

and GeF_6^{2-} salts. Vibrational spectra indicate that the GeF_5^- anion in NF_4GeF_5 has a cis-fluorine-bridged polymeric structure.

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Registry No. NF_4BF_4 , 15640-93-4; NF_4PF_6 , 58702-88-8; NF_4AsF_6 , 16871-75-3; $\text{NF}_4\text{Sb}_2\text{F}_{11}$, 58702-89-9; $(\text{NF}_4)_2\text{GeF}_6$, 58702-87-7; NF_4GeF_5 , 58702-86-6; NF_3 , 7783-54-2; BF_3 , 7637-07-2; AsF_5 , 7784-36-3; PF_5 , 7647-19-0; GeF_4 , 7783-58-6; CF_3NF_2 , 335-01-3; F_2 , 7782-41-4.

Supplementary Material Available: Listings of the observed x-ray powder diffraction patterns of NF_4PF_6 , NF_4GeF_5 , $(\text{NF}_4)_2\text{GeF}_6$, and NF_4BF_4 (4 pages). Ordering information is given on any current masthead page.

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Reactions of SnCl_2 and PbF_2 with CO, NO, and N_2 and of PbCl_2 , PbBr_2 , and PbI_2 with CO in Argon Matrices

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The reactions between metal halides such as SnCl_2 , PbF_2 , PbCl_2 , PbBr_2 , and PbI_2 and the ligands such as CO, NO, or N_2 in argon matrices have been studied by infrared spectroscopy. It has been found that the ligand bands shift to higher whereas the metal halide bands shift to lower frequencies by complex formation. The magnitude of these shifts has been used as a measure of the extent of σ donation from the ligand to the metal. The effects of changing the ligand, halogen, and metal on σ donation have been discussed based on observed shifts.

Introduction

In 1971, DeKock¹ first succeeded in the preparation of unstable and transient metal carbonyls such as $\text{Ni}(\text{CO})$, $\text{Ni}(\text{CO})_2$, and $\text{Ni}(\text{CO})_3$ in argon matrices by treating metal vapor directly with CO and elucidated their structures by infrared spectroscopy. Since then, a large number of novel coordination compounds have been synthesized, and their

structures have been studied in inert-gas matrices by infrared and Raman spectroscopy.² The reactivity of metal halides at matrix temperatures was first demonstrated by Bassler et al.,³ who confirmed the reactions of SiF_2 with BF_3 , CO, and NO by infrared spectroscopy. Recently, Van Leirsburg and DeKock⁴ treated linear triatomic metal halides (MX_2) with ligands (L) in argon matrices and confirmed the formation

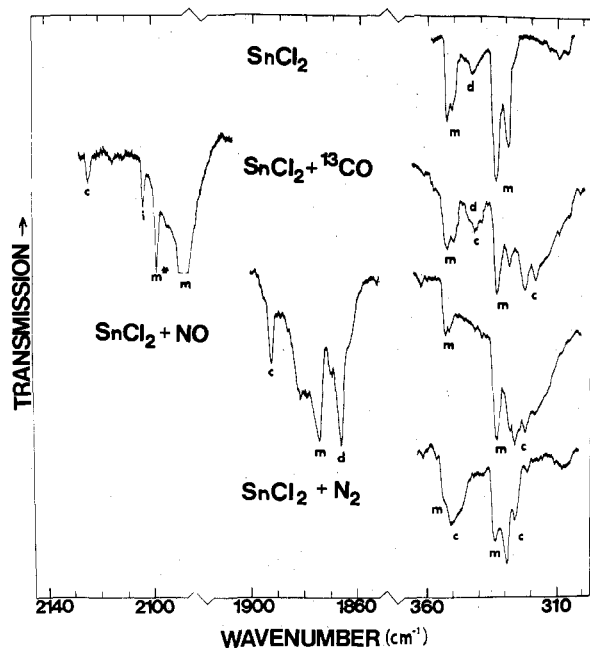


Figure 1. Infrared spectra of SnCl_2 , $\text{SnCl}_2^{13}\text{CO}$, SnCl_2NO , and SnCl_2N_2 in argon matrices.

of the MX_2L type complexes by observing the appearance of new bands in infrared spectra. Their study includes NiF_2L ($\text{L} = \text{CO}, \text{NO}, \text{N}_2, \text{O}_2$), NiCl_2L ($\text{L} = \text{CO}, \text{NO}, \text{N}_2$), and MF_2CO ($\text{M} = \text{Ca}, \text{Cr}, \text{Mn}, \text{Cu}, \text{Zn}$). In the case of the CO complexes, they observed the positive shifts of the CO stretching bands upon complex formation. As is well known, the CO stretching frequencies of the majority of metal carbonyls are lower than that of free CO.⁵ Except for the adsorbed CO,⁶⁻⁸ the systems studied by Van Leirsburg and DeKock provided the first example of isolated complexes exhibiting positive CO shifts. In order to gain a further insight into this interesting observation, we have studied the reactions of bent triatomic metal halides such as SnCl_2 and PbX_2 ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) with CO, NO, and N_2 in argon matrices and discussed the effects of changing the ligand, halogen, and metal on the $\text{MX}_2\text{-L}$ interaction by measuring their infrared spectra.

