of the low-temperature modification of $Mg_2NiD_{\sim 4}$ is therefore desirable.

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MCD Spectra of $M(CO)_5L$ Complexes (M = Cr, Mo, W; L = N Donor, P Donor)

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MCD spectra are reported and discussed for $M(CO)_5L$ complexes (M = Cr, Mo, W; L = PCl_3, $P(Ph)_3$, PMe_3, thiazole, pyridine, pyrazine, pyridazine, piperidine, and NMe_3). The results were used to assign the absorption bands of the $M(CO)_5L$ complexes. From the sign of the *A* term belonging to the lowest ligand field transition, it could be deduced that this transition is directed to the d_{z^2} orbital, a result that is of importance for the understanding of the photochemistry of these complexes. Furthermore, the magnitude of this *A* term decreases going from piperidine to NMe_3, thiazole, pyridine, pyrazine, and pyridazine. The MCD spectrum of $Cr(CO)_5PCl_3$ closely resembles that of $Cr(CO)_6$, indicating that the electron distribution within the metal d orbitals of this pentacarbonyl complex has nearly octahedral symmetry.

Introduction

The photochemistry of $M(CO)_5L$ complexes (M = Cr, Mo, W; L = N-donor ligand, P-donor ligand) has been investigated both in solution and in rare gas matrices at 10 K.[1-5] The complexes show release of CO upon high-energy excitation and loss of L upon low-energy irradiation.

$$M(CO)_5L \xrightarrow[X]{h\nu} M(CO)_5X + L$$

$$M(CO)_5L \xrightarrow[X]{h\nu'} M(CO)_4LX + CO$$

X = ligand in solution, "vacancy" in the matrix; $\nu' > \nu$

This photochemical behavior has been explained by means of the one-electron d-orbital energy diagram shown in Figure 1.

The relative positions of the occupied d orbitals were derived from photoelectron spectra of these complexes.[6] Furthermore, the wavelength dependence of the photochemical behavior could only be explained on the assumption that the excited state, in which the d_{z^2} orbital (a_1) is occupied, has a lower energy than the corresponding state with an occupied $d_{x^2-y^2}$ (b_1) orbital.[1,2,4] However, since no proof for this assumption has been given, we found it necessary to establish the order of the d_{z^2} and $d_{x^2-y^2}$ orbitals with MCD spectroscopy. So far only a few metal carbonyl complexes have been studied with MCD. Zandstra et al. reported a MCD study of $Mn(CO)_5Br$ and used this technique for the assignment of the LMCT transition $Br(\pi) \rightarrow d_{z^2}$.[7]

In the course of our investigations Zink et al. reported some preliminary results of the MCD spectra of $W(CO)_5L$ complexes (L = Br^-, CS, N_3^-). In agreement with the results for $Mn(CO)_5Br$[7] the lowest CT transition was assigned.[2] Preliminary MCD results concerning the lowest LF band and its assignment to the $^1E_a(b_2{}^2e^3a_1) \leftarrow {}^1A_1(b_2{}^2e^4)$ transition have been communicated by Schreiner[8] and Boxhoorn.[9] In this article we discuss the assignment of this lowest LF transition in detail. Also other bands in the spectra of the $M(CO)_5L$ complexes are assigned, and the influence of L on the magnetic moment of the lowest LF transition is described.

Results

The absorption spectra of the $Cr(CO)_5$ N-donor complexes show only one CT band at about 250 nm, which corresponds with a positive *A* term in the MCD spectrum in conflict with the assignment $^1A_1 \leftarrow {}^1A_1$ (CT transition) by Wensky.[10] A LF transition is detected at about 420 nm, which coincides with a positive *A* term in the MCD spectra for L = piperidine and NMe_3 (Figure 2). For L = thiazole, pyridine, pyrazine, and pyridazine the center of this *A* term does not coincide with the maximum of the absorption band. This is caused by the fact that these ligands possess low-lying π^* orbitals leading to CT transitions from the metal to the ligand L. These transitions show in contrast to the LF transitions a solvent dependence and give rise to a *B* term in the MCD spectra, close to the *A* term of the LF transition (Figure 3, Table II). For $Cr(CO)_5pyr$ (pyr = pyrazine) a MCD term corresponding to the MLCT transition could hardly be observed. $Cr(CO)_5pyr$ shows some weak intraligand transitions, but no MCD effect

