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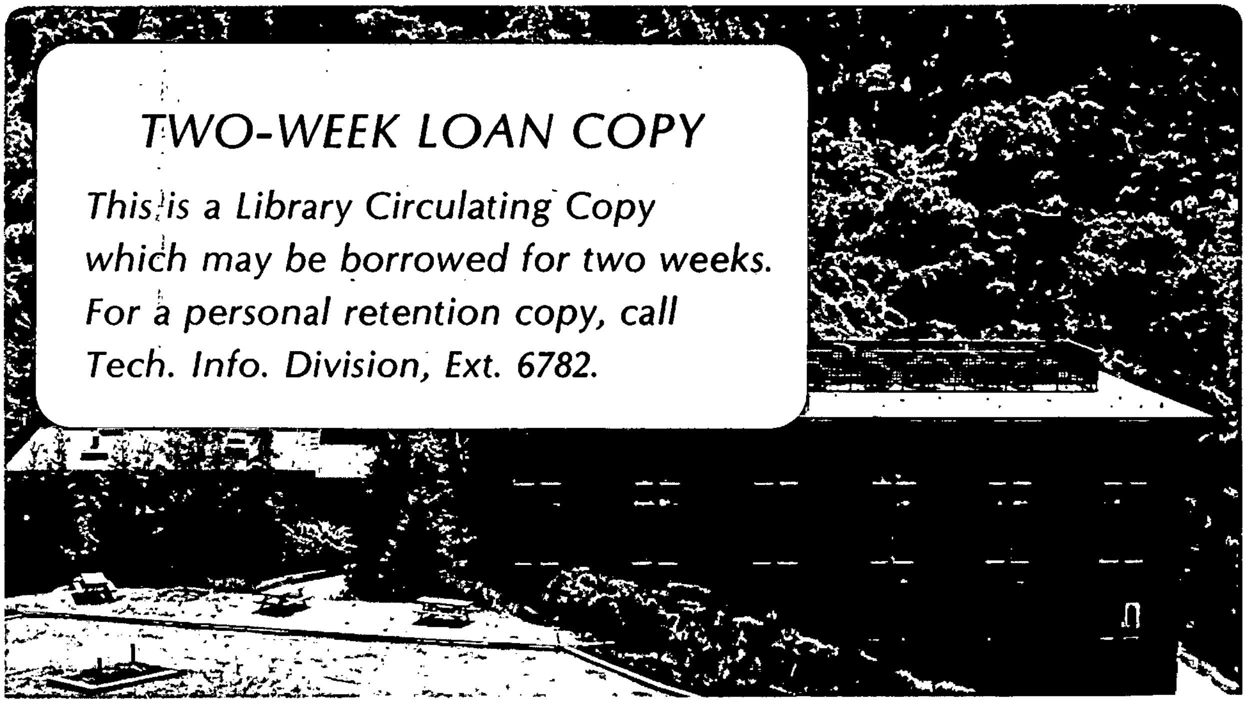

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DISCLAIMER

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An X-ray Photoelectron Spectroscopic Study of Transition Metal Thiocarbonyl and Thionitrosyl Complexes

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Transition metal thiocarbonyl and thionitrosyl complexes have received considerable attention in recent years.[2] It is of considerable interest to obtain information regarding the changes in bonding which occur when the oxygen atom of a coordinated CO or NO group is replaced with a sulfur atom. We have applied x-ray photoelectron spectroscopy, which can give information about valence electron distribution, to this problem. We have obtained the gas-phase core electron binding energies of four thiocarbonyl complexes, one thionitrosyl complex, and the corresponding non-thio complexes.

The binding energy data are presented in Table I. Probably the most significant feature of these data is the approximate constancy of the binding energies of the metal atom and the carbonyl groups upon replacing one of the CO groups by a CS group or upon replacing an NO group by an NS group. Most of the data indicate a slight lowering of the binding energies on going to the thio derivatives, but the uncertainties in the data are in most cases comparable to the measured shifts, and we must conclude that the replacements have little effect on the bonding in the rest of the complexes. It should be noted that this result is not generally observed; replacing a CO group by another group can have a marked effect on the metal and other ligands. For example on going from $Mo(CO)_6$ to $Mo(CO)_5P(CH_3)_3$, the carbonyl carbon binding energy decreases by 0.92 eV, the oxygen binding energy decreases by 0.83 eV, and the molybdenum binding energy decreases by 0.80 eV.[3]

