shown to be a stable surface species. In this case, however, there are indications that the nature of the complex changes with decreasing pH. Further, no evidence was found to indicate the existence of a cobalt(II) glycinate on the surface.

We have also measured the spectrum of the ligand, glycine, adsorbed on alumina at various pH values. While our data are in complete agreement with those of Coleman,[16] we have advanced a modified interpretation of the spectra obtained. We envisage a two-site adsorption process, invoking both zwitterionic glycine and glycinate species, the glycinate being more stable at high pH but present to a large extent throughout the pH 4–9 range.

Subsequent to submission of this article, Brown et al.[36] reported the IETS of several organic amines. They observe the NH stretching motion of NH_3^+ in the 2800-cm^{-1} region. This observation supports the analysis presented in this paper.

Acknowledgment. We thank the National Science Foundation for supporting this research in the form of Grant No. DMR-7820251.

Registry No. gly, 56-40-6; $KCo(gly)_2(NO_2)_2$, 15157-77-4; $Ni(gly)_2$, 13479-55-5; Ni(gly)Cl, 76430-69-8; *trans*-$Co(gly)_2$, 14281-74-4; Al_2O_3, 1344-28-1.

---

[36] Brown, N. M.; Floyd, R. B.; Nelson, W. J.; Walmsley, D. G. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 2335.

Contribution from the Department of Chemistry,
Northern Illinois University, DeKalb, Illinois 60115

Magnetic Circular Dichroism of Metal-to-Ligand Charge-Transfer Spectra of Hexacarbonyl and Hexacyano Complexes of *n*d^6 Electron Configuration

STEVEN K. CHASTAIN and W. ROY MASON*

Received June 13, 1980

Electronic absorption and magnetic circular dichroism (MCD) spectra are reported for $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ in acetonitrile solution and for $K_4[Fe(CN)_6]$, $K_4[Ru(CN)_6]$, and $K_4[Os(CN)_6]$ in aqueous solution. The spectral pattern observed in the MCD for the two allowed metal-to-ligand charge-transfer (MLCT) bands of $M(CO)_6$ is similar and consists of a positive *B* term for the band near 3.5 μm^{-1} and a negative *B* term for the band near 4.4 μm^{-1}. A weak negative *A* term was also observed at 2.9 μm^{-1} for $W(CO)_6$. The lowest energy allowed MLCT for each $M(CN)_6^{4-}$ complex exhibits a positive *A* term. The difference between the MCD for the lowest energy MLCT between the $M(CO)_6$ and $M(CN)_6^{4-}$ complexes is discussed in terms of relative metal p-orbital participation in the empty t_{1u} ligand-based MO.

Introduction

The intense electronic absorptions observed in the UV spectra of octahedral metal hexacarbonyl and hexacyano complexes of low-spin d^6 electron configuration were first assigned as metal-to-ligand charge transfer (MLCT) by Gray and Beach in 1963.[1] For example, the two bands near 3.5 and 4.4 μm^{-1} in $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ were interpreted as electron excitation from the filled, predominantly metal *n*d t_{2g} MO's to empty ligand-based t_{1u} and t_{2u} MO's, respectively (see Figure 1). Both bands were assigned as fully dipole-allowed ${}^1A_{1g} \rightarrow {}^1T_{1u}$ transitions even though the higher energy band was much more intense. A rationale for the intensity difference took note of the orbital composition of the t_{1u} MO's which contain contributions from the metal $(n + 1)$p orbitals, while the t_{2u} MO's are entirely ligand based. It was suggested that the p-orbital contribution in the t_{1u} MO's was responsible for the smaller transition dipole.[1,2] Similar bands given analogous assignments were identified in the spectra of $Fe(CN)_6^{4-}$, $Ru(CN)_6^{4-}$, and $Os(CN)_6^{4-}$, though the two allowed transitions were at higher energy and of more equal intensity.[1]