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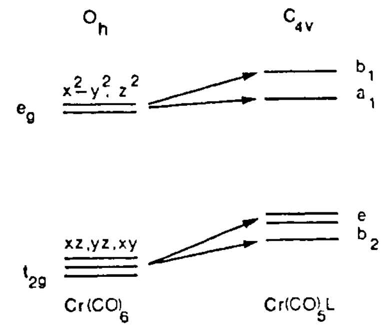

Figure 1. d-Orbital energy diagram for $Cr(CO)_6$ and $Cr(CO)_5L$ complexes.

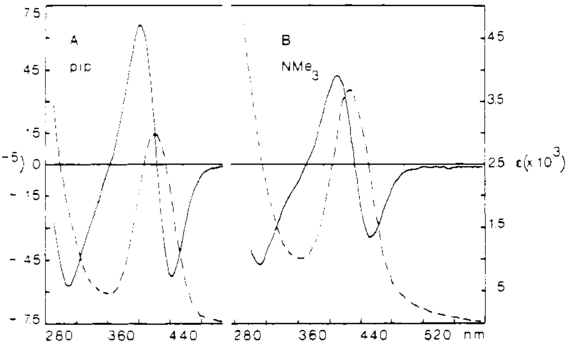

Figure 2. MCD (—) and absorption (---) spectra of $Cr(CO)_5pip$ (A) and $Cr(CO)_5NMe_3$ (B) in hexane.

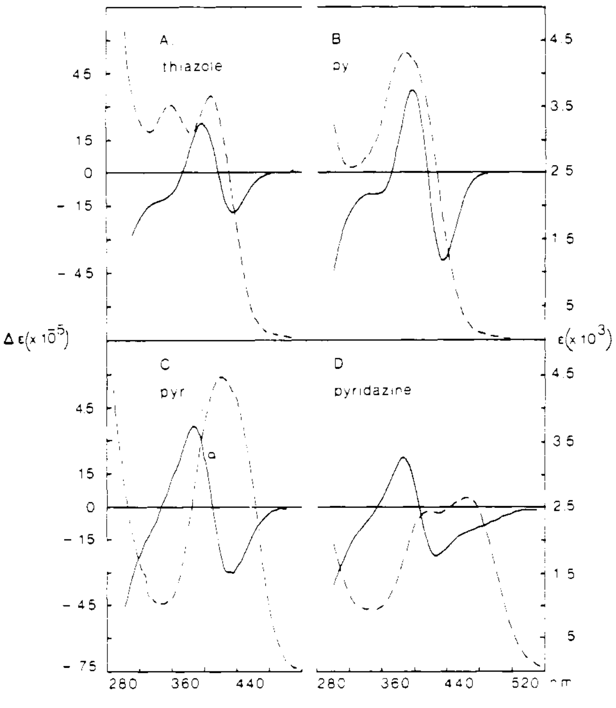

Figure 3. MCD (—) and absorption (---) spectra of $Cr(CO)_5L$ complexes in hexane: (A) L = thiazole; (B) L = pyridine; (C) L = pyrazine; (D) L = pyridazine.

could be observed for them. Apart from these MCD terms one more positive *B* term is observed for all N-donor complexes between 280 and 315 nm (see, e.g., Figure 3). The position of this term varies strongly with L and is, e.g., 311 nm for L = NMe_3 and 284 nm for L = pyridine. These N-donor complexes also show a change of slope of the MCD curve between 330 and 350 nm, which indicates the presence of a MCD term in that region.

