Table I. Data for $Cr_2(OAc)_4$ in $HOAc/H_2O$ Media[a]

$[H_2O]$, M	$\{H_2O\}$, M	$(K_D/4\epsilon)^{-1/2}$, 10^{-3} M $cm^{1/2}$	ϵ^{-1}, 10^{-3} M cm	ϵ, M^{-1} cm^{-1}	log (K_D/M)
8.32	27.5	0.033 ± 0.022[b]	5.95	168	−6.15 ± 0.3
8.88	28.4	0.025 ± 0.010	5.48	182	−6.4 ± 0.2
13.32	34.3	0.050 ± 0.026	5.84	171	−5.8 ± 0.25
14.98	36.1	0.073 ± 0.050	5.95	168	−5.45 ± 0.3
16.1	37.2	0.075 ± 0.035	5.59	178	−5.4 ± 0.2
20.3	40.9	0.110 ± 0.045	6.21	161	−5.1 ± 0.2
55.5	55.5				−4.35

[a] T = 25 °C, λ = 470 nm. [b] Limits of error are estimated as $(S/N)^{1/2}$ where S is the sum of squares of residuals in the least-squares fit of eq 4 and N is the number of data points.

storage vessels described previously,[3a] by using hypodermic syringes with glass needles. Concentrations were determined by weight, and chromium(II) concentrations were checked after measurement by titrating standard solutions of iodine in acetic acid, into the same cells, to a spectrophotometric end point.

Results

Writing the equilibrium in the generalized form

$$Cr^{II}_2 \overset{K_D}{\rightleftharpoons} 2Cr^{II} \qquad (1)$$

where Cr^{II}_2 and Cr^{II} denote the aggregates of all binuclear and all mononuclear species and assuming that absorption by the monomer is negligible at the wavelength used, we obtain the absorbance A as

$$A = \epsilon l\,[Cr^{II}_2] \qquad (2)$$

where ϵ is the extinction coefficient per mole of dimer and l is the path length. Defining the total chromium(II) concentration by

$$C = [Cr^{II}] + 2[Cr^{II}_2] \qquad (3)$$

and using $K_D = [Cr^{II}]^2/[Cr^{II}_2]$ we obtain

$$\frac{C}{2A^{1/2}} = \frac{A^{1/2}}{\epsilon l} + \left(\frac{K_D}{4\epsilon l}\right)^{1/2} \qquad (4)$$

Values of A were measured at 470 nm, at concentrations in the range C = 0.06–1.6 mM. Data were fitted to eq 4 to yield the parameters listed in Table I.

Cheng and Howald[5] correlated their results for the copper(II) acetate system with the molar concentration of water in the solvent mixture and found a fourth-power dependence, log K_D = −5.0 + 4.0 log $[H_2O]$, though an empirical equation log K_D = −4 + 0.29$[H_2O]$ gave an almost equally good fit. It seems preferable, however, to take the water *activity* as the basis of a correlation. In Figure 1, values of log K_D for both the chromium and the copper systems are plotted against log $\{H_2O\}$, where $\{H_2O\}$ is the activity calculated by using the data of Hansen et al.[9] Over the range of $\{H_2O\}$ for which the two sets of data overlap, the trends are parallel within experimental error, and in the case of the chromium data, it is noteworthy that our previous value of K_D for the 100% aqueous medium falls in line with the new data for acetic-acid water mixtures. The slopes of the lines, by least-squares fitting, are 6.3 ± 0.5. This could be interpreted by expanding eq 1 into the form $Cr_2(OAc)_4(OH_2)_2 + 6H_2O \rightleftharpoons 2Cr(OAc)_2(OH_2)_4$, but this neglects the possibility of replacement of coordinated H_2O by HOAc as the water activity is reduced. The conclusion we regard as significant at present is that the difference log $K_D{}^{Cr}$ − log $K_D{}^{Cu}$ is ca. 5.5. This is similar to the value 6.4 suggested previously for aqueous media by using an estimated value of log $K_D{}^{Cu}$. It was argued previously that this difference is the result of two opposing effects: the greater stability of the Cr–Cr bond compared with the Cu–Cu bond is partly offset by greater strength of the Cu–acetate bond compared with the Cr–acetate bond. A calculation based on reported stability constants assessed the latter effect as being equivalent to 1.6 units in log K_D; hence, the difference in metal–metal bond strengths is approximately 5.5 + 1.6 = 7.1 units, corresponding to 40 kJ mol^{-1}.

