Organometallics 1984, 3, 1786–1789

Absolute Integrated Infrared Intensities of the Carbonyl, Thiocarbonyl, and Selenocarbonyl Stretching Modes in the Chalcocarbonyl Complexes $Cr(CO)_5(CX)$ and $(\eta^6\text{-}C_6H_6)Cr(CO)_2(CX)$ (X = O, S, Se)[1]

Ione M. Baibich,[2a] Ann M. English,[2b] and Ian S. Butler*

Department of Chemistry, McGill University, Montreal, Quebec, Canada H3A 2K6

Received March 1, 1984

The absolute integrated IR intensities in CS_2 solution of the CO, CS, and CSe stretching modes in the chalcocarbonyl complexes $Cr(CO)_5(CX)$ and $(\eta^6\text{-}C_6H_6)Cr(CO)_2(CX)$ (X = O, S, Se) have been determined. From the intensity results and L matrix data from earlier general quadratic valence force field calculations for the same complexes, the CrCX bond dipole moment derivatives have been calculated and these decrease in the order μ'(CrCSe) > μ'(CrCS) > μ'(CrCO), suggesting that the π-acceptor capacities of the three chalcocarbonyl ligands decrease as CSe > CS > CO. While the intensities of ν(CO) modes in metal carbonyls have been extensively investigated, the present study represents the first detailed analysis of intensity data for ν(CS) and ν(CSe) modes in metal chalcocarbonyl derivatives.

Introduction

It is now well established that the absolute integrated IR intensities of CO and N stretching modes in transition-metal carbonyl and dinitrogen complexes are extremely useful in assessing the extent of π-electron delocalization in the CO[3-5] and N_2 groups.[6] The approach involves calculating the bond dipole moment derivatives μ'(MCO) and μ'(MNN) from the measured intensities of the vibrators. If electrical harmonicity is assumed, the absolute integrated IR intensity, A_i, of the ith fundamental of frequency, ν, is related to the molecular dipole moment by the expression[3]

$$A_i = (N\pi/3c)/(\partial\mu/\partial Q_I)_0^2 \qquad (1)$$

where N is the number of molecules per unit volume of sample, c is the velocity of light, and $\partial\mu/\partial Q_I$ is the rate of change of molecular dipole moment with respect of the normal coordinate Q_I of the vibration concerned. To obtain a physical meaning for $\partial\mu/\partial Q_I$, it is necessary to express this rate in terms of internal coordinates $\partial\mu/\partial r$. This is accomplished by assuming that on stretching a bond by ∂r, a moment $(\partial\mu/\partial R)\partial r$ is generated in the direction of the bond and, at the time of stretching of this bond, no other bond moments are produced in the molecule. Normal coordinates can be related to molecular symmetry coordinates (S_j) by eq 2, where L_{ij} are coefficients that are

$$Q_I = \sum_j L_{ij}^{-1} S_j \qquad (2)$$

functions of the molecular geometry, the atomic masses, and the vibrational potential energy function (which is obtained from detailed normal coordinate calculations). The L_{ij} values are eigenvectors generated by solving the vibrational secular equation

$$|FGL - \Lambda L| = 0 \qquad (3)$$

where F is a force constant matrix, G is the kinetic energy matrix, and Λ is a matrix associated with the vibrational frequencies such that $\lambda = {}^1/_4\pi^2c^2\bar{\nu}^2$ ($\bar{\nu}$ is the vibrational wavenumber). Finally, since symmetry coordinates can be expressed as linear combinations of internal bond coordinates (R_k), we have

$$S_j = \sum_k U_{jk}R_k \qquad (4)$$

where U is a real, unitary, and orthoganol transformation matrix and

$$\partial\mu/\partial Q_I = \sum_j\sum_k L_{ji}U_{jk}(\partial\mu/\partial R_k) \qquad (5)$$

Clearly, by combining eq 1 and 5, we have a relationship between A_i and $\partial\mu/\partial R_k$ [i.e., μ'(MCO) and μ'(MNN) in our case] that necessitates us knowing the L_{ij} values.[3]

