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Electronic Spectra of the Chromium Chalcocarbonyl Complexes, $Cr(CO)_5(CX)$ and $(\eta^6\text{-}C_6H_6)Cr(CO)_2(CX)$ (X = O, S, Se)

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The room-temperature electronic spectra of the chromium chalcocarbonyl complexes, $Cr(CO)_5(CX)$ and $(\eta^6\text{-}C_6H_6)Cr(CO)_2(CX)$ (X = O, S, Se), have been recorded in solution, and in some cases, in the gas phase. Assignments for the thiocarbonyl and selenocarbonyl spectra are proposed on the basis of the literature assignments for the parent all-CO derivatives. Overall, the data support the order of increasing electron withdrawing capacity of the chalcocarbonyl ligands as CO < CS < CSe.

Introduction

In recent years, there has been growing interest in the chemistry of transition metal thio-, seleno- [1], and tellurocarbonyl [2] complexes with emphasis on comparing the properties of the isostructural CS, CSe, and CTe ligands with those of CO. Whereas metal carbonyls have been known since 1890 [3], the first analogous metal thio-, seleno-, and tellurocarbonyls were not discovered until 1966 [4], 1975 [5], and 1980 [2], respectively. This situation is clearly related to the extreme instability of CS compared to CO, and the apparent non-existence of CSe and CTe, even at very low temperatures. As another part of our continuing research in this relatively new field of chalcocarbonyl chemistry, we now report the first electronic spectra of such complexes, in particular, $Cr(CO)_5(CX)$ and $(\eta^6\text{-}C_6H_6)Cr(CO)_2(CX)$ (X = S, Se). The spectra have been assigned by comparison with those of the related parent molecules, $Cr(CO)_6$ and $(\eta^6\text{-}C_6H_6)Cr(CO)_3$.

Experimental

The chromium chalcocarbonyl complexes were all prepared by the literature methods [6, 7] starting with $Cr(CO)_6$ (Alfa Inorganics, Inc.). The UV spectra were recorded on a Cary model 17 spectrophotometer (accuracy, ±0.4 nm; reproducibility, 0.25 nm; resolution, 0.1 nm). The chart scale and scan speed normally used were 15 nm in^{-1} and 0.5 nm sec^{-1}, respectively. The spectra were recorded at room temperature. For the solution spectra, a 2.0-mm quartz cell was used. All solutions were freshly prepared and were flushed with N_2 immediately prior to recording the spectra. For the gas phase spectra, a few small crystals of the volatile samples were placed in a 10-cm quartz cell.

Results and Discussion

The He(I) photoelectron spectra of $Cr(CO)_5(CS)$ [8] and $Cr(CO)_5(CSe)$ [9] have been reported, and a partial molecular orbital diagram was given for the thiocarbonyl complex. Bearing this diagram and that for the $Mn(CO)_5X$ (X = Cl, Br, I) [10, 11] species in mind, we have derived the diagram shown in Fig. 1 for the chalcocarbonyl complexes. The σ(CO) and σ(CX) energy levels have been put together as σ(CO, CX) in order to simplify the diagram.

The axial CO[CO(5)] shares the same metal orbitals with CX. There is a σ bond between Cr and the two ligands involving mainly the a_1 ($3d_{z^2}$, 4s, $4p_z$) metal orbitals and the σ carbon orbitals (2s, $2p_z$) which transform under C_{4v} symmetry as $3a_1 + b_1 + e$. The π-bonding M–CO(5) and M–CX orbitals involve the metal e ($3d_{xz}$, $3d_{xy}$) and the ligand π and π^* ($a_1 + a_2 + b_1 + b_2 + 4e$) molecular orbitals. The $4p_x$ and $4p_y$ (e) metal orbitals may also interact in the π-bonding, but they are mainly involved in σ-bonding. The four σ-bonds between Cr and the equatorial CO's in the xy plane are formed using the a_1 (4s, $3d_{z^2}$), b_1 ($3d_{x^2-y^2}$) and e ($4p_x$, $4p_y$) metal orbitals. For the π-bonding metal → equatorial CO's, the $3d_{xy}$ (b_2) and $3d_{yz}$, $3d_{xz}$ (e) metal orbitals participate.