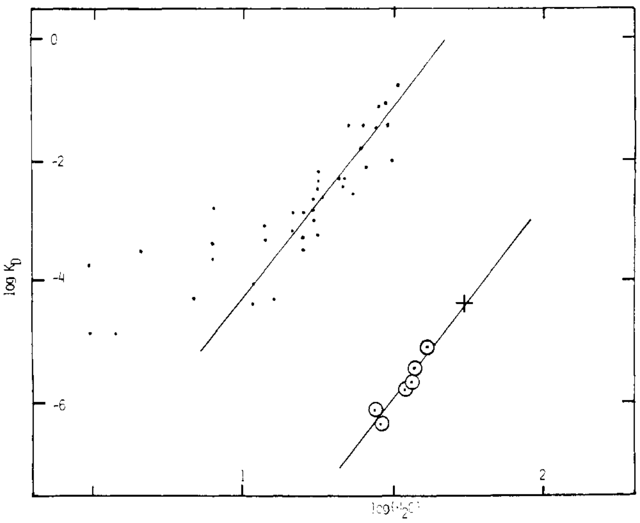

Figure 1. Plots of log K_D versus log $\{H_2O\}$ for the two reactions $M_2(OAc)_4 \rightleftharpoons 2M(OAc)_2$: upper line, M = Cu;[5] lower line, M = Cr; (⊙) this work; (+) ref 3. The lines are drawn by least-squares fitting (using data for log $\{H_2O\}$ > 1 in the Cu case).

Acknowledgment. L.M.W. held an SERC Research Studentship.

Registry No. $Cr_2(OAc)_4(OH_2)_2$, 14404-41-2.

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Infrared Spectroscopic Studies of the Interaction of ClF and Cl_2 with H_2Se, $(CH_3)_2Se$, and AsH_3 in Argon Matrices

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Received December 21, 1987

Charge-transfer complexes of the molecular halogens have been known for many years; for example, the interpretation of the UV/vis spectrum of the benzene–I_2 complex occurred in the 1940s, leading to a surge of interest in CT complexes.[1-7] The primary focus of work in this area has been on complexes of the heavier, less reactive halogens I_2 and Br_2, such that they could be studied in solution at room temperature.[8-11] Recently, a series of complexes of ClF and Cl_2 have been studied by using the matrix-isolation technique,[12-15] which is well suited to the study of more

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reactive materials. Bases with a range of different donor atoms have been studied, including oxygen, nitrogen, sulfur, and phosphorus, and the results interpreted qualitatively in terms of hard/soft acid/base theory.[4,16]

Very little is known about the complexes of ClF and Cl_2 with yet softer bases, having donor atoms in the fourth row of the periodic table (e.g. As and Se). Will the shift be greater than those observed to date, or will the orbital match between the Cl atom of the Lewis acid and its immediate neighbors S and P give rise to larger perturbations? Alternatively, will direct addition of the halogen occur? To answer these questions, a study was undertaken to isolate and characterize the products formed through the codeposition of ClF and Cl_2 with H_2Se, $(CH_3)_2Se$, and AsH_3 into argon matrices. Since the selenide and arsine compounds are quite reactive,[17] the matrix-isolation technique, which has been employed to study hydrogen-bonded complexes of the hydrogen halides with all of these compounds,[18-21] is ideally suited for the current study.

Experimental Study

Experiments were performed on conventional matrix-isolation equipment, which has been described previously.[22-24] Reactants were diluted by the matrix gas, argon, and deposited onto a CsI cold window at 15 K for roughly 22 h. Spectra were recorded over the range 180–4000 cm^{-1} on a Perkin-Elmer 983 infrared spectrometer at 1–3-cm^{-1} resolution. Matrix-to-reactant dilutions in the range of M/R = 100/1 to 1000/1 were employed, and twin-jet deposition was used throughout.

ClF (Pennwalt), Cl_2 (Matheson), and AsH_3 (Alphagaz) were obtained as gases and subjected to freeze–thaw purification at 77 K. $(CH_3)_2Se$ was introduced as the vapor above the liquid after freeze–thaw purification at 77 K. H_2Se was prepared as described previously by addition of concentrated (37%) HCl (Du Pont) to finely divided ZnSe (Alfa), condensing and freeze–thaw purifying the effluent gas at 77 K. Argon was used as the matrix gas without further purification.

