Registry No. $Cr(CO)_6$, 13007-92-6.

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Relative Energies of Metal–Metal Bonding and Nonbonding Molecular Orbitals in Bridged Diiron Complexes

Sir:

Both oxidation and reduction of compounds containing metal–metal bonds are normally accompanied by concurrent metal–metal bond cleavage and fragmentation.[1] This is taken as evidence that the highest occupied and lowest unoccupied molecular orbitals are strongly associated with the metal–metal interaction, the former being bonding and the latter antibonding. The situation with mononuclear transition-metal compounds is distinctly different in that the donor and acceptor orbitals are usually metal d orbitals which are essentially nonbonding with respect to the primary structure of the complex. There are, however, three classes of multinuclear metal compounds that can retain structural integrity in more than one molecular oxidation state: namely, those containing ligand-bridged metal–metal bonds, those with metal–metal multiple bonds, and those with closed-cluster structures.[2] This correspondence concerns the nature of the metal–metal interaction in the first of these classes.

Bridged dinuclear metal complexes have been the subject of numerous experimental and theoretical investigations. Previous discussions have focused on the metal–metal interaction vis â vis the metal-bridge interactions.[3–5] In this type of compound it has been clearly established that oxidation and reduction strongly affect the metal–metal distance.[6] It is logical that such a result be discussed in terms of electron gain or loss from high-lying orbitals associated with the metal–metal interaction. This interpretation is supported by the results of quantitative calculations on $Fe_2(CO)_6X_2$ complexes in which it was found that the lowest unoccupied molecular orbital is metal–metal antibonding while the highest occupied molecular orbital is metal–metal bonding.[4,7] In addition, it was found that the other metal d orbitals and ligand orbitals are at least 1–2 eV more stable than the metal–metal bonding orbital. On the other hand, recent structural work[8] and qualitative calculations[5] have drawn attention to the balance between the metal–ligand and metal–metal interactions in determining observed geometry and, in so doing, have implied that arguments restricted to consideration of the metal–metal interaction are incomplete.[9]

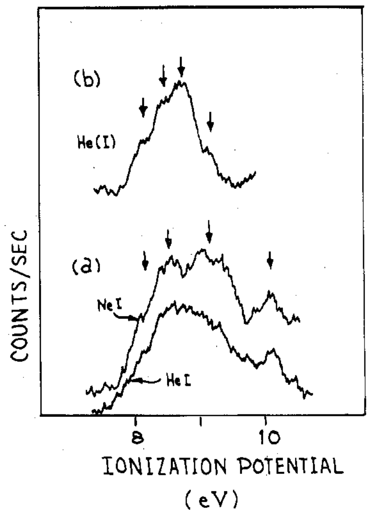

Figure 1. (a) The first band in the He I and Ne I photoelectron spectra of $Fe_2(CO)_6B_2H_6$. (b) The first band in the He I photoelectron spectrum of $Fe_2(CO)_6S_2$.

Recently, we have prepared[10] a diborane(6)-bridged diiron hexacarbonyl, $Fe_2(CO)_6B_2H_6$, which is formally and structurally[11] analogous to the class of bridged dinuclear metal compounds exemplified by $Fe_2(CO)_6S_2$. As $Fe_2(CO)_6B_2H_6$ is a volatile compound, we have obtained its UV photoelectron spectrum. Empirical assignment allows the relative energies of the metal orbitals to be investigated.[12] The band at lowest ionization potential in the He I and Ne I spectra of $Fe_2(CO)_6B_2H_6$ is shown in Figure 1. On the basis of an analysis of the complete spectrum in terms of the known behavior of model compounds containing the $Fe(CO)_3$ fragment,[13] relative intensity changes with photon energy,[14] and semiempirical molecular orbital arguments,[15] it is certain that this is the only band that contains the iron d ionizations.[16] Of the seven expected iron d ionizations, six are from orbitals which are essentially nonbonding with respect to the molecular framework while one is associated with the metal–metal bonding orbital. If the shoulder on this band is assigned to the latter ionization, then the implication[17] is that the metal–metal bonding orbital is only about 0.4 eV less stable than one of the iron nonbonding orbitals. However, there is no empirical justification for such an assignment, and the ionization associated with the metal–metal bonding orbital could well lie anywhere within the band.

As the structure of $Fe_2(CO)_6B_2H_6$ has not been conclusively established by diffraction techniques and as the calculations were carried out on ligands other than B_2H_6, we have also measured the photoelectron spectrum of $Fe_2(CO)_6S_2$. The band at lowest ionization potential in this spectrum is shown in Figure 1. Again, analysis of the whole spectrum in the manner described above demonstrates that the seven iron d ionizations are contained within this band. As indicated by the arrows in the figure, the onsets of four of the ionizations are evident; any one of these could correspond to the ionization of the metal–metal bonding orbital. The conclusion is the same. Removal of an electron from the metal–metal bonding orbital takes about the same amount of energy as removal from the metal–metal nonbonding orbitals.[18] The calculations for $Fe_2(CO)_6S_2$ referred to above,[4] however, indicate that the metal–metal bonding orbital is about 1.5 eV above the least stable of the six iron orbitals that are essentially nonbonding with respect to the molecular framework.

