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Metal to Ligand Charge-Transfer Spectra of Some Square-Planar Complexes of Rhodium(I) and Iridium(I)

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Solution electronic absorption and magnetic circular dichroism (MCD) spectral measurements at room temperature are reported for $[MX_2(CO)_2]^-$, *trans*-$[MCl(CO)(PPh_3)_2]$, $[M(Ph_2PCH_2CH_2PPh_2)_2]^+$, $[M(Ph_2PCHCHPPh_2)_2]^+$ (M = Rh(I) or Ir(I); $X^- = Cl^-$ or Br^-), and $[Ir(CN)_2(CO)_2]^-$. These complexes all exhibit intense absorptions in the visible and ultraviolet region, which are assigned as metal to ligand charge-transfer (MLCT) transitions from occupied metal d orbitals to the lowest energy π^* ligand orbitals. The MLCT spectra are interpreted within excited configurations involving only the lowest energy π^* ligand acceptor orbitals with metal spin–orbit coupling included. Detailed spectral assignments are presented, and the MCD spectra are interpreted with the aid of MCD terms calculated from spin–orbit wave functions.

Introduction

Metal to ligand charge-transfer (MLCT) spectra in transition metal complexes are ascribed to electronic excitations from occupied MO's, mainly of metal *n*d character, to empty ligand-based acceptor orbitals, usually of π symmetry. Excitation of this type may be viewed as an incipient oxidation of the metal ion, and the energetics of excitation reflect metal orbital stability and are related to redox properties of the metal ion in the complex. In square-planar complexes of d^8 electronic configuration, MLCT transitions have been identified in the electronic spectra of numerous complexes containing π-acceptor type ligands such as CN^-, CNR, CO, NO^+, PR_3, etc, which possess suitable low-energy empty orbitals.[2-5] In fact, in such complexes the MLCT states usually constitute the lowest energy allowed excited states and are therefore of considerable interest in formulating descriptions of electronic structure and electronic models for reaction pathways involving metal ion oxidation.

MLCT spectra in planar complexes have been characterized in greatest detail for cyano complexes, notably $[Ni(CN)_4]^{2-}$[2,6] and $[Pt(CN)_4]^{2-}$,[2,7-9] and perhaps to a lesser extent for some related alkyl isocyanide complexes of the type $[M(CNR)_4]^{n+}$ (M = Rh(I), Ir(I), Pt(II), Pd(II)).[4] There has been little systematic investigation of the factors which affect MLCT from one metal ion to another or between ligand systems for the same metal. Recently, MLCT spectra for a number of planar Rh(I) and Ir(I) complexes containing PR_3 and CO ligands were reported[3,5] and emissions were observed from low-lying MLCT states of several complexes containing the chelating bis(diphenylphosphino)ethane and bis(diphenylphosphino)ethylene ligands.[3] In contrast to the work on cyano complexes, however, detailed descriptions of MLCT states for complexes of Rh(I) and Ir(I) have yet to be formulated, and spectral assignments have been given in only a general way. The present report is prompted by our interest in advancing the understanding of the MLCT process in planar complexes and to provide a basis for more detailed descriptions of low-lying MLCT excited states. We report here some absorption and magnetic circular dichroism (MCD) spectral data for a variety of Rh(I) and Ir(I) complexes with several different types of ligands. Included are data for the complexes $[MX_2(CO)_2]^-$, *trans*-$[MCl(CO)(PPh_3)_2]$, $[M(Ph_2PCH_2CH_2PPh_2)_2]^+$, $[M(Ph_2PCHCHPPh_2)_2]^+$ (M = Rh(I), Ir(I); $X^- = Cl^-$, Br^-), and $[Ir(CN)_2(CO)_2]^-$. These results are compared with data reported[4] recently for complexes of the type $[M(CNC_2H_5)_4]^+$.

Experimental Section

The complexes $[(n\text{-}C_4H_9)_4N][RhX_2(CO)_2]$,[10] $[(n\text{-}C_4H_9)_4N][IrX_2(CO)_2]$[11] ($X^- = Cl^-$, Br^-), *trans*-$[RhCl(CO)(PPh_3)_2]$,[12] *trans*-$[IrCl(CO)(PPh_3)_2]$,[13] $[M(Ph_2PCH_2CH_2PPh_2)_2]Cl$,[14] and $[M(Ph_2PCHCHPPh_2)_2]Cl$[14] were all prepared by published procedures. The $[Ir(CN)_2(CO)_2]^-$ ion could not be isolated as a tetra-*n*-butylammonium salt owing to its high solubility, but it was prepared by the stoichiometric reaction of $[(C_2H_5)_4N]CN$ with $[(n\text{-}C_4H_9)_4N][IrCl_2(CO)_2]$ in CH_3CN solution prior to spectral measurements.[15] Spectral grade solvents were used throughout. Solutions of the air-sensitive Ir(I) complexes were carefully maintained under an N_2 atmosphere. Absorption spectral measurements were made using either a Cary Model 17 or a Cary Model 1501; MCD measurements were made using a Jasco ORD/UV-5 (equipped with a CD attachment) and a permanent magnet (field 10^4 G).

Results

Spectra. Electronic absorption and MCD spectral data for all the complexes studied are set out in Table I together for comparison with data reported recently for $[M(CNC_2H_5)_4]^+$. With the exception of a relatively weak band (ϵ 500–1600 in the Ir(I) complexes or 100–300 in the Rh(I) complexes) at low energy, all the bands are intense (ϵ 10^3–3×10^4). Further, the spectral pattern among complexes of the same metal are remarkably similar and are typified by the spectra of $[Rh(Ph_2PCHCHPPh_2)_2]^+$, $[Ir(Ph_2PCHCHPPh_2)_2]^+$, and $[Ir(CN)_2(CO)_2]^-$ shown in Figures 1–3, respectively.

