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## Synergistic Effects in Transition-Metal Complexes with Two or Three Ligands

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The collision-induced decomposition spectra of several complexes  $ML_1L_2^+$  and  $ML_1L_2L_3^+$ , where  $M = Mn, Fe, \text{ and } Co$  and  $L_i = CO, NO, H_2O, \text{ and } CH_3OH$ , are described. Treating branching ratios for ligand loss processes as equilibrium constants in these cases is justified empirically. Relative metal-ligand bond strengths derived from this treatment show antisymbiotic synergistic effects.

### Introduction

Synergistic effects occur in metal complexes having two or more ligands. The result of these effects is that the strengths of each metal-ligand interaction reflect the identity of the remaining ligands.<sup>1</sup> The present report describes such effects in ionic gas-phase transition-metal complexes with two, three, or four ligands. Synergistic effects appear to play an important role in determining fragmentation patterns in the collision-induced decompositions of the complexes.

Synergistic effects are evident in equilibrium constants for gas-phase ligand-exchange reactions of ionic transition-metal complexes with two ligands.<sup>2</sup> The measured equilibrium constants indicate that  $ML_1L_2^+$  is stabilized when  $L_1$  is a  $\pi$  acceptor and  $L_2$  is a  $\sigma$  donor. This is reflected in the average metal-ligand bond strengths in  $M(L_1)_2^+$ ,  $M(L_2)_2^+$ , and  $M(L_1)(L_2)^+$ . Rather than examining equilibria in competitive ligand-exchange reactions, the present study examines competitive loss of individual ligands from metal complexes activated in an energetic collision. This method probes individual bond strengths rather than average bond strengths and reveals an effect similar to that observed in the ligand-substitution studies. This method is applicable to several ligands including CO and  $H_2O$ , which are inaccessible to the ligand-substitution studies.

McLucky, Schoen, and Cooks<sup>3</sup> have described the connection observed between collision-induced decomposition of  $Ag^+$  complexes and metal-ligand bond strengths. Their treatment of the  $Ag^+$  results is a generalization of a similar treatment of the collision-induced decomposition of proton bound dimers by McLuckey, Cameron, and Cooks.<sup>4</sup> The present results on  $Mn^+$ ,  $Fe^+$ , and  $Co^+$  complexes are interpreted in a similar way.

In a typical experiment the metal complexes are formed by electron impact on volatile metal compounds or by ion molecule reactions in a chemical ionization source. The ion of interest is selected by a double-focusing mass analyzer and enters a collision chamber. The high-velocity ion suffers collisions in the collision chamber and forward-scattered products of glancing collisions enter a second mass analyzer. A mass spectrum of the collision products is obtained. For the ions examined in this study, such collision-induced decomposition (CID) spectra are typically dominated by peaks corresponding to ions formed by loss of one ligand. The basic assumption made in interpreting the results is that the most weakly bound ligand is most readily lost.

If certain assumptions are made about the kinetics of the ligand loss process, the extent to which loss of the weaker ligand is dominant can be treated quantitatively. Complex  $M^+L_1L_2$  may lose either  $L_1$  or  $L_2$ . Suppose the energy difference between the two channels is  $\Delta E$ . We then expect that the ratio of the two loss channels will be  $\exp(-\Delta E/kT)$  subject to two conditions. First, the preexponential factors (or frequency factors, or activation entropies) must be the same for both channels. Second, the reverse

Table I. CID Spectra of Ions Containing Mn

ion	rel intens of ions corresponding to loss of		
	CO	$H_2O$	$CH_3OH$
$MnCO(H_2O)^+$	0.733	0.017	
$MnCO(CH_3OH)^+$	0.756		0.007
$Mn(H_2O)(CH_3OH)^+$		0.517	0.209

activation energies for the ligand loss processes must be zero. The ligand loss processes are simple bond cleavages, so neither condition is extremely restrictive. We proceed on the basis that these conditions are satisfied by the processes of interest but with the awareness that this has not been proven. A rigorous argument in support of these assumptions would require a dynamical analysis that would be difficult even if the required potential surface were known. We rely instead on the internal consistency of the results to support the applicability of the method. Application of the method to other systems should similarly rely on tests of internal consistency. The general applicability of the method should not be uncritically assumed.