Equations relating absolute intensities, L_{ij}, and μ'(MCO) values (for example) for varying geometries have been derived over the past few years, especially by Darensbourg and co-workers.[3,4]

Several years ago, we reported the only IR intensity study to date for a CS stretching vibration in a metal thiocarbonyl complex.[5] We showed that the MnCS dipole moment derivative μ'(MnCS) for $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CS)$ is significantly greater than the μ'(MnCO) values. Since these dipole moment derivatives are considered to have direct bearing on the π-bonding properties of the CS and CO ligands, this result was taken as evidence of the greater π-acceptor ability of CS compared to CO. Although our analysis was satisfactory, it was only approximate because we had to assume that the CS stretching vibration was not coupled with any other vibrational modes of the same symmetry. A more rigorous treatment would have necessitated having the appropriate L matrix values from a complete normal-coordinate analysis, and these were unavailable.

We have recently completed general quadratic valence force field (GQVFF) calculations for the chalcocarbonyl complexes $(Cr(CO)_5(CS)$, $Cr(CO)_5(CSe)$,[7] and $(\eta^6\text{-}C_6H_6)$-$Cr(CO)_2(CX)$ (X = O, S, Se).[8] Consequently, we felt that

---

[1] Presented in part at the 64th Canadian Chemical Conference, Halifax, Nova Scotia, June 1981.

[2] Present addresses: (a) Department of Chemistry, Federal University of Rio Grande do Sud, Porto Allegre, Brazil. (b) Department of Chemistry, Concordia University, Montreal, Quebec, Canada H3G 1M8.

[3] For excellent reviews of the field, see: (a) Braterman, P. S. "Metal Carbonyl Spectra"; Academic Press: London, 1975. (b) Kettle, S. F. A.; Paul, I. *Adv. Organomet. Chem.* **1972**, *10*, 199.

[4] Darensbourg, D. J.; Nelson, H. H., III; Hyde, C. L. *Inorg. Chem.* **1974**, *13*, 2135 and references cited therein.

[5] Butler, I. S.; Johansson, D. A. *Inorg. Chem.* **1975**, *14*, 701 and references cited therein.

[6] Darensbourg, D. J. *Inorg. Chem.* **1972**, *11*, 1436 and references cited therein.

[7] English, A. M.; Plowman, K. R.; Butler, I. S. *Inorg. Chem.* **1981**, *20*, 2553.

0276-7333/84/2303-1786$01.50/0

Table I. Observed Positions, Absolute Integrated IR Intensities, and Associated Bond Dipole Moment Derivatives for the CO, CS, and CSe Stretching Modes of $Cr(CO)_5(CX)$ and $(\eta^6\text{-}C_6H_6)Cr(CO)_2(CX)$ (X = O, S, Se) in CS_2 Solution

complex (mol sym)	ν(CO), cm^{-1}	vib sym	abs intensity (I)[a]	CX specific intensity[b]	μ'(CrCX)[c]		μ'(sym)[d]/ μ'(antisym)
					EFFF	GQVFF	
$Cr(CO)_6$ (O_h)	1984.4 vs	t_{1u}	68.5	11.4	9.46		
$Cr(CO)_5(CS)$ (C_{4v})	2088.4 m	$a_1^{(2)}$	6.47	11.8			
	2017.3 s	$a_1^{(1)}$	9.47		10.0	10.2	1.07
	1989.0 vs	e	42.9		9.31	9.56	
	1261.0 s (CS)	a_1	14.0	14.0	11.1	11.1	
$Cr(CO)_5(CSe)$ (C_{4v})	2087.6 m	$a_1^{(2)}$	7.05	11.2			
	2023.4 s	$a_1^{(1)}$	9.93		10.3	10.5	1.15
	1991.8 vs	e	39.0		8.88	9.16	
	1077.4 s (CSe)	a_1	11.9	11.9	11.1	11.3	
$(\eta^6\text{-}C_6H_6)Cr(CO)_3$	1976 s	a_1	13.6	11.8	9.33		1.06
(C_{3v}, loc sym)	1904 s	e	21.8		8.81		
$(\eta^6\text{-}C_6H_6)Cr(CO)_2(CS)$	1969 s	a′	12.0	11.4	8.92		1.02
(C_s, loc sym)	1923 s	a″	10.7		8.72		
	1220 s (CS)	a′	9.65	9.65	9.18	9.33	
$(\eta^6\text{-}C_6H_6)Cr(CO)_2(CSe)$	1975 s	a′	11.3	10.3	8.65		1.06
(C_s, loc sym)	1932 s	a″	9.37		8.16		
	1028 m (CSe)	a′	8.75	8.75	9.55	9.85	