Spin–Orbit Calculations. There now seems to be little doubt that the bands in Rh(I) and Ir(I) complexes such as these are due to MLCT transitions.[3,5] The similarity in spectral pattern observed is taken to indicate that the MLCT transitions have essentially the same origin and therefore can be described by small perturbations on the same model. Figure 4 presents a simplified MO energy level scheme which will be useful in visualizing excited MLCT configurations. For the sake of generality, the symmetry labels in Figure 4 refer to a planar complex of D_{4h} symmetry and representations of lower symmetry may be easily correlated with those of D_{4h}. All of the complexes studied here, like the $[M(CNC_2H_5)_4]^+$ complexes, have fully occupied *n*d MO levels labeled $a_{1g}(z^2)$, $e_g(xz, yz)$, and $b_{2g}(xy)$ and have diamagnetic ground states. The MLCT transitions are interpreted as excitations from these occupied d orbitals to low-lying molecular orbitals derived from the CO and CN^- π^* orbitals, the phosphorus d orbitals of π symmetry, and the empty metal $(n + 1)p_z$ orbital. These MO's are expected to have the same symmetry as the metal $(n + 1)p_z$ orbital and will have the form $\sum \phi_\pi(\text{ligands}) + \lambda(n + 1)p_z$, where the sum is over ligands with appropriate empty acceptor orbitals and λ is a mixing coefficient. Furthermore, the influence of metal spin–orbit coupling in excited MLCT states is apparent in the spectra of the Ir(I) complexes as evidenced by the greater number of intense bands and the higher relative intensities of the weaker low-energy band compared to corresponding Rh(I) complexes. The free-ion spin–orbit coupling constant for Rh(I), ζ_{4d} is 1200 cm^{-1} while for Ir(I) ζ_{5d} is estimated to be in the range 3500–4000 cm^{-1}.[16] Detailed spectral assignments must therefore take spin–orbit effects into account.

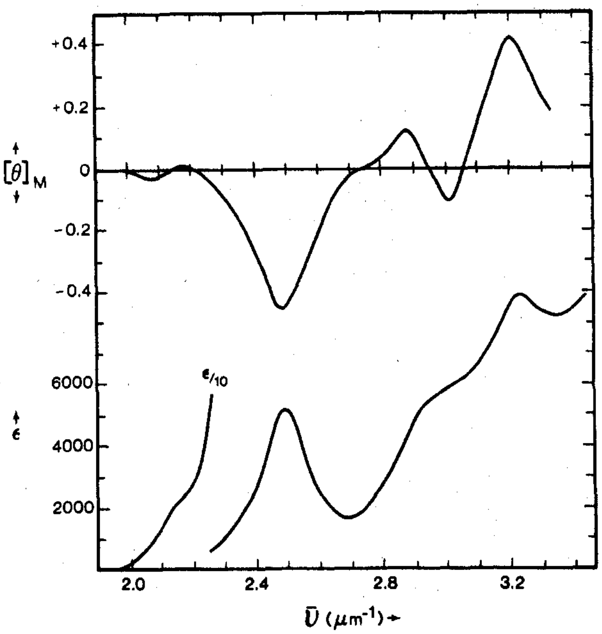

Figure 1. Electronic absorption (lower curve) and magnetic circular dichroism (upper curve) spectra for $[Rh(Ph_2PCHCHPPh_2)_2]Cl$ in CH_3CN solution.

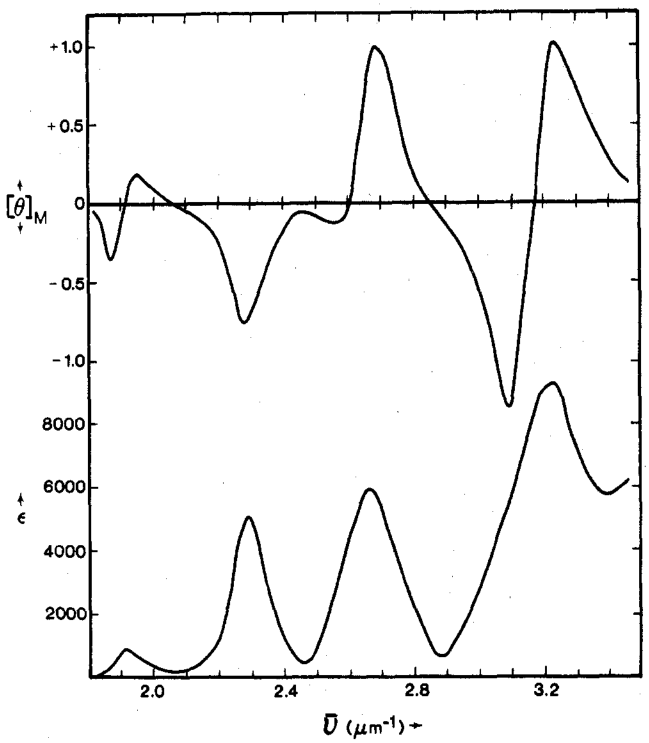

Figure 2. Electronic absorption (lower curve) and magnetic circular dichroism (upper curve) spectra for $[Ir(Ph_2PCHCHPPh_2)_2]Cl$ in CH_3CN solution.

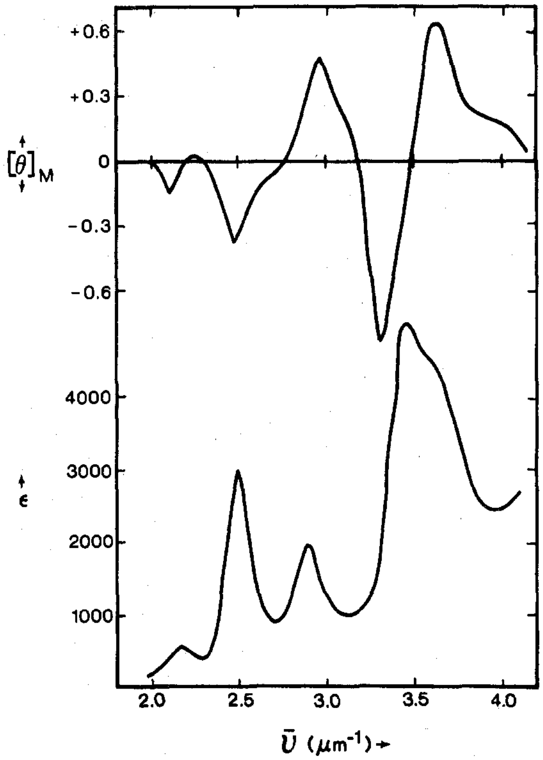

Figure 3. Electronic absorption (lower curve) and magnetic circular dichroism (upper curve) spectra for $[Ir(CN)_2(CO)_2]^-$ ion in CH_3CN solution.