All the electronic spectra of the $Cr(CO)_5(CX)$ (X = O, S, Se) complexes were recorded for the gas phase, while for $Cr(CO)_5(CS)$ and $Cr(CO)_6$, the spectra were also measured in CH_3CN solution. Table I summarizes the results and typical spectra are illustrated in Figs. 1 and 2. The d–d transitions that can arise for this system are:

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TABLE I. Electronic Spectra of $Cr(CO)_5(CS)$ (X = O, S, Se).

$Cr(CO)_6$						$Cr(CO)_5(CS)$						$Cr(CO)_5(CSe)$	
Vapor		CH_3CN soln.[a]				Vapor		CH_3CN soln.				Vapor	
λ_{max}(nm)	$\bar{\nu}_{max}(cm^{-1})$	λ_{max}(nm)	$\bar{\nu}_{max}(cm^{-1})$	$\epsilon_{max}(M^{-1}\ cm^{-2})^a$		λ_{max}(nm)	$\bar{\nu}_{max}(cm^{-1})$	λ_{max}(nm)	$\bar{\nu}_{max}(cm^{-1})$	$\epsilon_{max}(M^{-1}\ cm^{-2})$		λ_{max}(nm)	$\bar{\nu}_{max}(cm^{-1})$
196	50,900		>50,000										
224	44,600	228	43,600	85,000		207	48,300	223	44,800	b		203	49,300
	38,950[a]		38,850	3,500		228	43,800	235	42,600	58,800		230	43,500
278	36,000	280	35,700	13,100		275	36,400	275	36,400	b		273	36,600
	31,550[a]		31,550	2,670		291	34,400	305	32,800	56,300		306	32,700
	29,000		29,500	700		368	27,200					375	26,700
						404	24,800					420	23,800

[a] From Ref. 12. [b] Shoulders not resolved.

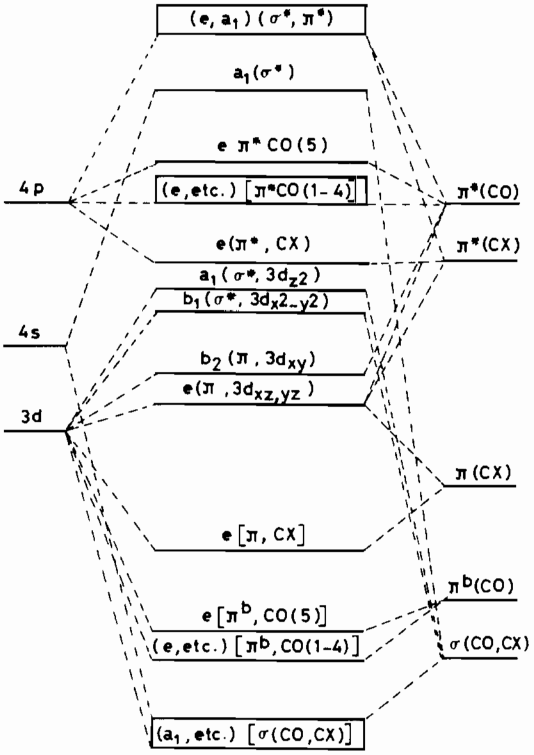

Fig. 1. Molecular orbital diagram for $Cr(CO)_5(CX)$ (X = O, S, Se).

