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Electronic Structure of Transition Metal Thiocarbonyl Complexes

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The He I photoelectron spectra of $Cr(CO)_5CS$, $W(CO)_5CS$, and η^5-$C_5H_5Mn(CO)_2CS$ have been obtained. It is observed that the ionizations which are associated predominantly with the highest occupied σ and π levels of the thiocarbonyl ligand are clearly separated from the other ionizations of these complexes and display quite different ionization band envelopes. The remaining ionization bands of these complexes are comparable to the bands observed in the ionization spectra of the corresponding carbonyl complexes. Molecular orbital calculations were performed on the chromium and manganese species. Besides predicting the correct order for the ionizations, the calculations are highly successful in giving a quantitative account of observed trends in ionization potentials between the carbonyl complexes and the thiocarbonyl complexes. As suspected, the thiocarbonyl ligand is found to be a better π-electron acceptor than the carbonyl ligand. However, consideration of this factor alone does not account for the observed trends in ionization potentials between carbonyl and thiocarbonyl complexes. The occupied thiocarbonyl σ and π levels also interact more strongly with the metal, and the electron density has increased at the carbon of the thiocarbonyl group. These factors have important implications for the properties of thiocarbonyl complexes.

Introduction

The synthesis and characterization of transition metal thiocarbonyl complexes have received much attention in the last few years.[1-10] A portion of the interest in these complexes is a consequence of their similarity, in terms of electronic structure and bonding capabilities, to the more common example of a carbonyl ligand. Preliminary investigations have also shown that thiocarbonyl complexes display some intriguing chemical and physical characteristics.[9-12] The electronic structure of thiocarbonyl has been investigated with photoelectron spectroscopy[13-15] and an ab initio calculation.[16] The interpretation of the bonding capabilities of CS is consistent with certain of the properties of the complexes, such as the strong metal–CS bonds and the low CS stretching frequencies. Consideration of the electronic structure of the isolated CS group is not sufficient, however, for describing the behavior of the total transition metal complex. Interpretations of relative small changes in the force constants of the remaining carbonyls after CS substitution,[17] the ir and Raman intensities,[18] the ^{13}C NMR shifts,[12] and certain substitution reactions[9] are contradictory.

The present work concerns the investigation, via photoelectron spectroscopy and theoretical calculations, of the electronic structure and bonding of transition metal thiocarbonyl complexes. He I photoelectron spectroscopy has proven to be a useful probe into the valence-electron structure of transition metal carbonyls[19,20] and a variety of other ligand groups.[21-26] These studies, when combined with theoretical calculations,[26-28] lead to a better understanding of the ionization process and the electronic interactions in the complexes. Angelici and Dombek[9] have recently prepared and characterized $Cr(CO)_5CS$ and $W(CO)_5CS$, and Butler and Fenster[7,10] have synthesized $CpMn(CO)_2CS$ ($Cp = \eta^5$-C_5H_5). These complexes are sufficiently stable and volatile for study by photoelectron spectroscopy. The study of these particular thiocarbonyls is especially appropriate because they are closely related to the carbonyl complexes $Cr(CO)_6$, $W(CO)_6$, and $CpMn(CO)_3$ which have already received considerable attention. The photoelectron spectra of the thiocarbonyl complexes are found to offer a bonus feature in that the ionization bands associated with the highest occupied σ and π levels of the CS group are clearly separated from the other ionization bands of the molecule. Thus these ionizations of the diatomic ligand may now be examined in detail.

Experimental and Computational Details

Photoelectron Spectra. Samples of $Cr(CO)_5CS$ and $W(CO)_5CS$ were provided by Dr. R. J. Angelici and Dr. B. D. Dombek, and the sample of $CpMn(CO)_2CS$ was supplied by Dr. I. S. Butler. Photoelectron spectra were measured using a Varian IEE-15 electron spectrometer in the uv configuration. All spectra were measured using argon (15.76 eV) as a single internal standard. The working resolution was less than 30 meV. Simultaneous observation of a number of reference gas ionization peaks showed the energy scale to be linear within less than 0.01 eV over a range of binding energies from 9 to 17 eV. All samples were admitted to the spectrometer via the variable-temperature inlet system. The volatility of each sample was appropriate for obtaining a well-defined spectrum at room temperature. The displayed spectra represent a time-averaged sum of individual scans through a binding energy range of 10 eV, stored in 1000 data channels. The duration of a single data collection scan was generally 100 s, and data were collected continuously for about 1 h. In addition, data for specific regions of the spectra were collected in greater detail over longer periods of time for more precise information regarding the band shapes and areas. The ionizations were carefully observed from initial introduction of the sample until the supply of sample had been depleted. There was no evidence of any transient behavior or decomposition. Each experiment was also repeated to ensure reproducibility.

Spectral Data Reduction. So that the ionization band potentials and shapes of these spectra could be described precisely, the low-binding-energy ionization bands were curve-fit with asymmetric Gaussian functions. The ability of this functional form to represent ionization bands accurately and the utility of this representation for interpreting ionizations have been discussed elsewhere.[29] The exact functional form used is an asymmetric Gaussian function defined as

$$C(E) = Ae^{-k} [(E - P)/W]^2$$

where E is the binding energy, $C(E)$ is the amplitude of peak, P is the position of the peak, $k = 4 \ln 2$, $W = W_h$, the apparent high-binding-energy side half-width for $E > P$, and $W = W_l$, the apparent low-binding-energy side half-width for $E < P$. Thus the variable parameters for each peak are A, P, W_h, and W_l. The baseline is assumed to be linear through short segments in the binding energy. The fit is weighted according to the value of each data channel. If two or more peaks overlap considerably, as occurs if some vibrational structure is partially resolved, the peaks used to fit the band are assumed to have the same left half-widths and also to have the same right half-widths.