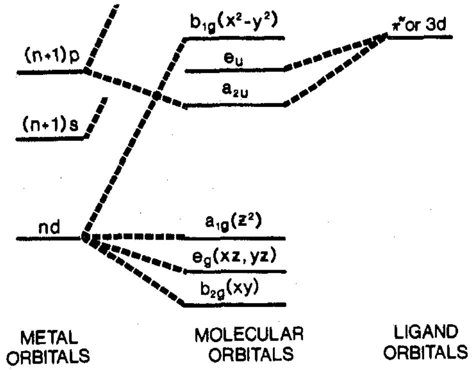

Figure 4. Simplified molecular orbital energy level diagram for planar complexes containing π-acceptor ligands.

Metal spin–orbit coupling has been treated in some detail for the MLCT excited states of $[Pt(CN)_4]^{2-}$,[7,8] some related cyanoamineplatinum(II) complexes,[8] and several $[M(CNC_2H_5)_4]^{n+}$ complexes.[4] Following the approach taken in these cases, spin–orbit calculations were performed for the allowed E_u and A_{2u} MLCT excited states of $[Ir(Ph_2PCHCHPPh_2)_2]^+$ and $[Rh(Ph_2PCHCHPPh_2)]^+$, which may be viewed as prototypical of the complexes examined here. The spin–orbit $E_u(i)$ and $A_{2u}(i)$ wave functions are given by eq 1 and 2 where a_i, b_i, etc. are mixing coefficients among the various singlet and triplet MLCT states in the absence of spin–orbit coupling. These states arise (see Figure 4) from $a_{1g}(z^2) \rightarrow a_{2u}$ $[{}^1A_{1g} \rightarrow {}^{1,3}A_{2u}]$, $e_g(xz, yz) \rightarrow a_{2u}$ $[{}^1A_{1g} \rightarrow {}^{1,3}E_u]$, and $b_{2g}(xy) \rightarrow a_{2u}$ $[{}^1A_{1g} \rightarrow {}^{1,3}B_{1u}]$. Calculated energies, which compare favorably with the experimental electronic absorption spectra are set forth in Table II, together with the resulting mixing coefficients.

$$|E_u(i)\rangle = a_i|E_u({}^3B_{1u})\rangle + b_i|E_u({}^3E_u)\rangle + c_i|E_u({}^1E_u)\rangle + d_i|E_u({}^3A_{2u})\rangle \quad (1)$$

$$|A_{2u}(i)\rangle = e_i|A_{2u}({}^3E_u)\rangle + f_i|A_{2u}({}^1A_{2u})\rangle \quad (2)$$

MCD Terms. To provide a basis for interpreting the MCD spectra, the spin–orbit wave functions were used to determine the sign and estimate the relative magnitudes of the MCD A and B terms expected for the MLCT transitions. The MCD A terms for the $E_u(i)$ states are given[7,8] by eq 3, where β is

$$A_i = (\beta/2)[-2|a_i|^2 + |b_i|^2 + |c_i|^2 + 2|d_i|^2]\,|c_i|^2\,|D({}^1E_u)|^2 \quad (3)$$

the Bohr magneton and $|D({}^1E_u)|^2 = |\langle {}^1A_{1g}|\mathbf{m}|{}^1E_u\rangle|^2$, the dipole

