

Conclusions

The complete single-crystal ESR and susceptibility tensors of this series of four low-spin, planar cobalt(II) complexes, together with solution absorption spectra in the near-IR and visible regions have been reported in this and the earlier paper.³ All data have been quantitatively reproduced within a common framework, the ligand field being parameterized within an orbital energy scheme appropriate to D_{2h} symmetry, or the angular overlap model in the true geometry augmented by a stabilization of the d_{z^2} function by interaction with a metal s function.

Approximate orbital diagrams throughout the series are compared in Figure 8. The theoretical treatment of the results, while qualitatively confirming the conclusions of the earlier doublet-restricted model, indicates the need for the present complete d^7 configurational basis, especially with respect to our conclusions relating to the nephelauxetic effect

and to trends along the series of particular concern to the role of the α -methyl hydrogen blocking groups. The conclusions of central chemical concern are (i) the π -acid role of the phosphine ligands in these systems, possibly via $d\pi$ - $d\pi$ bonding, evidenced by both aom e_π parameters and a much enhanced nephelauxetic effect, (ii) the extent of d - s configurational mixing in the system, depressing the d_{z^2} orbital by several thousand wavenumbers, and (iii) the indication of an indirect role for the blocking hydrogen atoms, in the mesityl and α -methylnaphthyl derivatives, in augmenting the d - s mixing process.

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Registry No. $\text{Co}(\text{PEt}_2\text{Ph})_2(\text{mesityl})_2$, 22622-24-8; $\text{Co}(\text{PEt}_2\text{Ph})_2(\alpha\text{-methylnaphthyl})_2$, 30975-77-0; $\text{Co}(\text{PEt}_2\text{Ph})_2(\text{C}_6\text{F}_5)_2$, 31116-45-7; $\text{Co}(\text{PEt}_2\text{Ph})_2(\text{C}_6\text{Cl}_5)_2$, 22638-77-3.

Contribution from Ames Laboratory—USDOE and the Department of Chemistry, Iowa State University, Ames, Iowa 50011

Comparative Mass Spectrometry of the Group 6B Hexacarbonyls and Pentacarbonyl Thiocarbonyls

GARY D. MICHELS, GERALD D. FLESCH, and HARRY J. SVEC*

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Mass spectra, ionization energies, fragmentation energies, ionic and neutral dissociation energies, and heats of formation for the title compounds are measured and compared. Substitution of CS for CO in going from $\text{M}(\text{CO})_6$ to $\text{M}(\text{CO})_5\text{CS}$ results in (a) a slight modification of the mass spectra, if only the $\text{M}(\text{CO})_n\text{CS}^+$ and M^+ ions are considered, (b) a lowering of the ionization energies by 0.1–0.4 eV, (c) a reduction of approximately 0.1 eV in the average M–CO bond energies in both the molecule and the molecular ion, and (d) a reduction of 3.0 ± 0.3 eV in the heats of formation of the molecules. Within each molecule or molecular ion the M–CS bond is stronger than the M–CO bonds by 1.5–2.0 eV. Both the M–CS and the M–CO bonds increase in strength in going from Cr to Mo to W. Comparison of calorimetric and mass spectrometric data for $\text{M}(\text{CO})_6$ indicates that each neutral CO fragment leaves the ionization site in its first vibrationally excited state.

Introduction

During the past decade there has been considerable experimental and theoretical interest in transition-metal thiocarbonyl complexes.^{1–3} Particular emphasis has been placed upon comparing the strengths of the M–CO and M–CS bonds. As a result the group 6B metal pentacarbonyl thiocarbonyls, $\text{M}(\text{CO})_5\text{CS}$, have received much attention recently. The preparation and chemistry of these compounds have been described.^{4–7} These studies reveal that CS forms a more stable M–C bond than does CO, activates the metal atom toward CO substitution (particularly in the trans position), and undergoes electrophilic addition and nucleophilic attack more readily than does CO. These conclusions are supported by matrix isolation studies,^{8,9} studies of vibrational spectra,¹⁰ and theoretical calculations.^{11,12}

In this paper we report the mass spectra, ionization energies, and heats of formation of the group 6B hexacarbonyls and pentacarbonyl thiocarbonyls. We also compare quantitatively the M–CO and M–CS bond energies in the pentacarbonyl thiocarbonyls. In the remainder of this paper, pentacarbonyl thiocarbonyl will be shortened to thiocarbonyl.

Experimental Section

The metal carbonyls were obtained from Alfa Inorganics, Inc., Beverly, MA, and were used without further purification. The thiocarbonyls were kindly provided by B. D. Dombek (Iowa State University, Ames, IA). Hexacarbonyl impurities in the chromium and tungsten thiocarbonyls were removed via preparative gas chro-

matography⁴ to yield a product >99.9% pure. The molybdenum compound is not sufficiently stable to be purified by this method and was used without further purification. The presence of 30–40% $\text{Mo}(\text{CO})_6$ impurity precluded obtaining experimental data for $\text{Mo}(\text{CO})_n^+$ ($n = 0$ –5).

The mass spectrometer used for this research has been described previously.¹³ The instrument consists of two 15-cm radius, 60° magnetic sectors in a horizontal plane. Positive and negative ions are obtained simultaneously from a single electron beam. The positive ions are extracted, accelerated, mass analyzed, and detected in one direction and the negative ions in the opposite direction. The ion source is at ground potential, and the analyzer tubes and collectors are at ± 2000 V. The ionizing electron current of 8 μA is confined by a magnetic field of 110 G. The nominal mass range is 1–350 and a 10% valley is achieved at mass 350. Ions are detected by a magnetic

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Table I. Mass Spectra of the Group 6B Hexacarbonyls and Pentacarbonyl Thiocarbonyls (Percent Total Ions)

ion	M = Cr		M = Mo		M = W	
	hex	thio	hex	thio	hex	thio
M(CO) ₆ ⁺	12		13		14	
M(CO) ₅ CS ⁺		15		14		13
M(CO) ₅ ⁺	1		2		2	
M(CO) ₄ CS ⁺		1		2		6
M(CO) ₄ ⁺	1		4		15	
M(CO) ₃ CS ⁺		3		13		14
M(CO) ₃ ⁺	2		28		30	
M(CO) ₂ CS ⁺		11		22		26
M(CO) ₂ ⁺	22	1	19		14	3
M(CO)CS ⁺		19		17		14
M(CO) ⁺	31	5	18	3	15	2
MCS ⁺		23		19		15
M ⁺	32	20	16	10	9	6

electron multiplier (Bendix Corp. Model M-310). Currents from this device are measured by a battery-operated electrometer amplifier (Keithley Model 601) whose 0–1-V output is referenced to ground through a unity-gain isolation amplifier.¹⁴