Because of the possibility of a quantitative failure of Koopmans' theorem,[17,19] it may well be that the calculations

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represent the ground state of the molecule more accurately than do the experimental band positions in the photoelectron spectra. Nonetheless, it must be emphasized that for an oxidation, the experimental ionization potentials constitute a more accurate measure of relative energetics. Thus, the simple model for oxidation of such compounds, involving removal of an electron from a single orbital identified with the metal–metal bond, is clearly oversimplified and may well be inaccurate. It seems, rather, that the situation approaches that for organometallic clusters in which the highest occupied orbitals are thought to be metal in character and essentially nonbonding with respect to the cluster skeleton.[20] To a boron chemist, who would view both $Fe_2(CO)_6B_2H_6$ and $Fe_2(CO)_6S_2$ as four-atom clusters[21] rather than bridged, metal–metal bonded dinuclear complexes, this is not too surprising. A complete discussion of the photoelectron spectra of these compounds will be given elsewhere.

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Registry No. $Fe_2(CO)_6B_2H_6$, 70130-42-6; $Fe_2(CO)_6S_2$, 58500-79-1.

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Comparative Photochemistry of *trans*-$[Cr(en)_2NH_3F]^{2+}$, $[Cr(NH_3)_5F]^{2+}$, and $[Cr(en)_x(NH_3)_{6-2x}]^{3+}$. Harmony and Discord with Recent Theory

Sir:

In two recently published papers,[1,2] Vanquickenborne and Ceulemans (VC) have presented a new theory of chromium(III) photochemistry, including both the prediction of the reaction modes of complexes and their stereochemistry. An earlier paper of ours[3] on the photochemistry of *trans*-$[Cr(en)_2NH_3F]^{2+}$ and $[Cr(NH_3)_5F]^{2+}$ reported that the results were in disagreement with the then-existing theories. Since they agree well with the new theory, at least as far as the prediction of the reaction modes is concerned, one purpose of this correspondence is to reinterpret those results in this light. Our other reasons for this correspondence relate to a study[4] of the photochemistry of $[Cr(en)_x(NH_3)_{6-2x}]^{3+}$ which confirms and strengthens the interpretation of the results[3] relating to the stereochemistry of axial and equatorial ammonia aquation in $[Cr(NH_3)_5F]^{2+}$. These results have very important implications for the VC theory of the stereochemistry[2] of such processes.

The first of our objectives requires spectroscopic parameters for the ligands of interest. Following the VC theory, we adopt for ethylenediamine and ammonia ϵ_σ 7183 and ϵ_π 0 cm^{-1} and for fluoride ϵ_σ 7633 and ϵ_π 1700 cm^{-1}. (These values ignore the small difference, 1.5%, in σ-donor strength of the first two ligands.) Hence, one calculates the $^4B_2/^4E$ spacing to be 1360 cm^{-1}, with ^4E being the lower of the two excited states, possessing 73.0% d_{z^2} character. Then, following eq 5 of ref 1, one finds for the ^4E state

$$I^*(\text{Cr–NH}_3) = (2 - 0.730)\epsilon_\sigma(\text{NH}_3) = 9125 \text{ cm}^{-1}$$

$$I^*(\text{Cr–en}) = [(2 \times 0.730 + 5)/4]\epsilon_\sigma(\text{en}) = 11\,600 \text{ cm}^{-1}$$

$$I^*(\text{Cr–F}) = (2 - 0.730)\epsilon_\sigma(\text{F}^-) + 3\epsilon_\pi(\text{F}^-) = 14\,800 \text{ cm}^{-1}$$

and for the $^4B_2$ state

$$I^*(\text{Cr–NH}_3) = 2\epsilon_\sigma(\text{NH}_3) = 14\,400 \text{ cm}^{-1}$$

$$I^*(\text{Cr–en}) = \tfrac{5}{4}\epsilon_\sigma(\text{en}) = 9000 \text{ cm}^{-1}$$

$$I^*(\text{Cr–F}) = 2\epsilon_\sigma(\text{F}^-) + 2\epsilon_\pi(\text{F}^-) = 18\,700 \text{ cm}^{-1}$$

On the basis of these calculated strengths for the various bonds, one expects that the ^4E state would lose predominantly ammonia and the $^4B_2$ predominantly ethylenediamine. (If the calculated bond-strength differences could be equated to activation-energy differences, then at room temperature ^4E would favor ammonia loss by a factor of 10^5, and $^4B_2$ would favor ethylenediamine loss by a factor of 10^{11}.) The qualitative predictions of the theory are in complete agreement with the proposals made in our earlier paper where we concluded that the observations required participation by two excited states, most probably ^4E and $^4B_2$, leading to preferential ammonia loss and ethylenediamine loss, respectively, and remove many of the difficulties of interpretation discussed there.[3]

At all wavelengths both modes of photolysis are observed, but with different apparent activation energies for long-wavelength irradiation. At long wavelengths the ethylenediamine mode has an activation energy of about 50 kJ mol^{-1}. It is not clear whether this corresponds to the difference in activation energy for aquation of the ^4E state with ethylenediamine or ammonia loss, respectively, or if it corresponds to excitation of ^4E to $^4B_2$, with subsequent preferential loss of ethylenediamine from that state. It could also correspond to some other possibility such as, for example, activated absorption to $^4B_2$ from the ground state. From the above calculations the naive expectations for the activation energies for the first two mechanisms are 30 and 16 kJ mol^{-1}, respectively,