Table I. Electronic Absorption and Magnetic Circular Dichroism Spectral Data

Band no.	Absorption $\bar{\nu}$, μm^{-1} (ϵ, $M^{-1}\,cm^{-1}$)	MCD $\bar{\nu}$, μm^{-1} ($[\theta]_M$)^a	Absorption $\bar{\nu}$, μm^{-1} (ϵ, $M^{-1}\,cm^{-1}$)	MCD $\bar{\nu}$, μm^{-1} ($[\theta]_M$)^a	Excited state
	$[\mathrm{Rh(Ph_2PCHCHPPh_2)_2}]\mathrm{Cl}^b$		$[\mathrm{Ir(Ph_2PCHCHPPh_2)_2}]\mathrm{Cl}^b$		
		2.08 (−0.04)		1.87 (−0.38)	
I	2.14 (205)^c	d 2.14 (0)	1.92 (970)	d 1.91 (0)	$E_u(1)$
		2.17 (+0.01)		1.94 (+0.19)	
II	2.49 (5230)	2.48 (−0.46)	2.29 (5100)	2.27 (−0.77)	$A_{2u}(1)$
				2.56 (−0.14)	
III	3.00 (5860)^c	2.88 (+0.12)	2.66 (6000)	2.68 (+0.98)	$E_u(2)$
		3.01 (−0.12)		3.09 (−1.31)	
IV	3.22 (8900)	3.20 (+0.42)	3.20 (9100)	d 3.17 (0)	$E_u(3)$, $A_{2u}(2)$
				3.24 (+1.09)	
	$[\mathrm{Rh(Ph_2PCH_2CH_2PPh_2)_2}]\mathrm{Cl}^b$		$[\mathrm{Ir(Ph_2PCH_2CH_2PPh_2)_2}]\mathrm{Cl}^b$		
				1.84 (−0.22)	
I	2.14 (124)^c	2.06 (−0.02)	1.92 (700)	d 1.91 (0)	$E_u(1)$
				1.97 (+0.12)	
II	2.48 (4600)	2.48 (−0.46)	2.28 (3900)	2.26 (−0.63)	$A_{2u}(1)$
				2.50 (−0.05)^c	
III		2.99 (−0.12)	2.65 (4100)	2.67 (+0.82)	$E_u(2)$
				3.07 (−1.52)	
IV	3.19 (9400)	3.19 (+0.41)	3.18 (8600)	d 3.15 (0)	$E_u(3)$, $A_{2u}(2)$
				3.23 (+1.52)	
	trans-$[\mathrm{RhCl(CO)(PPh_3)_2}]^e$		*trans*-$[\mathrm{IrCl(CO)(PPh_3)_2}]^e$		
				2.25 (−0.18)	$A_1(1)$
I			2.31 (530)	2.35 (+0.06)	$B_2(1)$
II	2.77 (3100)	2.74 (−0.30)	2.61 (2780)	2.60 (−0.39)	$B_1(1)$
		3.26 (−0.16)			$A_1(2)$
III	3.51 (15 000)	3.61 (+0.63)	2.98 (2370)	3.01 (+0.35)	$B_2(2)$
				3.39 (−0.82)	$A_1(3)$
IV			3.65 (5500)	3.64 (+1.24)	$B_2(3)$, $B_1(2)$
	$[(n\text{-}\mathrm{C_4H_9})_4\mathrm{N}][\mathrm{RhCl_2(CO)_2}]^b$		$[(n\text{-}\mathrm{C_4H_9})_4\mathrm{N}][\mathrm{IrCl_2(CO)_2}]^b$		
I			2.60 (530)	2.56 (−0.12)	$A_1(1)$, $B_2(1)$
II	2.98 (2700)	2.96 (−0.20)	2.85 (2380)	2.88 (−0.29)	$B_1(1)$
III			3.16 (2040)	3.21 (+0.33)	$B_2(2)$
				3.66 (−0.68)	$A_1(3)$
IV	3.70 (5400)^f	3.86 (+0.38)	3.86 (4700)	3.88 (+0.32)	$B_2(3)$, $B_1(2)$
V			4.23 (4200)	4.22 (+0.18)	$A_1(4)$, $B_2(4)$
	$[(n\text{-}\mathrm{C_4H_9})_4\mathrm{N}][\mathrm{RhBr_2(CO)_2}]^b$		$[(n\text{-}\mathrm{C_4H_9})_4\mathrm{N}][\mathrm{IrBr_2(CO)_2}]^b$		
I			2.60 (700)	2.53 (−0.11)	$A_1(1)$, $B_2(1)$
II	2.97 (2900)	2.96 (−0.14)	2.83 (2500)	2.81 (−0.28)	$B_1(1)$
III			3.13 (2450)	3.16 (+0.38)	$B_2(2)$
				3.53 (−0.66)	$A_1(3)$
IV	3.63 (6600)^f	3.77 (+0.42)	3.80 (6350)	3.80 (+0.42)	$B_2(3)$, $B_1(2)$
V			4.10 (5200)	4.13 (+0.44)	$A_1(4)$, $B_2(4)$
	$[\mathrm{Rh(CNC_2H_5)_4}]\mathrm{ClO_4}^{b,g}$		$[\mathrm{Ir(CNC_2H_5)_4}]\mathrm{ClO_4}^{b,g}$		
I	2.30 (260)	2.26 (−0.11)	2.14 (4600)	h	$E_u(1)$
II	2.63 (8400)	2.65 (−1.34)	2.38 (5500)		$A_{2u}(1)$
III	3.00 (3450)^c	2.95 (+0.33)	2.71 (4170)		$E_u(2)$
		3.21 (−1.93)			
IV	3.25 (24 500)	d 3.29 (0)	3.25 (6670)		$E_u(3)$, $A_{2u}(2)$
		3.35 (−1.93)			
		3.55 (+0.20)			
V	3.55 (2100)^c	d 3.59 (0)	3.56 (3850)		$E_u(4)$
		3.72 (−0.30)			
			$[\mathrm{Ir(CN)_2(CO)_2}]^{-\,b,i}$		
				2.11 (−0.13)	$A_1(1)$
I			2.17 (1570)	2.23 (+0.03)	$B_2(1)$
II			2.49 (2960)	2.48 (−0.37)	$B_1(1)$
				2.70 (−0.06)^c	$A_1(2)$
III			2.89 (1980)	2.96 (+0.47)	$B_2(2)$
				3.30 (−0.85)	$A_1(3)$
IV			3.45 (5030)	3.62 (+0.65)	$B_2(3)$, $B_1(2)$
V			3.60 (4450)^c	3.93 (+0.20)^c	$A_1(4)$, $B_2(4)$

[a] $[\theta]_M = 3300\Delta A/(MlH)$, where ΔA is the measured differential absorbance, M is the molar concentration, l is the path length in centimeters, and H is the magnetic field in gauss. [b] $\mathrm{CH_3CN}$ solution. [c] Shoulder; ϵ or $[\theta]_M$ at the given $\bar{\nu}$. [d] A term. [e] $\mathrm{CHCl_3}$ solution. [f] Broad band; $\Delta\nu_{1/2} \approx 0.55\ \mu m^{-1}$. [g] Reference 4. [h] MCD data could not be obtained due to photochemical decomposition in the time required for measurement. [i] Complex not isolated (see ref 15).