Results

Spectra of the individual reactants in argon matrices were recorded and found to be in agreement with literature spectra.[12-15,20,21,25-28a] In particular, blank spectra of ClF in argon showed a sharp doublet at 769/763 cm^{-1}, due to the parent ClF stretching mode with ^{35,37}Cl isotopic splitting. Weaker features were noticed to the red from 755 to roughly 720 cm^{-1}; these have been assigned to aggregate ClF, also with isotopic splittings. The spectrum of H_2Se was relatively weak and contained some HCl impurity, as evidenced by a feature at 2862 cm^{-1} and a band at 2657 cm^{-1} due to either the[29] $HCl{\cdot}H_2O$ or $HCl{\cdot}H_2Se$ complex. The blank spectrum of $(CH_3)_2Se$ in argon showed a medium band near 270 cm^{-1}, which does not exactly match any literature band. It does lie a bit to the blue to the skeletal C–Se–C deformation, which has been observed[8,28] in Raman spectra near 235 cm^{-1}. This band has escaped detection in the infrared to date, due to low intensity, but is probably so assigned here.

ClF Reactions. When ClF was codeposited with H_2Se in argon, a very strong product absorption at 580 cm^{-1} with a shoulder at 576 cm^{-1} dominated the spectrum. Additional new absorptions were noted at 1022, 2595, and 2886 cm^{-1}, the first coming near a parent mode of H_2Se at 1032 cm^{-1}.

The codeposition of ClF with $(CH_3)_2Se$ led to several new product absorptions (see Figure 1), the most intense of which dominated the spectrum at 448 cm^{-1}, with some unresolved structure on the low-energy side. In addition, a medium-intensity, somewhat broad band was observed at 300 cm^{-1}, along with a medium band at 972 cm^{-1} (near the parent CH_3 rocking mode at 958 cm^{-1}) and a weaker band at 1412 cm^{-1} (near a parent mode at 1426 cm^{-1}). A medium product absorption, containing some unresolved structure, was also noted at 1289 cm^{-1}, superimposed on a much weaker parent band at about the same position. In the codeposition experiments, this band was of comparable intensity to a nearby medium parent band at 1267 cm^{-1}, while in $(CH_3)_2Se$ blank experiments it was very weak. Finally, in more concentrated experiments, a weak, somewhat broad feature was observed at 500 cm^{-1}.

When ClF was codeposited with AsH_3 in argon, a very intense band at 465 cm^{-1} with unresolved structure to the red dominated the spectrum. Several product bands were recorded near a parent mode at 911 cm^{-1}, including a doublet of medium intensity at 890, 898 cm^{-1}, which overlapped this parent, and a strong band (more intense than the parent in these experiments) at 875 cm^{-1}, with a weaker overlapping band at 868 cm^{-1}. In addition, product absorptions were noted at 2194 and 2218 cm^{-1}, near the parent band at 2150 cm^{-1}.

Cl_2 Reactions. When Cl_2 was codeposited with H_2Se, a multiplet of medium intensity was observed, with peaks at 493, 498, 505, and 512 cm^{-1}. At higher Cl_2 concentrations, a product band was observed at 1022 cm^{-1} near a parent mode at 1032 cm^{-1}. Additional product bands were noted at 2690 and 2886 cm^{-1}.

The codeposition of Cl_2 with $(CH_3)_2Se$ led to a very intense, somewhat broad product absorption centered near 295 cm^{-1}. Additional product bands were noted, a medium doublet at 968, 971 cm^{-1} (near the 958-cm^{-1} parent), a medium band at 1289 cm^{-1} (similar to that described above for the $ClF/(CH_3)_2Se$ system), and a weak band at 1415 cm^{-1} to the red of a 1426-cm^{-1} parent mode.

When Cl_2 was codeposited with several experiments with AsH_3, a doublet of medium intensity was noted at 512, 519 cm^{-1}. In addition, a very strong multiplet with maxima at 892, 896, and 898 cm^{-1} was observed near the AsH_3 parent band at 911 cm^{-1}.

