clusters. This set of three structures is complete only with Fe. The clusters $[Co_8S_6(SPh)_8]^{4-,5-}$[13] and $Co_7S_6(PPh_3)_5Cl_2$[14] (with a structure similar to that of **5**) are known but no Co prismane has yet been synthesized. Interconversion of clusters with these cores by capping reactions may be feasible (with some dimensional change in the lower ring of **5**), inasmuch as the cores of $\mathbf{1}^{3-}$ ($[Fe_6S_6]^{3+}$, 69e) and **5** ($[Fe_7S_6]^{3+}$, 77e) differ by Fe(0) and those of **5** and **4** ($[Fe_8S_6]^{5+}$, 83e) by Fe(II). Indeed, **1** has been doubly capped with M = Mo(0) and W(0),[21] affording clusters with $[M_2Fe_6S_6]^{2+,3+}$ cores (82e, 81e). These are nearly isoelectronic with **4** and with cubic $Fe_8S_6Cl_8$, which, together with at least one other cluster product, has been isolated from the reaction system affording **5**. The syntheses, properties, and reactions of these and related clusters will be the subject of a future report. Lastly, our results together with the outstanding work of Fenske et al.[14,17] emphasize the advantage of phosphine ligands and low-polarity solvents in the assembly of high-nuclearity metal–sulfide clusters.

Acknowledgment. This research was supported by National Institutes of Health Grant GM 28856. We thank Professor B. M. Foxman for helpful advice and Professor D. Coucouvanis for a preprint of ref 7b. I.N. was supported by the Takemoto Oil & Fat Co., Ltd., Gamagori, Japan.

Supplementary Material Available: Tables of positional and thermal parameters for $Fe_7S_6(PEt_3)_4Cl_3$ (2 pages); a table of calculated and observed structure factors for $Fe_7S_6(PEt_3)_4Cl_3$ (14 pages). Ordering information is given on any current masthead page.

Department of Chemistry
Harvard University
Cambridge, Massachusetts 02138

I. Noda
B. S. Snyder
R. H. Holm*

Received June 2, 1986

Articles

Contribution from the Chemistry Department, College of General Education,
Osaka University, Toyonaka, Osaka 560, Japan

Singlet–Triplet Transitions of Aromatic Compounds Coordinating to a Paramagnetic Chromium(III) Ion

Takeshi Ohno,* Shunji Kato,*[†] Sumio Kaizaki,*[‡] and Ichiro Hanazaki*[§]

Received September 27, 1985

Chromium(III) compounds of 2,2′-bipyridine, 4,7-diphenyl-1,10-phenanthroline, acetylacetone, benzoylmethane, and phthalocyanine exhibit a fine structured absorption band with a moderate intensity below the strong band of the ligand excitation (^{1}LE). A mirror-image relation was observed between the absorption band of the chromium(III) compound and the phosphorescence band of the ligand coordinating to Be^{2+}, Zn^{2+}, or Rh^{3+}. The structured bands are assigned to a spin-allowed transition in which a quartet state composed of ^{3}LE and $^{4,2}(d^3)$ is excited. The intensities of the structured absorption bands are in agreement with those calculated on the basis of the intensity borrowing from the ^{1}LE transition via the charge-transfer excited state lying above. The assignment is consistent with the fact that a magnetic circular dichroism band of the chromium(III) compound was found in the same energy region as the structured absorption band.

