3.226 g), melting at −20 ± 2 °C. NMR (SO_2ClF, −60 °C) for $COCl_2$·AsF_5: $\delta(^{13}C)$ 155.9 ppm. For $COCl_2$: $\delta(^{13}C)$ 143.7 ppm. Dissociation pressure (temperature [°C], pressure [mm]): (−63, 5), (−60, 9), (−58, 12), (−51, 22), (−44, 49), (−43, 59), (−42, 66), (−40, 85), (−38, 104), (−37, 115), (−35, 143), (−32, 186), (−29, 230), (−28, 260), (−27, 292), (−26, 330), (−25, 375), (−24, 421), (−22, 481).

Preparation of $COCl_2$·SbF_5. Antimony pentafluoride (4.3 mmol) was dissolved at −78 °C in 5 mL of liquid $COCl_2$. After 5 min the solution became turbid and a precipitate formed. After 1.5 h, the excess of $COCl_2$ was pumped off at −78 °C, leaving behind 4.3 mmol of $COCl_2$·SbF_5 in the form of a white powder. Dissociation pressure and NMR data could not be measured due to rapid F−Cl exchange resulting in COClF formation.

Computational Methods. The optimized geometries, vibrational spectra and NMR chemical shifts of the O-coordinated carbonyl halide ·MF_5 (M = As, Sb) adducts were calculated using density functional methods. The B3LYP hybrid functional[13] and the Stevens, Basch, Krauss, Jasien, and Cundari effective core potentials and the corresponding valence double-ζ basis sets[14] were used. The basis set was augmented with a diffuse s+p shell[15] and a single Cartesian d polarization function on each atom.[16] These calculations, hereafter denoted as B3LYP/SBK+(d), were performed using Gaussian 94 and 98.[17] The calculated Hessian matrixes (second derivatives of the energy with respect to Cartesian coordinates) were converted to symmetry-adapted internal coordinates for further analysis with the program systems GAMESS[18] and Bmtrx.[19]

Results and Discussion

Synthesis and Properties of the COX_2·MF_5 (X = Cl, F; M = As, Sb) Adducts. Both SbF_5 and AsF_5 form with an excess of either $COCl_2$, COFCl or COF_2 exclusively O-coordinated 1:1 donor−acceptor complexes (eq 1).

$$MF_5 + COX_2 \xrightarrow[-78\ ^\circ C]{COX_2} \underset{(X = F, Cl;\ M = As, Sb)}{COX_2 \cdot MF_5} \qquad (1)$$

The 1:1 compositions were established by the observed material balances and for the COF_2/AsF_5 system by a tensimetric titration (vapor pressure−composition isotherm)[4] at −78 °C which gave evidence only for a 1:1 adduct. The resulting adducts are white solids which are thermally unstable and decompose reversibly to the starting materials, except for the $COCl_2$/SbF_5 system for which rapid irreversible fluorine−chlorine exchange is observed (eq 2).[11]

$$COCl_2 \cdot SbF_5 \rightarrow COClF + \text{“}SbF_4Cl\text{”} \qquad (2)$$

The oxygen-bridged nature of these adducts was established by vibrational and multinuclear NMR spectroscopy and the results

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Table 1. Thermochemical Data for the Dissociation of the $X_2CO{\cdot}MF_5$ Donor−Acceptor Adducts and Their Heats of Formation

	$H_d°$ [a] kcal/mol	T (1 atm)[b] °C	P_{298}[c] atm	$F°_{298}$[d] kcal/mol	$S°_{298}$[e] cal/deg mol	$H°_{f298}(X_2CO{\cdot}AsF_5)$[f] kcal/mol
$Cl_2CO{\cdot}AsF_5$	22.75	−16.8	22.78	−2.882	85.98	−370.81
$ClFCO{\cdot}AsF_5$	19.15	−34.5	56.15	−3.951	77.49	−416.61
$F_2CO{\cdot}AsF_5$	16.17	−41.5	50.19	−3.818	67.05	−464.33
$ClFCO{\cdot}SbF_5$	13.91	0.6	8.07	−0.826	49.41	−433.15

[a] Enthalpies of dissociation, calculated from the slope of the log P vs T^{-1} curves. [b] Extrapolated temperatures at which the dissociation pressures of the solid adducts would reach a dissociation pressure of 760 mm. [c] Extrapolated dissociation pressures at 298 K. [d] Values for the free energy change at 298 K. [e] Values for the entropy changes at 298 K. [f] Standard heats of formation of the solid adducts using the dissociation enthalpies of this work and the following literature values for the heats of formation: $H_f°_{298}(COCl_{2(g)}) = -52{,}600$; $H_f°_{298}(COFCl_{(g)}) = -102.00$; $H_f°_{298}(COF_{2(g)}) = -152.700$; $H_f°_{298}(AsF_{5\ (g)}) = -295.461$; $H_f°_{298}(SbF_{5\ (l)}) = -317.248$ kcal/mol.

from the theoretical calculations. Only for COClF with at least a 3-fold excess of SbF_5 does the formation of ionic salts containing the $ClCO^+$ cation become energetically more favorable (eq 3).[1]

$$COClF + 3SbF_5 \rightarrow ClCO^+Sb_3F_{16}^- \qquad (3)$$

The preferential formation of oxygen-coordinated 1:1 donor−acceptor adducts in these systems is in accord with the previous Raman study of the $COF_2{\cdot}MF_5$ (M = As, Sb) systems,[8] a ^{19}F NMR study of the $COClF{\cdot}SbF_5$ system,[7] and a tensimetric and IR spectroscopic study of the $COCl_2/AlCl_3$ system.[4]