Molecular Orbital Calculations. Molecular orbital calculations were performed for the purpose of providing a theoretical basis for an interpretation of the ionizations and the electronic structure of these complexes. Ab initio calculations have previously been performed on carbon monoxide[30,42] and carbon monosulfide,[16] as well as on chromium hexacarbonyl.[27] The electronic structure of η^5-cyclopentadienylmanganese tricarbonyl has also been described in detail.[31] The theoretical treatment of these systems may be extended to the corresponding thiocarbonyl complexes most easily via approximate molecular orbital methods. The Fenske method[32] of approximate molecular orbital calculations is well suited for this purpose. This method contains no empirical or variable parameters, and, therefore, it may serve as an unprejudiced aid for investigating electronic structure. The merits and limitations of this approach for investigating the electronic structure and bonding in transition metal carbonyls and other ligand systems and particularly for interpreting the ionizations of transition metal complexes are well documented.[23,24,33]

In these calculations, the atomic coordinates and basis functions, both of which are chosen in a totally nonarbitrary fashion, completely define the calculated results. The atomic coordinates are obtained from the available crystal structure data. The carbon–sulfur distance for these calculations of 1.534 Å is the same as that used in the earlier ab initio calculations on CS[16] and is essentially the same as the carbon–sulfur distance obtained from determination of the crystal structure of a rhodium thiocarbonyl complex.[34] This crystal structure determination also indicated that the metal–carbon (thiocarbonyl) distance was less than 0.03 Å shorter than the metal–carbon distance of the analogous carbonyl complex. Therefore, so that calculated trends in the electronic structures will reflect electronic effects only, the metal–carbon distances were assumed to be equivalent for both carbonyl and thiocarbonyl complexes. The metal–carbon and carbon–oxygen distances for $Cr(CO)_6$ were assumed to be 1.92 and 1.15 Å, respectively. The atomic coordinates for the calculation of $CpMn(CO)_2CS$ were derived from the crystal structure of $CpMn(CO)_3$.[35] The calculation on $CpMn(CO)_2CS$ parallels the previously reported calculation on $CpMn(CO)_3$.[31,36]

The variational basis set used in these calculations is a minimum atomic valence basis of contracted Slater-type functions. The functions for carbon, oxygen, and sulfur were determined from Clementi's atomic functions[37] as described previously.[38] The chromium and manganese 1s–3d functions were taken from Richardson et al.[39] In addition, 4s and 4p functions were included on the metal centers. For consistency with previous calculations, the chromium 4s and 4p exponents were taken to be 2.0 and 1.6, respectively, and the manganese 4s and 4p exponents were set to 2.0.

It is found in these calculations that certain of the canonical orbitals of the thiocarbonyl ligand are only slightly perturbed upon bonding in the metal complex. This partial separability of the total electron wave function of a transition metal complex has been discussed elsewhere in the context of the 3σ and 6σ orbitals of the carbonyl ligand[40] and many of the orbitals of an η^5-cyclopentadienyl ring.[31] If these particular orbitals are fixed to their form as determined in the isolated ligands, the size of the SCF problem is reduced substantially with only minor changes in the results. Furthermore, because the approximate wave function is then analyzed via perturbation theory, there is no more uncertainty in these results than in the results of a full-variational-basis calculation. In the case of the thiocarbonyl ligand, it is found that the 5σ orbital, which represents the C–S σ bond, and the 8σ orbital, which is virtual, may be deleted from variational treatment in the calculation of the total wave function of the complex without altering the results significantly. The 5σ orbital acts as if it were a ligand core orbital, even though this orbital is composed of atomic valence functions. The bonding of the thiocarbonyl group to a metal may be described quite accurately within the assumption that the ligand valence density moves in a potential provided by this frozen core. To be consistent with earlier calculations, the results reported in this paper refer to calculations in which the carbonyl 3σ and 6σ orbitals and the thiocarbonyl 5σ and 8σ orbitals have been deleted from variational treatment.

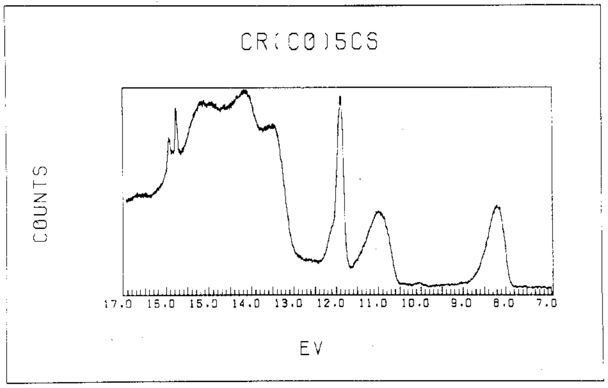


Figure 1.

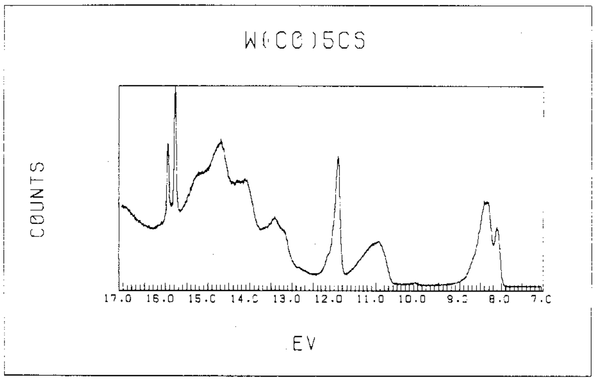


Figure 2.

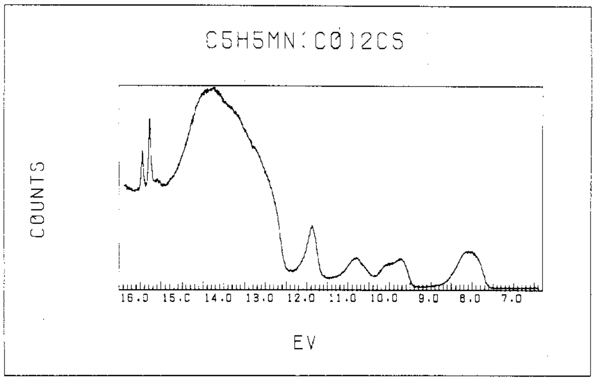


Figure 3.