Although the d^6 hexacarbonyl and hexacyano complexes have been the subject of several experimental and theoretical investigations since 1963,[2-8] the MLCT assignments have stood the test and now seem well established. Thus these complexes provide excellent prototypes for the study of MLCT in octahedral symmetry. Therefore as a consequence of our interest in magnetic circular dichroism (MCD) of MLCT transitions in complexes of lower coordination number, we turned naturally to the d^6 hexacarbonyl and hexacyano complexes to extend our understanding of the MLCT process. However there have been surprisingly few MCD studies of octahedral carbonyl and cyano complexes. The paramagnetic d^5 $V(CO)_6$ and $Fe(CN)_6^{3-}$ complexes have been investigated,[9,10] but their spectra are dominated by ligand-to-metal charge transfer (LMCT) and MCD *C* terms. The MLCT spectra of diamagnetic d^6 carbonyl or cyano complexes should exhibit only *A* and *B* MCD terms since the ground state is ${}^1A_{1g}$ in each case. The only earlier report of MCD for such a complex is limited to MCD spectra of $Fe(CN)_6^{4-}$,[11] in which a positive *A* term was found for the lowest energy intense band. The sign and approximate magnitude of the *A* term were shown to be consistent with a MLCT assignment.[11] In view of the limited data available for MLCT transitions of carbonyl and cyano complexes we report here some MCD spectra for $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ in acetonitrile and $Fe(CN)_6^{4-}$, $Ru(CN)_6^{4-}$, and $Os(CN)_6^{4-}$ in water.

Experimental Section

The hexacarbonyl complexes were purchased from Alfa-Ventron or Strem Chemicals, Inc., and purified by vacuum sublimation. Vapor-phase and actonitrile solution spectral band energies agreed favorably with previous reports,[1,2] but solution molar absorptivities differed in some cases. The origin of these differences is not known. The complexes are known to be photochemically reactive,[3,4,12] so care

---

[1] Gray, H. B.; Beach, N. A. *J. Am. Chem. Soc.* **1963**, *85*, 2922.

[2] Beach, N. A.; Gray, H. B. *J. Am. Chem. Soc.* **1968**, *90*, 5713.

[3] Wrighton, M. S. *Chem. Rev.* **1974**, *74*, 401.

[4] Wrighton, M. S.; Handeli, D. I.; Morse, D. L. *Inorg. Chem.* **1976**, *15*, 434.

[5] Johnson, J. B.; Klemperer, W. G. *J. Am. Chem. Soc.* **1977**, *99*, 7132.

[6] Trogler, W. C.; Desjardins, S. R.; Solomon, E. I. *Inorg. Chem.* **1979**, *18*, 2131.

[7] Alexander, J. J.; Gray, H. B. *J. Am. Chem. Soc.* **1968**, *90*, 4260.

[8] Clack, D. W.; Monski, M. *Mol. Phys.* **1976**, *31*, 1607.

[9] Schatz, P. N.; McCaffery, A. J.; Suëtaka, W.; Henning, G. N.; Ritchie, A. B. *J. Chem. Phys.* **1966**, *45*, 722. For a review of MCD spectroscopy see also: Stephens, P. J. *Annu. Rev. Phys. Chem.* **1974**, *25*, 201 and references cited therein.

[10] Barton, T. J.; Grinter, R.; Thomson, A. J. *J. Chem. Soc., Dalton Trans.* **1978**, 608.

[11] Stephens, P. J.; Mowery, R. L.; Schatz, P. N. *J. Chem. Phys.* **1971**, *55*, 224.

0020-1669/81/1320-1395$01.25/0

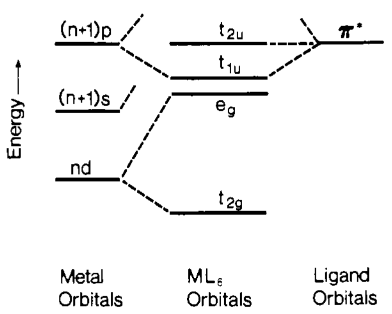

Figure 1. Simplified molecular orbital energy levels for the hexacarbonyl and hexacyano complexes.