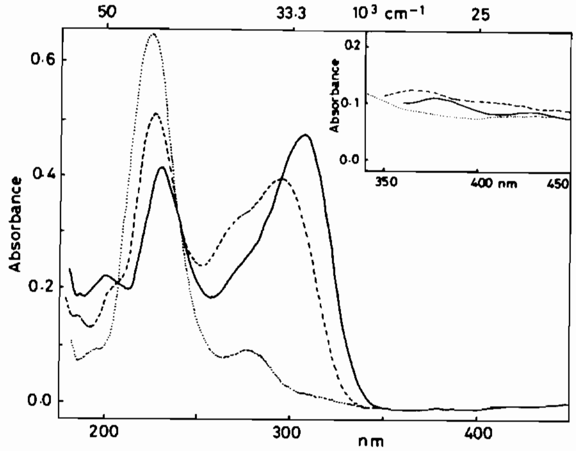

Fig. 2. Electronic spectra of $Cr(CO)_5CX$ (X = O, S, Se) in gas phase. (——) $Cr(CO)_5(CSe)$; (– – –) $Cr(CO)_5(CS)$; (· · ·) $Cr(CO)_6$. Insert shows the region at higher concentration.

$b_2[\pi, 3d_{xy}] \rightarrow b_1[\sigma^*, 3d_{x^2-y^2}]\ (^1A_1 \rightarrow {}^1A_2)$

$b_2[\pi, 3d_{xy}] \rightarrow a_1[\sigma^*, 3d_{z^2}]\ (^1A_1 \rightarrow {}^1B_2)$

$e[\pi, 3d_{xz,xy}] \rightarrow b_1[\sigma^*, 3d_{x^2-y^2}]\ (^1A_1 \rightarrow {}^1E)$

$e[\pi, 3d_{xy,yz}] \rightarrow a_1[\sigma^*, 3d_{z^2}]\ (^1A_1 \rightarrow {}^1E)$

Initially, we will restrict our analysis to a discussion of the gas phase spectra. By analogy with the

$Cr(CO)_6$ spectrum [10–14] the d–d transitions in $Cr(CO)_5(CX)$ are expected to be around 30,000 cm^{-1}. In fact, there is a weak, broad band for $Cr(CO)_5(CS)$ and $Cr(CO)_5(CSe)$ at 27,200 and 26,700 cm^{-1}, respectively, that can be assigned as one of the $^1A_1 \rightarrow {}^1E$ C_{4v} components of the O_h $^1A_{1g} \rightarrow {}^1T_{1g}$ transition. There is also a very weak, broad band at 24,800 (CS) and 23,800 cm^{-1} (CSe) which has been tentatively attributed to the orbitally forbidden $^1A_1 \rightarrow {}^1A_2$ d–d transition. These results are consistent with the lower binding energy found from photoelectron studies for the e and b_2 molecular orbitals in $Cr(CO)_5(CS)$ compared to the value for the corresponding t_{2g} molecular orbital in $Cr(CO)_6$ [8]. The analogous band in the magnetic circular dichroism spectra of $W(CO)_5(CS)$ has been assigned as charge transfer metal-to-CS [15, 16], but we consider that in the present case these bands are too weak to be charge-transfer bands.

The lowest-energy metal → π*CO charge transfer in $Cr(CO)_6$, $t_{2g} \rightarrow t_{1u}$ ($^1A_{1g} \rightarrow d^1T_{1u}$), is believed to lead to the transition in C_{4v} symmetry $b_2[\pi, 3d_{xy}] \rightarrow (e, e, a_1, a_2, b_1, b_2)\ [\pi^*, CO(1\text{–}4)]$ ($^1A_1 \rightarrow {}^1E, {}^1E, {}^1B_1, {}^1B_2, {}^1A_1, {}^1A_2$). By analogy with the band in $Cr(CO)_6$ (36,000 cm^{-1}), the bands found in the same region in the spectra of $Cr(CO)_5(CS)$ and $Cr(CO)_5(CSe)$ at 36,400 and 36,600 cm^{-1}, respectively, were assigned as the C_{4v} component of the octahedral $^1A_{1g} \rightarrow d^1T_{1u}$ charge transfer electronic transition. The shift to higher energies concurs with a reduction in the M–CO π-backbonding on replacement of one CO by a better π-acid suggesting that the order of π-acceptor capabilities of the chalcocarbonyl ligands as CO < CS < CSe. The *trans* counterpart of this transition, $b_2[\pi, 3d_{xy}] \rightarrow e[\pi^*CO(5)]$ ($^1A_1 \rightarrow {}^1E$), might be hidden by the broadness of the observed peak. In fact, there is an asymmetry in the peak to the high energy side, where the corresponding M → π*CO *trans* transition would be expected to appear.