strength of the fully allowed $^1A_{1g} \rightarrow {}^1E_u$ transition. The MCD B terms for the $E_u(i)$ and $A_{2u}(i)$ states cannot be given exactly because summations over all excited states are required. However, as a first approximation only contributions from all other $E_u(j)$ and $A_{2u}(j)$ states of eq 1 and 2 are included. With this approximation the summations reduce to

$$B[E_u(i)] = \Sigma B(E_u)_{ij} + \Sigma B(E_u, A_{2u})_{ik}$$

$$B[A_{2u}(i)] = \Sigma B(A_{2u}, E_u)_{ij}$$

Table II. Spin-Orbit Energies and Mixing Coefficients

State	Energy, μm^{-1} Calcd[a]	Energy, μm^{-1} Obsd[b]	$a(^3B_{1u})$	$b(^3E_u)$	$c(^1E_u)$	$d(^3A_{2u})$	$e(^3E_u)$	$f(^1A_{2u})$
				$[Ir(Ph_2PCHCHPPh_2)_2]^+$ [c]				
$E_u(1)$	1.93	1.92	−0.0067	−0.252i	−0.189	0.949		
$E_u(2)$	2.68	2.66	0.294	0.786i	−0.534	0.104		
$E_u(3)$	3.20	3.20	−0.204	0.550i	0.754	0.295		
$E_u(4)$	3.42		0.933	−0.129i	0.332	0.038		
$A_{2u}(1)$	2.29	2.29					0.582	0.813
$A_{2u}(2)$	3.06						0.813	−0.582
				$[Rh(Ph_2PCHCHPPh_2)_2]^+$ [d]				
$E_u(1)$	2.14	2.14	−0.0007	−0.095i	−0.076	0.992		
$E_u(2)$	2.99	3.00[e]	0.132	0.949i	−0.277	0.070		
$E_u(3)$	3.22	3.22	−0.142	0.287i	0.942	0.100		
$E_u(4)$	3.46		0.981	−0.086i	0.174	0.0058		
$A_{2u}(1)$	2.49	2.49					0.233	0.972
$A_{2u}(2)$	3.03	3.00[e]					0.972	−0.233

[a] See References 4, 7, and 8 for details; the phase conversions adopted here are the same used by Griffith.[17] [b] From absorption spectra in CH_3CN (see Table I). [c] Input parameters (μm^{-1}): ζ_{5d}, 0.30; $^1A_{2u}$, 2.55; $^3A_{2u}$, 2.05; ^1E_u, 3.03; ^3E_u, 2.80; $^3B_{1u}$, 3.35. [d] Input parameters (μm^{-1}): ζ_{4d}, 0.10; $^1A_{2u}$, 2.52; $^3A_{2u}$, 2.16; ^1E_u, 3.20; ^3E_u, 3.00; $^3B_{1u}$, 3.45. [e] Shoulder.

Table III. Calculated MCD Terms[a]

State	*A* term $\beta\lvert D(^1E_u)\rvert^2$	*B* term $\beta D(^1A_{2u})D(^1E_u)^*$	*B* term $\beta\lvert D(^1E_u)\rvert^2$
		$[Ir(Ph_2PCHCHPPh_2)_2]^+$	
$E_u(1)$	$+3.4 \times 10^{-2}$	-2.8×10^{-5}	-1.8×10^{-6}
$E_u(2)$	$+1.1 \times 10^{-1}$	$+1.8 \times 10^{-4}$	$+1.8 \times 10^{-6}$
$E_u(3)$	$+2.7 \times 10^{-1}$	$+6.0 \times 10^{-4}$	$+8.4 \times 10^{-5}$
$E_u(4)$	-8.9×10^{-2}	$+5.4 \times 10^{-6}$	-8.4×10^{-5}
$A_{2u}(1)$		-1.6×10^{-4}	
$A_{2u}(2)$		-5.9×10^{-4}	
		$[Rh(Ph_2PCHCHPPh_2)_2]^+$	
$E_u(1)$	$+5.7 \times 10^{-3}$	-6.0×10^{-6}	-4.4×10^{-8}
$E_u(2)$	$+3.6 \times 10^{-2}$	$+2.2 \times 10^{-4}$	-3.7×10^{-6}
$E_u(3)$	$+4.2 \times 10^{-1}$	$+2.9 \times 10^{-4}$	$+3.6 \times 10^{-5}$
$E_u(4)$	-2.9×10^{-2}	$+1.7 \times 10^{-6}$	-3.2×10^{-5}
$A_{2u}(1)$		-2.2×10^{-4}	
$A_{2u}(2)$		-2.8×10^{-4}	

[a] Calculated from the mixing coefficients of Table II; the quantity $\lvert D(^1E_u)\rvert^2$ is positive, while $D(^1A_{2u})D(^1E_u)^*$ is negative (see text); β is the Bohr magneton.

In these expressions $B(E_u)_{ij}$ and $B(A_{2u}, E_u)_{ij}$ are given by eq 4 and 5, where ΔE_{ji} is the energy difference between the jth

$$B(E_u)_{ij} = -(\beta/\Delta E_{ji})[2a_i^*a_j - b_i^*b_j - c_i^*c_j - 2d_i^*d_j]\, c_ic_j^*\, \lvert D(^1E_u)\rvert^2 \quad (4)$$

$$B(A_{2u}, E_u)_{ij} = -(\beta/\Delta E_{ji})[2^{1/2}e_i^*a_j + 2(2^{1/2})e_i^*b_j - (3/2)^{1/2}e_i^*d_j + (3^{1/2})f_i^*c_j]\, f_ic_j^*D(^1A_{2u})D(^1E_u)^* \quad (5)$$

and ith states, $D(^1A_{2u}) = \langle ^1A_{1g}|\mathbf{m}|^1A_{2u}\rangle$ and $D(^1E_u)^* = \langle ^1A_{1g}|\mathbf{m}|^1E_u\rangle^*$. Use is also made of the relations $B(E_u)_{ij} = -B(E_u)_{ji}$ and $B(E_u, A_{2u})_{ij} = -B(A_{2u}, E_u)_{ji}$. In eq 3–5 the quantity $\lvert D(^1E_u)\rvert^2$ is positive but $D(^1A_{2u})D(^1E_u)^*$ is negative with our choice of phase convention.[17] The integrals in the latter case can be approximated using pure metal d functions: $D(^1A_{2u})D(^1E_u) = -\langle d_{z^2}|m_z|a_{2u}(\pi^*)\rangle\langle d_{xz}|m_x|a_{2u}(\pi^*)\rangle$, where the $a_{2u}(\pi^*)$ MO function will involve the metal p_z and phosphorus 3d orbitals. These integrals are difficult to evaluate exactly, but integration over angular coordinates shows that they will be positive, making $D(^1A_{2u})D(^1E_u)^*$ negative overall. The *A* and *B* terms calculated from eq 3–5 are given in Table III. The *signs* of the terms are completely compatible with the experimental spectra (see Table I and Figures 1 and 2), and the relative magnitudes are also in qualitative agreement with the observed term magnitudes.