Thermochemical Properties. Based on the vapor pressure data given in the Experimental Section, plots of log P versus T^{-1} for the heterogeneous equilibria (eqs 4 and 5) give straight lines,

$$COX_2{\cdot}AsF_5(s) \rightleftharpoons COX_2(g) + AsF_5(g) \qquad (4)$$

$$COClF{\cdot}SbF_5(s) \rightleftharpoons COClF(g) + SbF_5(s) \qquad (5)$$

which can be described by the following equations:

$$COCl_2{\cdot}AsF_5\ (210-251\ K):\ \log P\ (mm) = -2486.13/T\ (K) + 12.5768$$

$$COClF{\cdot}AsF_5\ (186-231\ K):\ \log P\ (mm) = -2092.67/T\ (K) + 11.649$$

$$COF_2{\cdot}AsF_5\ (173-218\ K):\ \log P\ (mm) = -1767.12/T\ (K) + 10.5084$$

$$COClF{\cdot}SbF_5\ (230-263\ K):\ \log P\ (mm) = -3038.9/T\ (K) + 13.98$$

The thermochemical properties, derived from these data by standard procedures,[12] are summarized in Table 1. Literature values were used for the required heats of formation of AsF_5,[20] SbF_5,[21] and the carbonyl halides.[22] Table 1 shows that the stability of the $COX_2{\cdot}MF_5$ adducts decreases from SbF_5 to AsF_5, as expected for the decrease in Lewis acidity, and from $COCl_2$ to COF_2, as expected from a decreasing basicity of the oxygen with increasing electron density withdrawal by the more electronegative fluorine ligands. The decrease in the dissociation energy $\Delta H_d°$ from $COClF{\cdot}AsF_5$ to $COClF{\cdot}SbF_5$ should not be mistaken as an indication of a weaker adduct. The decrease in $\Delta H_d°$ is caused by the fact that at the investigated dissociation temperatures the SbF_5 decomposition product is a solid and not a gas. Therefore, the value of $\Delta H_d°$ is only one-half of that expected for the formation of 2 mol of gas from 1 mol of solid. The slopes of the log P versus T^{-1} curves, which are independent of the number of moles of gas in the decomposition products, reflect the expected stability trends, i.e., $COCl_2{\cdot}AsF_5$ > $COClF{\cdot}AsF_5$ > $COF_2{\cdot}AsF_5$ and $COClF{\cdot}SbF_5$ > $COClF{\cdot}AsF_5$. The same stability trend is also displayed by the extrapolated temperature values at which the adducts would reach a dissociation pressure of one atmosphere (see Table 1). A comparison of the data of Table 1 with the previously reported[4] dissociation pressure of 440 mm at 25 °C for $COCl_2{\cdot}AlCl_3$ suggests that the stability of the $COCl_2{\cdot}AlCl_3$ adduct is significantly higher than that of $COCl_2{\cdot}AsF_5$.

NMR Spectra. The results of our ^{13}C and ^{19}F NMR study are summarized in Table 2. In agreement with a previous observation,[7] difficulties were encountered in observing well resolved signals for some of the systems at low temperatures due to exchange phenomena. Table 2 shows that on formation of the donor−acceptor adducts both the ^{13}C and ^{19}F signals of the free carbonyl halides are shifted to lower fields, as expected from a deshielding of these nuclei by the electron-withdrawing effect of the Lewis acids. These shifts vary from about 5 to 20 ppm and appear to be larger for the stronger Lewis acid SbF_5. The magnitudes and directions of these shifts were confirmed by our theoretical calculations at the B3LYP/vdz+p level of theory using the GIAO method (see Table 2).

Since our NMR measurements were carried out at temperatures at which some of the adducts exhibit significant dissociation pressures, the possibility that the signals, observed for the carbonyl halide part of the adducts, might represent exchange-averaged spectra for an equilibrium mixture of COX_2 and $COX_2{\cdot}SbF_5$ had to be considered. For the COF_2-SbF_5 and $COClF-SbF_5$ systems it was found that the observed shifts and coupling constants of the signals, attributed to the free carbonyl halides and their SbF_5 adducts, remained unchanged whether an excess of carbonyl halide or SbF_5 was used, and only their relative intensities varied. Furthermore, in the ^{19}F spectrum of $COF_2{\cdot}SbF_5$ in SO_2ClF solution at −100 °C a well-resolved AX_4 pattern, characteristic for coordinated SbF_5,[7] was observed (δ −109.3, doublet, area of 4; δ −142.4, quintet, area of 1; $^1J(F-F) = 96$ Hz), indicating that the observed $COF_2{\cdot}SbF_5$ spectrum was not influenced by exchange processes. In addition to the $COF_2{\cdot}SbF_5$ signals, a separate resonance due to free nonexchanging COF_2 was observed at −179 ppm in the ^{19}F spectrum.