The mass spectrometer was modified¹⁵ to allow computer control (PDP12, Digital Equipment Corp.) of the instrument during the acquisition and processing of ionization efficiency (IE) data. The IE data were acquired at 0.05-eV intervals in the 2-V energy range immediately above the onset energy. The data were interpolated to 0.01-eV intervals. Then electron energy values E_n ($n = 1, 2, \dots, 15$) were found such that $I_{E_n}/I_{E_1} = n$ and $E_{15} - E_1 = 1.5$ eV, where I_{E_n} is the ion current measured at E_n . The energy values E_n ($n = 3, 4, \dots, 15$) were used to calculate voltage differences, ΔE_n , to be used in extrapolated voltage difference (EVD) plots.¹⁶ The voltage intercept was determined from the least-squares line through the 13 data points. Each intercept was determined from data collected on at least three different days. Xenon was used as the calibrant gas to determine the ionization energy of each compound. In ensuing appearance energy determinations, data for the molecular ion were used as the standard for the EVD calculations. All of the data processing was performed automatically by the computer. The printout consisted of the 15 values for ΔE_n and the EVD intercept. Plots of ΔE_n vs. n could also be printed.

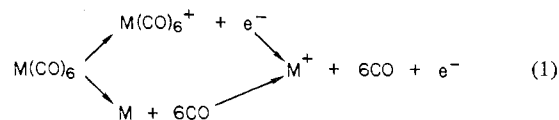
Results and Discussion

Mass Spectra. Mass spectra for the six compounds were obtained by using 50-eV electrons. The data as percent of total ions are presented in Table I. The spectrum for Mo(CO)₅CS is corrected for the Mo(CO)₆ impurity on the basis of the abundance of the Mo(CO)₆ observed and the previously determined mass spectrum of Mo(CO)₆.

The mass spectra of the hexacarbonyls reported here are in good agreement with those reported previously.^{17–20} Substitution of CS for CO in going from M(CO)₆ to M(CO)₅CS results in only a slight modification of the spectra, if only the M(CO)_nCS⁺ and M⁺ ions are considered. The other ions, M(CO)_n⁺, account for less than 10% of the total ions. Thus the probability of loss of a particular number of carbonyl ligands during the fragmentation of M(CO)₅CS is about the same as that for M(CO)₆. The low probability of the loss of CS is indicative that CS is bound more strongly to the metal than is CO. However, conclusions about the strengths of bonds based solely on mass spectra should be regarded with caution. Conclusive evidence can be obtained only from the energetics of the fragmentation processes.

Ionization Energies. Values determined for the ionization energies (I 's) of the hexacarbonyls and thiocarbonyls studied are listed in the first two rows of Table II. These values are, on the average, 0.02 ± 0.08 eV higher than the corresponding photoelectron values,^{12,21} indicating that good-quality measurements have been made. The I 's of the thiocarbonyls average about 0.3 eV lower than those for the respective hexacarbonyls. This correlates well with empirical evidence²² that substitution of a ligand in a metal carbonyl complex with one having a lower I will decrease the I of the resulting complex by 10–20% of the difference [$I(\text{CO}) - I(\text{CS}) = 2.67$ eV; $0.3/2.67 = 11\%$]. Within the framework of previous studies^{23,24} that relate this change in I to the relative σ -donor and π -receptor abilities of the ligand, these results suggest that CS is a stronger σ donor than CO. Although theoretical calculations¹² confirm that CS is a stronger σ donor than CO, the lower I 's in the thiocarbonyls were shown to be a consequence of donation from CS π -bonding orbitals rather than from the σ orbitals.

In addition to yielding qualitative insights into the nature of the bonding within these complexes, the I 's provide valuable information seldom used in bonding studies. Consider that the formation of M⁺ from M(CO)₆ may occur by two pathways:

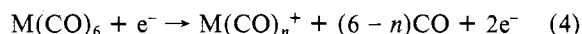


It follows that

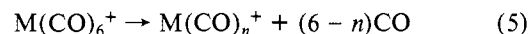
$$I[\text{M(CO)}_6] - I(\text{M}) = 6\bar{D}(\text{M-CO}) - 6\bar{D}(\text{M}^+-\text{CO}) \quad (2)$$

where $\bar{D}(\text{M-CO})$ and $\bar{D}(\text{M}^+-\text{CO})$ are the average bond dissociation energies in the molecule and molecular ion, respectively. Thus the difference between the I 's of the molecule and the central metal atom is equal to the difference between the total energies of the M–C bonds in the molecule and in the molecular ion. This source of bonding information is particularly useful in the quantitative evaluation of neutral bond energies from mass spectrometric data, since I 's determined by electron impact are usually accurate to ± 0.1 eV. Such information will be used later when bond dissociation energies are discussed.

Appearance Energies. When the molecular ion is used as the energy reference in the EVD determination of the appearance energy (A) of a fragment ion, the energy difference which is determined is really a fragmentation energy. For example, in the determination of $A[\text{M(CO)}_n^+]$ the IE data compared are those for the reactions



The energy difference is that for the reaction



Thus fragmentation energies are measured in this application of the EVD method. These measured energies are listed in Tables III and IV for the hexacarbonyls and thiocarbonyls, respectively. The appearance energies calculated from these fragmentation energies are listed in Table II. The identities of the neutral fragments, CO and CS, are unequivocal since $D(\text{C-O})$ and $D(\text{C-S})$ are much greater than $D(\text{M-C})$. The