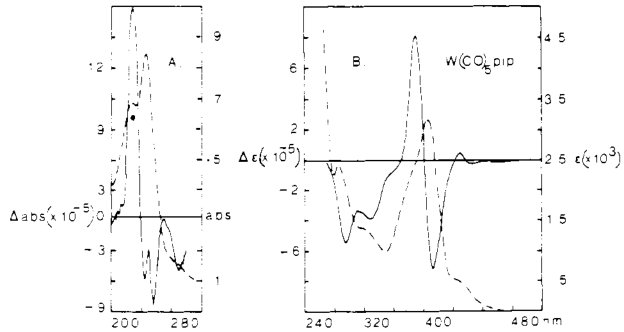

Figure 4. MCD (—) and absorption (---) spectra of $W(CO)_5pip$ in hexane: (A) between 200 and 300 nm; (B) between 270 and 520 nm (* = $W(CO)_6$, due to decomposition).

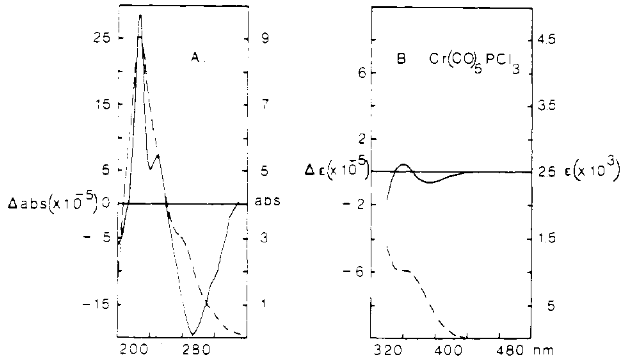

Figure 5. MCD (—) and absorption (---) spectra of $Cr(CO)_5PCl_3$ in hexane: (A) between 200 and 350 nm; (B) between 340 and 440 nm.

In contrast to the chromium complexes the absorption spectra of the molybdenum and tungsten complexes show several extra bands and shoulders, for which the right positions could only be deduced by using a curve-fitting procedure.[10] The same holds for the MCD spectra of these complexes, which show at least one more positive *B* term at 325 nm for $W(CO)_5pip$ (pip = piperidine). Furthermore, this tungsten complex possesses a positive *A* term coinciding with the weak ligand field $S \rightarrow T$ transition at 450 nm (see Figure 4). Going from the $Cr(CO)_5$ N-donor to the $Cr(CO)_5$ P-donor complexes, all absorption bands shift to higher energy as a result of increasing π back-bonding from the metal to the ligand L. This shift is also reflected in the MCD spectra. In the case of, e.g., $Cr(CO)_5PMe_3$ and $Cr(CO)_5P(Ph)_3$ the shape of the low-lying *A* term has totally changed. This is partly caused by overlap with MCD terms of the intense charge-transfer transitions and partly by the coincidence of several LF transitions as we will discuss later. A positive *B* term is detected for $Cr(CO)_5PMe_3$ and $Cr(CO)_5PCl_3$ coinciding with a band at 287 nm in the absorption spectrum of $Cr(CO)_5PCl_3$. The most striking observation is that for $Cr(CO)_5PCl_3$ a negative *B* term is found for the $Cr \rightarrow \pi^*(CO)$ transition at 225 nm contrary to $Cr(CO)_5PMe_3$, which shows a positive *A* term for the corresponding transition at 245 nm just as the N-donor complexes. It also has to be noted, however, that the appreciable shift of the position of this absorption band points to a change of character of the transition. Apart from this a negative *B* term was detected for the MLCT transition of the PCl_3 complex at 245 nm (see Figure 5). The absorption data in hexane solutions and the MCD results are collected in Tables I and II, respectively.