The previously reported[3,7] NMR data are for the most part ambiguous. Thus, the report[3] on the $COClF{\cdot}SbF_5$ adduct in SO_2ClF at −80 °C listed only ^{13}C data with a wide shift range of 150−175 ppm which do not permit a meaningful comparison with the signal of free COClF.

The other previous report[7] dealt only with the ^{19}F spectra of $COF_2{\cdot}SbF_5$, $COFCl{\cdot}SbF_5$ and $COF_2{\cdot}AsF_5$ in SO_2ClF solution and also contained some ambiguities. Thus, for $COF_2{\cdot}AsF_5$ no

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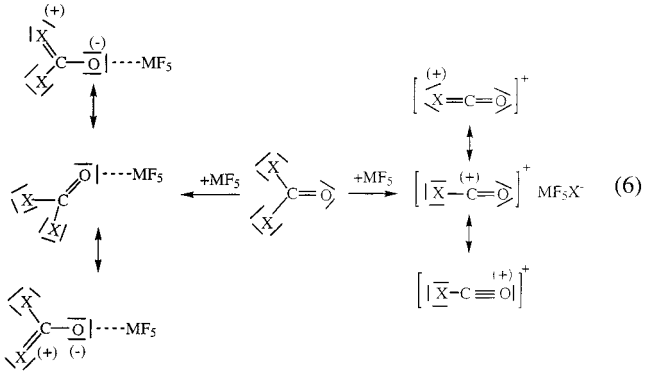
Table 2. Selected ^{13}C and ^{19}F NMR Parameters for COF_2, COClF, $COCl_2$, and Some of their Lewis Acid Adducts

	chemical shifts (ppm)				
	δ (^{13}C)		δ (^{19}F)		coupling constant (Hz)
	obsd[a]	calcd[b]	obsd[a]	calcd[b]	^1J ($^{13}C-^{19}F$) obsd[a]
COF_2[g]	130.0 (134.2)[c]	133.0	−18.3 (−23.0)[c] (−19.6)[d]	−28.7	308 (309)[c]
COClF	142.0 (140.5)[c]	143.6	59.7[a,c]	54.5	368 (366)[c]
$COCl_2$	143.7 (141.8)[c]	154.0	–	–	–
$COF_2 \cdot AsF_5$	137.8	137.4	−16	−20.4	330
$COF_2 \cdot SbF_5$[g]	145.5	139.7	2.5 (2.1)[d]	−12.6	325
$COClF \cdot AsF_5$	–	152.8[e] (152.8)[f]	–	59.0[e] (54.7)[f]	–
$COClF \cdot SbF_5$	163.8	157.7[e] (158.3)[f]	73.9	66.4[e] (58.5)[f]	383
$COCl_2 \cdot AsF_5$	155.9	167.7	–	–	–
$COCl_2 \cdot SbF_5$	–	176.3	–	–	–

[a] All data are from this study, unless noted otherwise, and were recorded in SO_2ClF solutions at −60 °C. [b] Calculated at the B3LYP/vdz+p level using the GIAO method. "vdz+p" denotes a mixed valence double zeta plus polarization basis set, constructed as follows: SBKJC effective core potentials and valence basis sets, augmented with a diffuse s+p shell and a single Cartesian d polarization function, were used for Sb and As. The 6-311G(d) basis set was used for all other atoms. [c] Data from Gombler, W. *Spectrochim. Acta, Part A* **1981**, *37*, 57. [d] Data from ref 7. [e] Isomer in which the fluorine ligand of COClF points toward the MF_5 molecule. [f] Isomer in which the chlorine ligand points toward the MF_5 molecule. [g] Recorded in SO_2ClF at −100 °C.

signal for coordinated COF_2 was observed at −100 °C, leading to the incorrect conclusion that even at this low-temperature complexation must be incomplete. Furthermore, for a concentrated $COClF/SbF_5$ solution at −80 °C, only signals due to free COF_2 and $COF_2 \cdot SbF_5$ were observed, while for a dilute solution at −95 °C a signal at 59.9 ppm was attributed to $COClF \cdot SbF_5$. However, this shift is almost identical to that of 59.7 ppm found in our study for free COClF and is quite different from that of 73.9 ppm, found by us for the $COClF \cdot SbF_5$ adduct. The previous report by Bacon, Dean, and Gillespie on the $COF_2 \cdot SbF_5$ adduct in SO_2ClF solution at −100 °C using an excess of SbF_5[7] is in excellent agreement with our findings (see Table 2) using either stoichiometric amounts or an excess of COF_2. In all cases, the shift of the COF_2 signal in the adduct was about 21 ppm downfield from that of free COF_2. It supports our conclusion that the stronger Lewis acid SbF_5 deshields the fluorine ligands of the coordinated carbonyl halides more strongly than AsF_5. Inspection of the $^1J(^{13}C-^{19}F)$ coupling constants of Table 2 shows that the C−F coupling increases upon complexation. This is in accord with the increased C−X bond strengths of the adducts, as shown by the valence bond structure (eq 6).

Vibrational Spectra and Theoretical Calculations. Vibrational spectra are well suited to distinguish between ionic salts and covalent donor−acceptor adducts.[1,23] As shown by the valence bond structures (eq 6), the C−O and C−X bond orders



and, therefore, also their stretching frequencies decrease and the C−X stretching frequencies increase, compared to the free COX_2 molecule. Furthermore, a $COX^+SbF_5X^-$ salt should exhibit only 18 normal modes, while a covalent donor−acceptor adduct should possess 24.