Discussion

The large extinction coefficients of the electronic absorption bands in the Rh(I) and Ir(I) complexes examined in this work, the temperature independence of band intensities in the spectra of $[M(Ph_2PCHCHPPh_2)_2]^+$, $[M(Ph_2PCH_2CH_2PPh_2)_2]^+$, and *trans*-$[MCl(CO)(PPh_3)_2]$,[3,5] the observed energy ordering Ir(I) < Rh(I) for the lowest absorption band in analogous complexes, and the ordering $CN^- < Cl^-$ in the $[IrX_2(CO)_2]^-$ complexes studied here and also in *trans*-$[MX(CO)(PPh_3)_2]$ complexes[5] all clearly indicate that the electronic transitions in question are MLCT in character and that a molecular orbital diagram such as shown in Figure 4 is appropriate. In the absence of spin-orbit coupling in excited MLCT configurations, only two allowed transitions of the d → $a_{2u}(\pi)^*$ type are expected: $^1A_{1g} \rightarrow {}^1A_{2u}$, which should exhibit a *B* term in the MCD, and $^1A_{1g} \rightarrow {}^1E_u$, which should have associated *A* and *B* terms in the MCD. Both the absorption and MCD spectra of the complexes examined here are clearly more complicated, and the need for including spin-orbit coupling is demonstrated. As spin-orbit coupling is increased, transitions to the E_u and A_{2u} components of the $^3A_{2u}$, ^3E_u, and $^3B_{1u}$ states will gain intensity and will exhibit MCD terms characteristic of the symmetry and parentage of the excited state(s). The MCD results therefore provide an important guide to the placement of the MLCT states, since the observation of an *A* term is consistent only with a degenerate E_u state. Further, the sign of the *A* term is dependent upon the symmetry properties of the orbitals involved in the transition. Thus, the E_u component from the $^3A_{2u}$ and ^3E_u states are expected to give rise to positive *A* terms, while the component from $^3B_{1u}$ is expected to give a negative *A* term (see eq 3).[4,7,8] Also the observed pattern of *B* term signs in the MCD spectra must be compatible with the relative placement of the MLCT states. The signs of the *B* terms of the A_{2u} and E_u states are not only dependent upon the symmetry properties of the orbitals involved in a given transition but also on the energy ordering of all other MLCT states. With these considerations, the input energies for the singlet and triplet states were chosen for the spin-orbit calculations for the $[M(Ph_2PCHCHPPh_2)_2]^+$ complexes (see Table II). Alternative choices of input energies substantially different from those used here did not give sensible results for both the absorption and MCD spectra (Tables II and III).

On the basis of the results of Tables II and III for the $[M(Ph_2PCHCHPPh_2)_2]^+$ complexes, band assignments were formulated for the Rh(I) and Ir(I) complexes examined in this work. These assignments are summarized in Table I and are briefly discussed below for each type of complex in turn.

$[M(Ph_2PCHCHPPh_2)_2]^+$ Cations. The results presented in Tables II and III allow a complete interpretation of both the absorption and MCD spectra for these cations. Band I is assigned as a transition to the $E_u(1)$ state whose parentage is predominantly $^3A_{2u}$. The greater band intensity observed for the Ir(I) complex compared to the Rh(I) complex is consistent with the greater spin–orbit coupling. The MCD reveals a positive *A* term and a positive *B* term for both complexes, consistent with the calculated results (Table III). Band II is assigned to $A_{2u}(1)$, derived from $^1A_{2u}$. The calculations show that this state has substantial ^3E_u character in the case of the Ir(I) complex but is nearly pure $^1A_{2u}$ in the Rh(I) complex. Band III is assigned to $E_u(2)$ which is mainly ^3E_u in character. The MCD does not show a clear *A* term for this state because the negative *B* terms associated with this state apparently makes a larger contribution to the observed MCD. The small negative ellipticity at 2.56 μm^{-1} for the Ir(I) complex is likely due to the negative component of a small positive *A* term. A negative *B* term is predicted for band III in good agreement with experimental spectra. Finally, band IV is assigned as $E_u(3)$ derived from ^1E_u, although the $A_{2u}(2)$ state of ^3E_u parentage is expected at slightly lower energy. It should be noted that the *B* terms calculated for the $E_u(3)$ and $A_{2u}(2)$ states are of nearly the same magnitude but of opposite sign, resulting from the close proximity of these two states. These terms may overlap sufficiently so as to give the appearance of a positive "pseudo" *A* term. The sign of this pseudo *A* term is the same as expected for the *A* term associated with $E_u(3)$ and thus would enhance the magnitude of this term in the observed spectra. The large positive *A* term at 3.17 μm^{-1} observed for the Ir(I) complex (Figure 2) is therefore interpreted as containing contributions both from the positive *A* term of $E_u(3)$ and from the pseudo *A* term resulting from $E_u(3)$ and $A_{2u}(2)$ lying close in energy. A similar situation has been identified in the spectra of $[Pt(CN)_4]^{2-}$ and $[Pt(CNC_2H_5)_4]^{2+}$.[4,7,8]

$[M(Ph_2PCH_2CH_2PPh_2)_2]^+$ Cations. The assignment of the absorption spectra and the interpretation of the MCD spectra for the $[M(Ph_2PCH_2CH_2PPh_2)_2]^+$ complexes can be made by an analogy to that for the $[M(Ph_2PCHCHPPh_2)_2]^+$ complexes since the spectra are virtually identical. The absorption and MCD spectra of the Rh(I) complex are somewhat less well resolved, but the intense features of both are clear. The close similarity of the spectra for the $Ph_2PCH_2CH_2PPh_2$ and $Ph_2PCHCHPPh_2$ complexes indicates that the MLCT is not very sensitive to the nature of the chelate and its structural and conformational details. Perhaps this is not surprising since the acceptor orbital on the phosphorus is visualized as nearly a pure 3d orbital which should not be markedly affected by whether or not the chelate backbone is saturated or unsaturated. Similarly, the donor orbitals on the phosphorus are not expected to be very different, apart from weak inductive effects.