The effective temperature characterizing the decomposition processes may depend on such factors as the time scale of the experiment and the mass and structure of the complexes. All the ions typically suffer a number of collisions in the source, which is run at relatively high pressure (estimated to be on the order of 0.1 Torr), and have the temperature of the source gas. Those ions that decompose, however, suffer high-energy collisions in the collision chamber. Of those ions that suffer high-energy collision only those scattered through a narrow range of angles with little or no momentum transfer are sampled in the collision-induced decomposition spectrum. The range of scattering angles sampled is determined by instrumental parameters. The effective temperature of the decomposing ions is probably more sensitive to those parameters than to the temperature of the source gas. McLuckey, Cameron, and Cooks<sup>4</sup> found in their study of proton affinities that the decomposition spectra of proton-bound dimers were consistent with temperatures in the range 400–500 K. Analyzing the present results does not require explicit assignment of an effective temperature, but the assumption that there is such a temperature helps to order metal-ligand bond strengths on the basis of the results.

### Experimental Section

The experiments were performed on the Kratos MS50TA instrument at the Midwest Center for Mass Spectrometry (MCMS) at the University of Nebraska, Lincoln, NE. This instrument has been described in detail elsewhere.<sup>5</sup> In brief it consists of a double-focusing, high-resolution mass spectrometer followed by a collision chamber and an electrostatic energy analyzer. A chemical ionization source was used. Ions were produced by electron impact on mixtures of metal carbonyls and ligand molecules. At the pressures that obtained in the source, primary ions produced by electron impact reacted with neutrals present to produce secondary ions. In the mixtures used metal-ligand complexes were among those secondary ions. The complexes of interest were selected by using the first mass analyzer and allowed to collide with He in the collision chamber. The energy analyzer functioned as a mass analyzer and provided a mass spectrum of the collision fragments. The collision

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**Table II.** CID Spectra of Ions Containing Fe

ion	rel intens of ions corresponding to loss of	
	CO	H <sub>2</sub> O
Fe(CO)(H <sub>2</sub> O) <sup>+</sup>	0.460	0.218
Fe(CO) <sub>2</sub> (H <sub>2</sub> O) <sup>+</sup>	0.732	0.081
Fe(CO) <sub>3</sub> (H <sub>2</sub> O) <sup>+</sup>	0.678	0.036

**Table III.** CID Spectra of Ions Containing Co

ion	rel intens of ions corresponding to loss of		
	CO	NO	H <sub>2</sub> O
Co(CO)(NO) <sup>+</sup>	0.564	0.258	
Co(CO)(H <sub>2</sub> O) <sup>+</sup>	0.351		0.304
Co(NO)(H <sub>2</sub> O) <sup>+</sup>		0.264	0.493
Co(CO)(NO)(H <sub>2</sub> O) <sup>+</sup>	0.642	0.131	0.056

energy was 6 kV, and the pressure in the collision chamber was sufficient to attenuate the beam by 50%. The spectra were signal averaged by using software developed at MCMS. The Mn-containing ions were generated by using Mn<sub>2</sub>(CO)<sub>10</sub>, the Fe-containing ions were generated by using Fe(CO)<sub>5</sub>, and the Co-containing ions were generated by using Co(NO)(CO)<sub>3</sub>. All samples were obtained commercially.

### Results

The results are listed in Tables I–III. The tables list the ions examined and the fraction of the total collision-induced fragmentation corresponding to loss of each ligand. In the case of Mn(CO)(H<sub>2</sub>O)<sup>+</sup>, for example, the peak corresponding to loss of CO to form Mn(H<sub>2</sub>O)<sup>+</sup> is 73.3% of the total of the intensities of all fragment ion peaks from Mn(CO)(H<sub>2</sub>O)<sup>+</sup>. The peak corresponding to loss of H<sub>2</sub>O is only 1.7% of the total fragment ion peak intensity. The Mn<sup>+</sup> peak accounts for most of the remaining intensity in the collision induced decomposition (CID) spectrum of this ion. The ions listed in Table I were prepared in the source of the mass spectrometer by ion molecule reactions between electron-impact-produced fragments of Mn<sub>2</sub>(CO)<sub>10</sub> and water and methanol added to the source gases.