The highest-energy metal → π*CO charge transfer in $Cr(CO)_6$ ($t_{2g} \rightarrow t_{2u}$) ($^1A_{1g} \rightarrow C^1T_{1u}$) is believed to transform under C_{4v} symmetry as $e\ [\pi, 3d_{xz,xy}] \rightarrow (e, e, a_1, a_2, b_1, b_2)\ [\pi^*, CO(1\text{–}4)]$ ($^1A_1 \rightarrow {}^1A_1, {}^1A_2, {}^1B_1, {}^1B_2, {}^1B_2, {}^1A_1, {}^1A_2, {}^1B_1, {}^1B_2, {}^1E, {}^1E, {}^1E, {}^1E$). In $Cr(CO)_6$, this band appears at 44,600 cm^{-1}, while in $Cr(CO)_5(CS)$ and $Cr(CO)_5(CSe)$, the band is shifted to lower energy (43,800 and 43,500 cm^{-1}, respectively). The order $Cr(CO)_6 > Cr(CO)_5(CS) > Cr(CO)_5(CSe)$ is in direct contradiction to what was expected on the basis of the π-acceptor capacities of the CS ligands. The explanation for this discrepancy is not clear at present. However, the photoelectron study on $Cr(CO)_5(CS)$ revealed that the t_{2g} level occurs at lower binding energy than in $Cr(CO)_6$ [8] suggesting that the M → π*CO transition should appear at lower energy because the separation in energy between the two levels (metal π and ligand π*) ought to be smaller. The intensity of this band decreases in the order $Cr(CO)_6 > Cr(CO)_5(CS) > Cr(CO)_5(CSe)$, again consistent with weaker M–CO π-backbonding on substitution of one CO by CX (X = S, Se). The bands at 48,300 (CS) and 49,300 cm^{-1} (CSe), which are attributed to the corresponding M → *trans*-CO π* transition $e\ [\pi, 3d_{xz,yz}] \rightarrow e\ [\pi^*, CO(5)]$ ($^1A_1 \rightarrow {}^1A_1, {}^1A_2, {}^1B_1, {}^1B_2$), follow the expected trend: there is a weakening of the M → *trans*-CO π-backbonding, which is reflected in the increase in energy for the transition.

The very intense band displayed at 34,400 [$Cr(CO)_5(CS)$] and 32,700 cm^{-1} [$Cr(CO)_5(CSe)$] is absent in $Cr(CO)_6$ and is assigned here as the M → CX charge transfer $b_2[\pi, 3d_{xy}] \rightarrow e\ [\pi^*CX]$ ($^1A_1 \rightarrow {}^1E$). This band shifts to lower energy on going from $Cr(CO)_5(CS)$ to $Cr(CO)_5(CSe)$, again supporting the apparent order of π-acceptor capacities of these ligands (CO < CS < CSe). The assignment of this band as M → CX charge transfer is also in accord with the energies of the π* orbitals of diatomic CO and CS since the CS π* orbitals are at lower energy than those of CO [8, 17, 18]. The extinction coefficients for the spectra in the gas phase were not determined, but a qualitative comparison of the spectra showed that this band is more intense for $Cr(CO)_5(CSe)$ than for $Cr(CO)_5(CS)$, suggesting a greater transition probability for M → CSe than for M → CS, again providing further evidence for CSe being a better π-acceptor than CS. It should be mentioned here that the π-acceptor order, CO < CS < CSe, is also substantiated from ^{13}C NMR data [19] and dipole moment derivatives obtained from IR intensity measurements for the CX stretching vibrations [20].