Experimental Section

Matrix reactions were performed by condensing reactants diluted in inert gases onto a 10 K CsI window cooled by a Cryogenic Technology Model 21 refrigerator. The window was housed in a brass vacuum shroud. Attached to the shroud was a brass cell in which an oven was contained. The oven consisted of an aluminum oxide cylinder for electrical insulation around a quartz cylinder which held the CaF_2 sample holder in place. Resistance wires were coiled between the quartz tube and sample holder. Thermal insulation between the oven and the 10 K window was provided by a $1/8$ in. thick brass plate which was part of the oven jacket with a $1/4$ -in. deposition port. To dissipate heat, water was circulated in copper tubes soldered to the outside of the oven jacket.

Metal halides used in the present work are SnCl_2 , PbF_2 , PbCl_2 , PbBr_2 , and PbI_2 , all of which were purchased from Ventron Corp., Danvers, Mass. The salts were loaded into the oven and outgassed at near their deposition temperature before the window was cooled. Gas samples were prepared on a glass vacuum line using standard procedures. Argon, nitrogen, nitric oxide, and carbon monoxide were purchased from Matheson Gas Products, Joliet, Ill. ^{13}CO (95% enriched) was purchased from Merck & Co., Inc., St. Louis, Mo. Concentrations of the reactants in argon varied from 0.1 to 4%.

Infrared spectra were measured during and after sample deposition on a Beckman IR-12 infrared spectrophotometer. High-resolution spectra were recorded using a $10 \text{ cm}^{-1}/\text{in.}$ chart expansion and a $4 \text{ cm}^{-1}/\text{min}$ chart speed. Calibration of frequency readings was made using the rotation-vibration bands of standard molecules. Reproducibility of the spectra was checked by running the spectra several

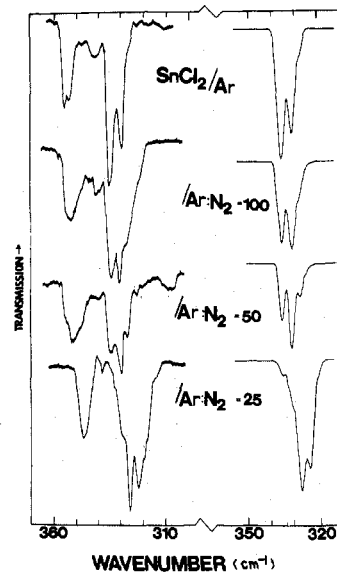


Figure 2. Infrared and computer-simulation spectra of the $\text{SnCl}_2\text{-N}_2$ system as a function of N_2 concentration in argon.

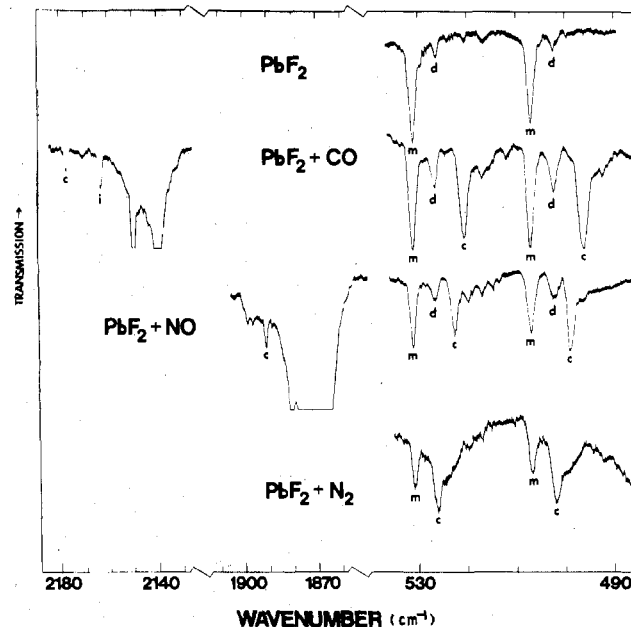


Figure 3. Infrared spectra of PbF_2 , PbF_2CO , PbF_2NO , and $\text{PbF}_2\text{-N}_2$ in argon matrices.

times. The average error in frequency reading was $\pm 0.3 \text{ cm}^{-1}$. In each spectrum shown in Figures 1-4, the optical density of the strongest peak was about 0.7.

Computer-simulation spectra were produced by a program which plots the sum of Gaussian bands of given frequencies, intensities, and widths. This technique has been used and described previously.⁹

Results

(1) **SnCl_2 Complexes.** The top curve of Figure 1 illustrates the infrared spectrum of SnCl_2 in an argon matrix at 10 K. This spectrum is in good agreement with that of earlier measurement by Andrews and Frederick.¹⁰ Following their assignments, the bands at 354.1 and 351.7 cm^{-1} are attributed to the symmetric and those at 334.2 and 329.9 cm^{-1} to the antisymmetric Sn-Cl stretching modes of the bent triatomic SnCl_2 monomer. Both modes exhibit two peaks due to the mixing of $\text{Sn}^{35}\text{Cl}_2$ and $\text{Sn}^{35}\text{Cl}^{37}\text{Cl}$, and their intensity ratio is about 3:2 as predicted from the percentage natural abundances of these isotopic molecules. In Figure 1, these peaks are marked by m (monomer). Warming the matrix to