[a] In units of 10^4 M^{-1} cm^{-2}. Average standard deviation ±0.18. [b] In units of 10^4 M^{-1} cm^{-2}. Obtained by dividing the sum of the CX absolute integrated intensities by the number of CX groups present.[3,20] [c] Calculated from the following equations.[13] $Cr(CO)_5(CX)$: X = O, $\mu'(CrCO) = (I_{CO})^{1/2}/6G_{CO}$; X = S, Se, $\mu'(CrCO)[a_1^{(1)}] = [L_{21}(I_{a_1}(2)^{1/2} - L_{22}(I_{a_1}(1)^{1/2}]/(L_{21}L_{12} - L_{11}L_{22})$, $\mu'(CrCO)(e) = (I_e)^{1/2}/2L_{11} \sin\theta$ where $\theta = 90°$, $\mu'(CrCX) = (I_{CX})/G_{CX})^{1/2}$(EFFF) $= I_{CX}/L_{CX}$ (GQVFF). $(\eta^6\text{-}C_6H_6)Cr(CO)_3$: $\mu'(CrCO)(a_1) = (1/\cos\alpha)(I_{a_1}/3G_{CO})^{1/2}$, $\mu'(CrCO)(e) = (1/\sin\alpha)(I_e/3G_{CO})^{1/2}$ where $\alpha = 53.3°$. $(\eta^6\text{-}C_6H_6)Cr(CO)_2(CX)$ (X = S, Se): $\mu'(CrCO)(a') = (1/\cos\alpha)(I_{a_1}/2G_{CO})^{1/2}$, $\mu'(CrCO)(a'') = (1/\sin\alpha)(I_{a''}/2G_{CO})^{1/2}$ where $\alpha = 44°$, μ'(CrCX) as for $Cr(CO)_5(CX)$. Note: $G_{CO} = 0.1458$, $G_{CS} = 0.1144$, $G_{CSe} = 0.09592$, and the GQVFF L matrix values (EFFF values in parentheses) for $Cr(CO)_5(CX)$ are as follows: X = S, $L_{11} = 0.3427$ (0.3517), $L_{12} = 0.1679$ (0.1489), $L_{21} = -0.1681$ (−0.1489), $L_{22} = 0.3428$ (0.3517), $L_{CS} = 0.3362$; X = Se, $L_{11} = 0.3409$ (0.3516), $L_{12} = 0.1717$ (0.1491), $L_{21} = -0.1719$ (−0.1491), $L_{22} = 0.3409$ (0.3516), $L_{CSe} = 0.3051$. For $(\eta^6\text{-}C_6H_6)Cr(CO)_2(CX)$: X = S, $L_{CS} = 0.3330$; X = Se, $L_{CSe} = 0.3004$. [d] sym = $a_1^{(1)}$, a_1, or a′ and antisym = e, e, or a″, respectively. [e] When calculated from the expression $\mu'(CrCO)[a_1^{(1)}] = \{[I_a(1) + I_a(2)]/G_{CO} - (1 + 4\cos^2\theta)\}^{1/2}$, the values are 10.5 (X = S) and 10.8 (X = Se), assuming $\theta = 90°$. These values are less reliable than those given in the table because in these calculations the $a_1(1)$ and $a_1(2)$ ν(CO) dipole moment derivatives must be assumed equal.[13]

we were in an ideal position to determine μ'(CrCO), μ'(CrCS), and μ'(CrCSe) accurately from the absolute integrated IR intensities of the CO, CS, and CSe stretching modes of these complexes since the required L matrix elements were readily available in these cases. Moreover, the bond dipole moment derivatives obtained would enable us to make a direct comparison of the π-electronic properties of the CO, CS, and CSe ligands in two series of isostructural complexes. At this point, it should be emphasized that, unlike CO, the CS and CSe species do not readily exist as free diatomic molecules; CS polymerizes above −160 °C, often explosively, while CSe has eluded isolation even at liquid helium temperatures.[9] Therefore, studies of the properties of the metal-stabilized entities are crucial in understanding the bonding behavior or these interesting chalcocarbonyl ligands. In this paper, we report the results of our absolute IR intensity measurements.