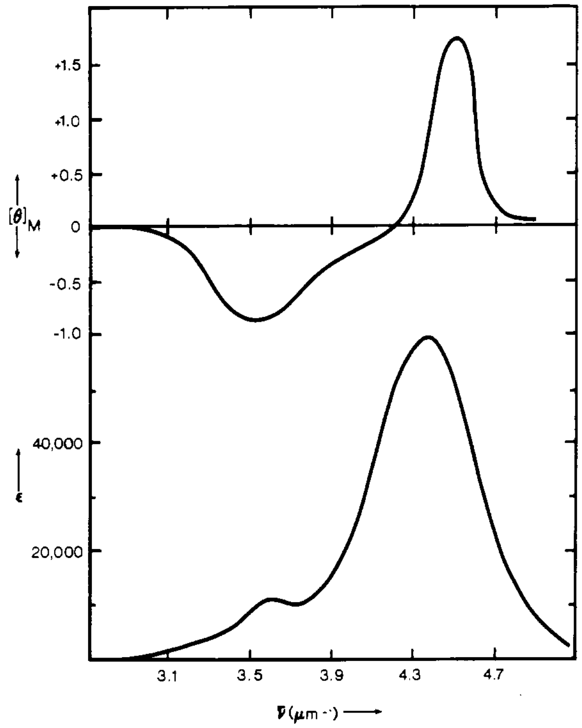

Figure 2. Absorption (lower curve) and MCD (upper curve) spectra for $Cr(CO)_6$ in acetonitrile.

was taken to protect solutions from light. The spectral measurements showed no changes during the time required to obtain data, and Beer's law was obeyed. Acetonitrile solutions were prepared with Spectrograde solvent.

$K_4Ru(CN)_6$ was purchased from Alfa-Ventron, while $K_4Fe(CN)_6 \cdot 3H_2O$ was reagent grade. $K_4Os(CN)_6$ was prepared as described previously.[13] Absorption spectra in water for these compounds agreed favorably with the previous reports.[1,7]

Absorption spectra were obtained with use of 1.00-cm quartz cells and a Cary 1501, while MCD measurements were made with use of 0.100-cm quartz cells and a JASCO ORD/UV-5 equipped with a circular dichroism attachment and a permanent magnet (field 1.0 T). The values of $[\theta]_M$ are estimated to be reliable to within ±5% below 4.2 μm^{-1} but to within ± 20% at higher energy due to lower signal to noise in the regions of high absorption.

Results and Discussion

Figures 2 and 3 present MCD and absorption spectra for $Cr(CO)_6$ and $W(CO)_6$, respectively, in acetonitrile; spectra for $Mo(CO)_6$ were of comparable quality. The most prominent MCD features for the two MLCT bands of each of the $M(CO)_6$ complexes are similar and consist of a positive *B* term (negative ellipticity) associated with the lower energy band near 3.5 μm^{-1} and a negative *B* term for the higher energy band near 4.4 μm^{-1}. A weak negative *A* term is also observed at 2.87 μm^{-1} for $W(CO)_6$ which has no counterpart in the spectra of $Cr(CO)_6$ or $Mo(CO)_6$. These latter complexes reveal only a broad unresolved shoulder in the ellipticity below the lowest energy intense MLCT band.

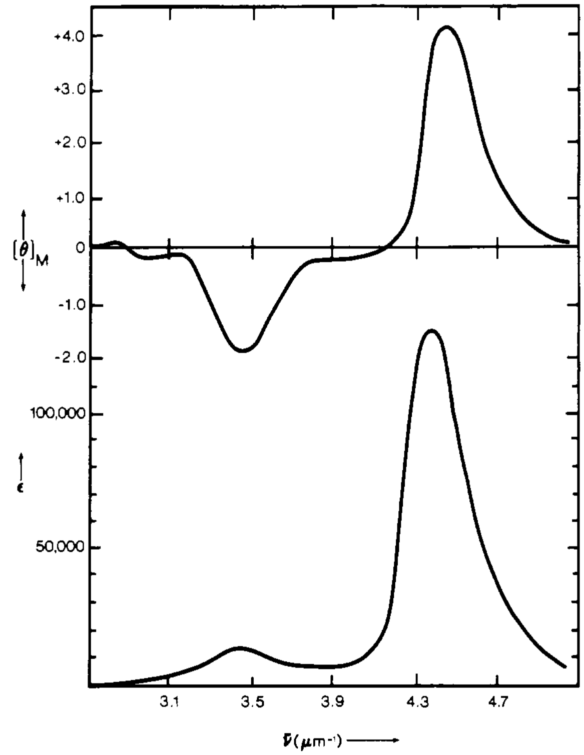

Figure 3. Absorption (lower curve) and MCD (upper curve) spectra for $W(CO)_6$ in acetonitrile.