Results

The He I ionization spectra are displayed in Figures 1–3. The two sharp ionization peaks between 15.5 and 16 eV in each spectrum correspond to the internal argon standard. The ionization bands in these spectra may be classified into four distinct categories which correspond to particular band shapes and binding energy regions. In region 1, between 7.5 and 10.5 eV, the ionization bands of these complexes appear remarkably similar to the ionization bands observed in the spectra of the analogous carbonyl complexes. In region 2, between 10.5 and 11.5 eV, and in region 3, between 11.5 and 12.5 eV, ionization bands are observed which have no similar counterparts in the spectra of the carbonyl complexes. The ionization band in region 2 of each spectrum is broad and has no resolved fine structure and apparently no ionization shoulders. The band in region 3 of each spectrum is sharp and intense and under

Table I. Ionization Data for $Cr(CO)_5CS$

Band	Ionization potential, eV	Rel amplitude	W_h	W_l	Rel area[a]
1	8.16	0.46	0.61	0.30	0.33
2	10.93	0.39	0.73	0.43	0.35
3	11.88	1	0.20	0.14	0.32
3′	12.08	0.15	0.20[b]	0.14[b]	
3″	12.17	0.06	0.20[b]	0.14[b]	

[a] Relative to total area of 1 for all bands in table. [b] Constrained parameters.

Table II. Ionization Data for $W(CO)_5CS$

Band	Ionization potential, eV	Rel amplitude	W_h	W_l	Rel area[a]
1	8.08				0.46
1′	8.25–8.35				
2	10.92	0.33	0.91	0.34	0.29
3	11.90	1	0.15	0.09	0.24
3′	12.03	0.26	0.15[b]	0.09[b]	
3″	12.16	0.13	0.15[b]	0.09[b]	

[a] Relative to total area of 1 for all bands in table. [b] Constrained parameters.

Table III. Ionization Data for η^5-$C_5H_5Mn(CO)_2CS$

Band	Ionization potential, eV	Rel amplitude	W_h	W_l	Rel area[a]
1[c]	7.81	0.37	0.44	0.24	0.34
	8.00	0.37[b]	0.44[b]	0.24[b]	
	8.23	0.37[b]	0.44[b]	0.24[b]	
1′	9.71	0.55	0.40	0.31	0.27
1″	10.07	0.35	0.40[b]	0.31[b]	
2	10.80	0.55	0.50	0.51	0.28
3	11.85	1	0.19	0.22	0.38
3′	11.98	0.46	0.19[b]	0.22[b]	
3″	12.14	0.17	0.19[b]	0.22[b]	

[a] Relative to total area of bands in table excluding 1′ and 1″. [b] Parameters constrained. [c] Three peaks were used for accurate representation of the band. No significance should be placed on the exact IP's except that the highest and lowest values indicate the possible range.

increased resolution displays an apparent vibrational progression on its high-binding-energy side. In region 4, between 12.5 and 16 eV, a broad, intense ionization spectrum is observed which, in the case of the chromium and tungsten complexes, exhibits a complex band envelope. This structure has been ascribed to ionization from carbonyl 5σ and 2π levels in carbonyl complexes[20] and to ionization from certain η^5-cyclopentadienyl ring levels in bis(η^5-cyclopentadienyl) complexes.[41]

The ionization potentials, peak shapes, relative peak amplitudes, and relative peak areas for bands up to a binding energy of 12.5 eV are presented in Tables I–III. The uncertainty of the ionization potentials and half-widths is in most cases less than ±0.02 eV. There is greater uncertainty in these values for bands which are appreciably overlapping, such as the bands in region 3 or the initial ionization band of $CpMn(CO)_2CS$. The relative amplitudes and areas are generally reproducible to within 5%.

Assignment and Interpretation of Ionizations

Table IV. Calculated Orbital Eigenvalues and Ionization Potentials of CS and CO

Eigenvalues of ab Initio Calculation, eV

	CO[42]		CS[16]	Δ
2π*	4.1	3π*	2.31	−1.79
5σ	−15.52	7σ	−12.80	2.72
1π	−17.77	2π	−12.61	5.16
4σ	−22.45	6σ	−18.83	3.62
3σ	−42.16	5σ	−30.12	12.04

Eigenvalues by This Method, eV

	CO		CS	Δ
2π*	−0.48	3π*	−2.09	−1.61
5σ	−13.85	7σ	−11.01	2.84
1π	−20.74	2π	−15.31	5.43
4σ	−22.55	6σ	−19.71	2.84
3σ	−41.76	5σ	−30.54	11.22

Observed Vertical Ionization Potentials, eV (Vibrational Frequencies, cm^{-1})

	CO[43] (2157)		CS[13–15] (1275)	Δ
5σ	14.01 (2160)	7σ	11.34 (1384–1290)	2.67
1π	16.91 (1610)	2π	12.90 (972–1050)	4.01
4σ	19.72 (1690)	6σ	16.06 (868)	3.66
3σ[44]	38.3	5σ	18.03 (1055)	20.27

Carbon Monosulfide. Before the available experimental and theoretical information is assembled into a consistent interpretation of these ionizations, and hence the electronic structure and bonding in these complexes, it is helpful to consider the electronic structure and ionization characteristics of carbon monosulfide. An ab initio calculation of the electronic structure of carbon monosulfide has been reported by Richards[16] which is comparable to Nesbet's ab initio calculation on carbon monoxide.[42] The eigenvalues of these two calculations, as well as the eigenvalues obtained from approximate calculations on CO and CS, are compared in Table IV. Also included in Table IV are the observed vertical ionization potentials of CO and CS labeled according to the molecular orbitals from which the electrons originate. Although the ab initio and approximate calculations differ slightly in the absolute energies of the eigenvalues, the two calculations agree quite closely in the shift of corresponding eigenvalues from CO to CS. It is the shift of these eigenvalues which is important to the present study. The eigenvalues of a molecular orbital calculation are frequently assumed to be related to the vertical ionization potentials through Koopmans' theorem.[45] Koopmans' theorem requires, in effect, that the remaining total electron density does not rearrange upon removal of an electron and that correlation and relativistic effects are not important.[46] Straightforward application of this theorem for the purpose of interpreting the ionizations of a single molecule may be erroneous.[26,31,47] Indeed, as the figures in Table IV show, it is observed that the two lowest binding energy bands of CS occur in the reverse order of the eigenvalues determined in the ab initio calculation. However, if those factors producing the discrepancies between the calculated eigenvalues and the observed ionization potentials of two similar systems are relatively constant, the trends in calculated eigenvalues between the two systems will be reflected in the trends in ionization potentials. Under certain conditions this latter assumption is also not valid.[48] However, in the case of CO and CS, it is found that the eigenvalues of the calculations may be used successfully to interpret the shifts in ionization potentials.