Experimental Section

All IR spectra were recorded on a specially modified Perkin-Elmer Model 337 grating spectrophotometer (slit width, ~2.0 cm^{-1}) coupled to a Sargent-Welch Model SRLG linear absorbance recorded. The spectra in the 2200–2800 cm^{-1} region were obtained at a recording rate of 40 cm^{-1} min^{-1} using the maximum frequency expansion possible (7.9 cm^{-1} $in.^{-1}$); calibrations were performed before each measurements using CO gas (2147.08 cm^{-1}) as a standard. In the 1350–900 cm^{-1} region, the recording rate was 13.33 cm^{-1} min^{-1} with an expansion scale of 2.59 cm^{-1} $in.^{-1}$; the spectra were calibrated against the polystyrene peak at 1601.4 cm^{-1}. Matched pairs of calibrated 0.1- and 1.0-mm NaCl solution cells were employed in the measurements.

Pure samples of the chalcocarbonyl complexes were prepared by the literature methods.[10,11] The samples were carefully weighed on a Cahn electrobalance (±0.01 mg) immediately following their purification by vacuum sublimation. The extremely volatile pentacarbonyls had to be placed in plastic capsules to prevent sublimation during the weighing process. The spectrograde CS_2 solvent was dried over molecular sieves and was flushed with nitrogen immediately prior to use. Fresh solutions were prepared each time, and the samples studied did not undergo decomposition during the recording time of the IR spectra (usually 5–10 min). The concentrations were varied so as to give bands between 15% and 65% transmittance range. At least three separate measurements were taken for each concentration. The areas of the bands, $[\int_{band} \ln (T_0T)\, d\nu]$, for an interval of about 40 cm^{-1} on either side of the band maximum, were found by cutting the bands and weighing them on the electrobalance. The chart paper used (Sargent S-72167) was calibrated for each set of spectra and was found to be uniform. Tne intensity results were reproducible and no wing corrections were performed owing to the sharpness of the peaks. Any bands that did overlap slightly were resolved by symmetry. The apparent integrated intensities (B) were measured for at least five different concentrations. The true integrated intensities (I) were determined by extrapolating[5,12,13] the B values to zero concentration using a standard linear regression analysis.

Results and Discussion

The observed peak positions and absolute IR intensities for the CO, CS, and CSe stretching vibrations of the six complexes investigated are given in Table I. The proposed

---

(8) English, A. M.; Plowman, K. R.; Butler, I. S. *Inorg. Chem.* **1982**, *21*, 338.

(9) For reviews on the chemistry of transition-metal thio- and selenocarbonyls, see: (a) Butler, I. S. *Acc. Chem. Res.* **1977**, *10*, 359. (b) Yaneff, P. V. *Coord. Chem. Rev.* **1977**, *23*, 183.

(10) English, A. M.; Plowman, K. R.; Baibich, I. M.; Hickey, J. P.; Butler, I. S.; Jaouen, G.; LeMaux, P. *J. Organomet. Chem.* **1981**, *205*, 177. (b) English, A. M.; Plowman, K. R.; Baibich, I. M.; Hickey, J. P.; Butler, I. S.; Jaouen, G.; LeMaux, P.; Thépot, J.-Y. *J. Organomet. Chem.* **1977**, *132*, C1.

(11) Butler, I. S.; English, A. M.; Plowman, K. R. *Inorg. Synth.* **1982**, *21*, 1.

(12) Brown, T. L.; Darensbourg, D. J. *Inorg. Chem.* **1967**, *6*, 971.