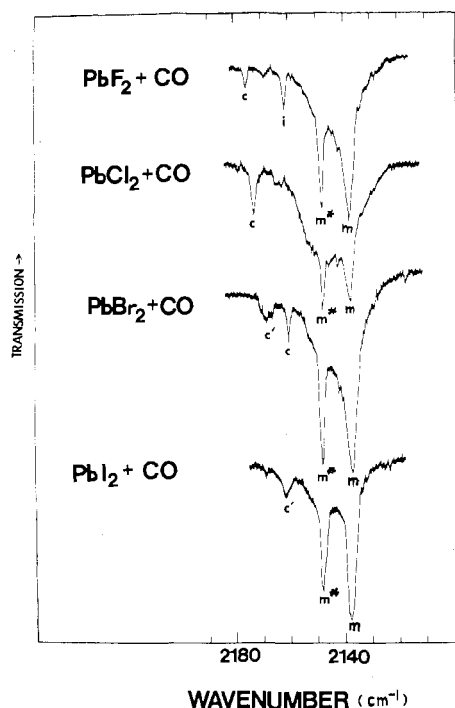


Figure 4. Infrared spectra of PbF_2CO , PbCl_2CO , PbBr_2CO , and PbI_2CO in argon matrices.

40 K followed by recooling to 10 K resulted in a marked decrease in the intensity of these monomer bands, leaving moderately intense bands at 343 and 352 cm^{-1} . Thus, the weak and broad band at 343 cm^{-1} (marked by d in Figure 1) has been assigned to the dimeric species (SnCl_2)₂. Apparently, another dimer peak at 352 cm^{-1} is hidden under the strong monomer band at the same frequency.

When SnCl_2 is treated with ^{12}CO in an argon matrix, four bands are observed at 2175.5, 2155, 2149, and 2138 cm^{-1} . Previously^{4,11} the bands at 2149 and 2138 cm^{-1} were assigned to monomeric and polymeric CO molecules, respectively. However, these assignments have been revised by Dubost and Abouaf-Marguin,¹² who confirmed by double-doping experiments that the former band at 2149 cm^{-1} is due to a CO-H₂O species (m*) whereas the latter at 2138 cm^{-1} originates in monomeric CO (m). The 2155- cm^{-1} band is due to HClCO impurity (i) resulting from the reaction of SnCl_2 with trace H₂O in the system.¹³ The 2175.5- cm^{-1} band (c) can be assigned to a novel SnCl_2CO complex. Then the positive shift of the CO stretching band upon complex formation with SnCl_2 is 37.5 cm^{-1} . All of these bands are shifted by ca. 48 cm^{-1} to lower frequencies when ^{13}CO is treated with SnCl_2 . In Figure 1, these four bands are located at 2127.8 (c), 2106.6 (i), 2101.2 (m*), and 2091.4 (m) cm^{-1} . The observed shift of 47.7 cm^{-1} from $\text{SnCl}_2^{12}\text{CO}$ to $\text{SnCl}_2^{13}\text{CO}$ is close to that expected for free diatomic CO molecule (48.3 cm^{-1}).

In the low-frequency region, two new bands are observed at 324.3 and 319.9 cm^{-1} in addition to those of unreacted SnCl_2 species discussed above. As expected, all of the frequencies in this region do not change by the ^{12}CO - ^{13}CO substitution. It is obvious from Figure 1 that these two bands (marked by c) are due to the antisymmetric stretching modes of $\text{Sn}^{35}\text{Cl}_2\text{CO}$ and $\text{Sn}^{35}\text{Cl}^{37}\text{ClCO}$, respectively.¹⁰ Then, the magnitude of the negative shift of the Sn-Cl stretching mode upon complex formation is ca. 10 cm^{-1} for both isotopic species. It is anticipated that the symmetric Sn-Cl stretching modes show similar negative shifts upon complex formation. If this is the case, the symmetric stretching bands of the complex are expected to overlap on the (SnCl_2)₂ band at 342

cm^{-1} . The appearance of two shoulder bands in this region seems to support this interpretation.

The third trace of Figure 1 illustrates the infrared spectrum of the SnCl_2NO complex. The NO molecule exhibits two bands at 1875.0 (monomer) and 1866.0 cm^{-1} (cis dimer) in an argon matrix.^{14,15} When it reacts with SnCl_2 , a new band appears at 1891.7 cm^{-1} (marked by c) which is assigned to the NO stretching mode of SnCl_2NO . Thus, the NO stretching bands give a positive shift of 16.7 cm^{-1} (relative to the monomer) by forming the complex. Previous workers⁴ did not assign the NO stretching bands of NiX_2NO (X = F, Cl) because of the complexity of the spectra in this region. In our case, no such complexity was observed as is seen in Figure 1. In the low-frequency region, two new bands are observed at 326.9 and 323 cm^{-1} which are assigned to the antisymmetric Sn-Cl stretching modes of $\text{Sn}^{35}\text{Cl}_2\text{NO}$ and $\text{Sn}^{35}\text{Cl}^{37}\text{ClNO}$, respectively. The average shift of these two bands by complex formation is 7.1 cm^{-1} which is smaller than that of SnCl_2CO . Similar shifts are expected for the symmetric Sn-Cl stretching modes. As seen in Figure 1, however, it was not possible to observe distinct bands in the 350-340- cm^{-1} region where the symmetric stretching bands due to the complex are expected to appear.