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Table II. Ionization and Appearance Energies (eV) of the Group 6B Hexacarbonyls and Pentacarbonyl Thiocarbonyls^a

ion	M = Cr		M = Mo		M = W	
	hex	thio	hex	thio	hex	thio
M(CO) ₆ ⁺	8.42 ± 0.03		8.46 ± 0.01		8.60 ± 0.02	
M(CO) ₅ CS ⁺		8.31 ± 0.03		8.18 ± 0.02		8.22 ± 0.01
M(CO) ₅ ⁺	9.85 ± 0.03	10.58 ± 0.07	10.02 ± 0.02	10.96 ± 0.20 ^b	10.30 ± 0.03	11.46 ± 0.14
M(CO) ₄ CS ⁺		9.39 ± 0.04		9.36 ± 0.05		9.74 ± 0.04
M(CO) ₄ ⁺	10.45 ± 0.03	11.12 ± 0.05	11.61 ± 0.02	12.39 ± 0.20 ^b	12.22 ± 0.03	13.12 ± 0.11
M(CO) ₃ CS ⁺		10.22 ± 0.04		11.02 ± 0.05		11.61 ± 0.04
M(CO) ₃ ⁺	11.35 ± 0.03	12.06 ± 0.05	13.29 ± 0.02	14.05 ± 0.20 ^b	14.06 ± 0.02	14.86 ± 0.11
M(CO) ₂ CS ⁺		11.12 ± 0.04		12.39 ± 0.09		13.46 ± 0.04
M(CO) ₂ ⁺	12.51 ± 0.04	13.52 ± 0.08	14.86 ± 0.02	15.82 ± 0.30 ^b	16.29 ± 0.04	17.21 ± 0.27
M(CO)CS ⁺		12.12 ± 0.04		14.46 ± 0.05		15.83 ± 0.04
M(CO) ⁺	14.03 ± 0.04	14.94 ± 0.08	16.52 ± 0.03	17.54 ± 0.30 ^b	18.36 ± 0.06	19.48 ± 0.21
MCS ⁺		13.68 ± 0.04		16.07 ± 0.09		18.07 ± 0.04
M ⁺	15.36 ± 0.03	16.16 ± 0.07	18.24 ± 0.06	19.12 ± 0.30 ^b	21.01 ± 0.05	21.97 ± 0.13

^a The uncertainty is the standard deviation of a single measurement. ^b The values and uncertainties for $A[\text{Mo}(\text{CO})_n^+]_{\text{T}}$ were estimated by comparison to $A[\text{Cr}(\text{CO})_n^+]_{\text{T}}$ and $A[\text{W}(\text{CO})_n^+]_{\text{T}}$. See text.

Table III. Fragmentation Processes and Their Energies for the Group 6B Hexacarbonyls

assumed process	$\Delta H, \text{eV}$		
	Cr(CO) ₆	Mo(CO) ₆	W(CO) ₆
M(CO) ₆ ⁺ → M(CO) ₅ ⁺ + CO	1.43 ± 0.01	1.56 ± 0.01	1.70 ± 0.02
→ M(CO) ₄ ⁺ + 2CO	2.03 ± 0.01	3.15 ± 0.01	3.62 ± 0.02
→ M(CO) ₃ ⁺ + 3CO	2.93 ± 0.01	4.83 ± 0.02	5.46 ± 0.01
→ M(CO) ₂ ⁺ + 4CO	4.09 ± 0.03	6.40 ± 0.02	7.69 ± 0.03
→ M(CO) ⁺ + 5CO	5.61 ± 0.02	8.06 ± 0.03	9.76 ± 0.05
→ M ⁺ + 6CO	6.94 ± 0.01	9.78 ± 0.06	12.41 ± 0.04

Table IV. Fragmentation Processes and Their Energies for the Group 6B Thiocarbonyls

assumed process	$\Delta H, \text{eV}$		
	Cr(CO) ₅ CS	Mo(CO) ₅ CS	W(CO) ₅ CS
M(CO) ₅ CS ⁺ → M(CO) ₄ CS ⁺ + CO	1.08 ± 0.03	1.18 ± 0.04	1.52 ± 0.04
→ M(CO) ₃ CS ⁺ + 2CO	1.91 ± 0.03	2.84 ± 0.04	3.39 ± 0.04
→ M(CO) ₂ CS ⁺ + 3CO	2.81 ± 0.03	4.21 ± 0.09	5.24 ± 0.04
→ M(CO)CS ⁺ + 4CO	3.81 ± 0.03	6.28 ± 0.04	7.61 ± 0.04
→ MCS ⁺ + 5CO	5.37 ± 0.03	7.89 ± 0.09	9.85 ± 0.04
→ M(CO) ₅ ⁺ + CS	2.27 ± 0.06	2.78 ± 0.20 ^a	3.24 ± 0.14
→ M(CO) ₄ ⁺ + CS + CO	2.81 ± 0.04	4.21 ± 0.20 ^a	4.90 ± 0.11
→ M(CO) ₃ ⁺ + CS + 2CO	3.75 ± 0.04	5.87 ± 0.20 ^a	6.64 ± 0.11
→ M(CO) ₂ ⁺ + CS + 3CO	5.21 ± 0.07	7.64 ± 0.30 ^a	8.99 ± 0.27
→ M(CO) ⁺ + CS + 4CO	6.63 ± 0.07	9.36 ± 0.30 ^a	11.26 ± 0.21
→ M ⁺ + CS + 5CO	7.85 ± 0.06	10.94 ± 0.30 ^a	13.75 ± 0.13

^a These values were calculated from the appearance energies given in Table II.

appearance energies of the fragments from the hexacarbonyls are in fair agreement with the values reported by previous investigators.¹⁷⁻²⁰

Note that values for $A[\text{Mo}(\text{CO})_n^+]_{\text{T}}$ are listed in Table II even though no experimental values were possible. The values listed were estimated from the values observed for $A[\text{Cr}(\text{CO})_n^+]_{\text{T}}$ and $A[\text{W}(\text{CO})_n^+]_{\text{T}}$. We define an appearance energy difference, ΔA_n , for $\text{Cr}(\text{CO})_n^+$ as in eq 6 where the subscripts

$$(\Delta A_n)_{\text{Cr}} = A[\text{Cr}(\text{CO})_n^+]_{\text{T}} - A[\text{Cr}(\text{CO})_n^+]_{\text{H}} \quad (n = 0-5) \quad (6)$$

T and H denote that the ions were produced from the thiocarbonyl and hexacarbonyl, respectively. Values of $(\Delta A_n)_{\text{Mo}}$ and $(\Delta A_n)_{\text{W}}$ are similarly defined. Examination of the data shows that the ΔA 's are relatively constant (0.80 ± 0.13 eV for the chromium compounds and 0.98 ± 0.14 eV for the tungsten compounds). It is reasonable to assume that the ΔA 's for the molybdenum compounds are also reasonably constant and midway, ± 0.2 eV, between the values for the chromium and tungsten compounds. Thus the values for $A[\text{Mo}(\text{CO})_n^+]_{\text{T}}$ were calculated by use of eq 7 with uncertainties estimated

$$A[\text{Mo}(\text{CO})_n^+]_{\text{T}} = A[\text{Mo}(\text{CO})_n^+]_{\text{H}} + \frac{(\Delta A_n)_{\text{Cr}} + (\Delta A_n)_{\text{W}}}{2} \quad (7)$$

to be 0.2 eV for the heavier ions and 0.3 eV for the lighter ions. Differences between $I[\text{Mo}(\text{CO})_5\text{CS}]$ and the appropriate values of $A[\text{Mo}(\text{CO})_n^+]_{\text{T}}$ are listed as fragmentation energies in Table IV.