(13) Darensbourg, D. J.; Brown, T. L. *Inorg. Chem.* **1968**, *7*, 959.

vibrational assignments have been verified by general quadratic valence force field (GQVFF) calculations.[7,8] The absolute intensity for the t_{1u} ν(CO) mode of $Cr(CO)_6$ in CS_2 solution (68.5 in practical units of 10^4 M^{-1} cm^{-2}) is in good agreement with the values obtained earlier for *n*-hexane (63.7)[14,15] and CCl_4 (70.7)[16] solutions. Also, our results for $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ in CS_2 solution ($I_{a_1} = 13.6$; $I_e = 21.8$) agree very closely with those for CCl_4 solution (13.4; 21.4)[17] and reasonably well with those for cyclohexane solution (11.1; 20.0).[18] There have been no detailed studies on the effect of solvent on the absolute IR intensities of ν(CO) modes, but since all our measurements were in the same solvent and the intensities of the ν(CO) modes of $Cr(CO)_6$ and $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ are reproducible when compared with the literature, it seems that solvent effects are minimal, provided that nonpolar solvents are used.[19] Values for the specific intensities[20] are included in Table I, but since these have been shown to be not particularly useful when attempting quantitative comparisons of intensities,[3] nothing more will be said about them here.

$Cr(CO)_5(CX)$ (X = O, S, Se) Complexes. The equations used to calculate the bond dipole moment derivatives for these derivatives are given in footnote *c* of Table I and were taken from ref 13. The dipole moment derivatives for the radial a_1 ν(CO) modes, $\mu'(\mathrm{CrCO})[a_1^{(2,}]$, have a dependence of cos θ_1 (where θ is the angle between the CrCO groups), and for θ close to 90° (as is the case in C_{4v} symmetry), a slight error in estimating θ would make a large difference in $\mu'(\mathrm{CrCO})[a_1^{(2)}]$. Thus, the expression for $\mu'(\mathrm{CrCO})[a_1^{(2)}]$ was not used in the present work. The dipole moment derivative for the e ν(CO) mode also depends on θ, in this case sin θ, but since sin θ is not very sensitive to changes in θ when $\theta \simeq 90°$, the expression shown can be used without any problem.

The dipole moment derivative for the CX modes (X = S, Se) were calculated by using the following equations: $\mu'(\mathrm{MCX}) = (I_{\mathrm{CX}}/G_{\mathrm{tt}})^{1/2}$ and $\mu'(\mathrm{MCX}) = (I_{\mathrm{CX}})^{1/2}/L_{\mathrm{CX}}$. In the first equation, it is assumed that there is no interaction with other stretching modes of the same symmetry in the molecule. In the other equation, CX and MC interactions are considered. Since ν(CX) is an a_1 mode, it would be expected to couple with the a_1 ν(CO) modes, but it has been shown[7] that the cross *L* matrix terms for these interactions are close to zero, and so such couplings were neglected. The *L* matrix values used for the dipole moment derivative calculations were obtained from the detailed normal-coordinate analyses of the $Cr(CO)_5(CX)$ complexes using both a GQVFF and an energy factored force field (EFFF).[7] The GQVFF *L* matrix values of importance to the present work are given in Table I (footnote *c*), together with similar results obtained with the EFFF approximation. For the latter approximation, the initial field was derived from that of $Cr(CO)_6$ and the wavenumbers of the enriched species were also used.[21]

There is no significant change in the dipole moment derivative for the $a_1^{(1)}$ ν(CO) mode for either force field but, if the CX vibrations are considered, the GQVFF gives a larger difference for ν(CSe) than for ν(CS). It is well-known that EFFF calculations are good approximations for CO vibrations because the CO modes are well separated in energy from the associated M–C modes.[3] On the other hand, ν(CS) and ν(CSe) are much closer in energy to their M–C counterparts, and when any interaction is ignored, the results obtained from force constant calculations are poor.[7]