It was possible to resolve carbon 1s peaks due to CS groups only in the case of the thiocarbonyl complexes with no organic ligands, i.e., $Cr(CO)_5CS$ and $W(CO)_5CS$. The carbon 1s spectrum of $W(CO)_5CS$ is shown in Fig. 1. The carbon binding energies of the CS groups are much lower than those of the CO groups. The observed carbon binding energy shifts of 2.24 and 2.15 eV for the chromium and tungsten compounds, respectively, are similar in magnitude to the corresponding shifts between OCS and CS_2 (2.1 eV) and between CO_2 and OCS (2.3 eV).[4] Undoubtedly the shifts are due to the lower electronegativity of sulfur compared to oxygen, and they indicate a much greater electron density on the carbon atom in a coordinated CS group than in a coordinated CO group. Similarly, the nitrogen binding energy of $CrC_5H_5(CO)_2NS$ is 2.02 eV lower than that of $CrC_5H_5(CO)_2NO$. Because of the increased electron density on the atoms attached to the metal, both the CS and NS groups must be stronger σ-donors than the CO and NO groups, respectively. It has been suggested that π-donor bonding to the metal is also important in CS and NS complexes.[5,6] To account for the fact that replacement of CO by CS, or of NO by NS, has little effect on the electron distribution of the remainder of the complex, we conclude that increased back-bonding largely compensates for the greater donor characters of the CS and NS groups. That is, CS and NS groups must be better π-acceptors than CO and NO groups, respectively. This same conclusion has been reached in most other studies of thiocarbonyl and thionitrosyl complexes.[5-8] However, Andrews[7] has pointed out that the relative π-acceptor to $(\sigma + \pi)$-donor ratios of CS and CO are a function of the effective electron density on the metal atom, with the π-acceptor to $(\sigma + \pi)$-donor ratio of CS being greater only when the metal has a relatively high electron density.

We have previously shown that the carbonyl oxygen 1s binding energies of the compounds in Table I are well correlated with the corresponding C-O stretching force constants and with the degree of back-bonding to the CO ligand.[9] Because the electronegativity of sulfur is greater than that of carbon (especially so because of the positive formal charge on sulfur in $^{-}C\equiv S^{+}$), the π^* orbital of CS is probably located mainly on the sulfur atom. Consequently the sulfur binding energy (or sulfur atomic charge) should be a good measure of the degree of back-bonding to the CS ligand. In accord with this expectation, we find that the sulfur binding energies of the thiocarbonyl compounds are fairly well correlated with the corresponding C-S stretching force constants[10] (correlation coefficient 0.955). We also find, as one would expect, that the oxygen 1s and sulfur 2p$_{3/2}$ binding energies of the compounds which contain both CO and CS groups are fairly well correlated (correlation coefficient 0.947).

Experimental Section

The binding energies were determined using procedures described previously.[11] As noted in Table I, some of the data were reported previously.[9] The cyclopentadienyl complexes and the hexacarbonyls of chromium and tungsten are volatile enough that we were able to obtain their spectra at room temperature. However, it was necessary to hold the $Cr(CO)_5CS$ and $W(CO)_5CS$ at 50°, and the benzene complexes at 70°, in order to obtain satisfactory spectra. In the elevated-temperature runs, the entire spectrometer (expect for the pumps, the detector preamplifier, and a few control valves) was enclosed in a thermostatted oven. This technique prevents condensation of sample in the analyzer chamber and consequently avoids possible deterioration of the electron focussing. Attempts to obtain the spectrum of $C_6H_6Cr(CO)_2CSe$ resulted in extensive decomposition of the complex within the spectrometer.

The synthetic methods and criteria of purity used for most of the compounds have been described previously.[9] The $C_6H_6Cr(CO)_2CS$, prepared by a general procedure used for arene$Cr(CO)_2CS$ complexes,[12] was purified on a silica gel column using 3:1 hexane-diethyl ether eluant and melted at 123°C with decomposition.

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Table I. Core Binding Energies (eV) of Transition Metal Carbonyls, Thiocarbonyls, Nitrosyl and Thionitrosyl[a]

Compound	O 1s[b]	C 1s(CO)[b]	C 1s(CS, CS + organic, or organic)	Metal $2p_{3/2}$ or $4f_{7/2}$	S $2p_{3/2}$
$C_6H_6Cr(CO)_3$	538.41(5)	292.07(8)	291.02(5)	581.08(5)	
$C_6H_6Cr(CO)_2CS$	538.33(9)	291.91(13)	290.83(9)	580.91(8)	167.78(11)
$Cr(CO)_6$	539.66(4)	293.16(5)		581.97(5)	
$Cr(CO)_5CS$	539.60(5)	293.07(8)	290.83(30)	581.70(6)	168.76(20)
$W(CO)_6$	539.54(4)	293.17(7)		37.92(5)	
$W(CO)_5CS$	539.50(5)	292.97(5)	290.82(16)	37.85(5)	168.69(13)
$C_5H_5Mn(CO)_3$	538.90(5)	292.30(7)	290.85(3)	646.72(3)	
$C_5H_5Mn(CO)_2CS$	538.97(4)	292.53(12)	290.83(4)	646.77(5)	168.57(6)
$C_5H_5Cr(CO)_2NO$	538.91(4)	292.51(12)	290.82(4)	581.77(5)	
$C_5H_5Cr(CO)_2NS$	539.12(5)	292.24(12)	290.65(3)	581.61(4)	168.38(7)

[a] The uncertainty in the last digit (estimated as twice the standard deviation determined by the least-squares fit) is indicated parenthetically. [b] The data in this column, except for the first two compounds, were reported previously in ref. 9.