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Table I. UV-Visible Absorption Maxima of $M(CO)_5L$ Complexes (nm)[a]

assignments	$d \rightarrow \pi^*(CO)$	$d \rightarrow \pi^*(CO)$	$d \rightarrow d$	$d \rightarrow d$	$d \rightarrow d$	$d \rightarrow \pi^*(L)$	intraligand transitions
$Cr(CO)_5PCl_3$	224	287			362	245	
$Cr(CO)_5P(Ph)_3$	227				≈357		
$Cr(CO)_5PMe_3$	248				333		224
$Cr(CO)_5$(thiazole)	246				408 (411)[b]	358 (358)	
$Cr(CO)_5$py	241				387 (410)[b]	387 (382)	
$Cr(CO)_5$pyr	244				422 (412)	422 (445)	320–330
$Cr(CO)_5$(pyridazine)	244				411 (405)	464 (467)	
$Cr(CO)_5NMe_3$	250				428		
$Cr(CO)_5$pip	250				422		
$Mo(CO)_5$pip[c]	250		≈285	≈305	396		
$W(CO)_5$pip[c]	246		288	≈330, 375	407, ≈450		

[a] Hexane solutions. [b] Values derived by using a curve-fitting program are shown in parentheses. [c] Exact positions can only be resolved after using a curve-fitting program.[10]

Table II. Positions of the MCD Terms of $M(CO)_5L$ Complexes (nm)

terms[a]	$-B$	$+B$	$+A$	$+B$	$+A$	?[b]	$+B$
$Cr(CO)_5PCl_3$	226	294			371		
$Cr(CO)_5P(Ph)_3$			*c*	*c*	355[d]		
$Cr(CO)_5PMe_3$			245	294	340[d]		
$Cr(CO)_5$(thiazole)			252	304	417		≈340
$Cr(CO)_5$py			252	284	416		350
$Cr(CO)_5$pyr			246	289	410		
$Cr(CO)_5$(pyridazine)			246	292	406	340[d]	≈480
$Cr(CO)_5NMe_3$			*c*	311	433		
$Cr(CO)_5$pip			252	310	422		
$Mo(CO)_5$pip			245	287	394		
$W(CO)_5$pip			239	295	402	325, 355[d]	

[a] Terms for the transitions in Table I. [b] Character and/or sign of the MCD term in doubt. [c] Not measured. [d] In doubt.

Discussion

$M(CO)_5$(N-donor ligand). It has already been mentioned in the Introduction that the d-orbital energy diagram of the $M(CO)_5L$ complexes (Figure 1) is derived both from the photoelectron results and from the photochemical behavior of these compounds. Going from $M(CO)_6$ to $M(CO)_5L$, the t_{2g} orbitals split into two levels with symmetry $e(d_{xz},d_{yz})$ and $b_2(d_{xy})$, respectively. The photoelectron spectra show that the e level is higher in energy than b_2.[6] From the observed release of L after long-wavelength irradiation of the $M(CO)_5L$ complexes, it has been deduced that the LF excited state in which the σ-antibonding d_{z^2} orbital, with symmetry a_1 being involved, is lower in energy than the state with $d_{x^2-y^2}(b_1)$.[1,2,4] This assumption did, however, not agree with the results from others,[11,12] and we wondered whether the MCD spectra could substantiate the validity of this conclusion.

For the lowest LF band two assignments are possible, depending on the relative order of the transitions to the $a_1(d_{z^2})$ and $b_1(d_{x^2-y^2})$ levels, viz., $^1E_a(b_2{}^2e^3a_1) \leftarrow {}^1A_1(b_2{}^2e^4)$ or $^1E_b(b_2{}^2e^3b_1) \leftarrow {}^1A_1(b_2{}^2e^4)$. Although both transitions give rise to an A term,[13] the sign of this MCD will be different for both transitions.

The sign of the A term for both transitions may be inferred from symmetry considerations by using a complex d-orbital basis, in which the orbital angular momentum operator is diagonalized.