Introduction

Electronic absorption bands of tervalent chromium compounds have been assigned to ligand field d–d transitions (LF), charge-transfer transitions (CT), and intraligand excitation transitions (LE).[1-4] Though most of the bands are structureless and ascribed to spin-allowed transitions of LF, CT, and LE, some structured bands with low intensity (molar absorption coefficient $\epsilon < 1$ M^{-1} cm^{-1}; 1 M = 1 mol·dm^{-3}) are characteristic of the spin-forbidden LF transition in the red region and those with high intensity ($\epsilon > 10^4$ M^{-1} cm^{-1}) are characteristic of LE in large ligands having conjugated π electrons in the visible and ultraviolet regions.[4] However, some well-structured bands with moderate intensity of 300–2000 M^{-1} cm^{-1}, which are seen on coordination of aromatic compounds to a chromium(III) ion, are left unassigned. For instance, 2,2′-bipyridine (bpy) coordinating to a paramagnetic chromium(III) ion presents a band at 22 000–26 000 cm^{-1} having three peaks with moderate intensity (300–2000 M^{-1} cm^{-1}) below an intense LE band at 32 050 cm^{-1}. König and Herzog,[5] who observed the strange band group of $[Cr(bpy)_3]^{3+}$ for the first time, found no explanation for the intensity and the band structure. More recently, Serpone et al.[6] observed a structured band in the electronic absorption spectra of several chromium(III) compounds of bpy or 1,10-phenanthroline. The intensities (270–1700 M^{-1} cm^{-1}) and energies (20 700–22 500 cm^{-1}) of the lowest bands varying with substituents in bpy and 1,10-phenanthroline could not be fully explained in terms of LF transition. Hanazaki et al.[7] assigned a similarly structured band group at 22 000–28 000 cm^{-1} of $Cr(acac)_3$ to a spin-allowed LE transition, which is intensified on coordination of acac to chromium(III) ion. According to them, the excited state is mainly constructed from the triplet excited state of aceylacetonate ion (^{3}LE) and the quartet and the doublet states of the metal center via direct coupling between unpaired electrons in the ligand and the metal center. However, since the transition energy to ^{3}LE was unknown at that time, some workers preferred to assign the first spike at 23 260 cm^{-1} to the LF transition.[8]

The aim of the present publication is to reexamine the moderate-intensity (300–2000 M^{-1} cm^{-1}), fine-structured bands of acetylacetonate ion, dibenzoylmethanate ion, 2,2′-bipyridine, 4,7-diphenyl-1,10-phenanthroline, and phthalocyaninate ion coordinating to a chromium(III) ion, which are observed at 24 000,

---

[†] Present address: Kobe-gakuin University, Igawadani, Nishi, Kobe 673, Japan.

[‡] Chemistry Department, Nara Women's University, Nara, Nara 630, Japan.

[§] Institute for Molecular Science, Myodaiji, Okazaki 444, Japan.

(1) Jørgensen, C. K. *Modern Aspects of Ligand Field Theory*; North-Holland: Amsterdam, 1971.
(2) Ballhausen, C. J. *Introduction to Ligand Field Theory*; McGraw-Hill: New York, Oxford, 1962.
(3) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984.
(4) Gouterman, M.; Hanson, L. K.; Khalil, G.-E.; Leenstra, W. R.; Buchler, J. W. *J. Chem. Phys.* **1975**, *62*, 2343–53.
(5) König, E.; Herzog, S. *J. Inorg. Nucl. Chem.* **1970**, *32*, 585–99.
(6) Serpone, N.; Jamieson, M. A.; Hoffman, M. Z.; Bolletta, F.; Maestri, M. *J. Am. Chem. Soc.* **1979**, *101*, 2907–16.
(7) (a) Hanazaki, I.; Hanazaki, F.; Nagakura, S. *J. Chem. Phys.* **1969**, *50*, 265–76. (b) Hanazaki, I.; Hanazaki, F.; Nagakura, S. *J. Chem. Phys.* **1969**, *50*, 276–86. (c) Hanazaki, I.; Nagakura, S. *Inorg. Chem.* **1969**, *8*, 648–54.
(8) Fatta, A. M.; Lintvedt, R. L. *Inorg. Chem.* **1971**, *10*, 478–81.

0020-1669/86/1325-3853$01.50/0 © 1986 American Chemical Society

20 000, 23 000, 22 000, and 8300 cm^{-1}, respectively, below the intense LE band. Absorption spectra at low temperature and magnetic circular dichroism spectra of the chromium(III) compounds were taken to resolve the complex bands into some components or vibronic peaks. Phosphorescence spectra of the ligands coordinating to light-metal ions were measured to obtain singlet–triplet transition energies of the ligands. Nanosecond laser photolysis spectroscopy was also utilized to identify the lowest excited state of a chromium(III) compound.