If we neglect any effects due to kinetic or excitation energies, the data represent the energies required to remove successive ligands from the molecular ion. This is evidenced by the monotonic increase in energy required with increased fragmentation.

Dissociation Energies. The energetics of the fragmentation processes provide a means of determining ionic bond dissociation energies. Usually such calculations have limited value because of indeterminate errors due to excess kinetic and excitational energies. However, in the case of the hexacarbonyls, the calculated values can be compared to combustion calorimetry values, which are known accurately. Any corrections found to be necessary should be applicable to the thiocarbonyl results since the compounds are similar, as are their fragmentations in the mass spectrometer. Thus the hexacarbonyl data are used to calibrate the mass spectrometer for the thiocarbonyl data. For this reason the hexacarbonyl results are discussed first.

Specific bond dissociation processes and the energies required for them are listed in Table V for the ions from the hexacarbonyls. With the exclusion of the first entry in each

Table V. Specific Bond Dissociation Energies (eV) of the Ions from the Group 6B Hexacarbonyls

dissocn process	bond dissoen energy		
	Cr	Mo	W
$M(CO)_6^+ \rightarrow M(CO)_5^+ + CO$	1.43	1.56	1.70
$M(CO)_5^+ \rightarrow M(CO)_4^+ + CO$	0.60	1.59	1.92
$M(CO)_4^+ \rightarrow M(CO)_3^+ + CO$	0.90	1.68	1.84
$M(CO)_3^+ \rightarrow M(CO)_2^+ + CO$	1.16	1.57	2.23
$M(CO)_2^+ \rightarrow M(CO)^+ + CO$	1.52	1.66	2.07
$M(CO)^+ \rightarrow M^+ + CO$	1.33	1.72	2.65
av \pm std dev	1.16 \pm 0.35	1.63 \pm 0.03	2.07 \pm 0.34

Table VI. Ionic Bond Dissociation Energies (eV) for $M(CO)_6$

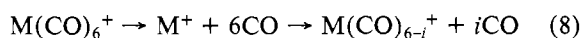
compd	$\bar{D}(M^+-CO)$				
	electron impact	calorimetric ^a	$\hat{D}(M^+-CO)^b$	Δ	SEE
Cr(CO) ₆	1.16 \pm 0.01	0.83 \pm 0.01	1.10 \pm 0.03	0.27	0.29
Mo(CO) ₆	1.63 \pm 0.01	1.35 \pm 0.01	1.61 \pm 0.01	0.26	0.06
W(CO) ₆	2.07 \pm 0.01	1.74 \pm 0.01	1.97 \pm 0.04	0.23	0.36

^a Calculated from eq 2 by using experimental values for $\bar{D}(M-CO)$,²⁷ $I[M(CO)_6]$ (this work), and $I[M]$.²⁶ ^b The uncertainties are those obtained for a random variation of one standard deviation in each of the fragmentation energies used in the calculations.

column, the entries are obtained by taking successive differences of the processes and energies listed in Table III. The values for the energies listed in each column represent six values of the M^+-CO bond energy. Differences in the values within each column are the result of variations in reorganizational energies of the ions. Differences in the values within each row are consistent with the conclusion that $D(W^+-CO) > D(Mo^+-CO) > D(Cr^+-CO)$.

For making comparisons between different compounds a single quantity is desired which is related to the specific bond dissociation energies of a molecule and which is free of reorganizational effects. Such a quantity is given by the average of the six dissociation energies and is called appropriately the average bond dissociation energy, $\bar{D}(M^+-CO)$. Because of the arithmetic involved, this bond energy is one-sixth the energy of the final process listed in Table III. These are the values listed in column 2 of Table VI. The precision is one-sixth that of the final process listed in Table III. This method of determining $\bar{D}(M^+-CO)$ has two advantages. First, only one fragmentation energy need be measured. Second, there are no reorganizational effects for the reaction since the fragmentation is complete. However, there are also disadvantages. Information available from the other fragmentation processes is ignored. More importantly, a single term does not adequately describe the bonding which occurs in molecules having more than one set of chemically equivalent bonds [e.g., $M(CO)_5CS$]. The energy to fragment such a molecule completely is described by a sum of terms, one for each set of equivalent bonds. To overcome these disadvantages, we developed a model to describe the fragmentation which occurs. Use of this model and a least-squares treatment of all the fragmentation energy data yields an energy term for each set of chemically equivalent bonds.

Consider the fragmentation reactions listed in Table III. To a first approximation the specific bond dissociations are equal, and reorganizational energies can be neglected. Thus the i th fragmentation can be envisioned as occurring with the breaking of all of the $M-CO$ bonds in the molecular ion, followed by the making of $(6-i)$ $M-CO$ bonds in the fragment ion.