It can be seen from Table I that the intensity and dipole moment derivative changes, caused by the coordination of a ligand, are not uniformly distributed between the e and a_1 ν(CO) modes. This was explained for $M(CO)_5L$ species by Anderson and Brown[22] using a molecular orbital model to calculate the IR intensities and dipole moment derivatives. This model considers only transfer of π-electron density during a vibration, although there is a σ-term contribution in the ground state of the molecule. They found that the intensity of the e mode is linearly related to the net charge on L and decreases as the π-acceptor ability of L increases. The inverse trend was found for the a_1 axial mode, its intensity increasing with the π-acceptor ability of L. The latter situation was attributed by Darensbourg and Brown[13,23] to a vibronic contribution[24] that arises from π-electronic charge transfer from the ligand to the metal to the axial CO, since the axial a_1 CO stretching vibration is polarized along the M–L axis, sharing the same d orbitals with L. This vibronic contribution is dependent on both the ability of L to hold its electron density and the demand made for these electrons during the a_1 axial CO vibration. In those cases where the π-ligands are extremely electron withdrawing, e.g., $SiCl_3$, there is a very small vibronic contributions to the $a_1^{(1)}$ mode.[23]

Darensbourg and Brown[13] have shown that for $M(CO)_5L$ species, when L is a π-ligand (P and As ligands), μ'-(MCO)(e) is smaller than when L is a σ-ligand (N ligands). However, if the μ'(MCO)(e) values for the π-ligand complexes are compared with that for $Mo(CO)_6$, there is no significant difference in the results. These observations were attributed to a combination of ligand properties: they increase the electron density on the metal, weakening the metal–carbonyl σ-bond but, at the same time, the ligands also act as π-acceptors and lower the energy of the π-orbitals. The axial a_1 dipole moment derivatives μ'-$(\mathrm{MCO})[a_1^{(1)}]$ for the π-ligands are enhanced over those for the σ-ligands as a result of the vibronic contribution π-ligand → metal → CO. Going back to Table I, the results strongly suggest that the order of π-acceptor strengths for the chalcocarbonyl ligands is CO < CS < CSe. If the a_1 axial ν(CO) dipole moment derivative is considered, the data show that CSe gives a larger vibronic contribution than CS. In addition, looking at the dipole moment derivatives for the e ν(CO) mode μ'(MCO)(e) there is a decrease in the order $Cr(CO)_6 > Cr(CO)_5(CS) > Cr(CO)_5(CSe)$. As the e mode dipole moment derivatives reflect the net π-electron density on the CO's, this means that the remaining CO's of $Cr(CO)_5(CS)$ have less available dπ metal electron density than the parent hexacarbonyl and that the CO's of $Cr(CO)_5(CSe)$ have less than $Cr(CO)_5(CS)$. The CS and CSe values are significantly higher than the CO values, and the CSe value is greater than that for CS. Here, it is obviously preferable to consider the results from the GQVFF calculations since the Cr–C and CX vibrations are known to couple.[7]

---

[14] Johansson, D. A. M.Sc. Thesis, McGill Universit, Montreal, Quebec, Canada, 1974.

[15] Abel, E. W.; Butler, I. S. *Trans. Faraday Soc.* **1967**, *63*, 45.

[16] Beck, W.; Nitzmann, R. E. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys. Biol.* **1962**, *17B*, 577.

[17] Klopman, G.; Noack, K. *Inorg. Chem.* **1968**, *7*, 579.

[18] Fischer, R. D. *Spectrochim. Acta* **1963**, *19*, 842.

[19] When the absolute intensity of the t_{1u} ν(CO) mode of $Cr(CO)_6$ is measured in tetrahydrofuran solution, the value is increased about 20% to 84.3.[14]

[20] This term was originally introduced by: Noack, K. *Helv. Chim. Acta* **1962**, *45*, 1847.

[21] Jones, L. H.; McDowell, R. S.; Goldblatt, M. *Inorg. Chem.* **1969**, *8*, 2349.

[22] Anderson, W. P.; Brown, T. L. *J. Organomet. Chem.* **1971**, *32*, 343.

[23] Darensbourg, D. J. *Inorg. Chim. Acta* **1970**, *4*, 597.

[24] Brown, T. L. *J. Chem. Phys.* **1965**, *43*, 2780.