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(10) The F_{C-S} values for $C_6H_6Cr(CO)_2CS$, $Cr(CO)_5CS$, $W(CO)_5CS$, and $C_5H_5Mn(CO)_2CS$ are (in mdyn Å^{-1}): 6.528, 7.677, 7.455, and 7.120, respectively. (A. M. English, Ph.D. thesis, McGill University, 1979;

J. Sedman, unpublished results.) The F_{C-S} calculations were based on the assumption of general quadratic valence force fields for these molecules; k_{C-S} values, calculated by the approximation of energy factoring of ν_{C-S}, are unreliable because of mixing of ν_{C-S} with lower energy vibrational modes.

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Figure Caption

Figure 1. Carbon 1s spectrum of $W(CO)_5CS$ vapor. The smaller peak, at 290.82 eV, corresponds to the CS group; the larger peak, at 292.97 eV, corresponds to the CO groups.

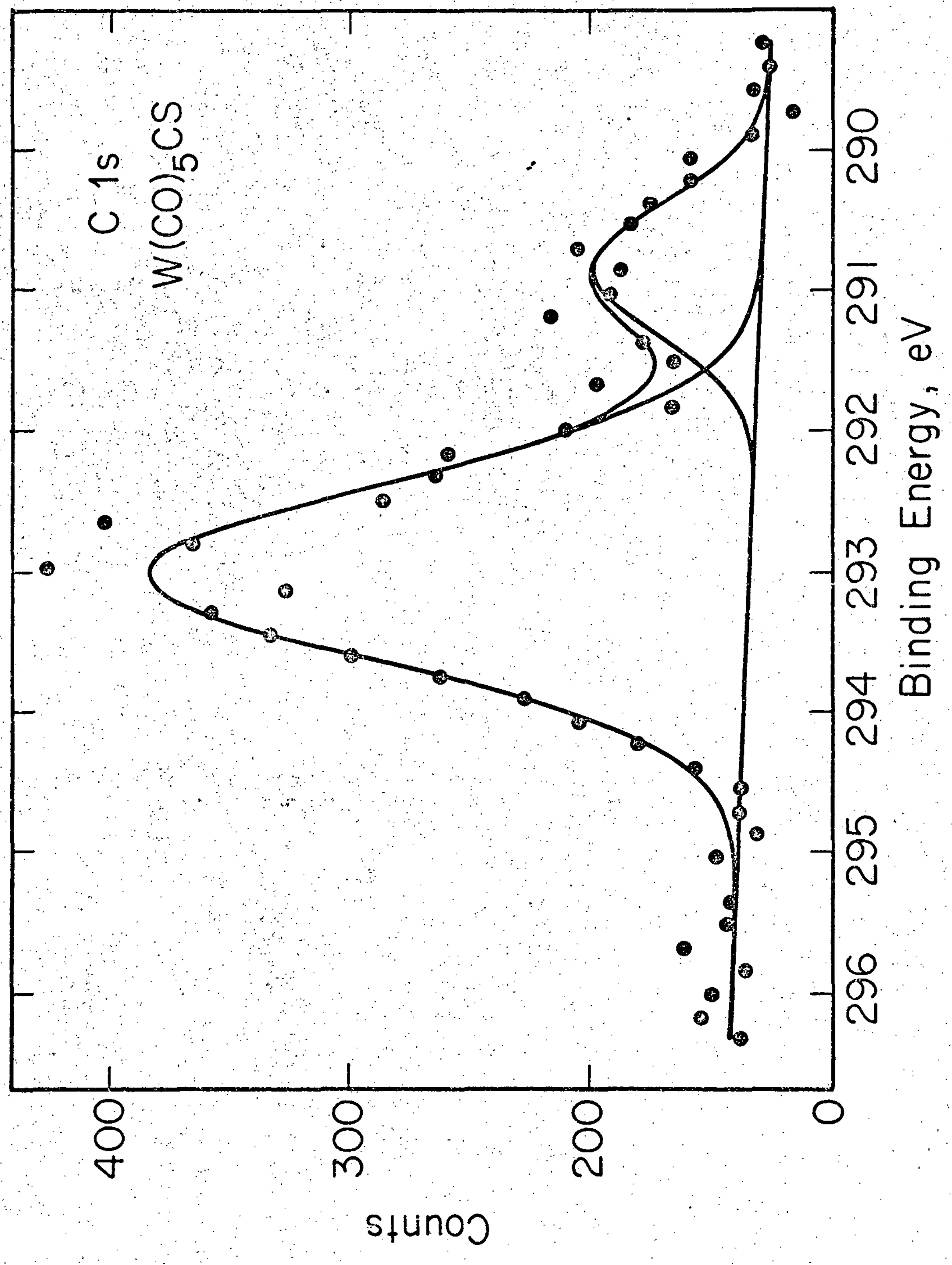
C 1s
W(CO)$_5$CS
Counts
0
200
300
400
296
295
294
293
292
291
290
Binding Energy, eV

Fig. 1

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