state, all of which are symmetry allowed for electric and magnetic dipole radiation.

The energy shifts exhibited by the absorption peaks within the series of homologous complexes, $M(acac)_2X_2$, also support the present assignment. Halogen substitution, from fluorine to iodine, decreases the effective charge on the central metal. SCF–CI calculations on acetylacetonate, with a positive charge as an outside perturbation, simulating the central ion, predict a low-energy shift of the first $\pi_3 \rightarrow \pi_4{}^*$ transition if the central metal charge is decreased.[6] This trend can be observed for all bands within the tin and the titanium series of compounds; in any case respective band components (cf. Table III) move to smaller wavenumbers upon substitution of halogens being able to form a bond of higher covalency. The observed shifts are not explained by a charge-transfer mechanism. An electron transfer from the acetylacetonate ligand to the metal center would be energetically favored for an increased positive charge on the metal. Fluoride ligands, therefore, would facilitate this transition, and complexes with chloride, bromide, etc. ligands would need more energy for this charge-transfer mechanism. However, the experimental results are opposite to this trend. An improved metal–acetylacetonate π bonding with higher effective charges on the metal[18] does not overcome the Coulomb attraction due to the central metal ion, since it is an off-diagonal perturbation in the bond matrix which is of second order with respect to the diagonal valence-state atomic orbitals. If the low-energy band in the titanium compounds would be charge transfer, the main π–π^* band at $(37-40) \times 10^3$ cm^{-1} should be split due to π bonding. However, the spectra of Figure 1 do not show any indication for this. From these reasons an interpretation of the observed bands through a charge-transfer mechanism can be rejected.[18] Predominant π-electron transfer from acetylacetonate to the central metal must be expected at higher energy. The optical electronegativity parameter for acetylacetonate, which has been set equal to 2.7,[11] should be corrected to a value significantly higher than 3; this parameter probably lies close to the value of other oxygen-donating ligands such as H_2O, acetate, or oxide, for which parameters of about 3.5 are derived.[33,37]

Conclusions

A comparison of optical spectra within a series of homologous complexes of closed-shell metal ions furnishes some evidence for establishing more reliable assignments of the measured absorption peaks. The problem of assigning the bands to π–π^* or charge-transfer mechanism and the breakdown of this classification due to π-electron delocalization over the whole molecule can be discussed with use of optical electronegativities of the central atom. Large metal electronegativities favor intermixing of charge transfer into π-electron states, which is the equivalent of increasing the metal–ligand π bonding. Enhanced metal–acetylacetonate π bonding, in turn, leads to a larger splitting of the π–π^* band components. The use of these relations may assist in spectral assignments from band splittings for other series of complex compounds, e.g., for open-shell metal ions.

Acknowledgment. The authors are grateful to the Fonds der Chemischen Industrie, Frankfurt, West Germany, for financial support.

Registry No. $Ge(acac)_2Cl_2$, 17112-69-5; $Sn(acac)_2F_2$, 25426-91-9; $Sn(acac)_2Cl_2$, 16919-65-6; $Sn(acac)_2Br_2$, 16919-66-7; $Sn(acac)_2I_2$, 16919-67-8; $Ti(acac)_2F_2$, 16986-93-9; $Ti(acac)_2Cl_2$, 16986-94-0; $Ti(acac)_2Br_2$, 16986-95-1; $Zr(acac)_2Cl_2$, 19555-94-3.

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Photoelectron Spectra of and Molecular Orbital Calculations on (η^5-Cyclopentadienyl)dinitrosylhalochromium and -tungsten

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The gas-phase ultraviolet photoelectron spectra are reported for the compounds $(\eta^5\text{-}C_5H_5)M(NO)_2X$, where M = Cr, W and X = Cl, Br, I. The observed spin–orbit splitting on the heavy atoms is used to assign and interpret the spectra. The results compare favorably with a Fenske–Hall molecular orbital calculation on the $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ species. Although the complexes are formally M(0) d^6, the calculations suggest that the "metal" electrons are highly delocalized onto the nitrosyls. This suggestion is supported by the similarity in the ionization energies of the chromium complexes to those of the isoelectronic $(\eta^5\text{-}C_5H_5)Fe(CO)_2X$ systems. Comparison of the ionization energy of the metal–halogen σ bonds suggests stronger W–X bonds than Cr–X bonds, which is consistent with the reactivity of the complexes and with the relative metal–chloride bond lengths.