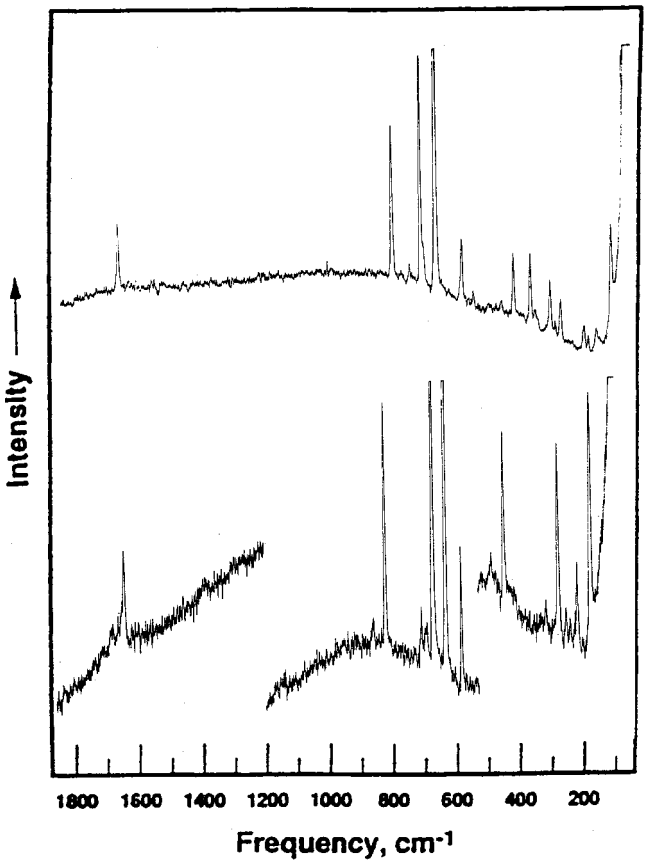


Figure 1. Raman spectra of solid $COCl_2 \cdot AsF_5$ (upper trace) and $COCl_2 \cdot SbF_5$ recorded at −130 °C.

The observed low-temperature Raman spectra of the solid 1:1 complexes of Cl_2CO and ClFCO with AsF_5 and SbF_5 are shown in Figures 1 and 2, and the observed frequencies are summarized in Tables 3 and 4. The large number of observed Raman bands, their frequency shifts relative to the free carbonyl halides,[24] and the excellent fit with the calculated frequencies and intensities (see Tables 3 and 4) leave no doubt that these complexes are O-coordinated donor−acceptor adducts.

Traditionally, the vibrational spectra of this type of covalent donor−acceptor adducts have been analyzed in terms of their

(23) Lindquist, I. Inorganic Adduct Molecules of Oxo-Compounds. In *Anorganische und Allgemeine Chemie in Einzeldarstellungen*, Becke-Goehring, M., Ed.; Academic Press Inc.: New York, 1963; Band IV.

Table 3. Calculated (B3LYP/SBK+(d) Vibrational Frequencies and Observed Raman Spectra of the $COCl_2 \cdot MF_5$ (M = As, Sb) Adducts and Their Analyses Based on the Point Groups of the Adducts and the Individual Donor and Acceptor Molecules