The trends in calculated eigenvalues between CO and CS are most easily understood in terms of the molecular orbital diagram in Figure 4. The sulfur atomic functions in the CS molecule are inherently less stable than those of the corresponding oxygen atomic functions in CO. The lower stability (in a sense, the lower electronegativity) of the sulfur functions contributes additional charge to the carbon center which in turn destabilizes the carbon functions and the carbon "lone pair" orbital, the 7σ. The interaction between the carbon and sulfur pπ orbitals is also reduced, resulting in a lower π* orbital, the 3π. The CS 3π orbital is still associated pre-

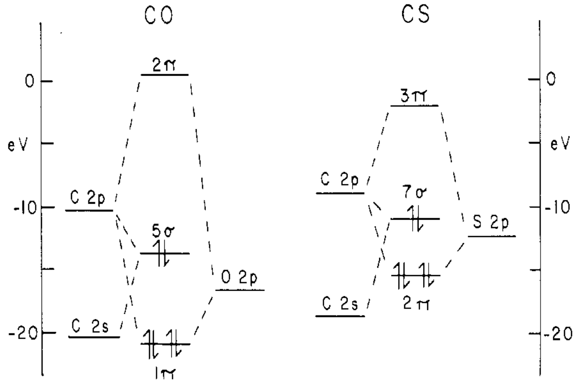


Figure 4. Molecular orbital diagrams of CO and CS.

dominantly with the carbon center (although it does contain an appreciable sulfur contribution) and should have an increased capability for accepting electrons from the metal. The eigenvalues of all the occupied orbitals of CS occur at higher energy in comparison to those of CO. The most striking change is in the eigenvalue of the CS π bonds, the 2π orbitals. These levels are destabilized by >5 eV. In fact, in the ab initio calculation of CS, the 2π orbitals are calculated to be the highest occupied orbitals. These orbitals are predominantly sulfur in character but also contain appreciable carbon character and may become significantly involved in metal–ligand interaction (vide infra).

$Cr(CO)_5CS$, $W(CO)_5CS$, and $CpMn(CO)_2CS$. The ionization bands of the transition metal thiocarbonyl complexes have been classified into four distinct categories which are characterized both by the shapes of the bands and by the binding energy regions in which they occur. The ionizations occurring in each region will now be analyzed in detail.

Region 1. The ionization bands which occur in this region of the spectra of the thiocarbonyl complexes are quite similar in appearance to the corresponding bands in the spectra of the carbonyl complexes. Consider first the initial ionization band of $Cr(CO)_5CS$. The fit of this ionization band with a single asymmetric Gaussian peak, as displayed in Figure 5, is quite similar to the fit of the corresponding band of $Cr(CO)_6$. The apparent left and right half-widths of this peak, 0.61 and 0.30 eV, respectively, are not much different from the corresponding values of 0.69 and 0.49 eV observed for $Cr(CO)_6$.[29] The only significant difference in these ionization bands is that for $Cr(CO)_5CS$, the band has shifted 0.25 eV to lower binding energy. In the spectrum of $Cr(CO)_6$, the first ionization band is attributed to removal of electrons from the predominantly metal t_{2g} orbitals. The molecule $Cr(CO)_5CS$, however, belongs to the point group C_{4v}, and the highest occupied orbitals, which are also predominantly metal d in character, will transform according to the e and b_2 representations. There is no evidence in the $Cr(CO)_5CS$ spectrum for a loss in degeneracy in these ionizations. The observations of lower binding energy and no significant loss of degeneracy for these metal ionizations appear to be inconsistent with the expected better π-acceptor ability of the CS ligand.

The initial ionization bands of $W(CO)_6$ and $W(CO)_5CS$ may provide further information on any loss of degeneracy caused by CS substitution. The initial band of both complexes displays a multiplet pattern caused by spin–orbit interactions in the positive ion. As Lloyd et al.[20] pointed out in their discussion of the spectrum of $W(CO)_6$, the $^2T_{2g}$ state of the positive ion is split into U' and E'' components. These states will differ in energy by three-halves the spin–orbit coupling term.[49] From degeneracy considerations the relative area of the two peaks, U':E'', should be near 2:1. In the spectrum of $W(CO)_5CS$, a slight flattening is observed on the top of the band assigned as the U'' component. This may indicate that the predominantly metal e and b_2 levels are separated by approximately 0.1 eV before spin–orbit interaction. However, the flattening may also be due to slightly different spin–orbit interactions in the positive ions and not to ground-state properties. Also, the tail of this ionization band for both complexes indicates that a short vibrational progression, ascribed to the CO stretching mode, is associated with each spin–orbit split component. The existence of this progression complicates a detailed band shape analysis.

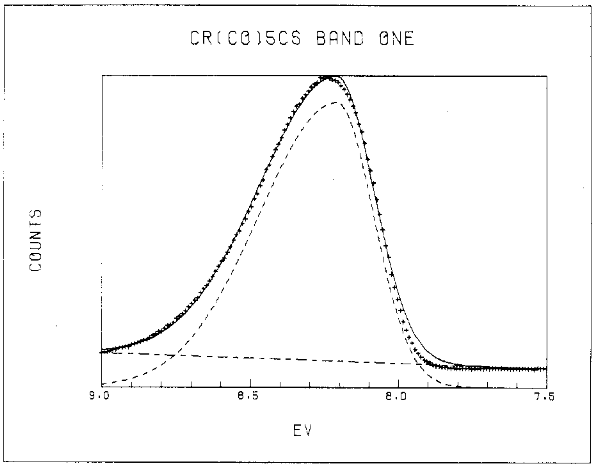


Figure 5. $Cr(CO)_5CS$ ionization band: plus signs, data values; dashed lines, curve-fit Gaussian peaks and baseline; solid line, fit sum.