It should be mentioned that the angle calculation[13] using the equation $\cos\theta = \{[L_{11}(I_{a_1}(2)/I_{a_1}(1)]^{1/2} - L_{12}\}/\{2L_{22} - 2L_{21}[I_{a_1}(2)/I_{a_1}(1)]^{1/2}\}$ gives an angle of 83° for both $Cr(CO)_5(CS)$ and $Cr(CO)_5(CSe)$. The results do not compare very favorably with the average value of 90° found for $Cr(CO)_5(CS)$ by X-ray diffraction measurements[25] and possibly further reflect the inadequacy of the use of IR intensities for such purposes, as pointed out originally by Kettle and Paul.[3]

(η^6-C_6H_6)$Cr(CO)_2(CX)$ (X = O, S, Se) Complexes. The measurement of the IR intensities for these derivatives was undertaken in an effort to study the ability of the arene to transfer, or to moderate, the electronic effects of CS and CSe on the carbonyls and to study further the bonding properties of these ligands. The CO specific intensities for this series decrease in the order CO > CS > CSe. Here, where there is no interaction between CO modes of the same symmetry, the specific intensity method can be reliable. But, even so, the dipole moment derivatives give a better indication of the bonding properties of these ligands because they take into account the geometry and interactions in the molecule. Table I shows the CO, CS, and CSe intensity and dipole moment derivative results. The latter were calculated from the equations given in footnote c of Table I from ref 13. The EFFF approximation $L_{11}^2 = G_{CO}$ was used in calculating the dipole moment derivatives for the CO vibrations since we had found earlier that there is no significant difference in the results for $Cr(CO)_5(CX)$ (X = S, Se) from those calculated with the general quadratic field. For the CX vibrations, again it can be seen that the GQVFF gives more reliable results. The L_{CX} values used had been calculated by assuming the complexes to be pseudooctahedral $Cr(C_2H_2)_3(CO)_2(CX)$ species, with the ring being treated as three double bonds trans to the carbonyls.[8] The angle between the CO's was taken as 88°. This was the value found from a combined X-ray and neutron diffraction study of (η^6-C_6H_6)$Cr(CO)_3$.[26] It was assumed that this angle does not vary appreciably for the CS and CSe complexes, as had been established earlier for the (η^6-$C_6H_5CO_2CH_3$)$Cr(CO)_2(CX)$ (X = O, S, Se) series.[27-29]

The results again suggest that the order of π-acceptor ability in this series of ligands is CO < CS < CSe. The dipole moment derivatives for the symmetric (a_1, a′) and antisymmetric (e, a″) ν(CO) modes decrease with an increase in π-acid character of the ligand, showwing less availability of dπ metal electrons for the carbonyl ligands. It would be expected that the dipole moment derivatives for the symmetric mode should increase as a consequence of the vibronic contribution from L, but this was not observed. Instead, the results showed that the ring acts as a "buffer" of the vibronic contribution to this mode. Similar results were obtained in studies on (η^5-C_5H_5)$M(CO)_2L$ complexes, where L = Mn[30] and Fe[31] and L are ligands that vary in π or σ strength. It was reported that the μ'(sym)/μ'(antisym) ratio, where μ'(sym) is the dipole moment derivative for the symmetric ν(CO) mode (a′) and μ'(antisym) is that for the antisymmetric ν(CO) mode (a″), did not vary significantly with the different L's, showing that there is no vibronic contribution L → M → CO. With use of a molecular orbital model, Anderson et al.[30] calculated the intensities and the dipole moment derivative ratios for *cis*-$M(CO)_2X_3L$ species. Their results showed that when X is a σ-bonded ligand, the ratio μ'(sym)/μ'(antisym) increases as the π-acceptor ability of L increases. In other words, there will be a vibronic contribution from L to the CO's. On the other hand, if X is a π-acceptor ligand, μ'(sym)/μ'(antisym) is insensitive to the nature of L, showing that X moderates the vibronic contribution from L to the CO's. This is the case for (η^6-C_6H_6)$Cr(CO)_2(CX)$ (X = O, S, Se); Table I shows that the μ'(sym)/μ'(antisym) ratio remains approximately constant (~1.05) in the three complexes.