***trans*-$[MCl(CO)(PPh_3)_2]$.** The spectra of the *trans*-$[MCl(CO)(PPh_3)_2]$ complexes are also quite similar to those of the $[M(Ph_2PCHCHPPh_2)_2]^+$ cations. For example, the absorption spectrum of *trans*-$[IrCl(CO)(PPh_3)_2]$ exhibits four bands, each of which lies ca. 0.3–0.4 μm^{-1} higher in energy than corresponding bands in $[Ir(Ph_2PCHCHPPh_2)_2]^+$, and the pattern observed in the MCD is also essentially the same. Regarding this latter feature, it should be noted that the degenerate $E_u(i)$ states of D_{4h} symmetry give rise to pairs of nondegenerate $A_1(i)$ and $B_2(i)$ states in the lower C_{2v} symmetry of the *trans*-$[MCl(CO)(PPh_3)_2]$ complexes. The absence of degenerate states predicts only *B* terms in the MCD. However if the $A_1(i)$ and $B_2(i)$ states are closely spaced in energy compared to bandwidths (near degeneracy), the MCD will exhibit overlapping *B* terms of opposite sign (pseudo *A* terms) and thus resemble the MCD for a D_{4h} complex. This appears to be the case in the region of bands I and IV. Here the negative MCD ellipticity at lower energy is assigned to the $A_1(i)$ state while the positive ellipticity at higher energy is assigned to the $B_2(i)$ state. In the case of the *trans*-$[RhCl(CO)(PPh_3)_2]$ complex, the weaker low-energy band (band I) is not observed, but bands II, III, and IV correspond to bands in the $[Rh(Ph_2PCHCHPPh_2)_2]^+$ spectra. The higher absorptivities of the bands in this Rh(I) complex are likely due to closer proximity to the higher energy, intense phenyl absorptions than in the case of the Ir(I) analogue. The similarity between the *trans*-$[MCl(CO)(PPh_3)_2]$ and $[M(Ph_2PCHCHPPh_2)_2]^+$ spectra shows that the MLCT is little affected by the symmetry reduction from nearly D_{4h} to C_{2v}. Furthermore, separate M → P and M → CO MLCT systems should be present in the *trans*-$[MCl(CO)(PPh_3)_2]$ complexes. The lack of resolution of these separate systems is likely due to their similarity in energy compared to bandwidths (typically 0.2–0.3 μm^{-1}).

$[MX_2(CO)_2]^-$ Anions. The geometry about the metal ion in these complexes is assumed to be cis,[10,11,18] and assignments are based on C_{2v} symmetry. With the exception of a high-energy band (band V), the spectra of the $[IrX_2(CO)_2]^-$ (X^- = Cl^-, Br^-, or CN^-) anions are also similar to that of $[Ir(Ph_2PCHCHPPh_2)_2]^+$ cations and can be assigned in an analogous fashion. Band V in each case appears on the high-energy side of the more intense band IV and is likely due to the states corresponding to $E_u(4)$ of $^3B_{1u}$ parentage (see Tables II and III). This state was not observed for $[Ir(Ph_2PCHCHPPh_2)_2]^+$ but was reported[4] for $[Rh(CNC_2H_5)_4]^+$ and assigned by virtue of the negative *A* term observed in the MCD. The negative *B* term observed for band V must correspond to the lower energy A_1 state, which is predicted to have a negative sign; the higher energy positive *B* term is not observed in any of these complexes. The spectra of the $[Ir(CN)_2(CO)_2]^-$ is red shifted ca. 0.3–0.4 μm^{-1} with respect to the two halide complexes. This observation is consistent with the greater π-acceptor ability of CN compared to Br or Cl. The greater acceptor ability is expected to lower the energy of the π^* acceptor MO in the complex (corresponding to a_{2u} in Figure 4). A similar observation has been noted recently for the *trans*-$[MX(CO)(PPh_3)_2]$ complexes.[5] The lack of resolution of separate M → CN^- and M → CO MLCT systems, as discussed in the case of the *trans*-$[MCl(CO)(PPh_3)_2]$ complexes, argues for similar energies for the two systems. In the case of the $[RhX_2(CO)_2]^-$ (X^- = Cl^- or Br^-) complexes, the spectra are less well resolved, and only the two most intense bands, II and IV, which correspond to nearly singlet excited states, appear in the spectra. Band IV is quite broad in each case and undoubtedly covers the additional weaker transitions expected in this energy region.

Electronic Structure. From the foregoing it is clear that the MLCT absorption and MCD spectra can be satisfactorily interpreted within excited configurations involving only the lowest energy a_{2u} ligand orbital. The inclusion of higher energy ligand orbitals such as e_u or b_{2u} (not shown in Figure 4) does not provide a satisfactory interpretation of the MCD results. Piepho et al.[7] have argued that in the case of $[Pt(CN)_4]^{2-}$, such excited configurations lead to the prediction of several E_u states which should exhibit negative *A* terms, and none are observed. These same arguments may be applied in the present case. Furthermore, the placement of the MLCT excited states consistent with the experimental spectra leads to the energy ordering of the occupied metal orbitals as $a_{1g}(z^2) > e_g(xz, yz) > b_{2g}(xy)$, provided differences in electronic repulsions are assumed to be small. Even admitting some ignorance to the details of repulsion differences, the ordering of excited states for the Rh(I) and Ir(I) complexes examined here parallels those for $[M(CN)_4]^{2-}$, $[M(CNR)_4]^{n+}$, and some cyanoamineplatinum(II) complexes.[4,7,8] As in these cases, the stabilization of the π-bonding $e_g(xz, yz)$ and $b_{2g}(xy)$ orbitals with respect to the nearly nonbonding or weakly σ-antibonding $a_{1g}(z^2)$ orbital is consistent with the π-acceptor character of the P-donor, CO, or CN^- ligands.