As in the case of the $Cr(CO)_5CS$ and $Cr(CO)_6$ spectra, the total band envelope of $W(CO)_5CS$ has shifted to lower binding energy in comparison to the band envelope of $W(CO)_6$. Using the peak of the E'' component as a reference, the shift is again 0.25 eV.

The initial ionization bands of $CpMn(CO)_2CS$ and $CpMn(CO)_3$[31] are also quite similar. These band envelopes are broadened, in comparison with the envelopes of the chromium complexes, by the reduced symmetry about the metal atom. Therefore, it is difficult to assess the additional splitting caused by the CS group, although an upper limit seems to be about 0.1 eV. Again, the band for the thiocarbonyl complex occurs at lower binding energy.

The ionization bands associated primarily with the ring e_1'' orbitals are also quite similar in the spectra of the two cyclopentadienyl complexes. Both bands display a distinct shoulder on their high-binding-energy side. The separation of this shoulder from the main peak in the spectrum of $CpMn(CO)_2CS$ is 0.36 eV, which compares favorably with the 0.39-eV separation observed in the spectrum of $CpMn(CO)_3$. The vertical ionization potential of this band for the thiocarbonyl complex occurs at about 0.2 eV lower binding energy than it does for the carbonyl complex.

Thus in each case, the ionizations of the carbonyl complex are shifted to lower binding energy in the thiocarbonyl-substituted species, and there is no apparent loss of degeneracy. Simple qualitative arguments based upon the better π-acceptor ability of CS compared to CO predicts just the opposite. Apparently a more sophisticated consideration of the structure of thiocarbonyls is necessary in order to understand these trends. Some clues are offered by examination of the ionization bands of the thiocarbonyl complexes which do not appear in the spectra of the corresponding carbonyl complexes.

Region 2. The band in region 2, at ~10.9 eV in each spectrum, is assigned as ionization from an orbital in which the predominant contribution is from the CS 7σ orbital. It is also conceivable that this band results from ionization of the orbital which is primarily CS 2π in character, although the following information, which is derived from band shifts,

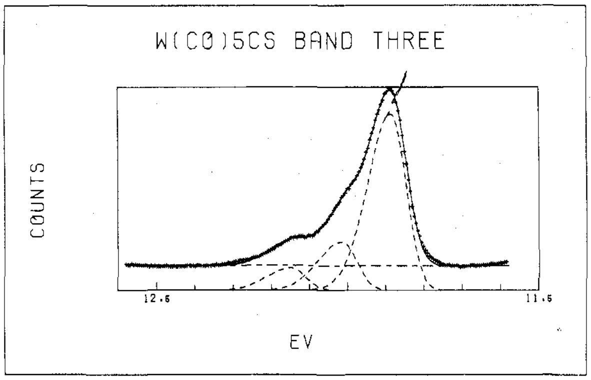


Figure 6. $W(CO)_5CS$ ionization band: plus signs, data values; dashed lines, curve-fit Gaussian peaks and baseline; solid line, fit sum.

shapes, and intensities in regions 2 and 3 of the spectra, favors the 7σ assignment. This ionization occurs at about 0.4 eV lower binding energy than the corresponding ionization of free CS. In the spectrum of free CS, ionization from this level produced a sharp ionization peak, as characteristic of a lone pair orbital. In the spectra of the thiocarbonyl complexes, the corresponding ionization band now has a half-width greater than 0.5 eV. This is undoubtedly caused by the interaction with the metal center. The shape of this band indicates that the ionization is now associated with removal of an electron from an orbital which is bonding in character. Since no fine structure could be resolved, the vibrational frequency associated with this band must be low.

Region 3. The band near 12 eV in each of the spectra is assigned to ionization from an orbital in which the major contribution is from the CS 2π orbital. This ionization occurs at about 1.0 eV lower binding energy than the corresponding ionization of free CS. This band is relatively sharp and intense and displays a short vibrational progression. This progression is most evident in the ionization band of $W(CO)_5CS$, which is displayed in Figure 6. As many as four vibrational components may be observed. The vibrational spacing of 0.13 eV corresponds to 1050 cm^{-1}, a value which is in close agreement with the frequency observed for the corresponding band of free CS. The reduction in frequency of this mode compared to the frequency of 1258 cm^{-1} observed for the same mode in the neutral complex[9] again indicates that the ionization is associated with removal of an electron from a bonding orbital. There is one significant difference in this ionization band in the spectra of the thiocarbonyl complexes as compared to the corresponding band in the spectrum of free CS. In the spectrum of free CS, the vertical ionization potential corresponds to the second component of the vibrational progression, whereas in the spectra of the thiocarbonyl complexes, the vertical ionization potential corresponds to the first component, and the intensity of successive components decreases rapidly. This indicates that, for the thiocarbonyl complexes, the potential curve of the positive ion does not shift as much with respect to the potential curve of the ground state as it does for free CS.

The vertical ionization potentials of the bands in regions 2 and 3 are relatively insensitive to the metal substitution. The measured binding energies for these bands in the spectrum of $Cr(CO)_5CS$ are essentially equivalent to the values obtained from the spectrum of $W(CO)_5CS$. These bands have shifted to slightly lower binding energy in the spectrum of $CpMn(CO)_2CS$. The maximum shift, which is only 0.1 eV, is observed for the band associated with the thiocarbonyl 7σ orbital.

Region 4. The remaining bands in these spectra arise from ionization of the highest occupied σ and π levels of the carbonyl and ring ligands. Because of the large number of ionizations occurring in region 4, it is difficult to analyze in detail any of the small changes which are observed. The ionization band at the onset of region 4 (near 13 eV) has been ascribed to ionizations associated primarily with the CO 5σ orbitals. It has been found that ionizations from both the CS 7σ and the CS 2π orbitals occur at lower binding energy than ionizations from the CO 5σ orbitals. Therefore, it is not surprising that these additional ionization bands are observed in regions 2 and 3, from 10 to 12.5 eV.