assignments, approx. mode descript			freq, cm^{-1}, intensities[a]			
			$COCl_2 \cdot AsF_5$		$COCl_2 \cdot SbF_5$[c]	
MF_5 C_{4v}	$COCl_2$ C_{2v}	$COCl_2 \cdot MF5$ C_s	obsd Ra	calcd (IR)[Ra]	obsd Ra	calcd (IR) [Ra]
	$\nu_1(A_1)$ 1827	$\nu(A')\nu$ C=O	1610[33]	1768(671)[43]	1587[14]	1718(740)[29]
	$\nu_4(B_1)$ 849	$\nu_2(A')\nu$ as CCl_2	978[11]	896(460)[9.7]	989[3.4]	930(430)[6.1]
$\nu_{7(E)}$		$\nu_3(A')\nu$ as MF_4	770[4]	734(127)[0.35]	708[2]	667(90)[2.2]
		$\nu_{16}(A'')\nu$ as MF_4	733[1]	736(152)[0.09]	−	667(114)[0.13]
$\nu_1(A_1)$		$\nu_4(A')\nu$ MF′	757[44]	742(153)[8.3]	683[22]	665(114)[5.5]
$\nu_2(A_1)$		$\nu_5(A')\nu$ s MF_4 in phase	698[100]	663(1.7)[30]	654[100]	617(5.7)[34]
	$\nu_2(A_1)$ 567	$\nu_6(A')$ ν s CCl_2	660[52]	597(8.4)[16.4]	676[66]	623(0.27)[3.9]
$\nu_4(B_1)$		$\nu_{17}(A'')$ ν s MF_4 out of phase	615[15]	597(0.21)[2.8]	608[16]	577(0.34)[2.3]
	$\nu_6(B_2)$ 580	$\nu_{18}(A'')$ δ MOCCl out of plane	592[2]	582(3.3)[0.02]	600sh	585(3.3)[0.08]
	$\nu_5(B_1)$ 440	$\nu_7(A')$ δ MOCCl in plane	538[22]	471(0.25)[4.6]	528[9]	484(2.7)[4.1]
$\nu_3(A_1)$		$\nu_8(A')$ δ sciss MF_4	402[19]	403(0.03)[1.6]	303[0.21]	307(0.12)[1.5]
$\nu_8(E)$		$\nu_{19}(A'')$ δ FMF_4 out of plane	391[4]	380(47)[0.26]	286[8]	287(53)[0.34]
		$\nu_9(A')$ δ FMF_4 in plane	380[11]	379(42)[0.33]	279[4]	283(46)[0.18]
	$\nu_3(A_1)$ 285	$\nu_{10}(A')$ δ sciss CCl_2	360[33]	308(46)[4.2]	394[37]	322(2.7)[5.1]
$\nu_6(B_2)$		$\nu_{11}(A')$ δ umbrella MF_4	328[15]	331(83)[2.4]	260[2]	262(141)[0.17]
$\nu_9(E)$		$\nu_{12}(A')$ δ as MF_4 in plane	304[29]	276(0.88)[1.7]	236[16]	221(0.90)[1.3]
		$\nu_{20}(A'')$ δ as MF_4 in plane	238[11]	278(0.63)[0.84]	−	233(0.48)[0.42]
		$\nu_{21}(A'')$ δ wag $COCl_2$	181[14]	165(0.20)[0.61]	190[21]	165(0.20)[0.85]
		$\nu_{13}(A')$ δ rock $COCl_2$	140[13]	125(1.2)[0.55]	146[22]	134(8.4)[0.91]
$\nu_5(B_1)$		$\nu_{22}(A'')$ δ pucker MF_4	−	115(0)[0]	−	119(0)[0.01]
		$\nu_{14}(A')$ νM−O	−	74(15)[0.04]	−	104(13)[0.15]
		$\nu_{15}(A')$ δM−O−C	−	49(1.9)[0.36]	−	60(0.04)[0.18]
		$\nu_{23}(A'')$ τ C−O	−	38(0.15)[1.2]	−	45(0.06)[0.88]
		$\nu_{24}(A'')$ τ M−O	−	16(0.09)[1.2]	−	24(1.0)[1.38]

[a] Calculated infrared and Raman intensities in km/mol and $Å^4$/amu, respectively. [b] Data from ref 24. [c] In the Raman spectrum of solid $COCl_2 \cdot SbF_5$ two additional bands were observed at 442[8] and 346[15] cm^{-1} which were of variable intensity and probably do not belong to the adduct (see text).

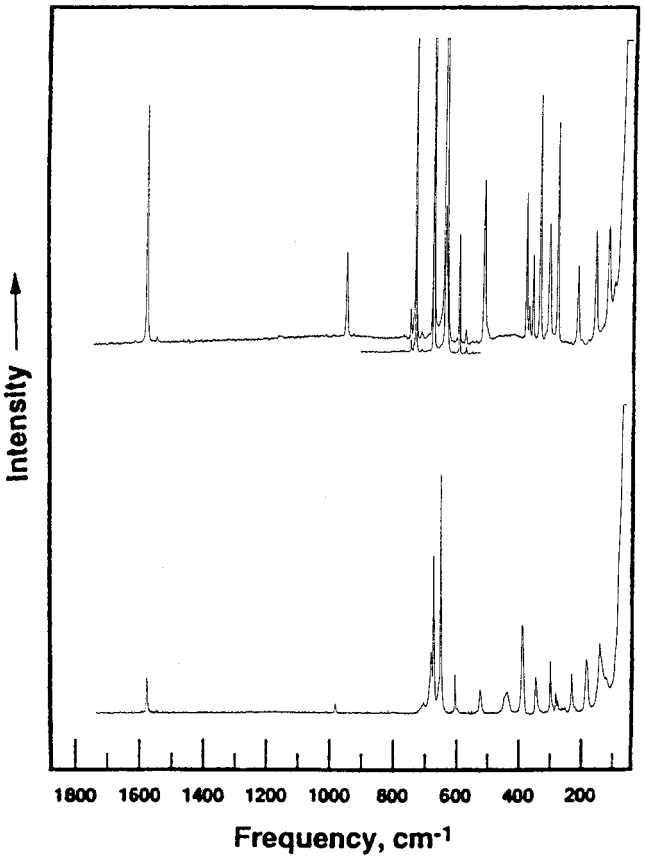


Figure 2. Raman spectra of solid $COClF \cdot AsF_5$ (upper trace) and $COClF \cdot SbF_5$ (lower trace) recorded at −130 °C.

separate components in their original point groups, ignoring the bridge modes and the splittings of degenerate modes caused by the symmetry lowering in the adducts. This approach has generally been quite useful and has permitted the analysis of the gross features of the spectra, particularly when the donor−acceptor interactions are relatively weak and the splittings of the degenerate modes are small. However, a rigorous analysis of the finer details of the observed spectra requires a treatment in the correct point group of the adduct, as shown in Table 3. The resulting agreement between the observed and calculated spectra of $COCl_2 \cdot AsF_5$ is very good. The fact that the observed carbonyl stretching frequency is lower and the CCl_2 stretching frequencies are higher than those calculated indicates that in the condensed phase the interactions between the carbonyl halides and the Lewis acids are stronger than those predicted for the free gaseous adducts. Therefore, the calculated optimized geometries, shown in Figure 3, are expected to exhibit somewhat longer M−O and shorter C−O bonds than those expected for the condensed phase. The theoretical results furthermore predict that the modes due to the M−O bridge should occur below 100 cm^{-1} and, hence, justify the traditional approach of neglecting the bridge modes in a vibrational analysis. Finally, it should be noted, that our normal coordinate analyses show that, contrary to the previous assignments[8] and those generally given for closely related C_{4v} MF_4F species,[25,26] the frequencies of the MF_5 deformation modes decrease in the following order: δ(scissor