Discussion

The codeposition of either ClF or Cl_2 with H_2Se, $(CH_3)_2Se$, or AsH_3 gave rise to new infrared absorptions that could not be attributed to either parent species. For studies involving H_2Se and AsH_3, spectra were relatively simple, and will be analyzed separately from the $(CH_3)_2Se$ studies (see below). The dominant feature in the H_2Se and AsH_3 studies was a new absorption recorded to lower energies of the parent halogen stretching mode. Additional bands were also noted near parent absorptions of the base molecule. Taken in the context of previous matrix studies[12-15] of charge-transfer complexes of ClF and Cl_2 with a variety of bases, the present results suggest that the individual reactants have remained intact but are perturbed in the product species, in contrast to a molecular rearrangement. Thus, the spectra support formation of a molecular complex for these systems, and at the concentrations employed, formation of the 1:1 complex is favored. Higher order aggregates may also appear in low concentrations, but the intensity of the product bands due to the 1:1 complex prevent their observation.

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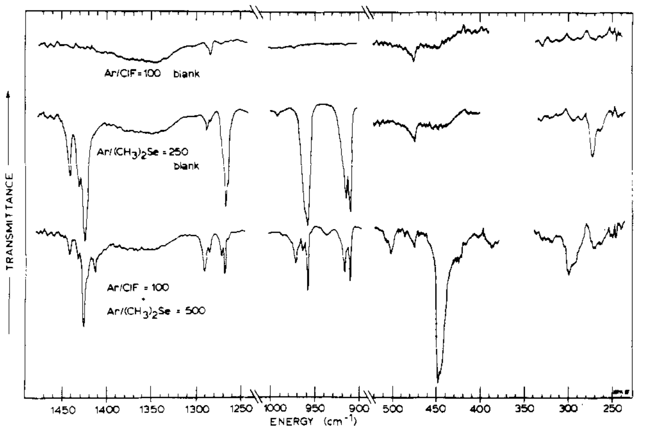

Figure 1. Infrared spectra arising from the codeposition of a sample of Ar/ClF with Ar/$(CH_3)_2Se$ at 15 K, over selected spectral regions, compared to blank spectra of the individual reactants.

The dominant feature observed to the red of the parent halogen mode is assigned, as in past studies, to the perturbed halogen stretching mode. This mode shifts to lower energy as electron density enters the lowest unoccupied molecular orbital on the halogen, an antibonding σ^* orbital. This interaction also causes an intensification of the halogen stretching mode and, in the case of Cl_2 complexes, activates the Cl–Cl stretch.[13,14,30-34] The bands at 580 and 465 in the ClF complexes with H_2Se and AsH_3 and the multiplets near 500 and 515 cm^{-1} in the analogous Cl_2 studies are assigned to the perturbed halogen stretch. The splittings and unresolved structure on the low-energy side can be attributed to chlorine isotopic splitting.

Since the base subunit is donating nonbonding electron density, only slight perturbations, if any, are expected in the base modes of the complex. This is the result seen in previous studies[12-15] and for the current complexes as well. As noted above, shifts were generally 20 cm^{-1} or less and are assigned by proximity to parent modes. For example, the product band around 1020 cm^{-1} in the H_2Se complexes is assigned to the H–Se–H bending mode, which occurs at 1032 cm^{-1} for parent H_2Se. The bands at 2595, 2690, and 2886 cm^{-1} are due to the HCl impurity from the synthesis of H_2Se, complexes of HCl with ClF and Cl_2, and the H_2Se complexes with ClF and Cl_2. For the AsH_3 complexes, the product absorptions just to the red of the 911-cm^{-1} parent are assigned to the perturbed symmetric deformation or "umbrella" mode of the AsH_3 subunit, while the bands near 2200 cm^{-1} are assigned to As–H stretching modes.

Previous studies[12-15] of CT complexes of ClF and Cl_2 have attempted to correlate the magnitude of perturbation to the halogen stretch (i.e. the shift) with the proton affinity of the base.[35] For a given donor atom (e.g. S), this correlation was nearly linear, with a greater proton affinity giving rise to a larger shift. However, this correlation does not hold when bases are compared with different donor atoms. The shifts, for example, for a series of O donors were approximately 50–100 cm^{-1}, while shifts of up to 300 cm^{-1} were observed for S donors, even though proton affinities for the two series are nearly equal. This variation has been qualitatively rationalized by using hard/soft acid/base theory.[4,13-16] Interaction of ClF and Cl_2 is thought to occur through the Cl atom, which is a "soft" acid center, and should interact more effectively with "soft" bases. Although H_2Se and AsH_3 have rather low proton affinities (171.2 and 179.2 kcal/mol, respectively), relatively large shifts are seen, particularly for the ClF complexes, as shown in Table I. The shifts are quite similar to those of the previously studied S bases and slightly less than those of the P bases, while considerably greater than those of the O bases. This is again consistent with the idea of strong interactions between soft acids and soft bases. Interestingly, AsH_3 perturbed the ClF stretch to a greater degree than did H_2Se, while for Cl_2 complexes, the opposite was observed.