The enthalpy of this i th fragmentation is equal to the energy required to break the six bonds, $6\hat{D}(M^+-CO)$, minus the en-

ergy gained in forming the product ion, $(6-i)\hat{D}(M^+-CO)$. Here $\hat{D}(M^+-CO)$ is the average bond dissociation energy calculated for this model of the fragmentation process. It is assumed that all the $M-CO$ bonds are equivalent within each ion, $M(CO)_{6-i}^+$, and from ion to ion. The six enthalpy equations for the $Cr(CO)_6$ fragmentations are

$$\begin{aligned} \hat{D}(Cr^+-CO) &= 1.43 \text{ eV} & 2\hat{D}(Cr^+-CO) &= 2.03 \text{ eV} \\ 3\hat{D}(Cr^+-CO) &= 2.93 \text{ eV} & 4\hat{D}(Cr^+-CO) &= 4.09 \text{ eV} \quad (9) \\ 5\hat{D}(Cr^+-CO) &= 5.61 \text{ eV} & 6\hat{D}(Cr^+-CO) &= 6.94 \text{ eV} \end{aligned}$$

The observational equations of this set of six equations in one unknown may be written in matrix form as given in (10).

$$\begin{bmatrix} 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \end{bmatrix} \hat{D}(M^+-CO) = \begin{bmatrix} 1.43 \\ 2.03 \\ 2.93 \\ 4.09 \\ 5.61 \\ 6.94 \end{bmatrix} \text{ or } \begin{bmatrix} 1.56 \\ 3.15 \\ 4.83 \\ 6.40 \\ 8.06 \\ 9.78 \end{bmatrix} \text{ or } \begin{bmatrix} 1.70 \\ 3.62 \\ 5.46 \\ 7.69 \\ 9.76 \\ 12.41 \end{bmatrix} \quad (10)$$

These observational equations were solved by least-squares methods²⁵ to yield the results listed in column 4 of Table VI. The precision listed is that obtained for a random variation of one standard deviation in each of the energy values in the six observational equations. This indicates that usual random errors in individual measurements have little effect on the value calculated for $\hat{D}(M^+-CO)$. Comparison of these values with those of column 2 show that the agreement is excellent. This is encouraging in view of the assumptions made in developing the observational equations.

The standard estimate of error (SEE) is a measure of how well the values calculated from the fragmentation agree with the observed data. The SEE is the root-mean-square value of the differences between the observed and calculated fragmentation energies. Values obtained for SEE for the hexacarbonyl fragmentation model are listed in column 5 of Table VI and indicate a reasonable accuracy for the model. The values are in agreement with the standard deviations listed in Table V, as expected.

The value of $\bar{D}(M^+-CO)$ can also be calculated from eq 2 by using the mass spectrometric values of $I[M(CO)_6]$ reported here, the I 's of the metal atoms²⁶ [6.76, 7.10, and 7.98 eV for Cr, Mo, and W, respectively] and $\bar{D}(M-CO)$'s from a recent calorimetric study²⁷ [1.11, 1.57, and 1.85 eV for $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$, respectively]. The resultant values for $\bar{D}(M^+-CO)$ are listed in column 3 of Table VI. These values are lower than those of column 4, and the difference is listed in column 5 of the table. The differences are surprisingly constant for all three compounds. The lack of a mass dependence eliminates fragment kinetic energies as a probable cause. Their magnitudes are too low to result from electronic excitations but are highly suggestive of vibrational excitations. In fact, the average, 0.25 eV, agrees with the vibrational fundamental²⁸ of CO, 0.27 eV. This leads to the interpretation that CO carries away one quantum of vibrational energy during the cleavage of the $M-CO$ bond. Direct evidence supporting this hypothesis was obtained by determining $I(CO)$ for the CO produced in the fragmentation of $Cr(CO)_6$ during electron impact. If CO is produced in its first ($v = 1$) vibrational state, its ionization energy should be lowered by 0.27

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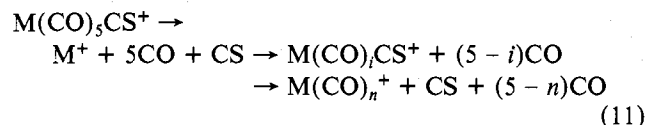
Table VII. Least-Squares Ionic Bond Dissociation Energies (eV)^a

compd	$\hat{D}(M^+-CO)_H$	$\hat{D}(M^+-CO)_T$	$\hat{D}(M^+-CS)$	SEE
Cr(CO) ₅ CS	0.90 ± 0.03	0.74 ± 0.02	2.46 ± 0.15	0.25
Mo(CO) ₅ CS	1.39 ± 0.13	1.26 ± 0.08	3.13 ± 0.52	0.20
W(CO) ₅ CS	1.84 ± 0.09	1.64 ± 0.05	3.82 ± 0.44	0.34

^a Calculated for the thiocarbonyls by assuming equivalence of the five M⁺-CO bonds and including a calculation for $\hat{D}(M^+-CO)_H$. The uncertainties are those obtained for a random variation of one standard deviation in each of the fragmentation energies used in the calculations.

eV. By use of a recently developed neutral-fragment mass spectrometer,²⁹ $I(\text{CO})$ for gaseous CO was determined to be 14.0 ± 0.1 eV. The value obtained for $I(\text{CO})$ for the CO fragment from Cr(CO)₆ is 13.7 ± 0.1 eV, as anticipated. Similar results have been observed for CO produced from ketones.³⁰ The experiment was not repeated by using Mo(CO)₆ or W(CO)₆ because their vapor pressures are too low to provide sufficient gas flow into the present neutral-fragment mass spectrometer.

From these studies of M(CO)₆ it is concluded that the calculations using mass spectrometric data do yield accurate values for the bond dissociation energies of the hexacarbonyls if a correction is made for vibrational excitation in the free ligands generated. Similar treatment of the mass spectrometric data for M(CO)₅CS should also yield accurate values for the bond dissociation energies involved. In this case the fragmentation is envisioned to occur in either of two ways:



If we neglect any effects caused by reorganization of the fragments, the energy of each process can be attributed to the making and breaking of M⁺-CS and M⁺-CO bonds. A series of observational equations can be generated in the same manner as was done for the hexacarbonyl compounds. It is assumed that the five M⁺-CO bonds in M(CO)₅CS⁺ are energetically equivalent but that they are different in energy from the M⁺-CS bond, and also different from the M⁺-CO bonds in M(CO)₆⁺. Three quantities can be calculated on the basis of this model: $\hat{D}(M^+-CO)_T$, $\hat{D}(M^+-CO)_H$, and $\hat{D}(M^+-CS)$. The subscripts T and H differentiate the M⁺-CO energy in those ions containing the CS ligand from those which do not. It is assumed that the M(CO)_n⁺ ions formed in the thiocarbonyl fragmentation are identical with those formed in the hexacarbonyl fragmentations. It is also assumed that the free CS is in its first vibrational state,²⁸ viz., 0.16 eV. Correcting the data from Table IV by 0.27 eV for each free CO and 0.16 eV for a free CS formed in the fragmentations permits generation of the observational matrix equations (12).