(24) (a) Shimanouchi, T. *J. Phys. Chem. Ref. Data* **1977**, *6*, 993 and references therein. (b) Shimanouchi, T. *Tables of Molecular Vibrational Frequencies, Consolidated Volume 1*; NSRDS-NBS39, Nat. Stand. Ref. Data Ser.; National Bureau Standards (U.S.): Gaithersburg, MD, 1972, and references therein.

(25) Siebert, H. Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie. *Anorganische und Allgemeine Chemie in Einzeldarstellungen*; Becke-Goehring, M., Ed.; Springer-Verlag: Berlin, 1966, Band VII.

(26) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds* 5th ed.; John Wiley & Sons: New York, 1997; Part A.

Table 4. Calculated (B3LYP/SBK + (d)) Vibrational Frequencies and Observed Raman Spectra of the $COClF{\cdot}MF_5$ (M = As, Sb) Adducts and Their Analyses Based on the Point Groups of the Adducts and the Individual Donor and Acceptor Molecules

assignments, approx mode descript			freq, cm^{-1}, intensities			
			$COClF{\cdot}AsF_5$		$COClF{\cdot}SbF_5$	
MF_5 C_{4v}	COClF C_s obsd[a]	$COClF{\cdot}MF_5$ C_s	obsd Ra	calcd[c] (IR)[Ra]	obsd Ra	calcd[c] (IR)[Ra]
	ν_1(A′) 1868	ν_1(A′) ν C═O	1701[40]	1826(695)[38]	1669[8]	1789(751)[25]
	ν_2(A′) 1095	ν_2(A′) ν CF	1220[1]	1167(416)[4]	1257(vs)[b]	1208(412)[2.0]
ν_7(E)		ν_3(A′) ν as MF_4	780[5]	735(147)[0.17]	712[2]	667(112)[2.0]
		ν_{16}(A″) ν as MF_4	732[5]	736(160)[0.06]		670(126)[0.22]
ν_1(A_1)		ν_4(A′) ν MF′	742[52]	743(173)[5.8]	689[42]	668(106)[4.0]
ν_2(A_1)		ν_5(A′) ν s MF_4 in phase	695[100]	663(2.2)[31]	651[100]	621(2.3)[28]
	ν_3(A′) 776	ν_6(A′) ν CCl	835[35]	781(47)[15]	842[21]	795(50)[13]
ν_4(B_1)		ν_{17}(A″) ν s MF_4 out of phase	616[16]	597(0.13)[3.1]	603[15]	578(0.36)[2.6]
	ν_6(A″) 667	ν_{18}(A″) δ MO CCl out of plane	580[4]	659(8.5)[0.32]	590[2]	660(2.4)[0.20]
	ν_4(A′) 501	ν_7(A′) δ MO CCl in plane	453[16]	520(2.1)[5.2]	470[15]	536(6.8)[3.4]
ν_3(A_1)		ν_8(A′) δ sciss MF_4	401[13]	404(0.01)[1.6]	301[18]	308(0.08)[1.6]
ν_8(E)		ν_{19}(A″) δ FMF_4 out of plane	390[4]	380(48)[0.25]	275[3]	287(53)[0.30]
		ν_9(A′) δ FMF_4 in plane	382[2]	379(43){0.26]		285(49)[0.29]
	ν_5(A′) 415	ν_{10}(A′) δ sciss ClCF	340[9]	420(0.29)[2.3]	337[3]	429(1.9)[2.4]
ν_6(B_2)		ν_{11}(A′) δ umbrella MF_4	325[3]	327(125)[1.9]	265[2]	264(134)[0.27]
ν_9(E)		ν_{12}(A′) δ as MF_4 in plane	306[10]	276(0.83)[1.0]	240[8]	223(0.98)[0.79]
		ν_{20}(A″) δ as MF_4 in plane	233[5]	278(0.69)[0.86]		232(0.77)[0.41]
		ν_{21}(A″) δ wag COClF	197[4]	164(0.12)[0.45]	198[20]	165(0.13)[0.73]
		ν_{13}(A′) δ rock COClF	148[17]	137(1.2)[0.13]		146(5.5)[0.60]
ν_5(B_1)		ν_{22}(A″) δ pucker MF_4		114(0)[0]		115(0)[0]
		ν_{14}(A′) ν M−O		76(15)[0.21]		109(14)[0.20]
		ν_{15}(A′) δ M-O−C		53(1.6)[0.31]		62(0.05)[0.27]
		ν_{23}(A″) τ C═O		36(0.13)[1.1]		41(0.06)[0.64]
		ν_{24}(A″) τ M−O		28(0.02)[0.51]		32(0.01)[0.81]

[a] Data from ref 2.4. [b] Frequency and intensity from the infrared spectrum. [c] The listed calculated frequencies are for the isomers in which the fluorine atom of the COClF unit is pointed toward MF_5.