In this basis we have d_{z^2} belonging to the a_1 representation, $d_{x^2-y^2}$ to b_1 and d_{xy} to b_2 and $d_{-1} = 2^{-1/2}(d_{xz} - id_{yz}) \equiv e(-1)$ together with $d_1 = -2^{-1/2}(d_{xz} + id_{yz}) \equiv e(+1)$ to the e representation of the C_{4v} point group. The excited-state functions for the $^1E(e \rightarrow a_1)$ and the $^1E(e \rightarrow b_1)$ states can be constructed from these one-electron orbitals with use of the tabulated V coefficients for point group C_{4v}.[14a] Leaving out doubly occupied orbitals, we find

$$|E_a(+1)\rangle = |e(-1)\rangle|a_1\rangle \qquad |E_a(-1)\rangle = |e(+1)\rangle|a_1\rangle$$

For the other excited state, we find

$$|E_b(+1)\rangle = |e(+1)\rangle|b_1\rangle \qquad |E_b(-1)> = |e(-1)\rangle|b_1\rangle$$

In this notation singlet functions are implied.

Selection rules for left- and right-handed circularly polarized light are derived from the matrix elements of the electric dipole moment operators $2^{-1/2}(m_x - im_y)$ and $2^{-1/2}(m_x + im_y)$, respectively, between the ground state $^1A_1$ and the excited state ^1E.

Using the same V coefficients and the symmetry properties of these operators, we readily find that LCP light is absorbed by the E(−1) component and RCP light by the E(+1) component of the excited state. In a magnetic field the degeneracy of the E states is lifted. This splitting is governed by the matrix elements of the magnetic dipole moment operator $-\beta L_z$ for a magnetic field directed along the z axis. The matrix elements of this operator are well-known,[14b] and for the energy shift, $\Delta E = \beta H\langle L_z\rangle$, we find, e.g.

$$\beta H\langle E_a(+1)|L_z|E_a(+1)\rangle = \beta H\langle e(-1)|l_z|e(-1)\rangle = -\beta H$$

So the $E_a(e \rightarrow a_1)$ state is split, the $E_a(-1)$ component being higher ($+\beta H$) and the $E_a(+1)$ component lower ($-\beta H$) while for the $E_b(e \rightarrow b_1)$ state we find exactly the opposite result, $E_b(+1)$ being the higher component and $E_b(-1)$ the lower one, in accordance with a magnetic moment $+\beta$ for the $E_a(e \rightarrow a_1)$ state and $-\beta$ for the $E_b(e \rightarrow b_1)$ state in units $\hbar$. The measured MCD is given by the difference in absorption for left- and right-handed circularly polarized light: $A_L - A_R$.

From the above considerations we predict for the $^1E_a(e \rightarrow a_1)$ transition a dispersion curve that is typical for a positive A term as at lower energy the RCP light is absorbed and at higher energy the LCP light is absorbed. In the same way we find a negative A term for the $^1E_b(e \rightarrow b_1)$ transition. These results may be obtained by using the method of reduced matrix elements;[7,14a] however, in this simple case a direct approach seems more appropriate. For all $M(CO)_5$ N-donor complexes positive A terms are observed, which means that the lowest LF transition is directed to the d_{z^2} orbital (a_1). This result agrees with the order of states derived from the photochemical data.

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The value of the MCD *A* term is related to the magnetic moment (μ) of the excited state according to the equation

$$A/D = \mu/2$$

D represents the dipole strength of the transition. From this equation we find for pure metallic 3d orbitals $\mu = 1.0\ \mu_B$ for the ${}^1E_a \leftarrow {}^1A_1$ transition, while by the method of moments a value for μ of 0.7 μ_B is deduced for the *A* term observed for $Cr(CO)_5pip$. A lower value of about 0.4 μ_B is obtained for $Cr(CO)_5NMe_3$. This decrease is probably caused by a lowering of local C_{4v} symmetry as a result of steric hindrance of the NMe_3 rotation around the metal–nitrogen bond.[15] A decrease of the magnetic moment with respect to the piperidine complex is also expected when the σ donation of the N-donor ligand decreases and/or the π back-bonding to the ligand L increases. This is in fact observed for the $Cr(CO)_5L$ complexes with L = thiazole, pyridine, pyrazine, and pyridazine. Direct calculation of μ is not possible for the pyridine and pyrazine complexes, because of the coincidence of LF and metal to ligand L charge-transfer transitions. This prevents the estimation of the dipole strength *D* of the LF transitions of the pyridine and pyrazine complexes. For L = thiazole and pyridazine, the separation between the MLCT and the LF band is sufficient to estimate *D*. For these complexes values of $\mu = 0.2\ \mu_B$ and $\mu = 0.4\ \mu_B$, respectively, are calculated from the spectra, which are indeed much lower than the corresponding value for the piperidine complex. For the pyridine and pyrazine complexes μ can only be obtained if a simple curve-fitting technique, which is based on the known positions of the LF transition (coinciding with the intersection of the MCD *A* term and the base line), is applied to the absorption band. In this way values of 0.4 μ_B and 0.6 μ_B are deduced for the magnetic moments of the pyridine and pyrazine complexes, respectively. The reliability of these two values is, however, very speculative.