$$\begin{bmatrix} 1 & 0 & 0 \\ 2 & 0 & 0 \\ 3 & 0 & 0 \\ 4 & 0 & 0 \\ 5 & 0 & 0 \\ 5 & 1 & -5 \\ 5 & 1 & -4 \\ 5 & 1 & -3 \\ 5 & 1 & -2 \\ 5 & 1 & -1 \\ 5 & 1 & 0 \end{bmatrix} \begin{bmatrix} \hat{D}(M^+-CO)_T \\ \hat{D}(M^+-CO)_H \\ \hat{D}(M^+-CS) \end{bmatrix} = \begin{matrix} \text{Cr} & \text{Mo} & \text{W} \\ \begin{bmatrix} 0.81 \\ 1.37 \\ 2.00 \\ 2.73 \\ 4.02 \\ 2.11 \\ 2.38 \\ 3.05 \\ 4.24 \\ 5.39 \\ 6.34 \end{bmatrix} & \text{or} & \begin{bmatrix} 0.91 \\ 2.30 \\ 3.40 \\ 5.20 \\ 6.54 \\ 2.62 \\ 3.78 \\ 5.17 \\ 6.67 \\ 8.12 \\ 9.43 \end{bmatrix} & \text{or} & \begin{bmatrix} 1.25 \\ 2.85 \\ 4.43 \\ 6.53 \\ 8.50 \\ 3.08 \\ 4.47 \\ 5.94 \\ 8.02 \\ 10.02 \\ 12.24 \end{bmatrix} \end{matrix} \quad (12)$$

The results of the least-squares solutions of these equations are listed in Table VII. The values for SEE are essentially equal to those in Table VI, indicating a similarly accurate fragmentation model. Note in particular that the values calculated for $\hat{D}(M^+-CO)_H$ are in excellent agreement with the calorimetric values for $\bar{D}(M^+-CO)$ listed in Table VI. This is strong evidence that values calculated from this model of fragmentation are reliable. Because of this agreement, the calorimetric values for $\bar{D}(M^+-CO)$ were substituted for $\hat{D}(M^+-CO)_H$ in the observational equations, and values for $\hat{D}(M^+-CO)_T$ and $\hat{D}(M^+-CS)$ were recalculated. The recalculated values are listed in the middle portion of Table VIII. Using the lower, calorimetric values for $\bar{D}(M^+-CO)$ has no effect on the values for SEE or the values calculated for $\hat{D}(M^+-CO)_T$ but results in slightly lower values for $\hat{D}(M^+-CS)$. The data clearly show that in the positive ion, the M⁺-CS bonds are considerably stronger than the M⁺-CO bonds. The M⁺-CO bonds in the thiocarbonyls are slightly weaker than the M⁺-CO bonds in the hexacarbonyls. These conclusions are in agreement with previously published results for the group 6B thiocarbonyl complexes.^{4,10} Analogous with the hexacarbonyl compounds, the M⁺-CO dissociation energies decrease in the order W > Mo > Cr. The M⁺-CS bond strengths show a similar dependence.

A recent electron-impact study³¹ of cyclopentadienyl-manganese thiocarbonyl and carbonyl complexes and a recent X-ray structural investigation³² of *trans*-W(CO)₄-(CNC₆H₁₁)CS have also shown the M-CS bond to be stronger than the M-CO bond. In contradiction to the present findings, the electron-impact results³¹ show the M⁺-CO bonds in the thiocarbonyl complexes to be slightly stronger than those of the carbonyl analogues. This discrepancy can presumably be attributed to a crossover in the electronic properties³³ of CS and CO.

Experimental evidence⁷ and force constant calculations¹⁰ suggest that the five carbonyl ligands of the M(CO)₅CS complexes are not equivalent. One of them, presumably the CO trans to CS, may be more weakly bound than the rest. On this basis the data of Table IV may be fit to a second model wherein the weak bond is denoted $\hat{D}(M^+-CO)_T$ and the strong bonds are denoted $\hat{D}(M^+-CO)_H$. For the purpose of generating the observational equations, the assumption is made that the weaker M⁺-CO bond is broken first. Also, the calorimetric value for $\bar{D}(M^+-CO)_H$ is substituted for $\hat{D}(M^+-CO)_H$. The resulting observational matrix equations are given in (13).

$$\begin{bmatrix} 1 & 0 & 0 \\ 1 & 1 & 0 \\ 1 & 2 & 0 \\ 1 & 3 & 0 \\ 1 & 4 & 0 \\ 1 & 4 & 1 \\ 1 & 4 & 1 \\ 1 & 4 & 1 \\ 1 & 4 & 1 \\ 1 & 4 & 1 \\ 1 & 4 & 1 \end{bmatrix} \begin{bmatrix} \hat{D}(M^+-CO)_T \\ \hat{D}(M^+-CO)_H \\ \hat{D}(M^+-CS) \end{bmatrix} = \begin{matrix} \text{Cr} & \text{Mo} & \text{W} \\ \begin{bmatrix} 0.81 \\ 1.37 \\ 2.00 \\ 2.73 \\ 4.02 \\ 6.26 \\ 5.54 \\ 5.90 \\ 6.22 \\ 6.34 \end{bmatrix} & \text{or} & \begin{bmatrix} 0.91 \\ 2.30 \\ 3.40 \\ 5.20 \\ 6.54 \\ 9.32 \\ 9.19 \\ 9.35 \\ 9.46 \\ 9.43 \end{bmatrix} & \text{or} & \begin{bmatrix} 1.25 \\ 2.85 \\ 4.43 \\ 6.53 \\ 8.50 \\ 11.83 \\ 11.19 \\ 11.52 \\ 11.77 \\ 12.24 \end{bmatrix} \end{matrix} \quad (13)$$

The dissociation energies calculated from these sets of equations are tabulated in the lower portion of Table VIII. The values for SEE indicate a slightly better fit of the observed and calculated data for Mo(CO)₅CS and W(CO)₅CS. There may be slight reductions in the M⁺-CS dissociation energies, but, more significantly, the destabilizing effect of the CS ligand