Introduction

Although $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ was first reported in 1956,[1] it was not until recently that improved synthetic procedures have led to detailed studies on the entire series of chromium, molybdenum, and tungsten derivatives.[2,3] These studies have revealed considerable chemical and structural differences between the chromium and tungsten species. Upon reaction with $AgBF_4$, $CpCr(NO)_2Cl$ (Cp = $\eta^5\text{-}C_5H_5$) goes smoothly to the 16-e complex $[CpCr(NO)_2]BF_4$, but $CpW(NO)_2Cl$ does not react unless a donor, D, is present in which case the product is $[CpW(NO)_2D]BF_4$.[2] Also, the chromium complexes can be alkylated with CH_3MgI while the tungsten complexes cannot.[2] This difference in reactivity could be due to a difference in the M–Cl bond strength, in the relative size of the metals, or in their respective stability at low coordination number and electron count. Recent X-ray crystal structures of $CpM(NO)_2Cl$ (M = Cr, W) have shown the two complexes to be isostructural.[3] The Cr–Cl bond distance was 2.321 (1) Å while the W–Cl bond distance was 2.386 (3) Å. Compared to the M–Cp and M–N distances, the W–Cl distance is short relative to the Cr–Cl distance. This result was interpreted as indicating an exceptionally weak Cr–Cl bond; however, the Mn–Cl bond distance in $Mn(CO)_5Cl$ is 2.367 Å.[4] It may be that the Cr–Cl

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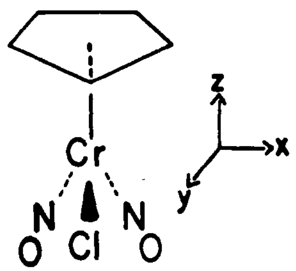

Figure 1. Structure of $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$. The geometry was idealized from the X-ray structure: C–C = 1.380 Å, C–H = 1.084 Å, Cr–Cl = 2.321 Å, Cr–N = 1.717 Å, N–O = 1.158 Å, Cr–N–O = 180°, Cl–Cr–N = 100°, and N–Cr–N = 94°. The coordinate system at Cr is also shown.

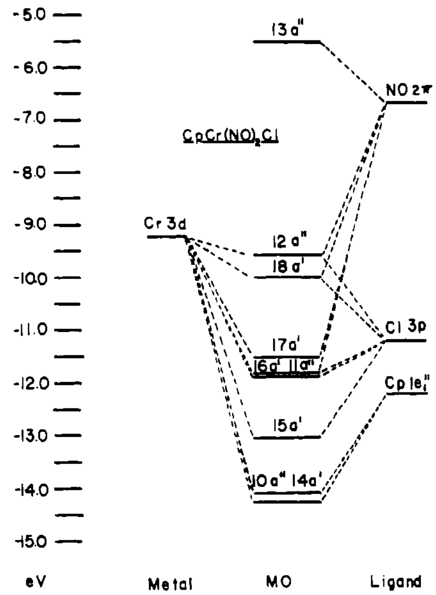

Figure 2. Molecular orbital diagram of $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$. The energy values were obtained from a Fenske–Hall calculation. The dashed lines indicate the principal contributions to each molecular orbital.

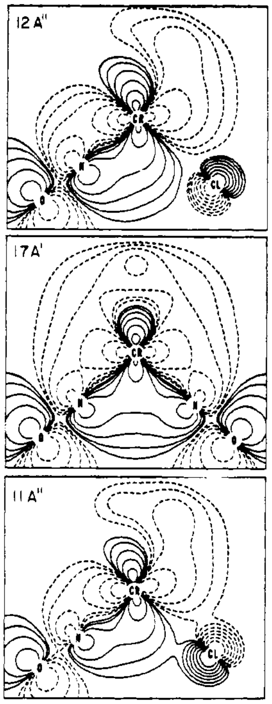

Figure 3. Orbital plots of the 12a'', 17a', and 11a''. The a'' orbitals are plotted in the Cl–Cr–NO plane, while the 17a' is plotted in the ON–Cr–NO plane. The lowest contour values are ±2.44 × 10^{-4} e au^{-3}, and each succeeding contour differs from the previous one by a factor of 2.0.

bond is perfectly normal for a first transition series M–Cl bond, which one would expect to be weaker than the M–Cl bond of a second or third transition series metal, or it may be that the W–Cl bond is stronger than a typical W–Cl bond. The paucity of structures with low-oxidation-state M–X bonds makes a comparison difficult.

We have undertaken an investigation of the electronic structure of these compounds using both ultraviolet photoelectron spectroscopy (PES) and parameter-free Fenske–Hall molecular orbital (MO) calculations.[5] In addition to the questions already raised about the M–X bond, we are interested in the substantial charge rearrangement that one would expect to occur when two excellent donors, Cp^- and X^-, and two excellent acceptors, NO^+, are bonded to the same zero-oxidation-state metal. With the exception of $Fe(CO)_2(NO)_2$,[6] there have been few PES–MO studies on dinitrosyls of any type. Especially important to assigning and interpreting the PES is the study of a series of complexes which include heavier elements. When clearly observed, the band splittings due to the spin–orbit coupling of these heavy atoms are useful in making assignments and in interpreting the results.[7,8] Simple intensity arguments are less useful in these low-symmetry species. A comparison of our results with a previous PES–MO study of the isoelectronic $(\eta^5\text{-}C_5H_5)Fe(CO)_2X$ species[9] should provide some detailed insight into the relative delocalization of a metal dinitrosyl.