Table I. Band Positions (cm^{-1}) for the Perturbed Halogen Stretching Mode for Complexes of ClF and Cl_2 with Selected Bases in Argon Matrices

base	ν_{ClF}	ν_{Cl_2}	PA[b]	ref
	769	550		
NH_3	600		204.0	15
PH_3	406	512	188.6	14
AsH_3	465	519	179.2	*a*
H_2S	631	516	170.2	13
H_2Se	580	512	171.3	*a*
$(CH_3)_2O$	682		192.1	12
$(CH_3)_2S$	471	360	200.6	13
$(CH_3)_2Se$	448[c]	295[c]		*a*

[a] This work. [b] Proton affinity of the base, in kcal/mol, from ref 35. [c] Possible assignment; see text.

Interpretation of the experiments involving $(CH_3)_2Se$ is somewhat less straightforward. The product bands near 970, 1289, and 1415 cm^{-1} fall near modes of parent $(CH_3)_2Se$, and are readily assigned by analogy (and by comparison to previous studies) to a perturbed CH_3 rocking mode, symmetric deformation, and antisymmetric deformation, respectively. The bands in the low-energy region, however, have two possible interpretations. The first is that formation of a 1:1 complex has occurred, as with the previously studied systems. In this case, the halogen stretching modes would be assigned to the bands at 448 and 295 cm^{-1} for the ClF and Cl_2 complexes, respectively. Although the proton affinity of $(CH_3)_2Se$ is not known, these are in good accord with the analogous $(CH_3)_2S$ complexes, where these modes were observed at 471 and 360 cm^{-1}, respectively. This interpretation, however, does not readily account for the product band at 300 cm^{-1} for the $ClF{\cdot}(CH_3)_2Se$ complex. One possibility is the intermolecular stretching mode between acid and base subunits, although this mode generally lies below 200 cm^{-1}. This mode was observed at 260 cm^{-1} for the $ClF{\cdot}PH_3$ complex,[14] but on the basis of a shift of the Cl–F stretching mode, the PH_3 complex was more strongly bound and involves a lighter base subunit. Consequently, it is unlikely that the intermolecular stretch would come as high as 300 cm^{-1}. An alternative explanation would be assignment to the perturbed C–Se–C deformation mode, which lies in the mid-200-cm^{-1} range for parent $(CH_3)_2Se$.

A second interpretation of the spectral features is that direct addition to the central Se atom has occurred, forming a four-coordinate Se compound. Previous researchers[8,11] have suggested that this type of reaction occurs in solution, involving $(CH_3)_2Se$ and heavier halogens. One group[1] studied the solution reaction of $(CH_3)_2Se$ with Cl_2, and postulated formation of $(CH_3)_2SeCl_2$, with an intense Se–Cl stretching mode at 293 cm^{-1}. Within the framework of this structural interpretation, the 448- and 300-cm^{-1} bands in the ClF system would be assigned to Se–F and Se–Cl stretches, while the band at 295 cm^{-1} may be assigned to the antisymmetric Cl–Se–Cl stretch. The Se–F stretching modes in several hypervalent selenium compounds have been observed[36] around 470 cm^{-1}, which is consistent with the 448-cm^{-1} band observed here. Overall, the spectral evidence presented here is probably insufficient to make a definitive distinction between formation of a 1:1 molecular complex and a four-coordinate Se addition product.

Acknowledgment. The authors gratefully acknowledge support of this research by the National Science Foundation through Grant CHE 87-21969. N.P.M. thanks the University Research Council of the University of Cincinnati for a summer fellowship.

Registry No. Cl_2, 7782-50-5; ClF, 7790-89-8; H_2Se, 7783-07-5; AsH_3, 7784-42-1; Me_2Se, 593-79-3.

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