The MLCT transitions themselves give rise to a *B* term in the MCD spectrum, which is found at higher energy with respect to the *A* term for L = thiazole and pyridine and at lower energy for L = pyridazine. For L = pyrazine, a MCD term could hardly be observed for the MLCT transition.

All complexes show a change of the slope of the MCD curve between 330 and 350 nm, an effect which is most pronounced for $W(CO)_5pip$. This point of inflection is tentatively assigned to a very weak MCD term corresponding to the ${}^1E_b(b_2{}^2e^3b_1{}^1) \leftarrow {}^1A_1(b_2{}^2e^4)$ transition for which a negative *A* term is expected. The point of inflection is found at nearly the same position for all pentacarbonyls with a nitrogen-donor ligand L. This agrees with the fact that when a constant energy separation is assumed between the $d_{x^2-y^2}$ and d_{xy} levels of all these pentacarbonyls, the shift of the ${}^1E_b(b_2{}^2e^3b_1) \leftarrow {}^1A_1(b_2{}^2e^4)$ transition within this series will only depend on the splitting ($\Delta\pi$) between the occupied orbitals. This splitting is directly deduced from the photoelectron spectra and only varies from 2580 cm^{-1} for $Cr(CO)_5py$ (py = pyridine) to 2180 cm^{-1} for $Cr(CO)_5(thiazole)$.[6] The $W(CO)_5pip$ complex shows a positive *B* term at 325 nm, which is not found for the corresponding Cr and Mo compounds, and therefore probably belongs to a spin-forbidden transition.

The positive *B* term, found between 284 and 311 nm for all nitrogen-donor complexes, corresponds to a very weak band in the absorption spectrum. We assign this MCD term to the symmetry-forbidden ${}^1B_2(b_2{}^1e^4a_1{}^1) \leftarrow {}^1A_1(b_2{}^2e^4)$ LF transition, because of the variation of its position with L. No such shifts are expected for the fourth (forbidden) LF transition ${}^1A_2(b_2{}^1e^4b_1{}^1) \leftarrow {}^1A_1(b_2{}^2e^4)$, which represents a transition from d_{xy} to $d_{x^2-y^2}$ and therefore will hardly depend on L. For the very intense metal to CO charge-transfer band at about 250 nm a positive *A* term is observed, which means that this band belongs to an ${}^1E \leftarrow {}^1A_1$ transition in contrast to the assignment of Wensky.[10]