Examination of the results in Table I suggests that both H<sub>2</sub>O and CH<sub>3</sub>OH are substantially more strongly bound to Mn<sup>+</sup> than is CO. It also appears that CH<sub>3</sub>OH is somewhat more strongly bound than H<sub>2</sub>O. As discussed above this can be treated by assuming the product ratios are determined by the relative energies of the reactions channels. From the data in Table I on Mn(CO)(H<sub>2</sub>O)<sup>+</sup>, for example we deduce that

$$D(\text{Mn}(\text{CO})^+ - \text{H}_2\text{O}) - D(\text{Mn}(\text{H}_2\text{O})^+ - \text{CO}) = kT \ln(0.733/0.017) = 3.8kT \quad (1)$$

where  $T$  is an undetermined effective temperature. This can be related to values of  $D(\text{M}^+ - \text{L})$  as shown in Figure 1. In Figure 1,  $E_1$  and  $E_2$  are  $D(\text{ML}_1^+ - \text{L}_2)$  and  $D(\text{ML}_2^+ - \text{L}_1)$ , respectively. Similarly,  $E_3$  and  $E_4$  are  $D(\text{M}^+ - \text{L}_1)$  and  $D(\text{M}^+ - \text{L}_2)$ , respectively. Examination of Figure 1 shows that  $E_1 - E_2 = E_4 - E_3$ . In the case of MnCO(H<sub>2</sub>O)<sup>+</sup> this implies that

$$D(\text{Mn}(\text{CO})^+ - \text{H}_2\text{O}) - D(\text{Mn}(\text{H}_2\text{O})^+ - \text{CO}) = D(\text{Mn}^+ - \text{H}_2\text{O}) - D(\text{Mn}^+ - \text{CO}) \quad (2)$$

Substituting from (1) into (2) we find that

$$D(\text{Mn}^+ - \text{H}_2\text{O}) - D(\text{Mn}^+ - \text{CO}) = 3.8kT \quad (3)$$

Applying a similar analysis to the data on Mn(CO)(CH<sub>3</sub>OH)<sup>+</sup> and Mn(H<sub>2</sub>O)(CH<sub>3</sub>OH)<sup>+</sup> gives

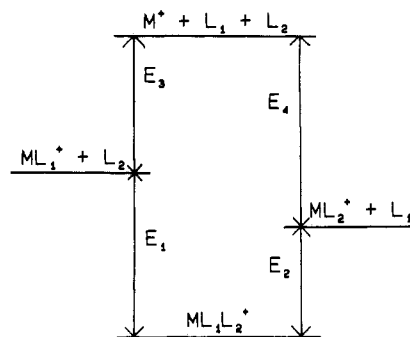
$$D(\text{Mn}^+ - \text{CH}_3\text{OH}) - D(\text{Mn}^+ - \text{CO}) = kT \ln(0.756/0.007) = 4.7kT \quad (4)$$

$$D(\text{Mn}^+ - \text{CH}_3\text{OH}) - D(\text{Mn}^+ - \text{H}_2\text{O}) = kT \ln(0.517/0.209) = 0.9kT \quad (5)$$

Note that subtracting (3) from (4) gives

$$D(\text{Mn}^+ - \text{CH}_3\text{OH}) - D(\text{Mn}^+ - \text{H}_2\text{O}) = 0.9kT \quad (6)$$

which is in good agreement with (5). Thus it appears that in this

**Figure 1.** Relationships between bond dissociation energies in  $\text{ML}_1\text{L}_2^+$ .

case the Mn<sup>+</sup> complexes all decompose with the same characteristic temperature. This provides support for the method of analysis.