Relative Band Areas. Besides the information which may be obtained from the band shapes and potentials, certain additional information may be derived from the relative band areas observed in these spectra. This information is also included in the ionization data tables for the spectrum of each complex. In the spectrum of $Cr(CO)_5CS$, the ratio of the area of the first band to the area of the second band is nearly 1:1. Because the first band is attributed to six electrons from the predominantly metal d levels and the second is attributed to only two electrons from the predominantly CS 7σ level, this ratio indicates that the cross section for ionization of these ligand electrons must be greater than the cross section for ionization of the metal electrons. The low cross section for metal ionizations compared to that for ligand ionizations has been observed in the spectra of other transition metal complexes.[20,21,31,50] The ratio of the area of band 2 to the area of band 3 is also nearly 1:1 in this spectrum, despite the fact that band 2 is associated with two CS σ electrons and band 3 is associated with four electrons from the predominantly CS 2π orbitals. The low cross section for the CS 2π ionizations compared to the CS 7σ ionizations is consistent with observation of low relative π–σ-band areas in the spectra of N_2 and CO.[51,52]

Some interesting trends are observed in these relative cross sections when the spectra of similar complexes are compared. For example, a cursory comparison of the spectrum of $W(CO)_5CS$ with that of $Cr(CO)_5CS$ reveals that the intensity of the first band has increased significantly in relation to the other bands. This is an example of the so-called "heavy atom effect",[20] in which replacement of an atom in a molecule by another which is below it in the periodic table causes the relative intensity of ionization bands associated with that center to increase. Lloyd et al.[20] compared the spectrum of $W(CO)_6$ with that of $Cr(CO)_6$ and concluded that the relative cross section for ionization of tungsten d levels is approximately twice as great as that for ionization of chromium d levels. In the spectra of the tungsten and chromium thiocarbonyl complexes, the two ionization bands between 10 and 12.5 eV are clearly separated from all other ionization bands and may conveniently be used as standard references for the comparison of the tungsten and chromium cross sections. If the band in region 3 (which has been ascribed to the CS 2π level) is assumed to have the same absolute area in the two spectra, then the tungsten cross section is 1.9 times greater than the chromium cross section. On the other hand, if the band in region 2 is assumed to have the same absolute area in the two spectra, then the tungsten cross section is only 1.7 times greater than the chromium cross section. The discrepancy in these values is most likely caused by unequal amounts of metal character mixing with the CS 2π and the CS 7σ levels. The lower relative cross section value obtained using the band in region 2 as a reference indicates that the band in region 2 is associated with a greater amount of metal character,[51] which is consistent with attributing this band to ionization from the M–CS σ bond.

The relative cross sections of $CpMn(CO)_2CS$ are more difficult to analyze because some bands overlap. Indications are that the cross sections of the metal levels and the CS levels of $CpMn(CO)_2CS$ bear much the same relationships to each other as those of $Cr(CO)_5CS$. In the spectrum of $CpMn(CO)_2CS$ it is also possible to compare the cross section for the metal ionizations to the cross section for ring ionizations. The ratio of the area of the metal band to the ring band is ~1.3:1, which is significantly larger than the ratio of 0.94:1 observed in the spectrum of $CpMn(CO)_3$. According to the cross section theory of Schweig and Thiel,[51] the principal contributions to an orbital cross section are the one-center effects. Also, as mentioned previously, ligand ionization bands are often more intense than metal d ionization bands. Although other explanations may be possible in more sophisticated theory, the increase in the relative area of the metal d ionization band from $CpMn(CO)_3$ to $CpMn(CO)_2CS$ is consistent with greater metal–thiocarbonyl interaction than metal–carbonyl interaction.

Electronic Structure of Transition Metal Thiocarbonyl Complexes

An indication of the electronic interactions in transition metal thiocarbonyl complexes has been provided by observing the kinetic energy distribution of ionized electrons. The binding energy, shape, and vibrational progression of an ionization band are clues to the bonding character of the orbital, and the relative intensities are evidence for its spatial distribution in the molecule. The differences in ionization potentials of the bands of a thiocarbonyl complex from those of the analogous carbonyl complex are related to differences in the electronic structures of CS and CO. These ionization characteristics must be interpreted with extreme caution. As already indicated, certain features of the ionization spectra of the thiocarbonyl complexes are somewhat surprising in light of the known structure of CS in comparison to CO. For instance, although the electronic structure of CS has been found to be much different from that of CO, the degeneracy of the t_{2g} ionizations of $Cr(CO)_6$ does not appear to be lifted in the spectrum of $Cr(CO)_5CS$. Also, the metal ionizations of the thiocarbonyl complexes consistently occur at lower binding energy than the metal ionizations of the carbonyl complexes, which seems to be in contradiction to the expected better π-acceptor ability of the thiocarbonyl ligand. As found in the discussion of the electronic structures of CO and CS, the approximate calculations reproduce well the trends between the two species, and Koopmans' theorem is adequate for comparing the ionizations of CO and CS. Therefore it is to be expected that molecular orbital calculations on the full complexes will help resolve the apparent inconsistencies.

The molecular orbital diagrams of $Cr(CO)_6$ and $Cr(CO)_5CS$ are compared in Figure 7. The ordering of the occupied levels as obtained from these calculations is the same as that determined from the photoelectron spectra, although the calculated eigenvalues are generally larger than the measured binding energies. This is also generally the case for ab initio calculations. The experimental trends in ionization potentials between $Cr(CO)_6$ and $Cr(CO)_5CS$ are accurately reproduced by the eigenvalues of these calculations. For instance, the predominantly metal e and b_2 levels of $Cr(CO)_5CS$ are calculated to be separated by only 0.1 eV. This result is interesting in light of the fact that the calculations also indicate that the thiocarbonyl ligand is a significantly better π-electron accepting group than the carbonyl group. The overlap of the CS 3π orbital with the metal orbitals is 0.12, which compares favorably with the CO 2π–metal overlap of 0.13. Because the separation in energy of the CS π^* orbitals from the occupied metal levels is less, they accept 0.60 electron in comparison to the 0.51 electron accepted by the CO π^* orbitals. Despite the increased interaction of the CS π^* orbitals with the metal e orbitals, the calculations actually indicate that the e level is destabilized just slightly above the b_2 level. Analysis of these calculations reveals that the primary factor producing this order of the metal levels is the increased metal interaction with the C–S occupied π bond. It has already been noted in the comparison of CS with CO that the greatest difference between the eigenvalues of these two species lies in the relative instability of the CS occupied π bond and the appearance of its ionization band gives evidence of its interaction with the metal center. The tendency to stabilize the metal e levels through increased interaction with the CS π^* orbitals is offset by the greater interaction with the CS π orbitals. These interactions produce a stronger metal–carbon bond and a correspondingly weaker carbon–sulfur bond.