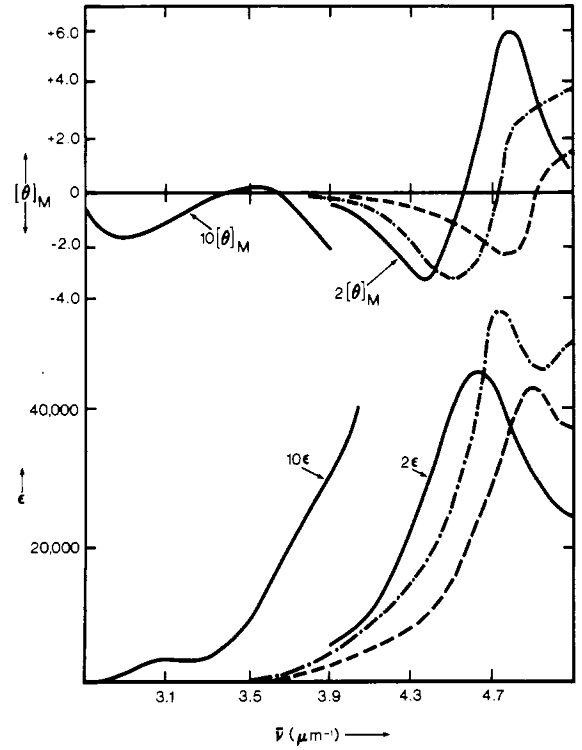

Figure 4. Absorption (lower curves) and MCD (upper curves) spectra for the hexacyano complexes in water: —, $Fe(CN)_6^{4-}$; - - -, $Ru(CN)_6^{4-}$; -·-, $Os(CN)_6^{4-}$.

Figure 4 presents MCD and absorption spectra for $Fe(CN)_6^{4-}$, $Ru(CN)_6^{4-}$, and $Os(CN)_6^{4-}$ in water. All three complexes exhibit a positive *A* term for the lowest energy

---

(12) Nasielski, J.; Colas, A. *Inorg. Chem.* **1978**, *17*, 237.

(13) Pesek, J. J.; Mason, W. R. *Inorg. Chem.* **1979**, *18*, 924.

Table I. Electronic Absorption and MCD Spectral Data

	absorption			MCD		
complex (solvent)	band no.	ν, μm^{-1}	ϵ, M^{-1} cm^{-1}	ν, μm^{-1}	$[\theta]_M$	assignt[a]
$Cr(CO)_6$ (CH_3CN)	I	3.12 sh	2 400	3.120 sh	−0.21	$^1T_{1g}$
	II	3.58	10 600	3.52	−0.98	$^1T_{1u}$
	III	4.35	59 200	4.50	+1.72	$^1T_{1u}$
$Mo(CO)_6$ (CH_3CN)	I	3.05 sh	2 020	3.09 sh	−0.19	$^1T_{1g}$
	II	3.47	15 130	3.46	−1.43	$^1T_{1u}$
	III	3.71	7 640	3.78 sh	−0.37	$^1T_{2g}$
	IV	4.30	106 000	4.27	+2.2	$^1T_{1u}$
$W(CO)_6$ (CH_3CN)	I	2.85 sh	1 360	2.83 2.87 2.99	+0.045 0 −0.179	$^3T_{1g}$
		3.04 sh	1 600			
	II	3.17 sh	2 620			$^1T_{1g}$
	III	3.46	12 800	3.47	−1.50	$^1T_{1u}$
	IV	3.67 sh	7 160			$^1T_{2g}$
	V	3.86	6 060	3.80 sh	−0.25	
	VI	4.38	130 000	4.48	+4.0	$^1T_{1u}$
$K_4Fe(CN)_6$ (H_2O)	I	3.10 sh	331	2.85	−0.098	$^1T_{1g}$
	II	3.75 sh	2 210	3.51	+0.008	$^1T_{2g}$
	III	4.61	22 800	4.39 4.53 4.75	−0.85 0 +1.5	$^1T_{1u}$
	IV	5.05 sh	12 700			$^1T_{1u}$
$K_4Ru(CN)_6$ (H_2O)	I	4.15 sh	5 710			
	II	4.88	43 500	4.82 4.88	−2.2 0	$^1T_{1u}$
$K_4Os(CN)_6$ (H_2O)	I	4.72	54 600	4.56 4.72 4.98 sh	−3.14 0 +3.0	$^1T_{1u}$