Experimental and Theoretical Section

Preparation. The compounds $CpCr(NO)_2Cl$ and $CpW(NO)_2Cl$ were prepared by published procedures.[2] The bromide and iodide derivatives were prepared by reacting 500 mg of $CpM(NO)_2Cl$ with a 15-fold excess of NaX (X = Br or I) in 30 mL of THF and stirring at room temperature for 18 h. The THF was then removed in vacuo and the residue extracted with dichloromethane. The extracts were filtered through a 2 × 8 cm column of Florisil, and the solvent was removed from the filtrate under reduced pressure. Materials obtained in this manner produced satisfactory analytical results.

Spectroscopy. The photoelectron spectra were taken on a Perkin-Elmer Model PS-18 photoelectron spectrometer. The argon doublet was used as an internal standard. The resolution (fwhm) was always better than 50 meV for the argon $^2P_{3/2}$ band. The temperature range for vaporization of these compounds was 70–75 °C.

Theoretical Calculations. The MO calculation for $CpCr(NO)_2Cl$ was done on an Amdahl 470 V/6 computer using the nonempirical method of Fenske and Hall.[5] The Cr(+1) functions were those of Richardson[10] with 4s and 4p exponents of 2.0.[11] Clementi functions were used for C, N, O, and Cl.[12] An exponent of 1.2 was used for all hydrogens. The bond lengths and angles were taken from the X-ray crystal structure. The symmetry of the molecule is C_s, and the coordinate system has the *yz* plane as the plane of reflection.

Theoretical Results

We will begin by describing the results of the MO calculation and the general features of the bonding in $CpCr(NO)_2Cl$ which will make the presentation of the spectral results clearer, The coordinate system and geometry are shown in Figure 1. All of the complexes have 60 valence electrons and in C_s symmetry have 18 doubly occupied orbitals of a' symmetry

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and 12 doubly occupied orbitals of a″ symmetry.

The molecular orbital diagram for CpCr(NO)$_2$Cl is shown in Figure 2. Only the upper valence levels are shown. With the exception of the 13a″, which is unoccupied, these levels correspond to the bands one might expect to see at low ionization energy (IE). The two highest occupied orbitals, 18a′ and 12a″, are separated by 0.41 eV and are mixtures of Cr 3d, Cl 3p, and NO 2π. Both orbitals are π bonding between the Cr 3d and NO 2π but π antibonding between the Cr 3d and Cl 3p. This character is illustrated in a contour plot of the 12a″ in the Cl–Cr–NO plane, which is at the top of Figure 3. The 18a′ is similar but contains less chromium and more chlorine character.

The next MO is the 17a′ which is 45% NO 2π and 30% Cr 3d. A plot of this orbital in a plane containing Cr and both N's is shown in the center of Figure 3. It is in this orbital that one 2π orbital from each NO overlaps in a ligand–ligand bonding type interaction to lower their energy and become a strong π acceptor in this plane. The MO is also stabilized to some degree by interaction with the empty e$_2$″ Cp orbital. The 16a′ and 11a″ orbitals are nearly degenerate and form a pair of Cr–Cl π bonding MO's with a higher percentage of chlorine than chromium character and some NO 2π character, especially in the 16a′. A contour plot of the 11a″ orbital in a plane containing Cl, Cr, and NO is shown at the bottom of Figure 3. The delocalized nature of the orbital is clearly evident. The MO is both Cr–Cl π bonding and Cr–NO π bonding. The 16a′ MO is related to this MO, but it contains less Cl character and both more Cr and more NO character. The 15a′ is the major component of the Cr–Cl σ bond and is mostly chlorine in character. The 10a″ and 14a′, which are only split by 0.2 eV, form the major component of the Cp–metal bond. These MO's are mainly Cp and arise from the 1e$_1$″ π orbitals of C_5H_5 stabilized by interaction with the metal. Previous comparisons between the PES and Fenske–Hall MO results indicate that these levels are calculated to be too stable and the IE will occur at lower energy than predicted.[9]

If one assumes that the Cp ring effectively occupies three coordination sites, the complex can be described as a six-coordinate Cr d^6 complex. In an O_h complex such as Cr(CO)$_6$, these six electrons occupy the t$_{2g}$ levels, which are predominately metal in character. In our lower symmetry chlorine complex, this d^6 system corresponds closely to the 12a″, 18a′, and 17a′ orbitals. The reason for the large splitting between the 17a′ and the closely spaced 12a″,18a′ pair is the strong π-acceptor power of two adjacent NO$^+$ ligands, which conspire to lower the energy of the 17a′, and the strong π-donor power of Cl$^-$, which pushes both the 18a′ and 12a″ to higher energy.