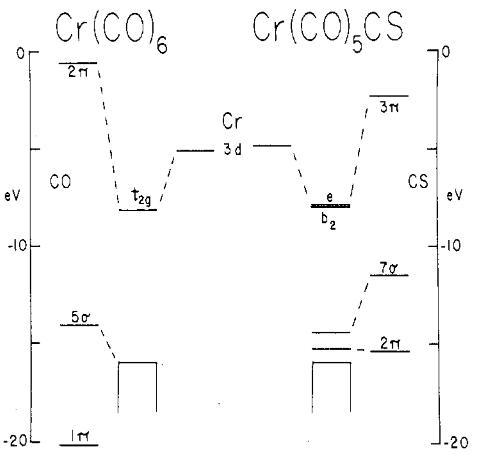
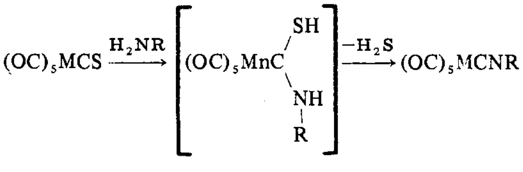


Figure 7. Molecular orbital diagrams of $Cr(CO)_6$ and $Cr(CO)_5CS$.

The net shift of the eigenvalues of the metal levels from $Cr(CO)_6$ to $Cr(CO)_5CS$ is also interesting. Although the CS ligand has accepted additional electrons from the metal, leaving the metal with a greater positive charge, the resulting metal eigenvalues occur higher in energy. The destabilization is calculated to be 0.1–0.2 eV, which compares well with the observed shift of 0.25 eV. Analysis of the calculations reveals that this shift is caused primarily by the difference in the electron distribution of CS as compared to that of CO. The sulfur atom, being less electronegative than the oxygen atom, produces a greater electron density at the carbon atom. This additional electron density at the carbon atom results in a destabilization of the metal levels.

Comparison of the σ-donating ability of the thiocarbonyl group with the σ-donating ability of the carbonyl group is difficult from this theoretical approach because of the interaction of these orbitals with the metal virtual 4s and 4p orbitals. These calculations indicate that the CS group is a slightly better σ-electron donor, as expected. It must be remembered that this improved donor ability is a result of the additional charge on the carbon center, both from the less electronegative sulfur atom and from the improved π-acceptor ability of CS, which destabilizes this lone-pair orbital. Thus the donor orbital can only partially reduce the electron density that has accumulated at the carbon center. It cannot overcompensate for the change in charge distribution to produce a net lower electron density at the carbon center.

These results are consistent with the other physical and chemical characteristics of thiocarbonyl complexes although, as illustrated in this case by the photoelectron ionizations, special care must be exercised when an interpretation is made. For example, thiocarbonyls are known to react readily with amines, presumably through a mechanism of the form[9]



$$(OC)_5MCS \xrightarrow{H_2NR} \left[(OC)_5MnC\begin{matrix} SH \\ NH \\ R \end{matrix} \right] \xrightarrow{-H_2S} (OC)_5MCNR$$

Reactions of this type have traditionally been described as nucleophilic attack of the amine at the carbon center of CS. This behavior seems to be contrary to the expected increase of electron density at this carbon center. It is more reasonable that the reaction is frontier controlled[53] rather than charge controlled. The highest occupied molecular orbital (HOMO) of the amine is the lone pair. This orbital prefers to interact with the lowest unoccupied molecular orbital (LUMO) of the complex. In this respect the amine may be considered to be "lumophilic", a concept which often parallels nucleophilicity. In this case, however, the LUMO of the complex is the carbon-sulfur π antibond. Combination of the amine with this level will destroy the multiple-bond character between the carbon and sulfur and yield the observed products.

Another interesting property of thiocarbonyl complexes is the intensity of their stretching bands in the ir and Raman spectra.[18,54] Compared to those of carbonyls, the ir bands are strong while the Raman activity is extremely weak. The increased intensity of the carbonyl ir stretch is not surprising since the predicted dipole moment derivative of free CS[16] is also greater than that of free CO.[42] (Experimentally, the dipole moment of CO is −0.1 D compared to −2.0 D for CS.[55]) In fact, the dipole moment derivative for the group MnCS determined from the ir intensities is not as much greater than that for the carbonyl groups[18] as would be predicted from the free ligands. This may be explained by the electron density buildup at the carbon center. The very weak thiocarbonyl Raman intensities are even more surprising in terms of preliminary considerations based upon the free ligands. In a general sense, the Raman intensity is dependent upon the square of the polarizability derivative. In qualitative terms, the replacement of the oxygen atom with the more polar sulfur atom should increase the polarizability. In molecular orbital terms, the empty π^* levels of CS are lower in energy and the filled π levels are considerably higher in energy. The closer proximity of these levels should increase the polarizability. In metal thiocarbonyls, however, these levels are also coupled through the metal π levels. The C–S stretch lowers the CS π^* orbitals and increases their carbon character, thus increasing their interaction with the metal. The CS π levels are destabilized with stretching, but they also acquire less carbon character and their interaction with the metal levels is diminished. These two competing influences will tend to reduce the change in polarizability along a stretching mode and hence weaken the Raman activity, as is observed.