[a] From ref 1, 2, and 7.

MLCT band. Because of poor signal to noise it was not possible to obtain reliable MCD measurements in the range of the higher energy MLCT bands reported previously[1,7] above 5 μm^{-1}. Also only $Fe(CN)_6^{4-}$ exhibited measurable MCD features at energies lower than the MLCT band. These features consist of weak *B* terms which correspond roughly to shoulder absorptions assigned[1,7] to ligand field (LF) transitions.

Detailed absorption and MCD spectral data are set out in Table I. The conventional assignments[1,2,7] are also included for reference.

The MCD spectra clearly show that there is a difference in the nature of the lowest energy MLCT band between the $M(CO)_6$ and $M(CN)_6^{4-}$ complexes. While the *A* term observed for the MLCT band of the $M(CN)_6^{4-}$ complexes was anticipated, the *B* terms observed for the two MLCT bands of the $M(CO)_6$ complexes seem puzzling in view of the assignments to transitions to degenerate T_{1u} excited states. Both of the MLCT transitions are expected to exhibit *A* terms. *B* terms result from interstate mixing in the magnetic field and are always present regardless of the degeneracy of the states involved. *A* terms, on the other hand, depend upon the magnetic moment of the degenerate excited state as given by eq 1[9] (*D* is the dipole strength of the transition, β is the Bohr

$$A/D = i\beta\langle T_{1u}x|\mathbf{L}_z + 2\mathbf{S}_z|T_{1u}y\rangle \qquad (1)$$

magneton, and $\mathbf{L}_z$ and $\mathbf{S}_z$ are orbital and spin angular momentum operators, respectively). The absence of *A* terms for the two MLCT bands must be interpreted as a quenching of the excited-state angular momentum in the $M(CO)_6$ complexes.

In order to examine the source of the angular momentum quenching, values of *A*/*D* were estimated with use of eq 1 and some approximations. The $|T_{1u}x\rangle$ and $|T_{1u}y\rangle$ functions were constructed from the t_{2g}, t_{1u}, t_{2u} one-electron MO functions with use of octahedral coupling coefficients.[14] The t_{2g} MO's were approximated by pure *n*d functions[15] and the t_{2u} MO's by standard linear combinations[16] of π^*-ligand 2p functions for both CO and CN^-. The t_{1u} MO's, however, consist of π^*-ligand 2p functions together with a contribution from the metal (*n* + 1)p orbitals and will have the form $|t_{1u}(i)\rangle = a_i|(\pi^*)\rangle + b_i|(n+1)p\rangle$, where a_i and b_i are mixing coefficients. Finally one-electron matrix elements of angular momentum were evaluated in the standard way retaining only one-center integrals.[9] Values of *A*/*D* estimated with use of these approximations are collected in Table II. The magnitude of *A*/*D* contributions from the T_{1u} states of triplet parentage must be