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Table VIII. Least-Squares Ionic Bond Dissociation Energies (eV) for the Thiocarbonyls^a

compd	$\bar{D}(M^+-CO)_H$	$\hat{D}(M^+-CO)_T$	$\hat{D}'(M^+-CO)_T$	$\hat{D}(M^+-CS)$	SEE
Cr(CO) ₆	0.83 ± 0.01				
Mo(CO) ₆	1.35 ± 0.01				
W(CO) ₆	1.74 ± 0.01				
Cr(CO) ₅ CS		0.74 ± 0.02		2.29 ± 0.10	0.26
Mo(CO) ₅ CS		1.27 ± 0.09		2.97 ± 0.42	0.21
W(CO) ₅ CS		1.62 ± 0.05		3.59 ± 0.28	0.35
Cr(CO) ₅ CS		0.78 ± 0.06	0.65 ± 0.11	2.26 ± 0.14	0.26
Mo(CO) ₅ CS		1.41 ± 0.22	0.84 ± 0.44	2.82 ± 0.61	0.13
W(CO) ₅ CS		1.82 ± 0.17	1.07 ± 0.23	3.32 ± 0.34	0.27

^a The middle portion of the table contains values calculated by assuming all five M⁺-CO bonds are equivalent; those for the lower portion were calculated by assuming four equivalent stronger bonds and one weaker bond. Calorimetric values of $\bar{D}(M^+-CO)_H$ are listed in the upper portion for comparison. The uncertainties are those obtained for a random variation of one standard deviation in each of the fragmentation energies used in the calculations.

is limited to the weaker M⁺-CO bond. This destabilizing effect increases significantly going from Cr to Mo to W. Dissociation energies of the remaining four carbonyls are essentially the same as those of M(CO)₆⁺. The relative energy ordering, W > Mo > Cr, is preserved in all cases.

On the basis of the calculations from these two fragmentation models (five equivalent M-CO bonds or four equivalent strong bonds and one weak bond) and experimental ligand substitution evidence (specific trans substitution⁷ in W(CO)₅L, ambiguous results³⁴ for Mo(CO)₅L and random substitution³⁴ in Cr(CO)₅L) it is reasonable to assume that the four strong-one weak bond model is the better description for W(CO)₅CS, that the five equivalent bond model is the better description for the Cr(CO)₅CS, and that the description for Mo(CO)₅CS is somewhere between.

Neutral Dissociation Energies. Bond energies in the molecule and the molecular ion for complexes of the type M(CO)₆ are related according to eq 2. The analogous relationship for M(CO)₅CS complexes is

$$I[M(CO)_5CS] - I(M) = 5\hat{D}(M-CO)_T + \hat{D}(M-CS) - 5\hat{D}(M^+-CO)_T - \hat{D}(M^+-CS) \quad (14)$$

where it is assumed that the five carbonyls are equivalent and the substitution of \hat{D} for \bar{D} has been made. Except for the neutral dissociation energies, $\hat{D}(M-CO)_T$ and $\hat{D}(M-CS)$, all the terms of this equation are known. The dissociation energy $\hat{D}(M-CO)_T$ can be estimated if it is assumed that the differences in the M-CO dissociation energies of the molecule and the molecular ion are the same for the thiocarbonyls as for the hexacarbonyls:

$$\bar{D}(M^+-CO)_H - \bar{D}(M-CO)_H = \hat{D}(M^+-CO)_T - \hat{D}(M-CO)_T \quad (15)$$

The dissociation energies used for the left side of the equation are the calorimetric values presented earlier, and values for $\hat{D}(M^+-CO)_T$ are taken from Table VIII. The values calculated for $\hat{D}(M-CO)_T$ are listed in the middle portion of Table IX. Substitution of the appropriate values into eq 10 yields values for $\hat{D}(M-CS)$ which are also listed in the middle portion of Table IX. Similar calculations for the four strong-one weak bonding model can also be made. The values calculated for that model are listed in the lower portion of Table IX.

It is seen that in the molecule, as in the molecular ion, the M-CS bond is much stronger than the M-CO bonds. The presence of the CS ligand slightly weakens the M-CO bond (equivalent bond model) or has little effect on four of the M-CO bonds while appreciably weakening the fifth M-CO bond (four strong-one weak model). The data also indicate that $\hat{D}(Cr-CS) > \hat{D}(Cr^+-CS)$, $\hat{D}(Mo-CS) \approx \hat{D}(Mo^+-CS)$,

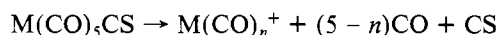
Table IX. Least-Squares Neutral Dissociation Energies (eV) for the Thiocarbonyls^a

compd	$\bar{D}(M-CO)_H$	$\hat{D}(M-CO)_T$	$\hat{D}'(M-CO)_T$	$\hat{D}(M-CS)$
Cr(CO) ₆	1.11 ± 0.01			
Mo(CO) ₆	1.57 ± 0.01			
W(CO) ₆	1.85 ± 0.01			
Cr(CO) ₅ CS		1.02 ± 0.02		2.46 ± 0.14
Mo(CO) ₅ CS		1.50 ± 0.19		2.92 ± 0.47
W(CO) ₅ CS		1.72 ± 0.15		3.29 ± 0.30
Cr(CO) ₅ CS		1.06 ± 0.16	0.91 ± 0.21	2.43 ± 0.17
Mo(CO) ₅ CS		1.64 ± 0.32	1.07 ± 0.54	2.77 ± 0.62
W(CO) ₅ CS		1.92 ± 0.27	1.17 ± 0.33	3.04 ± 0.35

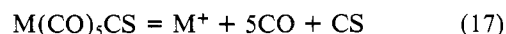
^a The middle portion of the table contains values calculated by assuming all five M-CO bonds are equivalent; those in the lower portion were calculated by assuming four equivalent stronger bonds and one weaker bond. Calorimetric values for $\bar{D}(M-CO)_H$ are listed in the upper portion for comparison. The uncertainties are those obtained for a random variation of one standard deviation in each of the fragmentation energies used in the calculations.

and $\hat{D}(W-CS) < \hat{D}(W^+-CS)$, although the uncertainties are large.