However, the proposed M–CX charge transfer assignment does not agree with the photoelectron results for $Cr(CO)_5(CS)$ [8]. If the energies of the metal orbital (8.16 eV) and π*CS (~2.2 eV) are considered, the difference will be 5.96 eV (~48,000 cm^{-1}) which is an unrealistic value. In addition, the ligand CS–metal charge-transfer $e\ [\pi, CS] \rightarrow b_1\ [\sigma^*, 3d_{x^2-y^2}]$ ($^1A_1 \rightarrow {}^1E$), which would be expected at lower energy, because of the high-energy of the 2π occupied CS orbitals, was not detected here. It is believed that this band is hidden underneath the intense and broad charge-transfer bands in the spectra. Perhaps this is the reason that the band at 44,600 cm^{-1} [M → π*CO, $Cr(CO)_6$] is anomalously shifted to lower energy.

From a comparison of the $Cr(CO)_5(CS)$ spectra in the vapor phase and in CH_3CN solution, it can be seen that the solvent generally induces a shift in the bands to lower energy. The only band that remains unchanged is the first M → π*CO charge transfer (36,400 cm^{-1}). A similar solvent effect for $Cr(CO)_6$ was attributed [11] to interactions with the solvent in the cases where the excited state levels are more exposed, for example, when they are more localized on the ligand. In the case of the second M → π*CO

TABLE II. Electronic Spectra of $(\eta^6\text{-}C_6H_6)Cr(CO)_2(CX)$ (X = O, S, Se) in Et_2O Solution.

$(\eta^6\text{-}C_6H_6)Cr(CO)_3$		$(\eta^6\text{-}C_6H_6)Cr(CO)_2(CS)$		$(\eta^6\text{-}C_6H_6)Cr(CO)_2(CSe)$		Direction of charge transfer
λ(nm)	$\bar{\nu}$(cm^{-1})	λ(nm)	$\bar{\nu}$(cm^{-1})	λ(nm)	$\bar{\nu}$(cm^{-1})	
		~195	51,300 (~1.5)	~195	51,300 (~1.5)	
215	46,500 (2.8)	220	45,400 (1.4)	220	45,400 (0.94)	Cr → CO ring → Cr → CO
255	39,200 (0.62)	260	38,500 (1.8)	270	37,000 (1.5)	Cr → CO Cr → CX
312	32,000 (1.0)^a	325	30,800 (1.2)	331	30,200 (1.0)	Cr → ring

$^a\epsilon_{max}$ in parentheses ($\times 10^4$ M^{-1} cm^{-2}).

charge transfer band, which shifts appreciably to lower energy, it was proposed that [for $Cr(CO)_6$] the $4t_{1u}$ level is stabilized by interaction with solvent dipoles, which is what happened in the present case.

Finally, the band for $Cr(CO)_6$ assigned as the d–d transition, $^1A_{1g} \rightarrow {}^1T_{2g}$ (38,950 cm^{-1}) could not be detected in the present work. This band should occur between the two intense charge transfer bands and it was assigned tentatively for $Cr(CO)_6$ through a Gaussian analysis and by comparison with the $W(CO)_6$ and $Mo(CO)_6$ spectra [12].

The electronic spectra of the $(\eta^6\text{-}C_6H_6)Cr(CO)_2(CX)$ (X = O, S, Se) complexes were recorded in Et_2O solution with the aim of studying the changes in the transition energies upon substitution of a CO group in $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ by CS or CSe. The observed transition energies are given in Table II. The bands of $(\eta^6\text{-}C_6H_6)Cr(CO)_2(CX)$ (X = S, Se) were assigned by analogy with the spectrum of the parent tricarbonyl. The agreement of the band positions and intensities obtained for the tricarbonyl in this work with those reported in the literature is quite good. Typical spectra of the three chalcocarbonyl complexes are illustrated in Fig. 4. All the bands appear at lower energy in the order $(\eta^6\text{-}C_6H_6)Cr(CO)_3 < (\eta^6\text{-}C_6H_6)Cr(C)_2(CS) < (\eta^6\text{-}C_6H_6)Cr(CO)_2(CSe)$. The band at ~30,000 cm^{-1}, which was assigned as a Cr → ring charge transfer transition, does not change significantly in intensity, although there is a broadening in the CS and CSe complexes due presumably to the lowering of symmetry. The band at around 38,000 cm^{-1}, which was assigned as Cr → CO charge transfer in $(\eta^6\text{-}C_6H_6)Cr(CO)_3$, shifted to lower energy in the CS and CSe derivatives and increased greatly in intensity. It is thought, by analogy with the spectra of the $Cr(CO)_5(CX)$ species analyzed earlier, that these bands are associated with M → π^*CS charge-transfer. The corresponding M → π^*CO charge-transfer transition might be hidden underneath this