Table II. Values of *A*/*D* for Excited States

excited state	*A*/*D*, β	excited state	*A*/*D*, β
	$\lvert T_{1u}\rangle$ States of $t_{2g}^5t_{1u}$		
$^1T_{1u}$	$^1/_4(3\lvert a_i\rvert^2 - 2\lvert b_i\rvert^2)$	$^3T_{2u}$	$-^1/_8(5\lvert a_i\rvert^2 + 2\lvert b_i\rvert^2)$
$^3T_{1u}$	$^1/_8(11\lvert a_i\rvert^2 - 2\lvert b_i\rvert^2)$	^3E_u	$-\lvert a_i\rvert^2$
	$\lvert T_{1u}\rangle$ States of $t_{2g}^5t_{2u}$		
$^1T_{1u}$	$-^3/_4$	^3E_u	−1
$^3T_{1u}$	$+^5/_8$	$^3A_{2u}$	+2
$^3T_{2u}$	$-^{11}/_8$		
	LF States of $t_{2g}^5e_g$		
$\lvert ^1T_{2g}\rangle$	$+^1/_2$	$\lvert T_{1g}(^3T_{1g})\rangle$	$+^5/_4$
$\lvert ^1T_{1g}\rangle$	$+^1/_2$	$\lvert T_{2g}(^3T_{1g})\rangle$	$-^5/_4$
	Forbidden Singlet MLCT States		
$\lvert ^1T_{2u}(t_{2g}^5t_{1u})\rangle$	$-^1/_4(3\lvert a_i\rvert^2 - 2\lvert b_i\rvert^2)$	$\lvert ^1E_u(t_{2g}^5t_{1u})\rangle$	0
		$\lvert ^1E_u(t_{2g}^5t_{2u})\rangle$	0
$\lvert ^1T_{2u}(t_{2g}^5t_{2u})\rangle$	$+^3/_4$		

---

[14] Griffith, J. S. "The Theory of Transition Metal Ions"; Cambridge University Press: Cambridge, England, 1964.

[15] The t_{2g} MO functions also contain a contribution from the ligand π^* orbitals, but this contribution is expected to be small since the energy deifference between the metal *n*d orbitals and the ligand orbitals is more than 3 μm^{-1}. That the t_{2g} MO's are *predominantly* metal *n*d orbitals is also supported by calculations.[2,5,6]

[16] Ballhausen, C. J. "Molecular Electronic Structures of Transition Metal Complexes"; McGraw-Hill: New York, 1979.

weighted in proportion to the strength of metal spin–orbit coupling which varies ζ_{3d}Cr(0) ≈ 220 cm^{-1} < ζ_{4d}Mo(0) ≈ 650 cm^{-1} < ζ_{5d}W(0) ≈ 2100 cm^{-1}.[14] From the similarity of the pattern of the two intense MLCT bands for all three carbonyl complexes contributions from triplet states must not be very large, even for W(CO)$_6$, and thus the T_{1u} excited states must be *predominantly* singlet. It may be remarked also that degenerate T_{2u} and E_u MLCT states are expected from the $t_{2g}{}^5t_{1u}$ and $t_{2g}{}^5t_{2u}$ excited configurations, and several degenerate LF states have been assigned at energies near the lower energy-allowed MLCT. Values of A/D for transitions to these states are also included in Table II, but their contribution to the observed MCD should be small because they are dipole forbidden (D is small).

From the A/D value for the lowest energy MLCT, which is predominantly $^1T_{1u}$, the sign and magnitude depends upon two contributions—a positive contribution proportional to $|a_i|^2$ from the π^*-ligand component and a negative contribution proportional to $|b_i|^2$ from the $(n+1)$p component. The difference in the MCD results for the lowest energy MLCT between the M(CO)$_6$ and M(CN)$_6{}^{4-}$ complexes can be rationalized in terms of a difference in the relative contributions of these two components. Atomic spectral data[17] show that the energies of the $(n+1)$p orbitals above the nd orbitals are 7–8 μm^{-1} for the free Fe(II), Ru(II), and Os(II) metal ions. Thus the d–p separation is larger than the lowest MLCT in the cyano complexes, which would argue for a low participation of the $(n+1)$p orbitals in the t_{1u} orbitals, i.e., $b_i \approx 0$. A positive A term resulting from the π^*-ligand component would be expected and is consistent with the sign of the observed A term. This conclusion is the same as that reached earlier for Fe(CN)$_6{}^{4-}$,[11] but a comparison here of the A term magnitudes with experiment is probably not significant due to the approximations involved. In contrast the d–p separation for Cr(0), Mo(0), and W(0) is only 2.5–3 μm^{-1},[17] which is less than the lowest energy MLCT. This would argue for a considerably greater $(n+1)$p orbital contribution to the t_{1u} MO's in the carbonyl complexes. To give a zero A term within experimental error requires $a_i/b_i \approx 0.82$ or nearly equal contributions of π^*-ligand orbitals and $(n+1)$p orbitals in the t_{1u} MO's. The angular momentum contributions from these two components cancel, giving virtually no magnetic moment for the lowest MLCT state.