The reaction between SnCl_2 and N_2 in argon was studied over a wide range of the N_2 concentration. The bottom curve of Figure 1 shows the results obtained for 2% N_2 in argon. In this case, no band assignable to the N_2 stretching mode was observed in the high-frequency region possibly due to weak interaction between SnCl_2 and N_2 . This is contrasted to the cases of $\text{Ni}(\text{N}_2)_{1-4}$ and $\text{Pd}(\text{N}_2)_{1-3}$ complexes¹⁶ for which strong N_2 stretching bands were observed in the 2200-2000- cm^{-1} spectral region. Figure 2 shows the variation of the low-frequency spectra as a function of the N_2 concentration. The top curve is the infrared spectrum of unreacted SnCl_2 discussed above. When 1% N_2 was introduced into the sample (second curve) and treated with SnCl_2 , two bands of nearly equal intensity (antisymmetric stretching bands) were observed at 334.2 and 329.8 cm^{-1} which are exactly the same frequencies as those of unreacted $\text{Sn}^{35}\text{Cl}_2$ and $\text{Sn}^{35}\text{Cl}^{37}\text{Cl}$, respectively. However, the intensity of the latter band increased relative to that of the former, and a new shoulder appeared at ca. 327 cm^{-1} . When the N_2 concentration in argon increased to 2% (third curve), three distinct peaks were observed at 334.2, 329.9, and 326.7 cm^{-1} with an approximate relative intensity of 3:5:2. These results can be explained if we assume that the bands due to unreacted SnCl_2 (334.2 and 329.8 cm^{-1}) are overlapped with those of SnCl_2N_2 (329.8 and 326.7 cm^{-1}) and the concentration of the latter increases as the N_2 concentration increases. When the N_2 concentration reached 4% in argon, two new bands were clearly observed at 326.1 and 322.3 cm^{-1} with a shoulder at ca. 330 cm^{-1} (bottom curve). These two new bands have been assigned to the $\text{SnCl}_2(\text{N}_2)_2$ complex. If we compare the antisymmetric Sn-Cl stretching frequencies of free $\text{Sn}^{35}\text{Cl}_2$ with those of the 1:1 and 1:2 complexes, the shift amounts to 4.4 cm^{-1} for the 1:1 complex and 8.1 cm^{-1} for the 1:2 complex.

In order to confirm the above assignments, we have attempted computer simulation of the infrared spectra which are shown on the right corner of Figure 2. Due to wide spectrophotometer slits used in this region, the half-bandwidths were assumed to be 3.0 cm^{-1} in all cases. The two frequencies characteristic of the unreacted SnCl_2 and its 1:1 and 1:2 complexes are already given in the above. The relative intensities of $\text{Sn}^{35}\text{Cl}_2$, $\text{Sn}^{35}\text{Cl}^{37}\text{Cl}$, and $\text{Sn}^{37}\text{Cl}_2$ peaks were taken to be 9:6:1 in all cases.¹⁷ It was assumed that to form the 1:1 complex 20% of the SnCl_2 reacted in the 1% N_2 experiment and 50% reacted in the 2% N_2 experiment. In the 4% N_2 experiment, we assumed a mixture of 80% $\text{SnCl}_2(\text{N}_2)_2$, 15%

SnCl_2N_2 , and 5% SnCl_2 . As is seen in Figure 2, the computer-simulated spectra thus obtained are in good agreement with the observed spectra in all cases. Similar changes in band shape are also occurring in the symmetric stretching bands near 350 cm^{-1} . Since these bands did not give any distinct peaks by complex formation, no attempts have been made to simulate these spectra.

(2) **PbF₂**. When PbF_2 was deposited in argon, two bands of nearly equal intensity were observed at 531.4 and 507.2 cm^{-1} (top curve of Figure 3). Following the frequency order observed for PbCl_2 and SnCl_2 ,¹⁰ these two bands have been assigned to the symmetric and antisymmetric Pb-F stretching modes, respectively, of the bent PbF_2 monomer (marked by m).¹⁸ A warm-up experiment to 40 K followed by recooling to 10 K reduced the intensity of these peaks by ca. 50% and increased the intensity of the weak bands at 526.9 and 502.4 cm^{-1} (marked by d). Therefore, the latter two bands have been assigned to the PbF_2 dimer.

When PbF_2 was treated with 1% CO in argon, the spectrum shown in the second curve of Figure 3 was observed. In the high-frequency region, the CO exhibits two bands at 2149 and 2138 cm^{-1} which have already been discussed. The band at 2162 cm^{-1} (marked by i) can be assigned to the CO complex with HF which was produced by the reaction of PbF_2 with traces of H_2O in the system.⁴ The new band (marked by c) at 2176.4 cm^{-1} has been assigned to the CO stretching band of the novel PbF_2CO complex. This frequency is slightly lower than those of MF_2CO complexes (2200 – 2183 cm^{-1} for $M = \text{Cr, Mn, Ni, Cu, and Zn}$) studied by Van Leirsburg and DeKock.⁴ In the low-frequency region, two new bands appear strongly at 520.6 and 496.3 cm^{-1} (marked by c) which are assigned to the symmetric and antisymmetric Pb-F stretching modes of PbF_2CO . The average shift of these two bands by complex formation is 10.8 cm^{-1} .