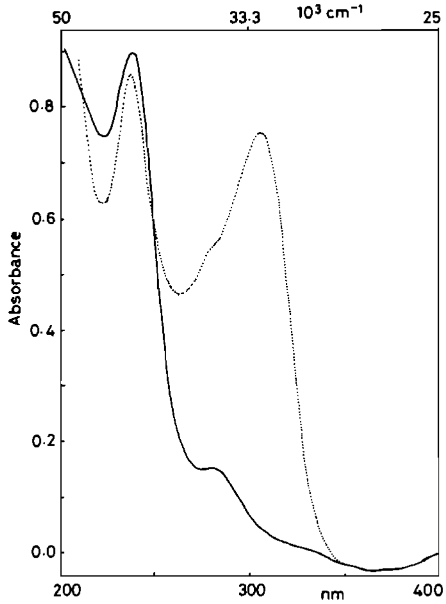

Fig. 3. Electronic spectra of $Cr(CO)_5(CX)$ (X = O, S) in CH_3CN solution. (——) $Cr(CO)_6$; (– – –) $Cr(CO)_5(CS)$.

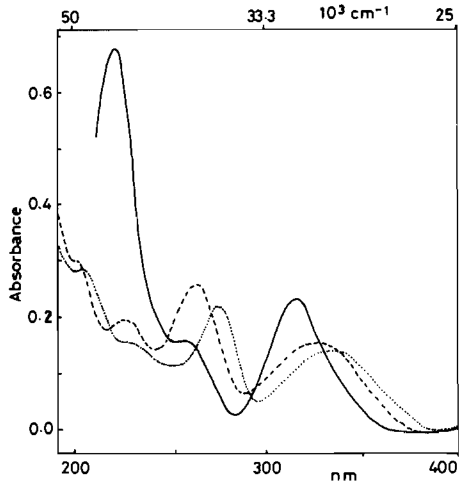

Fig. 4. Electronic spectra of $(\eta^6\text{-}C_6H_6)Cr(CO)_2(CX)$, (X = O, S, Se) ($Et_2O$ solution). (——) $(\eta^6\text{-}C_6H_6)Cr(CO)_3$; (– – –) $(\eta^6\text{-}C_6H_6)Cr(CO)_2(CS)$; (· · ·) $(\eta^6\text{-}C_6H_6)Cr(CO)_2(CSe)$.

band or between the other bands. The order of the lowering in energy of the M → CX band is consistent with increase in π-acid capability of these ligands: CO < CS < CSe. The peak at ~46,000 cm^{-1}, assigned as both ring → M → π^*CO and M → π^*CO for the tricarbonyl, appears to have lost its degeneracy in the CX derivatives, in agreement with the results for $Cr(CO)_5(CX)$. The lowering of energy of the bands, however, is inconsistent with the first ionization energies found for these complexes by photoelectron spectroscopy [9]: the observed binding energies of the electrons in the HOMO's are 7.29, 7.32 and 7.36 eV, for the CO, CS and CSe complexes, respectively. These results are at variance with those for the $Cr(CO)_5(CX)$ derivatives. There is a stabilization of the high occupied levels, which would lead to higher energies for the electronic transitions, *i.e.*, opposite to what is observed. The rationalization of these observations must await a full molecular orbital treatment of the complexes.

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