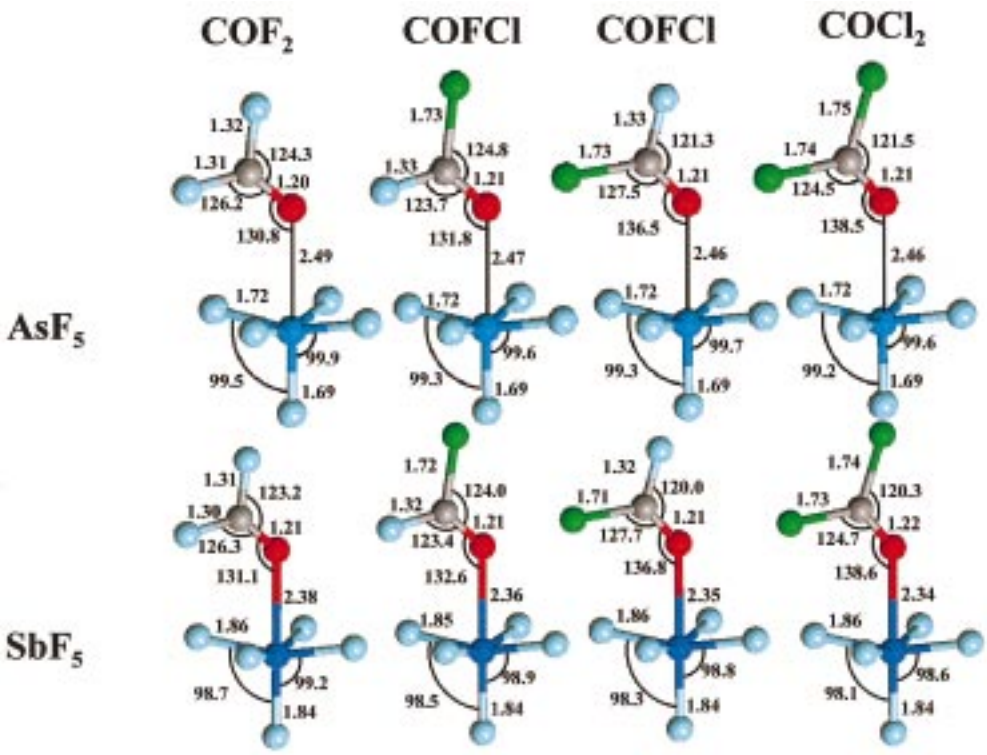


Figure 3. Geometries optimized at the B3LYP/SBK+(d) level for $COCl_2{\cdot}MF_5$, $COClF{\cdot}MF_5$ and $COF_2{\cdot}MF_5$ (M = As (Sb)). The optimized geometries of the free carbonyl halides at the same level are as follows: $COCl_2$, *r*CO = 1.195 Å, *r*CCl = 1.772 Å, ∠OCCl = 123.8°; COClF, *r*CO = 1.192 Å, *r*CCl = 1.755 Å, *r*CF = 1.345 Å, ∠OCCl = 126.6°, ∠OCF = 123.9°; COF_2, *r*CO = 1.189 Å, *r*CF = 1.332 Å, ∠OCF = 126.2°. As expected, in the adducts the C−O bonds are longer, the C−X bonds are shorter, and the O−C−X angles are smaller than in the free carbonyl halides.

MF_4 in plane) > δ(FMF_4) > δ(umbrella MF_4) > δ(asym MF_4 in plane).

The observed Raman spectra of $COCl_2{\cdot}MF_5$ (M = As, Sb) agree very well with the calculations, except for two extra bands observed for $COCl_2{\cdot}SbF_5$ at 442 and 346 cm^{-1}. These bands occur in the Sb−Cl region and are tentatively attributed to some halogen exchange between $COCl_2$ and SbF_5 which is known[11] to occur rapidly at slightly elevated temperatures.

For the $COClF{\cdot}MF_5$ adducts, two conformers are possible because either the fluorine or the chlorine ligand of COClF could

Table 5. Calculated (B3LYP/SBK+(d)) Vibrational Frequencies and Literature[a] Raman Spectra of the $COF_2 \cdot MF_5$ (M = As, Sb) Adducts and Their Analyses