It is interesting that the energies of the MLCT excited states for a given metal ion depend upon the number of acceptor ligands in the complex. For example, among the Ir(I) complexes the energy of the lowest energy MLCT state decreases in the order $[IrX_2(CO)_2]^-$ ($X^- = Cl^-$ or Br^-; two acceptor ligands) > *trans*-$[IrCl(CO)(PPh_3)_2]$ (three acceptor ligands) > $[Ir(CNC_2H_5)_4]^+$ ~ $[Ir(CN)_2(CO)_2]^-$ ~ $[Ir(Ph_2CHCHPPh_2)_2]^+$ ~ $[Ir(Ph_2PCH_2CH_2PPh_2)_2]^+$ (four acceptor ligands). This trend, though not large, is consistent with stabilization of the lowest energy empty MO (a_{2u} in Figure 4) as additional acceptor ligands are added. In contrast, the π-donor properties of the ligands appear to have little effect on the MLCT spectra. There is almost no difference in the spectra of the $[MX_2(CO)_2]^-$ ions for $X^- = Cl^-$ or Br^-. Further, there is very little difference between the spectral pattern observed for the $[Ir(CN)_2(CO)_2]^-$ anion and the $[Ir(Ph_2PCHCHPPh_2)_2]^+$ cation. Since there are no filled π orbitals on the P-donor ligands, this similarity indicates that the filled π orbitals of CN^- or CO have little effect on the stability of the $e_g(xz, yz)$ or $b_{2g}(xy)$ occupied metal π orbitals.

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Registry No. $[Rh(Ph_2PCHCHPPh_2)_2]Cl$, 22754-44-5; $[Ir(Ph_2PCHCHPPh_2)_2]Cl$, 36390-37-1; $[Rh(Ph_2PCH_2CH_2PPh_2)_2]Cl$, 15043-47-7; $[Ir(Ph_2PCH_2CH_2PPh_2)_2]Cl$, 15390-38-2; *trans*-$[RhCl(CO)(PPh_3)_2]$, 15318-33-9; *trans*-$[IrCl(CO)(PPh_3)_2]$, 15318-31-7; $[(n\text{-}C_4H_9)_4N][RhCl_2(CO)_2]$, 17966-76-6; $[(n\text{-}C_4H_9)_4N][IrCl_2(CO)_2]$, 53993-19-4; $[(n\text{-}C_4H_9)_4N][RhBr_2(CO)_2]$, 30191-99-2; $[(n\text{-}C_4H_9)_4N][IrBr_2(CO)_2]$, 62637-68-7; $[Ir(CN)_2(CO)_2]^-$, 62637-67-6.

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Synthesis and Characterization of Cobalt(II) Halide and Pseudohalide Complexes of 4-*N*,*N*-Dimethylaminopyridine

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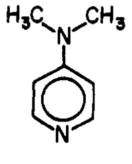
Six new halide and pseudohalide complexes of Co(II) with 4-*N*,*N*-dimethylaminopyridine (4-DMAP) have been prepared and are of the type $Co(4\text{-}DMAP)_2X_2$ (X is Cl, Br, I, NCO, NCS, or NCSe). Shifts which occur upon complexation of bands in the 1600–1800-cm^{-1} region, assigned to 4-DMAP nucleus stretching modes, confirm that the pyridine nitrogen is coordinated. The pseudohalides are N bonded to Co as evidenced by their ν_{CN} integrated absorption coefficients of approximately 1.2×10^5 M^{-1} cm^{-2}. In the temperature range 300–78 K the halide complexes are magnetically normal (4.6 μ_B at 300 K) whereas the pseudohalide complexes are magnetically subnormal (4.0 μ_B at 300 K). Ligand field spectra of the complexes are typical of C_{2v} Co(II) complexes and show the normal spectrochemical series for *Dq*. On the basis of the values of *Ds* calculated from a C_{2v} model the complexes exhibit increasing distortion from T_d symmetry in the series *N*CO < I < Br < *N*CS ~ Cl < *N*CSe. The presence of the strongly electron-donating 4-dimethylamino group does not markedly affect the electronic and structural properties of these complexes.

Introduction

A very large number of pseudotetrahedral complexes of chromophoric type CoN_2X_2 containing pyridine or its derivatives have been prepared and characterized.[1] In many cases variations in the electronic properties of a series of such complexes have been interpreted in terms of steric and electronic characteristics of the pyridine substituent. For example Haigh et al.[2] have related the metal–pyridine nitrogen stretching frequency of a series of substituted pyridine complexes to the electron-withdrawing ability of the substitutent. Also Nathan and Ragsdale[3] have related N–O stretching frequencies of a series of substituted pyridine *N*-oxides to their respective substituent constants, σ_{pyO}.[4] To study the effect of substitution on electronic properties of complexes containing pyridine substituted with groups capable of conjugation with the ring we have prepared and characterized the cobalt(II) halide and pseudohalide complexes of the strong base 4-*N*,*N*-dimethylaminopyridine (4-DMAP, I).



I

Herein we report results of this work and observe that the presence of this particular substituent does not markedly affect the properties of these complexes but rather their electronic and structural properties are similar to other C_{2v} Co(II) complexes.[5]

Experimental Section

Materials. 4-*N*,*N*-Dimethylaminopyridine was purchased from Aldrich Chemical Co. and used without purification. $CoCl_2\cdot 6H_2O$, $Co(NCS)_2$, and $CoBr_2$ were purchased from Ventron Corp. and used as received. CoI_2 was prepared from concentrated HI and $CoCO_3$.