The Fenske–Hall calculations should give a qualitative interpretation of the spectra, but we should not expect them to reproduce experimental IE's or even give the correct order for all the levels. We have already pointed out one problem in the placement of the 1e$_1$″ Cp-to-metal bonding MO's. Even though the order of the IE's may not correspond exactly, we will use the labels as given in Figure 2 to refer to the IE's principal characteristic. One must remember that the experimental IE's really refer to ground and excited *states* of the ion relative to the ground *state* of the molecules. The assignment of these *states* in terms of orbitals is only an approximation, although a very convenient one. We will also use this orbital labeling scheme for systems with large spin–orbit coupling even though the corresponding double-group-state labels would be more rigorous. In the double group corresponding to C_s, spin–orbit coupling mixes the previous ^{2}A′ and ^{2}A″ states and all of the states in the ion correspond to the $^2E_{1/2}$ representation. Because group theory has now lost its advantage, we will continue to refer to the states in terms of their parentage in C_s symmetry. Although this is a good approximation for species with lighter atoms and for species with large molecular splittings, it can be a very poor approximation in some cases.

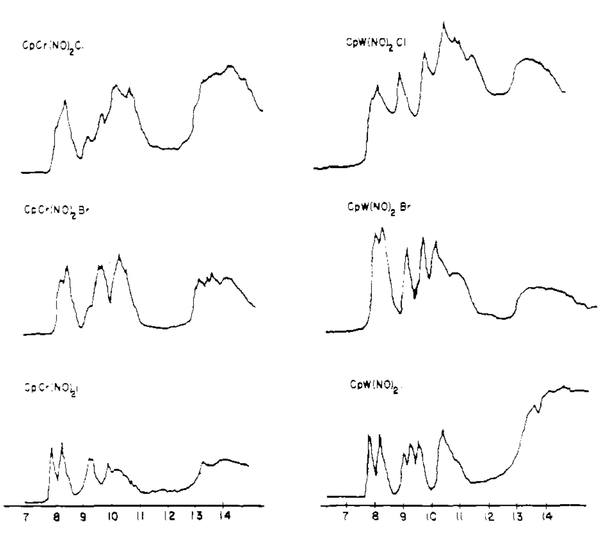

Figure 4. Photoelectron spectra of the (η^5-C_5H_5)M(NO)$_2$X complexes (M = Cr, W; X = Cl, Br, I).

Spectroscopic Results

The spectra of the complexes CpM(NO)$_2$X (M = Cr, W; X = Cl, Br, I) are shown in Figure 4. In all the spectra there exists in the region between 12 and 15 eV a large, very broad band. The lack of fine structure in this band is typical of bands with a number of close, overlapping ionizations. The ionizations of the Cp 1a$_2$″, 3e$_2$′, and 3e$_1$′ and the NO 5σ and 1π are assumed to be within this region. The relative intensity of this band varies because of the difficulty in maintaining a constant probe temperature and a constant He flow toward the end of the single slow scan. Although every effort was made to minimize these problems and the spectra shown are the best of numerous runs, the relative intensity of bands with very different IE's will not be very accurate. The IE for the lower energy bands and their assignments which are made below are collected in Table I.

CpCr(NO)$_2$Cl. The first band in this spectrum is 1 eV wide and is taken to be two separate ionizations at 8.17 and 8.39 eV. We have assigned them to be the 12a″ and 18a′ metal–halogen π^* ionizations. The next band at 9.18 eV is much less intense than the first and corresponds to the 17a′ ionization, mainly NO 2π character. The chromium–chlorine π bond, the 16a′ and 11a″ orbitals, are assigned as the next band at 9.70 eV. The next two bands are the most intense in the spectrum and are poorly resolved. The Cp 1e$_1$″ ionizations, the 14a′ and 10a″, are assigned to the band at 10.26 eV. The 15a′, the chlorine–chromium σ bond, appears at 10.72 eV. This reversal of the order of the Cr–Cp and Cr–Cl bands from that predicted by the calculation is not unexpected as previous work has shown that the Cp IE's are predicted to be too large by the Fenske–Hall technique.