$Cr(CO)_5$(P-donor ligand). Going from N-donor to P-donor ligands, the absorption maxima are blue shifted. For the lowest ligand field transition a positive *A* term is found in the MCD, in agreement with the N-donor complexes. However, this *A* term has partly collapsed and also partly disappeared under the intense MCD terms of the CT transitions. The decrease of the *A* term will probably be caused by coincidence of different LF transitions in the case of these P-donor complexes.[16] A very striking result is the different MCD effect observed for $Cr(CO)_5PMe_3$ and $Cr(CO)_5PCl_3$ in the region 225–250 nm. The absorption band of $Cr(CO)_5PMe_3$ at 248 nm corresponds with an *A* term in the MCD spectrum in agreement with the N-donor complexes. The 225-nm band of $Cr(CO)_5PCl_3$, however, corresponds to a *B* term, a result which is in accordance with the MCD effect of $Cr(CO)_6$ in this region.[17] It has to be noted that not only the character of the MCD term but also the positions of the absorption bands of $Cr(CO)_5PCl_3$ are closely analogous to those of $Cr(CO)_6$.[17] This result is in agreement with the PES spectrum of $Cr(CO)_5PCl_3$, which shows a coincidence of the e and b_2 metal orbitals.[18] It also agrees with the fact that the photochemical behavior of this complex can only be explained if it is assumed that the $d_{x^2-y^2}(b_1)$ and $d_{z^2}(a_1)$ levels nearly coincide.[16] Apparently, the distribution of electron density within the metal orbitals of $Cr(CO)_5PCl_3$ has nearly octahedral symmetry as it has for $Cr(CO)_6$. The *B* term of $Cr(CO)_5PCl_3$ at about 290 nm is not assigned to a LF transition as in the case of the N-donor complexes but to a metal to CO CT transition as for $Cr(CO)_6$. Apart from these *B* terms $Cr(CO)_5PCl_3$ shows one more negative *B* term at 245 nm, which belongs to the metal to PCl_3 CT transition.

Experimental Section

The $M(CO)_5L$ complexes were prepared from the corresponding $M(CO)_6$ molecules by adding the ligand L to the hexacarbonyl in a refluxing hydrocarbon solvent or by adding the ligand to the tetrahydrofuran–pentacarbonyl complex, which was prepared by irradiation of the hexacarbonyl in a photochemical reactor (Rayonet Type RPR-208). The preparative details have been described in the literature.[4,6,19] Exceptions are the synthesis of $Cr(CO)_5NMe_3$ and $Cr(CO)_5PMe_3$, which could more easily be obtained by the method of Koelle[20] and of Connor,[21] respectively. All complexes were characterized by infrared spectroscopy and by elemental analysis. Decomposition of the N-donor complexes in highly diluted hexane solutions was detected in the absorption spectra. Therefore no reliable extinction coefficients could be obtained for these complexes in the UV region.

The MCD spectra were recorded with a homemade instrument, which essentially consisted of a Hilger and Watts Model D 330 monochromator, a Morvue Model PEM-3 photoelastic modulator, and a PAR Model 186 synchrohet-lock-in amplifier. The magnetic field was provided by a superconducting magnet from Oxford Instruments Model Spectromag 4. The instrument has a sensitivity of about $5 \times 10^{-6}\ \Delta A$ units, and it could be used reliably in the spectral region of 750–220 nm. The concentrations were chosen such that the optical density was about 0.75. The spectra were measured with a band-pass of 3 nm at a magnetic field strength of 7.0 T and were corrected for the base line. The spectra were recorded at room

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temperature. Between 200 and 220 nm the MCD spectra are less reliable. Absorption spectra were measured on a Perkin-Elmer Hitachi 200 spectrophotometer. Solvents (Merck Uvasol) were dried and used without further purification.

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Registry No. Cr(CO)$_5$PCl$_3$, 18461-41-1; Cr(CO)$_5$PPh$_3$, 14917-12-5; Cr(CO)$_5$PMe$_3$, 26555-09-9; Cr(CO)$_5$(thiazole), 55293-31-7; Cr(CO)$_5$py, 14740-77-3; Cr(CO)$_5$pyr, 66179-02-0; Cr(CO)$_5$(pyridazine), 54070-89-2; Cr(CO)$_5$NMe$_3$, 15228-26-9; Cr(CO)$_5$pip, 15710-39-1; Mo(CO)$_5$pip, 19456-57-6; W(CO)$_5$pip, 31082-68-5.