It is appropriate to note here that this analysis applies only to parallel competing processes and not to sequential processes. The relative abundance of ions formed from a common precursor is given by the ratio of the rate constants for the two decompositions. Hence, we obtain the relationships used here. The relative abundances of parent and daughter species such as  $\text{ML}_1^+$  and  $\text{M}^+$  are not simply related in the way that  $\text{ML}_1^+$  and  $\text{ML}_2^+$  abundances are related.  $\text{M}^+$  is presumably formed from  $\text{ML}_1\text{L}_2^+$  species that acquire enough energy in the collision to lose both ligands sequentially. It is necessary to assume that this does not deplete the  $\text{ML}_1^+$  or  $\text{ML}_2^+$  abundances in such a way that their ratio can no longer be characterized by an effective temperature. The validity of this assumption is essentially a result of this study and rests on the internal consistency of the data described above.

The data in Table II exhibit an example of a synergistic effect. The loss of CO dominates the decomposition spectra to a remarkably increasing extent as the number of CO ligands increases. This occurs to an extent exceeding that expected from the increase in the degeneracy of CO loss with increasing number of CO ligands. In terms of the treatment used for the Mn<sup>+</sup> data the data on Fe(CO)(H<sub>2</sub>O)<sup>+</sup> suggest

$$\begin{aligned} D(\text{Fe}(\text{CO})_n^+ - \text{H}_2\text{O}) - D(\text{Fe}(\text{CO})_n^+ - \text{CO}) &= kT \ln(0.460/0.218) = 0.7kT \quad (n = 0) \\ &= kT \ln(0.732/(2 \times 0.081)) = 1.5kT \quad (n = 1) \\ &= kT \ln(0.678/(3 \times 0.036)) = 1.8kT \quad (n = 2) \end{aligned} \quad (7)$$

Note that the intensity of the CO loss peak is divided by  $n$  in  $\text{Fe}(\text{CO})_n(\text{H}_2\text{O})^+$  to account for the degeneracy of the CO loss process. The difference in the strengths of the H<sub>2</sub>O and CO bonds to the metal increases substantially as the number of CO ligands increases. This suggests a synergistic effect in which the additional CO ligands either weaken the metal CO interaction, strengthen the metal H<sub>2</sub>O interaction, or do both.

An interestingly different synergistic effect is evident in the data in Table III. In this case there are as many as three different ligands attached to the metal. When the ligands are attached to the metal in pairs, the apparent relative bond strengths are quite different than they are when all three ligands are attached to the metal. Consider CO and NO:

$$D(\text{Co}^+ - \text{NO}) - D(\text{Co}^+ - \text{CO}) = kT \ln(0.564/0.258) = 0.8kT \quad (8)$$

but

$$D(\text{Co}(\text{H}_2\text{O})^+ - \text{NO}) - D(\text{Co}(\text{H}_2\text{O})^+ - \text{CO}) = kT \ln(0.642/0.131) = 1.6kT \quad (9)$$

Addition of H<sub>2</sub>O to the complex increases the difference between the apparent bond strengths of NO and CO to the metal. Consider CO and H<sub>2</sub>O:

$$D(\text{Co}^+ - \text{H}_2\text{O}) - D(\text{Co}^+ - \text{CO}) = kT \ln(0.351/0.304) = 0.1kT \quad (10)$$

but

$$D(\text{Co}(\text{NO})^+-\text{H}_2\text{O}) - D(\text{Co}(\text{NO})^+-\text{CO}) = kT \ln (0.642/0.056) = 2.4kT \quad (11)$$

Addition of NO to the complex very substantially increases the difference between the apparent bond strengths of H<sub>2</sub>O and CO to the metal. Finally, consider NO and H<sub>2</sub>O:

$$D(\text{Co}^+-\text{NO}) - D(\text{Co}^+-\text{H}_2\text{O}) = kT \ln (0.493/0.264) = 0.6kT \quad (12)$$

but

$$D(\text{Co}(\text{CO})^+-\text{NO}) - D(\text{Co}(\text{CO})^+-\text{H}_2\text{O}) = kT \ln (0.056/0.131) = -0.9kT \quad (13)$$

Addition of CO to the complex actually inverts the order of the apparent bond strengths of NO and H<sub>2</sub>O to the metal. Note that subtracting (10) from (8) gives

$$D(\text{Co}^+-\text{NO}) - D(\text{Co}^+-\text{H}_2\text{O}) = 0.7kT \quad (14)$$

in good agreement with (12).