CpCr(NO)$_2$Br. The first band in the "bromide" spectrum shows two definite ionizations separated by 0.25 eV. The splitting between these ionizations is similar to that observed in the "chloride" spectrum even though one might expect it to increase due to the increase in the spin–orbit coupling of the halogen. The region between 9.2 and 10.4 eV shows two large, broad bands. The band at lower ionization potential has a shoulder at 9.21 eV, which is assigned as the 17a′ ionization. This band has shifted very little from its position in the chloride spectrum, where it was at 9.18 eV. The next band at 9.66 eV is similar in energy to 16a′ and 11a″ ionizations (metal–halogen π) in the chloride spectrum and will have the same assignment although its character is now assumed to have

Table I. Ionization Energies and Assignments for CpM(NO)$_2$X Complexes[a]

X	M		assignt
	Cr	W	
Cl	8.17	8.03	12a″
	8.39	8.29	18a′
	9.18	9.05	17a′
	9.70	9.95	16a′, 11a″
	10.26	10.63	10a″, 14a′
	10.72	11.61	15a′
Br	8.16	8.02	12a″
	8.41	8.34	18a′
	9.21	9.18	17a′
	9.66	9.75	16a′
	9.66	10.21	11a″
	10.31	11.00	15a′, 10a″, 14a′
I	7.86	7.87	12a″
	8.22	8.24	18a′
	9.28	9.09	16a′
	9.28	9.34	17a′
	9.28	9.66	11a″
	9.88	10.44	15a′
	10.33	10.99	10a″, 14a′

[a] Estimated errors are ±0.05 eV.

more chromium and less halogen. The next band at 10.31 eV is very close to the cyclopentadienyl ionizations of the chloride compound and is assigned to the 10a″ and 14a′. The 15a′, the bromine–chromium σ bond, is assigned as being degenerate with the 10a″ and 14a′ ionizations. In the "chloride" spectrum, the Cr–Cl σ bond appears at 10.72 eV, which is 0.4 eV higher in energy than the Cr–Br σ band. This result is expected since bromine typically has a lower ionization energy than chlorine.

CpCr(NO)$_2$I. The first band in the spectrum of the iodine compound is split into two peaks separated by 0.36 eV. This increase in splitting is expected since iodine has larger spin–orbit coupling than bromine. Again, these first two peaks are assigned to ionizations from the 12a″ and the 18a′ orbitals. However, while they were mainly chromium in character in the "chloride" spectrum and about half chromium and half bromide in the "bromide" spectrum, they are now mainly iodine in character. The second band in the iodine spectrum at 9.28 eV is less intense than the first and is almost degenerate with the 17a′ ionization from the two previous spectra, although it appears much broader and much higher in intensity. The 16a′ and 11a″ ionizations will be assigned as being degenerate with the 17a′ band in this spectrum, which explains the increase in intensity and bandwidth. The next band in the spectrum shows two distinct peaks located at 9.88 and 10.20 eV. The first peak is sharp while the second shows the typical broadness of the cyclopentadienyl ionizations. The first peak will be assigned the 15a′ ionization, the chromium–iodine σ bond. Since iodine typically has a lower ionization potential than bromine, its ionization should appear at a lower energy. The Cr–Br σ ionization was 0.38 eV lower in energy than that of the Cr–Cl σ, and now the Cr–I σ ionization is 0.46 eV lower in energy than that of the Cr–Br σ. Then, the second peak in this band at 10.20 eV will be assigned as the 10a″ and 14a′ ionizations from the cyclopentadiene ring.

CpW(NO)$_2$Cl. The first band in this spectrum is unsymmetrical with a shoulder on its left hand side. In the spectrum of CpCr(NO)$_2$Cl, this first band was assigned to the 12a″ and 18a′ ionizations, which were mainly chromium in character. This band in the tungsten spectrum is broader and shows a slightly larger splitting since tungsten has larger spin–orbit coupling. The second band at 9.05 eV will be assigned the nitrosyl 2π ionization, the 17a′. The tungsten–chlorine π-bond ionization, the 16a′ and 11a″, appears as the next band at 9.95 eV and probably has higher Cl than W character. The band at approximately 10.6 eV, which is extremely unsymmetric, is due to the cyclopentadienyl $1e_1''$ ionizations, the 10a″ and 14a′. The chlorine–tungsten σ ionization, the 15a′, is therefore assigned as the peak at 11.61 eV.

CpW(NO)$_2$Br. The first band here is split into two peaks at 8.02 and 8.34 eV. The greater separation between these peaks cannot be understood if the character of this first peak is still mainly metal. As in the spectrum of CpCr(NO)$_2$Br, this first band will be assigned to the 12a″ and 18a′ and is a mixture of approximately half bromine and half tungsten. The second band at 9.18 eV has not shifted from its position in the "chloride" spectrum and will therefore be assigned as the nitrosyl 2π ionization, the 17a′. The third and fourth bands at 9.75 and 10.63 eV are approximately symmetrically spaced about the π-bond ionization in CpW(NO)$_2$Cl because of the combined presence of both W and Br spin–orbit coupling. The very broad band around 11.0 eV is assigned the cyclopentadienyl $1e_1''$ and the bromine–tungsten σ-bond ionizations, the 10a″, 14a′, and 15a′ ionizations, respectively.