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Donor Properties of Metallomacrocyclic Tetrapyrrole Pigments with *sym*-Trinitrobenzene

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The interactions of metallo derivatives of macrocyclic tetrapyrrole pigments, pheophytin *a* (pheo), phthalocyanin (phth), and tetraphenylporphyrin (TPP) with *sym*-trinitrobenzene (TNB) have been studied with use of spectroscopic methods. These macrocyles form 1:1 molecular complexes with the acceptor. The association constants (K) for the interactions follow the decreasing order of binding as pheo > phth > TPP. The divalent metal ions influence the values of K for the various metallo TPP derivatives, and the relative order of stabilities decrease as Co > Cu ≈ VO > Ni > Zn. The stereochemistry of M(TPP) and the electronic configuration of the metal ions are shown to contribute to the magnitudes of K. The acceptor strongly quenches the fluorescence of the metallo macrocycles, and the quenching constant decreases as pheo > phth > TPP. The formation of exciplexes is postulated on the basis of the rate of bimolecular quenching constants and solvent effects.

Studies on molecular complexes of natural and synthetic tetrapyrrole pigments with diverse organic molecules have received considerable attention in the past few years.[1–5] In principle, the tetrapyrrole pigments can function both as a donor and an acceptor.[6] Introduction of metal ions can alter this behavior depending on their oxidation states and coordination numbers. In an earlier study involving porphyrins and various acceptors, it has been suggested that charge-transfer forces contribute to a small extent to the binding strength of these complexes.[7] We have been interested in the molecular complexation of macrocyclic systems in general, and the present study is directed toward the ability of tetrapyrrole pigments to form molecular complexes with a π acceptor, *sym*-trinitrobenzene (TNB), and the functional role of metal ions in the binding characteristics. The major objective is to elucidate the mode and site of interaction between donor and acceptor so that the additional knowledge of properties and functions of bioanalogues, chlorophyll, and heme might be gained.

The tetrapyrrole pigments chosen for the study are pheophytins *a* (pheo), phthalocyanin (phth), and 5,10,15,20-tetraphenylporphyrin (TPP) as their Zn(II) derivatives. The different macrocycles provide a range of sizes and chromophores; TPP is a N$_4$ chromophore with four benzene rings at the 5, 10, 15, and 20 positions, phth is a N$_8$ chromophore with four benzene rings fused to the pyrrole moieties, and pheo is a N$_4$ chromophore with an additional cyclopentanone ring in the tetrapyrrole skeleton (Figure 1). The TPP derivatives of the different divalent metal ions VO, Co, Ni, Cu, Zn, Cd, and Pd are chosen for study to define the functional role of these in the donor capacity of the pigments. Electronic absorption spectral methods have been used to evaluate the binding constants and associated thermodynamic properties. Emission data are also used to probe into the possible formation of exciplexes in these systems. The ^{1}H NMR measurements are valuable in ascertaining the site of interaction in these complexes. The ESR data are useful in assessing the axial perturbation on complexation. The results of these studies are informative in arriving at the nature of the stabilization forces and the relative orientations of the donor and acceptor.

Experimental Section

The Zn(II) derivative of pheo, phth, and TPP were prepared according to the published methods.[8–10] TPP was obtained from Aldrich Chemicals and the metal derivatives were synthesized and purified as described elsewhere.[9] TNB was obtained from BDH and crystallized twice from benzene (mp 122 °C). The solvents were purified and distilled and purged with pure dry nitrogen before use. The visible absorption spectral method has been used for the determination of association constants. The sample handling and other details concerning the spectrometers used are the same as described earlier.[11] The concentration of the metallo macrocycles was held constant (10^{-5} M), and that of TNB was varied (10^{-4}–10^{-1} M). A Perkin-Elmer MPF 44A spectrometer was used for fluorescence measurements. The ESR spectra were recorded on a Varian E109 ESR spectrometer using toluene glasses.

Results and Discussion

The visible absorption spectra of the metallomacrocycles exhibit well-defined intense absorption bands, the position of which depends on the nature of the metal ion and the macrocycle. Addition of TNB lowers the intensities of these bands, indicating the formation of molecular complexes. More than

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