In comparison to these appreciable differences in structure in the thiocarbonyl ligand, the changes in the electronic structure in the remaining metal carbonyl portion of the molecule are relatively small. This is a consequence of the fact that, although the thiocarbonyl group reduces the electron density at the metal available for back-bonding to the CO groups, the metal levels have also been destabilized. The net result is a slightly weaker M–CO bond. The M–CO overlap population in $Cr(CO)_6$ is calculated to be 0.680, while the overlap population with a cis carbonyl in $Cr(CO)_5CS$ is 0.652. The overlap population with the trans carbonyl is still lower at 0.618. These results are in agreement with the observations that the trans carbonyls of $M(CO)_5CS$ complexes are labilized toward thermal substitution with ligands L.[56]

The calculations on $CpMn(CO)_3$ and $CpMn(CO)_2CS$ exhibit many of the same features. The molecular orbital diagrams for these two complexes are shown in Figure 8. Again the calculated order of the levels is in agreement with the order of the ionization bands. The trends in observed ionization potentials from $CpMn(CO)_3$ to $CpMn(CO)_2CS$ are also accounted for quite well by the calculated eigenvalues. The shift in the metal ionizations, without a significant change in the shape of the band, is a result of the same factors discussed in the context of the chromium complexes. Because there is less competition for the back-bonding electrons in the manganese–η^5-cyclopentadienyl complexes as compared to the chromium complexes, the CO and CS ligands are able to accept additional π-bonding electrons from the manganese. This results in stronger metal–carbon bonds and weaker carbon–oxygen and carbon–sulfur bonds in comparison to those in the chromium complexes. These points have been discussed previously.[31]

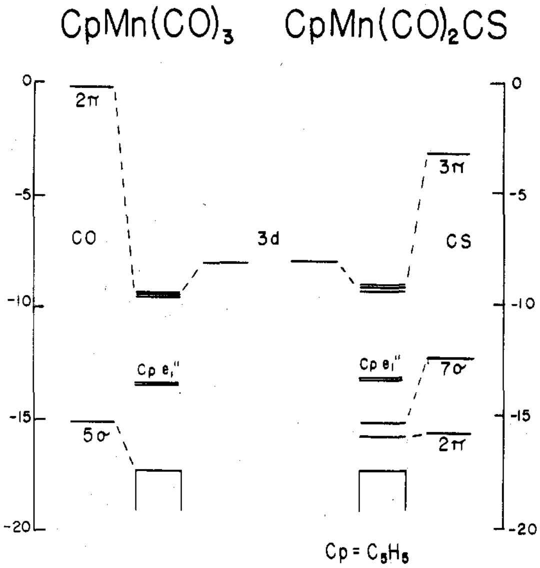


Figure 8. Molecular orbital diagrams of η^5-$C_5H_5Mn(CO)_3$ and η^5-$C_5H_5Mn(CO)_2CS$. Energy is in eV.

The predominantly ring e_1'' ionizations also occur at lower binding energy for the $CpMn(CO)_2CS$ complex than for the $CpMn(CO)_3$ complex. The calculations reproduce this trend despite the greater positive charge at the metal and the slightly greater positive charge on the ring. Again, analysis of the calculations reveals that this shift is a result of the greater electron density on the carbon atoms of CS, which destabilizes both the metal levels and the ring levels.

It is worth noting that the downfield ^{13}C shift of the thiocarbonyl carbon of $C_5H_5Mn(CO)_2(CS)$ is the largest yet found for any compound.[12] It is unlikely that this shift is due to any reasonable changes in charge at the carbon center. Rather, the shift may again be accounted for by the mutual interactions of the CS π and π^* levels with the metal π levels. As found in this investigation, the changes in these π interactions are the greatest differences between the electronic structures of metal carbonyls and metal thiocarbonyls.

Thus analysis of the ionization spectra of thiocarbonyl complexes, coupled with theoretical calculations, has led to a consistent description of the electronic structure, bonding, and related properties of these species. The structure of the entire metal complex must be evaluated. Consideration of just the bonding capabilities of the isolated ligands is not sufficient. Also, extreme caution must be exercised when relating the physical and chemical properties of these systems to their electronic structure. Even in the case of the ionization potentials, interpretations based upon first principles only are in serious error. It is in these instances that theoretical calculations, which are not prejudiced by empirical or variable parameters, are a valuable complementary aid to assessing molecular behavior.

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Registry No. $Cr(CO)_5CS$, 50358-90-2; $W(CO)_5CS$, 50358-92-4; η^5-$C_5H_5Mn(CO)_2CS$, 31741-76-1.

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Photochemistry and Photoisomerization of Five- and Six-Coordinate d^6 Transition Metal Thiocarbonyl Complexes in Low-Temperature Matrices

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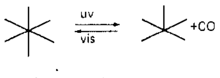
Uv photolysis (λ 300 ± 10 nm) of $M(CO)_5CS$ (M = Cr or W) in Ar or CH_4 matrices at 20 K produces a mixture of two isomeric forms of $M(CO)_4CS$ and molecular CO. There is no evidence for loss of CS under these conditions. The relative yield of the two isomers depends both on the photolysis time and the matrix material. Quantitative analysis of band positions of the ir spectra of the ^{13}CO-enriched compounds and qualitative analysis of the band intensities show that both isomers have square-pyramidal structures: one has C_{4v} symmetry with the CS group in the axial position, and the other C_s symmetry with a basal CS group. Both isomers have visible absorption bands (for $Cr(CO)_4CS/Ar$ λ_{max} C_{4v} 525 nm and C_s 562 nm). Irradiation with visible light of wavelength corresponding to the tail of the absorption band of one form of $M(CO)_4CS$ isomerizes it into the other form. Longer periods of irradiation with unfiltered visible light regenerates the parent $M(CO)_5CS$ molecule. Polarized photochemistry is used to assign the symmetries of the irradiated bands, and full uv–visible data are reported.

Introduction

Matrix isolation has already had considerable success in elucidating the structures of unstable transition metal carbonyl species.[1] The photolysis of the d^6 hexacarbonyl compounds, $M(CO)_6$ (M = Cr, Mo, and W), has produced particularly interesting results.[2-4] On irradiation with uv light, the octahedral $M(CO)_6$ molecule loses carbon monoxide to form a square-pyramidal $M(CO)_5$ fragment.[3] This pentacarbonyl has a visible absorption band, the exact position of which depends on both the metal and the matrix material.[4] Most surprisingly, irradiation of $M(CO)_5$ with light, corresponding to the wavelength of this absorption, regenerates the hexacarbonyl, $M(CO)_6$.



We have investigated the photochemistry of the analogous pentacarbonyl thiocarbonyl molecules, $M(CO)_5CS$ (M = Cr