CpW(NO)$_2$I. The first band (12a″, 18a′) is distinctly split into two separate peaks of equal intensity, indicating high iodine character in this tungsten–iodine π^* ionization. The next band is split into three peaks where it would be expected that the nitrosyl 2π and the tungsten–iodine π ionizations would be located. The tungsten–halogen π ionizations were split by 0.5 eV in the spectrum of CpW(NO)$_2$Br so it would be expected that these two ionizations would be split more in the iodine compound because of the increased spin–orbit coupling of iodine. Therefore, the peaks at 9.09 and 9.66 eV will be assigned the 16a′ and 11a″ ionizations. The peak at 9.34 eV is the nitrosyl 2π, the 17a′ ionization. In this spectrum, assignments according to the C_s molecular parentage may be particularly poor. The 16a′, 17a′, and 11a″ are all closely spaced, they all contain significant tungsten character, and will all mix under W spin–orbit coupling. The next band is about 1-eV broad, which would indicate multiple ionizations. The W–I σ bond, the 15a′, would be expected to have a lower ionization energy than the bromine ionization, and therefore the peak at 10.44 eV is assigned as resulting from the 15a′. The higher ionization energy side of this broad band, around 11 eV, would then be the ring $1e_1''$ ionizations.

Discussion

It is relatively rare that the PE spectra of low-symmetry metal complexes can be assigned unambiguously without the aid of theoretical calculations or careful comparison of the spectra in a series of related complexes. Both approaches have been useful in this study; the latter was particularly helpful when we could observe the spin–orbit splitting in complexes containing one or more heavy atoms. Although one might question the assignment of an individual spectrum, our assignments of all the spectra fit a pattern which provides convincing evidence that they are correct.

This pattern is illustrated in Figure 5, which shows "experimental" MO diagrams for all of the complexes. The diagrams were constructed by using experimental IE's for the negative of the MO energies. The metal, M, and Br atomic orbital (AO) energies were taken to have the same value and placed halfway between the 18a′,12a″ pair and the 16a′,11a″ pair. This somewhat arbitrary placement is based in part on previous results for Re(CO)$_5$X[7], and its accuracy is not critical to our arguments. The metal AO energies are kept the same for the other halogens. From the differences in the IE of the halogen lone pair in CH$_3$X,[13] the Cl AO energy is placed 0.6 eV lower and the I AO energy is placed 0.8 eV higher than that of Br. With these diagrams one can easily follow the change in the 18a′,12a″ pair (M–X π^*) from mostly metal

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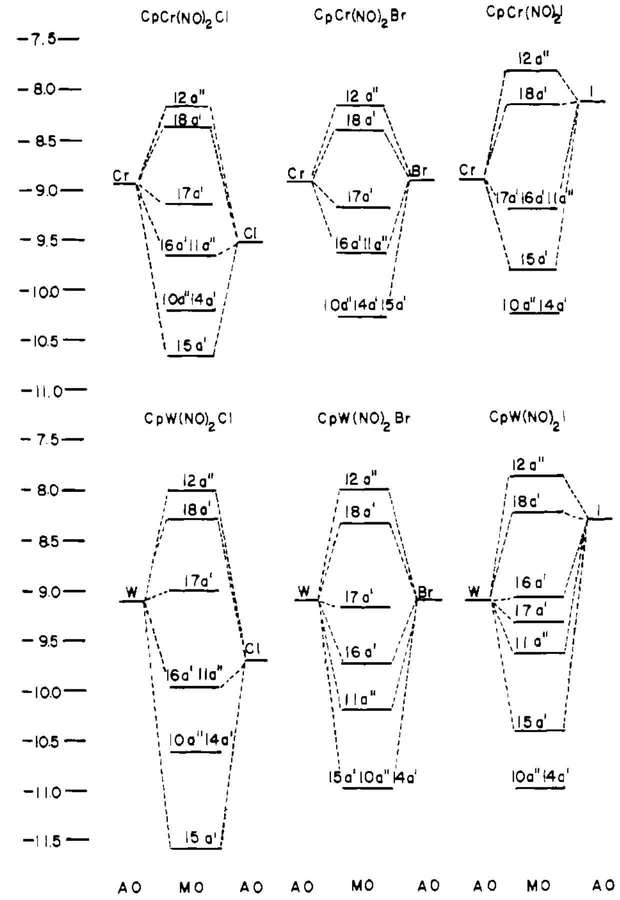

Figure 5. Experimental molecular orbital diagrams. The MO energies correspond to the negative of the experimental ionization energy.