A similar experiment was carried out with 1% NO (third curve of Figure 3). In the NO stretching region, a new band appears at 1891.4 cm^{-1} (labeled by c) together with those of the NO monomer (1875.0 cm^{-1}) and the cis dimer (1866 cm^{-1}). The former band is assigned to the PbF_2NO complex. In this case, the NO stretching band has been shifted by 16.4 cm^{-1} to higher frequency as a result of complex formation. The spectrum in the low-frequency region is similar to that observed for the PbF_2CO complex. Two new bands at 522.6 and 498.7 cm^{-1} (labeled by c) are assigned to the PbF_2NO complex. The average shift of these two bands by complex formation is 8.7 cm^{-1} which is by 2 cm^{-1} smaller than the case of PbF_2CO .

The bottom curve of Figure 3 shows the infrared spectrum of PbF_2 treated with 1% N_2 in argon. Again, no N_2 stretching bands were observed in the high-frequency region. In the low-frequency region, four distinct bands were observed. It is obvious that the bands at 531.4 and 507.2 cm^{-1} are due to the unreacted PbF_2 monomer. However, the bands at 526.6 and 502.2 cm^{-1} can be assigned either to the PbF_2N_2 complex or to the PbF_2 dimer. We have assigned them to the PbF_2N_2 complex because of the following reason. At the initial stage of the deposition, the monomer bands grew faster than the complex bands. When the Ar- N_2 flow rate was doubled in the middle of the experiment, the growth rate of the complex bands increased markedly relative to the monomer bands. At the end of deposition, the spectrum shown in Figure 3 was obtained. It is expected that an increase in the flow rate would increase the Ar: PbF_2 ratio, resulting in a decrease in the dimer concentration. If the bands labeled by c were due to the dimer, their intensities would have decreased rather than increased as we observed.

(3) **PbCl₂, PbBr₂, and PbI₂**. The infrared spectrum of PbCl_2 in an argon matrix has been reported previously.¹⁰ Our results

are in good agreement with those of previous workers. The two bands at 321.6 and 299.9 cm^{-1} are assigned to the symmetric and antisymmetric Pb-Cl stretching modes of the bent $\text{Pb}^{35}\text{Cl}_2$ molecule, respectively. When CO in argon was treated with PbCl_2 , a new band appeared at 2174.5 cm^{-1} (marked by c in Figure 4) in the CO stretching region which has been assigned to the PbCl_2CO complex. Similar bands have already been observed at 2176.4 cm^{-1} for PbF_2CO and at 2175.5 cm^{-1} for SnCl_2CO . This band is shifted to 2126 cm^{-1} in $\text{PbCl}_2^{13}\text{CO}$ as expected from a simple diatomic model calculation. In the low-frequency region, two bands at 321.6 and 299.9 cm^{-1} are shifted to 315.2 and 292.6 cm^{-1} , respectively, upon complex formation. These bands are accompanied by unresolved shoulder bands due to the $\text{Pb}^{35}\text{Cl}^{37}\text{ClCO}$ species.

The infrared spectra of PbBr_2 and PbI_2 in argon matrices have not been studied previously. No attempts have been made in the present study to measure the Pb-Br and Pb-I stretching bands mainly due to experimental difficulties encountered in the region below 200 cm^{-1} . Figure 4 shows the infrared spectra of PbBr_2 and PbI_2 treated with CO in the CO stretching region. In the case of PbBr_2 , one broad band centered at 2170 cm^{-1} (labeled c') and a sharp band at 2161.2 cm^{-1} (labeled c) were observed. The former band grew at the expense of the latter band when the matrix was warmed to 40 K. Thus, the latter has been assigned to PbBr_2CO . However, the nature of the former band is not obvious. It may be due to some higher aggregate involving both PbBr_2 and CO.

When PbI_2 was treated with CO, one new band was observed at 2162 cm^{-1} . However, this band persists even at 40 K and is probably a counterpart of the 2170 cm^{-1} band observed for the PbBr_2CO system. As will be shown in a subsequent paper,¹⁹ the CO stretching frequency of HgI_2CO is at 2143 cm^{-1} in an argon matrix. Thus, it is quite probable that the CO stretching band of PbI_2CO is hidden under the moderately intense CO- H_2O band near 2149 cm^{-1} (m*).

Discussion

It is well known²⁰ that the ligands such as CO, NO, and N_2 act as σ donors (bases) by donating electrons to the metal and also as π acceptors (acids) by accepting electrons from the metal. The σ donation tends to raise the CO stretching frequency since the electrons are removed from its weakly antibonding 5σ orbital. On the other hand, the π back-donation tends to lower the CO frequency since the electrons enter into its antibonding π orbital. In the majority of metal carbonyls in which the neutral metal atom interacts with CO, these two bonding mechanisms are synergic because the metal must dissipate the negative charge accumulated by σ donation through π back-bonding. The CO stretching frequencies of the majority of metal carbonyls (2100 – 1800 cm^{-1}) are lower than that of free CO⁵ because π back-bonding is dominant in these compounds.