Neutral Heats of Formation. The appearance energy data also yield information about the heats of formation of Cr(CO)₅CS, Mo(CO)₅CS, and W(CO)₅CS in the gas phase. Consider the dissociative ionization of the hexacarbonyls and thiocarbonyls to common ions:



The difference of the two appearance energies for each M(CO)_n⁺ (after correction for excitation energy in each free ligand) gives a value for the enthalpy of the ligand substitution reaction. These values and their averages are listed in Table X. From the average values and the known heats of formation of Cr(CO)₆, Mo(CO)₆, W(CO)₆, CO, and CS (-9.41 ± 0.02,²⁷ -9.49 ± 0.02,²⁷ -9.16 ± 0.03,²⁷ -1.146 ± 0.002,³⁵ and +2.93 ± 0.09 eV,³⁶ respectively), values for ΔH_f° [Cr(CO)₅CS(g)], ΔH_f° [Mo(CO)₅CS(g)], and ΔH_f° [W(CO)₅CS(g)] are calculated to be -6.3 ± 0.2, -6.4 ± 0.3, and -6.2 ± 0.2 eV, respectively. These results are in agreement with heat of formation, -6.6 ± 0.1, -6.5 ± 0.3, and -6.5 ± 0.1 eV, respectively, calculated directly from corrected appearance potentials of the metal ions:



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Table X. Substitution Energies (eV) for $M(\text{CO})_5\text{CS} + \text{CO} \rightarrow M(\text{CO})_6 + \text{CS}$

related ion	M = Cr	M = Mo ^a	M = W
$M(\text{CO})_5^+$	0.84	1.05	1.27
$M(\text{CO})_4^+$	0.78	0.89	1.01
$M(\text{CO})_3^+$	0.82	0.87	0.91
$M(\text{CO})_2^+$	1.12	1.07	1.03
$M(\text{CO})^+$	1.02	1.13	1.23
M^+	0.91	0.99	1.07
av \pm std dev	0.92 ± 0.13	1.00 ± 0.30	1.09 ± 0.14

^a The number for $\text{Mo}(\text{CO})_n^+$ is the average of $\text{Cr}(\text{CO})_n^+$ and $\text{W}(\text{CO})_n^+$ and results from the method used to estimate $A[\text{Mo}(\text{CO})_n^+]$. The larger uncertainty reflects the uncertainty of the estimate.

The averages of these determinations, -6.4 ± 0.2 , -6.4 ± 0.3 , and -6.3 ± 0.2 eV, are preferred values for $\Delta H_f^\circ[\text{Cr}(\text{CO})_5\text{CS}(\text{g})]$, $\Delta H_f^\circ[\text{Mo}(\text{CO})_5\text{CS}(\text{g})]$, and $\Delta H_f^\circ[\text{W}(\text{CO})_5\text{CS}(\text{g})]$, respectively.

Summary and Conclusions

The mass spectrometer has been used to determine and/or compare the values of several thermodynamic parameters of the group 6B hexacarbonyls and pentacarbonyl thiocarbonyls. From these results we conclude that for these compounds (1)

fragmentation of the molecular ion in the mass spectrometer results in vibrational excitation of the free ligands produced, (2) substitution of CS for CO in $M(\text{CO})_6$ lowers the ionization energy of the molecule by 0.1-0.4 eV, (3) the M-CS bond is significantly stronger than the M-CO bonds in all three pentacarbonyl thiocarbonyls, in both the molecule and the molecular ion, and (4) the calculations of the four strong-one weak bonding model are supportive of the hypothesis that substitution of the CS ligand for the one of the CO ligands results in weakening of the M-CO bond trans to the CS ligand.

These studies support the conclusions drawn from theoretical and experimental research performed elsewhere^{8-12,22-24,31,32} and show that the electron-impact mass spectrometer can be a useful and reliable tool for probing the physical chemistry of inorganic molecules.

Acknowledgment. We wish to acknowledge Duane Dombeck, who provided the pentacarbonyl thiocarbonyls, William Deissler, who measured the ionization energy of the CO from chromium hexacarbonyl, and R. J. Angelici for his interest and cooperation. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under Contract W-7405-eng-82.

Registry No. $\text{Cr}(\text{CO})_6$, 13007-92-6; $\text{Cr}(\text{CO})_5\text{CS}$, 50358-90-2; $\text{Mo}(\text{CO})_6$, 13939-06-5; $\text{Mo}(\text{CO})_5\text{CS}$, 50358-91-3; $\text{W}(\text{CO})_6$, 14040-11-0; $\text{W}(\text{CO})_5\text{CS}$, 50358-92-4.

Contribution from the Department of Chemistry,
Rutgers, The State University of New Jersey, Newark, New Jersey 07102

The Association of Optically Active Ions. 2. The Pfeiffer-Active System Tris(1,10-phenanthroline)zinc(II) with Adenosine 5'-Monophosphate and Related Compounds

CLIFFORD CHING-YU LEE and PAUL HEMMES*

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The system tris(1,10 phenanthroline)zinc(II) with adenosine 5'-monophosphate shows remarkable Pfeiffer activity. Noteworthy is the fact that the related compounds adenosine and α -ribose phosphate show little or no Pfeiffer activity in the pH range studied. The pH dependence indicates that a number of processes occur. At low pH the effect is most pronounced. It is concluded that short-range interaction between the purine base and the ligand rings is intimately involved in the ionic association process. The enhancement of the Pfeiffer effect in the protonated species may be due to a charge-transfer interaction from the ligands to the environmental compound. Protonation of the purine base would therefore make it a better electron acceptor. All Pfeiffer-active systems are shown by Job's method to involve 2 mol of environmental compound/mol of zinc complex.

Pfeiffer activity¹ is the nonadditivity of optical activity which sometimes results when a labile racemic component is added to a nonlabile optically active species. The two major mechanisms which have been proposed to account for this effect are the formation of diastereomeric ion pairs^{2a,b} and the shifting of the racemization equilibrium due to an asymmetric electric field, leading to unequal activity coefficients and thus unequal concentrations.^{3a,b} We have found a system which we feel clearly shows that the former mechanism provides a better description of the process. In addition this system provides

some insight into the nature of the bonding between the components of the ion pairs.

Experimental Section

We have investigated the optical activity of the system 0.01 M tris(1,10-phenanthroline)zinc(II) with 0.02 M sodium adenosine 5'-monophosphate as a function of pH, as well as the system containing the same cation but 0.02 M sodium D-ribose phosphate. In addition we have studied solutions of 0.020 M adenosine with and without the zinc complex also as a function of pH.

The cation was prepared by mixing stoichiometric amounts of the ligand with a concentrated zinc chloride solution. (The 5'-AMP, 3',5'-c-AMP, and sodium D-ribose phosphate were obtained from Sigma Chemical Co. and were used as received.) All other reagents were obtained from Fisher Scientific Co. and were used without further purification.

Optical rotations were measured at the sodium D line on a Rudolph polarimeter fitted with a photoelectric detector using a filtered sodium

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