### Discussion

These results are most simply interpreted as illustrative of the destabilizing effect that  $\pi$ -acceptor ligands can have on one another. In  $\text{Fe}(\text{CO})_n(\text{H}_2\text{O})^+$ , for example, the M-H<sub>2</sub>O bond exceeds the M-CO bond by an amount that increases with  $n$  (eq 7). The effect is most dramatic in the  $\text{Co}(\text{NO})(\text{CO})(\text{H}_2\text{O})^+$  system. While NO is more strongly bound than H<sub>2</sub>O to Co<sup>+</sup> (eq 12), the NO ligand is more weakly bound than H<sub>2</sub>O to  $\text{Co}(\text{CO})^+$  (eq 13). CO, NO, and H<sub>2</sub>O are all  $\sigma$  donors, but only CO and NO are  $\pi$  acceptors. The results suggest that in these cationic systems there is competition between  $\pi$  acceptors for electron density to form  $\pi$  bonds to the metal. Hence there is a mutually destabilizing effect of two or more  $\pi$  ligands on the same center.

It could be argued that these effects are the result of strengthening the metal-water interaction as other ligands are added to the complex. Water is small and polar, and its interaction with the cation center should be primarily electrostatic. Additional ligands inevitably decrease the concentration of charge on the metal and should weaken rather than strengthen the electrostatic interaction with water. Weakening of the interactions with  $\pi$

ligands thus seems the best explanation of the observed effects.

The effects observed here might be discussed in terms of "antisymbiosis". As defined by Pearson, the principle of antisymbiosis states that two soft ligands mutually trans to each other have a destabilizing effect on each other when attached to a class b metal.<sup>6</sup> In the present case CO and NO are "soft" ligands, and H<sub>2</sub>O is a "hard" ligand. Class a metals tend to be metals in their highest oxidation state and tend to bind hard ligands more strongly than soft ligands.<sup>7</sup> Class b metals tend to be metals in lower oxidation states and tend to bind soft ligands more strongly.<sup>8</sup> Class b metals tend to form covalent bonds, and class a metals tend to form more electrostatic bonds.<sup>8</sup> Co<sup>+</sup> is Co(I) and is known to form strong covalent bonds readily. R-X bonds (where X = halogen, alkyl groups, or H) add oxidatively to Co<sup>+</sup>.<sup>9</sup> This would suggest Co<sup>+</sup> to be a class b metal. In any event the present results show that a pair of soft ligands attached to Co<sup>+</sup> destabilize each other. In the complexes with two ligands, the ligands might reasonably be expected to be trans to one another, but the present experiments do not explicitly determine the structures of the complexes. The Pearson approach does not distinguish between  $\pi$  and  $\sigma$  donors or acceptors but only between "hard" and "soft" ligands.

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**Registry No.**  $\text{MnCO}(\text{H}_2\text{O})^+$ , 112374-36-4;  $\text{MnCO}(\text{CH}_3\text{OH})^+$ , 112374-37-5;  $\text{Mn}(\text{H}_2\text{O})(\text{CH}_3\text{OH})^+$ , 112398-35-3;  $\text{Fe}(\text{CO})(\text{H}_2\text{O})^+$ , 112374-38-6;  $\text{Fe}(\text{CO})_2(\text{H}_2\text{O})^+$ , 112374-39-7;  $\text{Fe}(\text{CO})_3(\text{H}_2\text{O})^+$ , 112374-40-0;  $\text{Co}(\text{CO})(\text{NO})^+$ , 61816-95-3;  $\text{Co}(\text{CO})(\text{H}_2\text{O})^+$ , 112374-41-1;  $\text{Co}(\text{NO})(\text{H}_2\text{O})^+$ , 112374-42-2;  $\text{Co}(\text{CO})(\text{NO})(\text{H}_2\text{O})^+$ , 112374-43-3.

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