In the case of the MX_2CO interaction, the situation is different from the above. The metal atom in MX_2 is expected to be much more positive than the neutral metal. Thus, the donation of σ electrons does not accumulate negative charge on the metal. Hence, π back-bonding is insignificant. Thus, the observed positive shifts in the MX_2CO type complexes can be interpreted largely in terms of σ donation. It is expected that the CO stretching frequency becomes higher as more electrons are removed from its antibonding orbital. If so, the CO stretching frequency may serve as a measure of σ donation. According to gas-phase data,²¹ the CO stretching frequency of neutral CO is 2143 cm^{-1} whereas that of CO^+ is 2184 cm^{-1} . Thus, a donation of a unit charge raises the frequency by ca. 40 cm^{-1} . In the present work, the maximum shift observed is $+38.4\text{ cm}^{-1}$ for PbF_2CO . If the metal accepts σ electrons, the oxidation state of the metal is lowered, and this results in

Table I. Observed Frequencies of Metal Halides, Ligands, and Their Complexes in Argon Matrices at 10 K (cm^{-1})

Compd	$\nu(\text{L})$	$\Delta\nu(\text{L})^a$	$\nu_{\text{g}}^-(\text{MX})$	$\Delta\nu_{\text{g}}^-(\text{MX})$	$\nu_{\text{as}}^-(\text{MX})$	$\Delta\nu_{\text{as}}^-(\text{MX})$
$\text{Sn}^{35}\text{Cl}_2$			354.1		334.2	
$\text{Sn}^{35}\text{Cl}_2$ $\text{Cl}_2^{12}\text{CO}$	2175.5	+37.5	343	-11	324.3	-9.9
$\text{Sn}^{35}\text{Cl}_2\text{NO}$	1891.7	+16.7	<i>b</i>	<i>b</i>	326.9	-7.3
$\text{Sn}^{35}\text{Cl}_2\text{N}_2$	<i>c</i>	<i>c</i>	350	-4	329.8	-4.4
PbF_2			531.4		507.2	
$\text{PbF}_2^{12}\text{CO}$	2176.4	+38.4	520.6	-10.8	496.3	-10.9
PbF_2NO	1891.4	+16.4	522.6	-8.8	498.7	-8.5
PbF_2N_2	<i>c</i>	<i>c</i>	526.6	-5.8	502.2	-5.0
$\text{Pb}^{35}\text{Cl}_2$			321.6		299.9	
$\text{Pb}^{35}\text{Cl}_2$ $\text{Cl}_2^{12}\text{CO}$	2174.5	+36.5	315.2	-6.4	292.6	-7.3
$\text{PbBr}_2^{12}\text{CO}$	2161.2	+23.2	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
$\text{PbI}_2^{12}\text{CO}$	$\sim 2149^d$	$\sim 10^d$	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>

^a Relative to free monomeric ^{12}CO (2138.0 cm^{-1}) or NO (1875.0 cm^{-1}). ^b Not possible to determine. ^c Too weak. ^d $\pm 5\text{ cm}^{-1}$.

the lowering of the MX_2 stretching frequencies.²² Thus, the magnitude of negative shifts of the MX_2 stretching bands may also be used as a measure of σ donation. In the following, the effect of changing the ligand, halogen, and metal on σ donation will be discussed based on the observed shifts of the ligand and MX_2 vibrations.

First, the effect of changing the ligand can be seen in the SnCl_2L (Figure 1) and PbF_2L (Figure 3) series. As is shown in Table I, the magnitude of negative shifts of the MX_2 stretching bands follows the order $\text{CO} > \text{NO} > \text{N}_2$. In terms of the Sn-Cl stretching force constant, this corresponds to the decrease in its value (in $\text{mdyn}/\text{\AA}$ units) in the same order: $0.10 (\text{CO}) > 0.07 (\text{NO}) > 0.04 (\text{N}_2)$. These results indicate that CO is the best, NO is the next, and N_2 is the poorest σ donor in the series. The same order is found in the NiF_2L series studied by Van Leirsburg and DeKock.⁴

The effect of changing the halogen is seen in the $\text{PbX}_2\text{-CO}$ series shown in Figure 4. The CO stretching frequencies of these complexes follow the order $\text{PbF}_2 > \text{PbCl}_2 > \text{PbBr}_2 > \text{PbI}_2$. This result is interpreted as indicating that the σ -accepting tendency of PbX_2 decreases in the above order since the ionicity of the Pb-X bond decreases in the same order. The observed dependence of the CO stretching band on the halogen cannot be attributed to the mass effect of the halogen because of the following reasons: (1) a pure mass effect would probably lower the CO stretching frequency when it forms a complex with MX_2 ; (2) as stated before, the $^{12}\text{CO}\text{-}^{13}\text{CO}$ shift of MX_2CO is close to that of free CO, indicating little participation of MX_2 in the CO stretching vibration; (3) according to earlier workers,⁴ the CO stretching frequency of NiCl_2CO (2189 cm^{-1}) is higher than that of ZnF_2 (2186 cm^{-1}). The reverse frequency order is expected if the mass effect is the main factor in determining the CO frequency. Thus, the observed dependence of the CO stretching frequency on the halogen must be attributed to the electronic effect.