in the Cl complexes to mostly halogen in the I complexes. The nearly constant IE for the 17a′ (NO 2π) is shown. It is not clear if the apparent trend toward higher IE in the W case is significant since the effects of spin–orbit coupling will be to mix the character of the 17a′ with the 16a′,11a″ pair. The splitting of the 16a′, 11a″ pair (M–X π) is small except for the two complexes with the largest spin–orbit effects, $CpW(NO)_2Br$ and $CpW(NO)_2I$. The 14a′,10a″ pair (Cp $1e_1''$) are at a similar energy in all the complexes. One of the most important features, which is obvious in the diagrams but not the spectra, is the decrease in the IE (increase in MO energy) of the 15a′ along the series Cl, Br, and I. This energy shift parallels the change in the halogen's AO energy and lends credence to our assignment.

Although diagrams of this type are helpful in interpreting the spectra, they should not be taken too literally. As mentioned before, we are really observing the energies of states of the ion in the experimental IE and it is only an approximation to view these state energies as corresponding to a MO energy. The assignments of species with heavy atoms presents further problems because the spin–orbit coupling mixes the $^2A''$ and $^2A'$ states. This problem is especially important in $CpW(NO)_2Br$ and $CpW(NO)_2I$ where spin–orbit coupling mixes the states arising from the 16a′ and 11a″ ionizations in $CpW(NO)_2Br$ and those arising from 16a′, 17a′, and 11a″ ionizations in $CpW(NO)_2I$. This mixing of states is probably less important for the 18a′,12a″ ionizations because these already have a substantial splitting due to molecular interactions.

The overall qualitative agreement with the Fenske–Hall calculation on $CpCr(NO)_2Cl$ is excellent. The calculation correctly predicts a larger splitting for the 18a′,12a″ pair than for the 16a′,11a″ pair. The 18a′,12a″ splitting arises primarily from direct ligand–ligand interactions. They also predict larger Cr character for the 18a′,12a″ pair and larger Cl character for the 16a′,11a″ pair in agreement with the trends in the spectra. The large separation between the IE of the 18a′,12a″ pair and that of the 17a′ is evident in the MO results. The most serious error made by the calculations is that they predict $Cp(1e_1'')$ orbitals, the 14a′,10a″ pair, to be too stable relative to the Cr–Cl σ-bonding pair, the 15a′. Even with this problem, which was previously known,[9] the overall agreement is excellent.

Our results can be compared with those of the $CpFe(CO)_2X$ series.[9] This series is isoelectronic with our $CpCr(NO)_2X$ series and involves the replacement of a $Fe(CO)_2$ group with a $Cr(NO)_2$ group. The splitting of the 18a′,12a″ pair is essentially constant in the spectra of the Fe complexes, while for the Cr series the splitting is the same in the spectra of the Cl and Br complexes but increases slightly in the spectra of the I complex. In the Fe series this constancy was explained as two competing effects. As the Fe–X distance increases (Cl to Br to I), the direct ligand–ligand interaction with the halogen decreases, which decreases the splitting of the 18a′,12a″ pair. Compensating for this decrease was the increase in halogen character of the 18a′,12a″ pair with the concomitant increase in spin–orbit coupling, which increases the splitting. The larger metal radius of Cr compared to Fe suggests that the splitting due to the ligand–ligand interactions would be less for the Cr complexes. This is consistent with the observed smaller absolute splitting in the Cr–Cl and Cr–Br spectra and with the increase in splitting of the Cr–I spectrum, where the large spin–orbit coupling of I would dominate the splitting. In the case of the W, where one has an even larger metal radius, one observes a steady increase in this splitting from 0.26 eV in $CpW(NO)_2Cl$ to 0.32 eV in $CpW(NO)_2Br$ and to 0.37 eV in $CpW(NO)_2I$.

In general the 16a′,11a″ splitting seems to be smaller in the Cr series than in the Fe series. These results may be a reflection of larger delocalization of the M–X π system onto the nitrosyls in the chromium complexes. This increased delocalization is dramatically illustrated by the increase in the IE of the 17a′ (from 8.87 to 9.22 eV) when $Fe(CO)_2$ is replaced by $Cr(NO)_2$. In the Fe series, this MO is mainly metal. If it remained mainly metal in the Cr series, the IE would have to decrease because of the lower effective nuclear charge of Cr. The only way for this IE to increase is for the character to change from metal to nitrosyl. This confirms the prediction of the MO calculations that 17a′ has substantial NO 2π character. In a sense, the electron density is following the change in the nuclear charge as $Fe(CO)_2$ changes to $Cr(NO)_2$.