It is difficult to draw any firm conclusions from the sign or magnitude of the B term which is observed for the lowest MLCT in the M(CO)$_6$ complexes since in order to do so coupling with all other excited states would have to be considered. The coupling between the two $^1T_{1u}$ states would not be zero, but the difficulty in the evaluation of the integrals, many of which are two centered, precludes any definite statement regarding the B term contribution from this interaction.

The rationale for the angular momentum quenching in the higher energy MLCT transition is not very clear. Since the t_{2u} orbitals are entirely ligand based, the quenching due to a contribution from metal orbitals is excluded. Two possible explanations are (1) a large distortion in the $^1T_{1u}$ excited state which would remove the degeneracy and thus quench the angular momentum and (2) the presence of orbitally forbidden and/or spin-forbidden states with large angular momentum contribution of opposite sign to the $^1T_{1u}$ state. Neither of these explanations is entirely satisfactory and cannot be distinguished from our present results. Comparative information from the cyano complexes was not available. A low-temperature MCD experiment might be able to demonstrate the presence of orbitally forbidden states since these would be vibronically allowed and their contribution would be temperature dependent. Obviously further experimental work is necessary to understand the quenching in the high-energy MLCT band of the carbonyl complexes.

The small negative A term observed for W(CO)$_6$ at 2.9 μm^{-1} which is absent in the other two carbonyl complexes is interesting and probably signals the presence of a spin-forbidden state. To be consistent with the $^3T_{1g}$ LF assignment[1,2] would require the state to be the T_{2g} spin-orbit component of $^3T_{1g}$. The spin-forbidden MLCT states $T_{1u}(^3E_u)$ and $T_{1u}(^3T_{2u})$ from the lower energy $t_{2g}{}^5t_{1u}$ excited configurations are also predicted to have negative A terms and would be expected to be at lower energy than the $^1T_{1u}$ state at 3.46 μm^{-1}. Thus an alternate assignment of the 2.9-μm^{-1} band might be to a spin-forbidden MLCT. However, the intensity of such a transition would be temperature independent in contrast to a LF band. The previous low-temperature measurements[2] on this band indicate a small reduction of intensity on cooling, which would argue for the LF assignment.

Added Note. While our paper was under review Hezemans et al. reported the MCD spectra of Cr(CO)$_6$, Mo(CO)$_6$, and W(CO)$_6$ in hexane solution.[18] The experimental spectra compare favorably with the spectra we report here, except that no mention is made by Hezemans et al. of the weak negative A term we observe for W(CO)$_6$. The interpretation of the MCD spectra given by these workers, especially the lack of the expected positive A term for the lowest energy MLCT band, is quite similar to the one advanced here independently and depends on a balance of orbital coefficients. The authors conclude that if the balance "is disturbed...the CT transitions may acquire observable A terms". Here we draw attention to our comparison of the carbonyl complexes with the cyano complexes where we expect the orbital coefficients a_i and b_i to be quite different and therefore the observed A terms for the cyano complexes reasonable.

Registry No. Cr(CO)$_6$, 13007-92-6; Mo(CO)$_6$, 13939-06-5; W(CO)$_6$, 14040-11-0; K$_4$[Fe(CN)$_6$], 13943-58-3; K$_4$[Ru(CN)$_6$], 15002-31-0; K$_4$[Os(CN)$_6$], 20740-36-7.

---

(17) Moore, C. E. *Natl. Bur. Stand. (U.S.) Circ.* **1958**, *No. 467*, Vols. II and III.

(18) Hezemans, A. M. F.; Van De Coolwijk, J. F. M.; Stufkens, D. J.; Boxhoorn, G. *Chem. Phys. Lett.* **1980**, *73*, 550.