Finally, estimations of the angles for these complexes were made from the intensity data using the equation $\tan^2\alpha = I_{sym}/I_{antisym}$, where α is the angle between the CO's divided by two in C_{3v} and C_s symmetries, respectively.[3] For (η^6-C_6H_6)$Cr(CO)_3$, α = 52°, which leads to an angle between the CO groups of 86°, i.e., 2° lower than reported for this complex.[26] For (η^6-C_6H_6)$Cr(CO)_2(CX)$ (X = S, Se), the angles found were 83° and 80°, respectively. Although there are no data available from X-ray studies for these complexes, the results seem unrealistic when compared with X-ray results[27-29] for (η^6-$C_6H_5CO_2CH_3$)$Cr(CO)_2$ (X = O, S, Se) (angle $\simeq$ 88° in all three cases). These discrepancies could possibly be attributed to interaction of the ligands with the solvent. In any event, it appears that one must use IR intensities cautiously when attempting to calculate bond angles between the oscillators concerned.

The intensity and dipole moment derivative data obtained for the two series of chalcocarbonyl complexes studied in the present work indicate that the order of π-acceptor ability of these ligands is CO < CS < CSe in agreement with earlier ^{13}C NMR measurements for various thio- and selenocarbonyl derivatives[32] and, more importantly, with ab initio molecular orbital calculations for the free and complexed CO, CS, and CSe ligands.[33] In addition, "vibronic contributions" of CS and CSe could be detected and it is tempting to suggest that these effects reflect the π-donor capabilities of the ligands, since these vibronic contributions are a measure of the ligand → metal → CO charge-transfer energy. The μ'(CrCS) (~10.0) values are close to the μ'(MnCS) values (11.1) obtained for (η^5-C_5H_5)$Mn(CO)_2(CS)$.[5]

In conclusion, it is clear that dipole moment derivatives are extremely useful in probing the π-bonding interactions of π-acid ligands, as originally suggested by Brown and Darensbourg.[12]

Acknowledgment. I.M.B. would like to thank CAPES (Brazil) for the award of a graduate fellowship. I.S.B. especially thanks the CEGB Berkeley Nuclear Laboratories, England, and the CNRS Laboratoire de Chimie de Coordination, Toulouse, France, for their hospitality while on sabbatical during which period this paper was written. The research was generously supported by grants from NSERC (Canada) and FCAC (Quebec).

Registry No. $Cr(CO)_6$, 13007-92-6; $Cr(CO)_5(CS)$, 50358-90-2; $Cr(CO)_5(CSe)$, 63356-87-6; (η^6-C_6H_6)$Cr(CO)_3$, 12082-08-5; (η^6-C_6H_6)$Cr(CO)_2(CS)$, 63356-86-5; (η^6-C_6H_6)$Cr(CO)_2(CSe)$, 63356-85-4.

---

(25) Saillard, J.-Y.; Grandjean, D. *Acta Crystallogr., Sect. B* **1978**, *B34*, 3318.

(26) Rees, B.; Coppens, P. *Acta Crystallogr., Sect. B* **1973**, *B29*, 2516.

(27) Saillard, J.-Y.; Grandjean, D. *Acta Crystallogr., Sect. B.* **1976**, *B32*, 2285. Carter, O. L.; McPhail, A. T.; Sim, G. A. *J. Chem. Soc. A* **1967**, 1619.

(28) Saillard, J.-Y.; Le Borgne, G.; Grandjean, D. *J. Organomet. Chem.* **1975**, *94*, 409.

(29) Saillard, J.-Y.; Grandjean, D. *Acta Crystallogr., Sect. B* **1978**, *B34*, 3772.

(30) Anderson, W. P.; Brill, T. B.; Schoenberg, A. R.; Stanger, J., Jr. *J. Organomet. Chem.* **1972**, *44*, 161.

(31) Darensbourg, D. J. *Inorg. Chem.* **1972**, *11*, 1606.

(32) Cozak, D.; Butler, I. S.; Baibich, I. M. *J. Organomet. Chem.* **1979**, *169*, 181.

(33) Saillard, J.-Y.; Grandjean, D.; Caillet, P.; Le Beuze, A. *J. Organomet. Chem.* **1980**, *190*, 371.