The effect of changing the metal has been thoroughly studied by earlier workers.⁴ Similar to the case of CO adsorbed on zeolites,⁶ they obtained a linear relationship between the CO stretching frequency and the electric field due to MX_2 at the carbon atom and attributed the deviation of CuF_2 and NiF_2 from the straight line to the anisotropic d-electron configuration of these metals. We could not find any single parameter (polarizability, electronegativity, etc.) which gives a better correlation with the frequency. In this paper, we simply regard the CO frequency as a measure of the σ donation or the electrophilic property of the metal in metal halides. Combining our results with those of earlier workers, we obtain the following orders of the CO stretching frequencies

(cm^{-1}): $\text{CuF}_2 (2210) > \text{NiF}_2 (2200) > \text{CrF}_2 (2188) > \text{ZnF}_2 (2186) > \text{MnF}_2 (2183) > \text{CaF}_2 (2178) > \text{PbF}_2 (2176); \text{NiCl}_2 (2189) > \text{SnCl}_2 (2176) > \text{PbCl}_2 (2175)$.

Previously, Brown and Darenbourg⁷ proposed a relationship between the frequency and the intensity of adsorbed CO molecules. In the present work, no attempts have been made to examine such a relationship because it was technically difficult to compare the CO intensity of the MX_2CO complexes prepared under different deposition conditions in inert-gas matrices.

Complex Formation and Structure. Thus far, we have assumed that observed spectral changes are due to complex formation and not to matrix effects. The possibility of the latter may be ruled out by the following argument. Suppose that the spectral changes shown in Figure 2 are caused by matrix effects through nearest-neighbor interactions. If SnCl_2 occupies a substitutional site in an argon matrix, it will have 12 nearest neighbors (argon atoms). If 2% of the argon atoms are replaced by N_2 molecules in the lattice, simple calculations show that about 78% of the SnCl_2 will be completely surrounded by argon, 19% will have one N_2 , and 2% will have two N_2 molecules in its inner coordination sphere. Here, we neglect the possibility of SnCl_2 dimerization. As discussed in the previous section, our computer-simulation analysis indicates that about 50% of the SnCl_2 reacted to form the SnCl_2N_2 complex. Thus, the observed percentage is much higher than that predicted from purely random mixing of the reactants in argon matrices. The above result then suggests that at least 31% of the SnCl_2 reacted with N_2 through a collision process before the matrix isolation process is completed on the CsI window. Diffusion experiments show, however, that further complex formation can occur when the matrix is warmed to ca. 35 K.

It should also be noted in the experiment shown in Figure 2 that the Sn-Cl stretching frequency decreases stepwise by changing the N_2 concentration. This observation suggests that there is a stepwise formation of the 1:1 and 1:2 complexes. Although not shown in Figure 2, the spectrum of SnCl_2 was measured in a pure N_2 matrix. In this case, the antisymmetric stretching bands were observed at 318 and 316 cm^{-1} . These frequencies are much lower than those of SnCl_2N_2 and $\text{SnCl}_2(\text{N}_2)_2$ in argon matrices and suggest the formation of even higher complexes such as $\text{SnCl}_2(\text{N}_2)_{3,4}$ since the N_2 matrix effect alone cannot account for such large shifts.

The present results do not provide definitive information about the structure of the MX_2L type complex. Earlier workers^{4,6} assumed that CO is coordinated to a metal in the end-on fashion through its carbon atom. Since the electronegativity of oxygen is much greater than that of carbon, σ donation is most likely to occur from the 5σ orbital of CO located mainly on the carbon atom. By similar reasoning, NO may coordinate to a metal through its nitrogen atom. Thus far, no side-on structure has been reported for molecular N_2 complexes. Thus, we surmise the end-on structure in all cases. On the basis of $^{35}\text{Cl}\text{-}^{37}\text{Cl}$ isotopic frequencies, Andrews and Frederick¹⁰ calculated the Cl-M-Cl angles of SnCl_2 and PbCl_2 to be 90-100°. We have carried out similar calculations on the MCl_2L type complexes and found very little changes in these angles upon complex formation. This result suggests that the interaction with CO, NO, or N_2 is not strong enough to cause any drastic changes in electron distribution and hybridization in the MX_2 molecule. The fact that no M-L stretching bands were observed in the low-frequency region also suggests that the interactions between MX_2 and these ligands are much weaker than those found in $\text{Ni}(\text{N}_2)_{1-4}$ and $\text{Pd}(\text{N}_2)_{1-3}$.¹⁶

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Registry No. SnCl_2 , 7772-99-8; $\text{Sn}^{35}\text{Cl}_2$, 58734-92-2; $\text{SnCl}_2^{13}\text{CO}$, 58815-37-5; $\text{Sn}^{35}\text{Cl}_2^{12}\text{CO}$, 58815-38-6; SnCl_2NO , 58815-39-7; $\text{Sn}^{35}\text{Cl}_2\text{NO}$, 58815-40-0; SnCl_2N_2 , 58815-41-1; $\text{Sn}^{35}\text{Cl}_2\text{N}_2$, 58815-42-2; PbF_2 , 7783-46-2; $\text{PbF}_2^{12}\text{CO}$, 58815-43-3; PbF_2NO , 58815-44-4; PbF_2N_2 , 58815-45-5; $\text{Pb}^{35}\text{Cl}_2$, 36677-74-4; PbCl_2CO , 58815-33-1; $\text{Pb}^{35}\text{Cl}_2^{12}\text{CO}$, 58815-34-2; $\text{PbBr}_2^{12}\text{CO}$, 58815-35-3; $\text{PbI}_2^{12}\text{CO}$, 58815-36-4.