Comparison of the M–X σ-bond IE in the $Mn(CO)_5X$ series[14] and $Re(CO)_5X$ series[7] with the $CpCr(NO)_2X$ and $CpW(NO)_2X$ series provides a possible rationale for the difference in the reactivity of the Cl in the Cr complex compared to the W complex. The Re–X σ bonds are more stable (higher IE) than the Mn–X σ bonds by an average of 0.2 eV. The corresponding difference between $CpW(NO)_2X$ and $CpCr(NO)_2X$ is 0.9 eV. In all cases the M–X σ IE of $CpCr(NO)_2X$ is smaller than that of $Mn(CO)_5X$, while the IE of $CpW(NO)_2X$ is larger than that of $Re(CO)_5X$. Since the net M–X bond is primarily σ in character, one might expect rather similar chemistry for the M–X bond in $Mn(CO)_5X$ and $Re(CO)_5X$ but rather different chemistry for this bond in $CpCr(NO)_2X$ and $CpW(NO)_2X$. Although one must be cautious in overinterpreting these differences in IE's, they are consistent with the difference in the reactivity of these species. We believe this is one of few examples where the PES can be compared so directly to the complexes reactivity.

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Structural Studies of the Hydrogen Storage Material Mg_2NiH_4.
1. Cubic High-Temperature Structure

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The structure of the high-temperature modification of Mg_2NiD_4 has been determined from neutron powder diffraction data collected at 280 °C. It is face-centered cubic (space group $Fm3m$, with $a = 6.507$ (2) Å) with the metal atoms occupying anti-fluorite positions and the D atoms surrounding the Ni atoms in a disordered configuration of yet unknown local symmetry. The average structure resembles the K_2PtCl_6 structure type. The average metal–deuterium distances are d(Ni–D) = 1.49 (3) Å and d(Mg–D) = 2.305 (3) Å.

Introduction

Magnesium–nickel alloys are considered promising materials for energy storage applications.[2a] A compound of central interest is Mg_2Ni because it forms a ternary hydride Mg_2NiD_4[2b] having a favorable hydrogen-to-metal weight ratio of 3.8% and because its presence improves considerably the hydriding kinetics of the binary hydride MgH_2.

Contrary to other hydrogen storage materials such as FeTi[3-5] and $LaNi_5$[6] structural information on this compound is scarce. Gavra et al.[7] have shown from an X-ray study that Mg_2NiH_4 forms a cubic high-temperature (HT) phase with lattice constant $a = 6.490$ Å which transforms between 245 and 210 °C into a low-temperature (LT) phase of low symmetry. The metal atom arrangement of the HT phase was suggested to be of the anti-fluorite type. The positions of the H atoms and the overall symmetry of the structure have not been determined.

In this article we report on final neutron diffraction results on the HT (β') phase of the deuteride $Mg_2NiD_{3.9}$, corresponding to improved experimental conditions with respect to a preliminary account of the results which has been presented recently.[8] Moreover, in the present article the bonding of $Mg_2NiD_{3.9}$ will be discussed and compared to that in similar systems.

Table I. Crystal Data for the High-Temperature Phase (β') of $Mg_2NiD_{3.9}$ at 280 °C and 22 bar of D_2

space group	$Fm3m$ (No. 225)
lattice const	$a = 6.507$ (2) Å
atom positions	4 Ni in (4a) 0, 0, 0 etc. 8 Mg in (8c) $^1/_4$, $^1/_4$, $^1/_4$ etc. ~16 D in (24e) x_D, 0, 0
fractional coord x_D	0.229 (1)[a] (0.229 (5))[b]
occupancy of D atom sites	0.69 (2)[a] (0.77 (10))[b]
temp factors	
B(Ni,Mg)	1.3 (2) Å^2 [a] (1.2 (8) Å^2)[b]
B(D)	7.6 (3) Å^2 [a] (9 (2) Å^2)[b]
R factors	5.6%[a] (8.1%)[b]

[a] Based on simultaneous profile refinement[9] of $Mg_2NiD_{3.9}$ and MgD_2.[15] [b] Based on least-squares refinement of integrated neutron intensities.

Experimental Section

The sample preparation is described in ref 8. In order to avoid large Bragg peaks from the container, we filled a Cu-coated vanadium tube with the sample and kept it under a constant pressure of 22 bar of D_2. This tube was placed into a second, coaxial vanadium tube which was evacuated and heated by electrical current to temperatures up to 300 °C. The assembly was mounted on a two-axis diffractometer ($\lambda = 2.346$ Å) at the reactor Saphir in Würenlingen, Switzerland, and a neutron diffraction pattern was recorded at $T = 280$ °C (Figure 1a). The pattern was analyzed by a special profile refinement technique[9] in which the contributions due to the MgD_2 impurity phase were taken into account. As shown in Figure 1b, 11 reflections were retained for the structure determination of $Mg_2NiD_{3.9}$. The results

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