assignments, approx mode descript			freq, cm^{-1}, intensities			
			$COF_2 \cdot AsF_5$		$COF_2 \cdot SbF_5$	
MF_5 C_{4V}	COF_2 C_{2v} obsd[b]	$COF_2 \cdot MF_5$ C_s	obsd Ra	calcd (IR)[Ra]	obsd Ra	calcd (IR)[Ra]
	$\nu_1(A_1)$ 1928	$\nu_1(A')\nu$ C=O	1788[12]	1896(704)[22]	1770[9]	1866(753)[13]
	$\nu_4(B_1)$ 1249	$\nu_2(A')\nu$ as CF_2	1402[5]	1314(407)[4.2]	1436[4]	1360(398)[3.3]
$\nu_7(E)$		$\nu_3(A')\nu$ as MF_4	776[7]	736(146)[0.48]	716[19]	669(108)[2.0]
		$\nu_{16}(A'')\nu$ as MF_4	~735[7]	736(117)[0.11]	701[29]	669(108)[0.12]
$\nu_1(A_1)$		$\nu_4(A')\nu$ MF′	765[18]	746(142)[6.1]	673[82]	671(98)[4.1]
$\nu_2(A_1)$		$\nu_5(A')\nu$ s MF_4 in phase	701[100]	664(2.8)[26]	658[100]	622(2.2)[23]
	$\nu_2(A_1)$ 965	$\nu_6(A')$ ν s CF_2	1037[20]	993(3.7)[9.8]	1050[28]	1013(26)[10]
$\nu_4(B_1)$		$\nu_{17}(A'')$ ν s MF_4 out of phase	615[16]	597(0.28)[3.1]	600[23]	578(0.64)[2.6]
	$\nu_6(B_2)$ 774	$\nu_{18}(A'')$ δ $MOCF_2$ out of plane	792[3]	756(74)[0.56]	774[6]	757(43)[0.52]
	$\nu_5(B_1)$ 626	$\nu_7(A')$ δ $MOCF_2$ in plane	673[4]	623(13)[1.5]	coincid.[d]	634(16)[3.3]
$\nu_3(A_1)$		$\nu_8(A')$ δ umbrella MF_4	406[13]	405(0.02)[1.7]	303[28]	309(0.09)[1.6]
$\nu_8(E)$		$\nu_{19}(A")$ δ FMF_4 out of plane	351[4][e]	381(48)[0.19]	285[5]	288(52)[0.19]
		$\nu_9(A')$ δ FMF_4 in plane		380(45)[0.20]		285(50)[0.21]
	$\nu_3(A_1)$ 584	$\nu_{10}(A')$ δ sciss CF_2	606[4]	575(3.9)[1.0]	606 sh	581(3.0)[1.0]
$\nu_6(B_2)$		$\nu_{11}(A')$ δ sciss MF_4	328[7]	332(96)[0.68]	265[14]	268(101)[0.19]
$\nu_9(E)$		$\nu_{12}(A')$ δ as MF_4 in plane	308[9]	276(0.95)[1.1]	226[14]	222(2.8)[0.98]
		$\nu_{20}(A'')$ δ as MF_4 in plane	238[4]	277(0.84)[1.0]	242[14]	232(1.3)[0.69]
		$\nu_{21}(A'')$ δ wag COF_2	−	165(0.05)[. 19]	194[19]	167(0.04)[0.37]
		$\nu_{13}(A')$ δ rock COF_2	−	142 (5.4)[0.07]	−	163(20)[0.17]
$\nu_5(B_1)$		$\nu_{22}(A'')$ δ pucker MF_4	−	108(0)[0]	−	112(0)[0]
		$\nu_{14}(A')$ ν M−O	−	87(14)[0.15]	−	115(7.9)[0.09]
		$\nu_{15}(A')$ δ M−O−C	−	55(0.82)[0.01]	−	65(0)[0.03]
		$\nu_{23}(A'')$ τ C=O	−	42(0.01)[0.47]	−	47(0)[0.40]
		$\nu_{24}(A'')$ τ M−O	−	24(0.20)[0.27]	−	34(0.20)[0.25]

[a] The observed frequencies were taken from ref 8. [b] Data from ref 24. [c] Weak bands shown in the figures but not listed in the tables of ref 8. [d] Coincidence with either 658[100] or 673[82]. [e] Figure 3 of ref 8 shows weak bands in the 380 cm^{-1} region, which might also belong to ν_{19} and ν_9 of the adduct.

be oriented toward the MF_5 group. The two conformers differ only very little in energy (~0.1 kcal/mol) and their calculated vibrational spectra are almost identical. Therefore, the observed Raman spectra do not allow to distinguish between the two conformers, and the ones with the fluorines pointing toward the MF_5 groups were chosen for our analyses (see Table 4). The MF_5 bands in their COClF adducts agree well with those of the corresponding $COCl_2$ adducts, but the deviations between the observed and calculated bands for the COClF part of the adducts are larger than those for the $COCl_2$ adducts.

For the $COF_2 \cdot MF_5$ adducts, good quality Raman spectra have previously been reported[8] by Chen and Passmore, and their experimental data are compared with our calculations in Table 5. Again, the overall agreement is very satisfactory.

A comparison of the relative changes of the carbonyl halide stretching frequencies within the $COCl_2 \cdot MF_5$, $COFCl \cdot MF_5$ and $COF_2 \cdot MF_5$ series shows that the strength of the adducts increases from COF_2 to $COCl_2$ and from AsF_5 to SbF_5, i.e., with increasing basicity of the donor and increasing acidity of the acceptor. Hence, $COCl_2 \cdot SbF_5$ is the strongest and $COF_2 \cdot AsF_5$ the weakest adduct within this series.

Conclusion

Even with strong Lewis acids, such as AsF_5 or SbF_5, the carbonyl halides, $COCl_2$, COFCl, and COF_2, preferentially form O-coordinated donor−acceptor adducts. The stability of the adducts increases with increasing basicity of the donor, i.e., from COF_2 to $COCl_2$, and with increasing acidity of the acceptor, i.e., from AsF_5 to SbF_5. This conclusion is strongly supported by thermochemical measurements, vibrational and multinuclear NMR spectroscopy and theoretical calculations.

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