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Single-Crystal Electronic Spectrum of Tetraphenylarsonium Oxotetrachlorochromate(V), $[(\text{C}_6\text{H}_5)_4\text{As}][\text{CrOCl}_4]$, and an ab Initio Calculation of the Bonding and Excited States of Oxotetrachlorochromate(V)

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Polarized single-crystal electronic spectral data have been recorded for $[(\text{C}_6\text{H}_5)_4\text{As}][\text{CrOCl}_4]$ at ca. 300 °K and at temperatures approaching that of liquid helium. The features observed are assigned with the aid of ab initio configuration interaction calculations. The experimental and theoretical data are consistent with the two lowest energy absorptions at ca. 13 and 18 kK, respectively, arising from the transitions $d_{xy} \rightarrow d_{xz,yz}$ and $\text{Cr}-\text{O}(\pi) \rightarrow \text{Cr}-\text{O}(\sigma^*)$, respectively. It is shown that the band at ca. 18 kK cannot be due to the $d_{xy} \rightarrow d_{x^2-y^2}$ transition as is commonly assumed. Several intense absorptions are observed above ca. 20 kK and these are ascribed to particular ligand \rightarrow chromium charge-transfer transitions.

The electronic structures of the d^1 monooxo chromophores VO^{2+} , CrO^{3+} , and MoO^{3+} have received considerable attention,¹⁻¹⁶ particularly since the pioneering molecular orbital (MO) studies of Gray et al.^{17,18} However, ambiguities still persist in the interpretation of the electronic spectra of, and bonding in, the complexes of these cations. As part of a detailed study of the electronic structure of these systems we have completed a single-crystal polarized electronic spectral study of $[(\text{C}_6\text{H}_5)_4\text{As}][\text{CrOCl}_4]$ in conjunction with all-electron ab initio MO calculations of the ground and excited states of this anion. This combined approach has provided new and definitive electronic spectral data for a CrO^{3+} complex and an improved basis not only for the assignment of such data but also for a discussion of the nature of the bonding within the $[\text{CrOCl}_4]^-$ ion.

Experimental Section

$[(\text{C}_6\text{H}_5)_4\text{As}][\text{CrOCl}_4]$ was prepared as described previously³ and recrystallized from dried CH_2Cl_2 . Anal. Calcd for $\text{C}_{24}\text{H}_{20}\text{AsCl}_4\text{CrO}$: C, 48.6; H, 3.4; Cl, 24.0; Cr, 8.8. Found: C, 48.5; H, 3.5; Cl, 24.1; Cr, 8.9. X-ray crystallographic studies¹⁹ have shown that this salt crystallizes in the space group $P4/n$ with $Z = 2$, the Cr atoms thus lying on a crystallographic fourfold axis of symmetry (c) and a diagram of the unit cell is shown in Figure 1.

Electronic Spectral Studies. Absorption spectra (10–30 kK) were recorded at ca. 300 °K at temperatures approaching that of liquid helium on a Cary 14 spectrophotometer equipped with Nicol prisms, for suitably thinned single crystals of $[(\text{C}_6\text{H}_5)_4\text{As}][\text{CrOCl}_4]$ mounted on glass microscope slides in orientations which permitted the electric vector of the incident beam to be polarized parallel to and perpen-

Table I. Electronic Spectral Characteristics of $[(\text{C}_6\text{H}_5)_4\text{As}][\text{CrOCl}_4]$

Absorption max, ^a kK			
Single crystal		CH_2Cl_2 soln, room temp	Oscillator strength
Room temp	Liq He temp		
13.4 ($xy > z$)	12.9 ₆ ($xy \gg z$) 13.4 ₅ sh ($xy \gg z$) 13.8 ₅ ($xy \gg z$) 14.4 ₅ ($xy \gg z$) 15.3 ₈ ($xy \gg z$)	13.1 ^b	1.8×10^{-4}
18.1 ($xy \gg z$)	17.8 ($xy \gg z$) 18.2 ($xy \gg z$) 18.5 ($xy \gg z$) 18.7 ($xy \gg z$)	18.1	9.3×10^{-4}
21 sh ($xy > z$)	20.3 ^c (xy and z) 22 ($xy \gg z$)	24.8	7.1×10^{-2}
23 sh ^d	23 sh (xy and z)		
25 sh ^d	24. ₅ sh ($z, p?$)	36.8	9.6×10^{-2}

^a Estimated error ca. ± 1 in the last significant figure quoted.

^b Recorded for $[(\text{C}_2\text{H}_5)_3\text{N}][\text{CrOCl}_4]$. ^c Possibly comprising two or more components. ^d Only seen in z polarization; xy too intense. Key: sh, shoulder; p, polarized.

dicular to the crystallographic c axis. The low-temperature spectra were obtained with the glass slide mounted on the copper block of an Oxford Instruments continuous-flow cryotip. The copper block was cooled to ca. 4 °K and the system allowed to equilibrate for at least 30 min before the spectrum was recorded. Figure 2 and Table