Experimental Section

The following abbreviations are used for ligands: acetylacetonate ion = acac; dibenzoylmethanate ion = dbm; 2,2′-bipyridine = bpy; 4,7-diphenyl-1,10-phenanthroline = dp-phen; phthalocyanate ion = PC; oxalate ion = ox; ethylenediamine = en; 3-chloroacetylacetonate ion = acacCl; 3-bromoacetylacetonate ion = acacBr; malonate ion = mal; tetrasulfonylphthalocyaninate ion = TSPC; 2,2′:6′,2″-terpyridine = terpy; dimethylformamide = DMF.

Literature methods were used to prepare and purify the following compounds: $[Cr(bpy)_3](ClO_4)_3\cdot 2H_2O$,[9] $Cr(acac)_3$,[10] $Cr(dbm)_3$,[10] Cr(PC)(OH),[11] $K[Cr(ox)_2(bpy)]$,[12] $[Cr(ox)(bpy)_2]Cl$,[12] $[Cr(acac)(en)_2]Cl_2$,[13] $[Cr(acac)_2(en)]Cl\cdot 1.5H_2O$,[13] their 3-halogeno acetylacetonato complexes $[Cr(acacCl)_3$[13] and $Cr(acacBr)_3$,[13] $Be(acac)_2$,[14] $Be(dbm)_2$,[14] and $[Rh(bpy)_3]Cl_3\cdot 4.5H_2O$.[15] $Na[Cr(mal)_2(bpy)]$ was obtained as follows. One gram of $CrCl_3(DMF)(bpy)$ was dissolved in 10 mL of a H_2O–dimethylformamide (1:1) mixture containing 0.54 g of malonic acid and 0.54 g of Na_2CO_3 on a water bath at about 70 °C. After the reaction mixture changed from green to red, the solution was filtered off. The filtrate was allowed to stand in a refrigerator overnight. Then, red crystals were obtained. This crude compound was recrystallized from methanol–ether. Anal. Calcd for $Na[Cr(mal)_2(bpy)]\cdot 2.5H_2O$: C, 40.01; H, 3.57; N, 5.83. Found: C, 40.14; H, 3.50; N, 5.73. Formation of $Zn(terpy)^{2+}$ in solution containing the free ligand and excess $Zn(NO_3)_2$ was spectroscopically ascertained PbPC (Tokyo Kasei) was purified by vacuum sublimation.

The absorption spectra of the chromium(III) compounds in a mixed solvent of methanol and ethanol (1:4) were measured at 77 K with a Shimadzu MPS-5000 spectrophotometer. The emission spectra of Zn(II) compounds and Be(II) compounds were obtained at 77 K with a Hitachi MPF-2A spectrofluorometer. The magnetic circular dichroism (MCD) spectra were recorded in a magnetic field of 1.5 T (1 T = 10^4 G) with a Jasco MOE-1 spectropolarimeter in aqueous solutions at room temperature. Absorption spectra of excited Cr(PC)(OH) in *N,N′*-dimethylacetamide (DMA) and PbPC in dimethyl sulfoxide (Me_2SO) were obtained by means of nanosecond laser photolysis kinetic spectroscopy.[16]

Theory

The aim of this section is to estimate a probability of optical transition to an excited state with a configuration of ^3LE of an aromatic compound (L) coordinating to a paramagnetic chromium(III) ion. The quartet multiplicity wave functions for a five-electron system of $CrLA_4$, two from the aromatic compound (L) and three from the chromium(III) ion, are constructed in the following way. The zero-order functions for the ground state (^4G), the lower charge-transfer states (^4CTa and ^4CTs), and the lower ligand excited states with a local multiplicity of singlet ($^4(^1LE)$) and triplet ($^4(^3LE)$) are expressed as[7b]

$$^4G = |d_od_sd_aq\bar{q}| \tag{1}$$

$$^4CTs = |d_oq^*d_aq\bar{q}| \tag{2}$$

$$^4CTa = |d_od_sq^*q\bar{q}| \tag{3}$$

$$^4(^1LE) = (1/2)^{1/2}[|d_od_sd_a\bar{q}q^*| - |d_od_sd_aq\bar{q}^*|] \tag{4}$$

$$^4(^3LE)(1) = (1/6)^{1/2}[2|\bar{d}_od_sd_aqq^*| - (|d_od_sd_a\bar{q}q^*| + |d_od_sd_aq\bar{q}^*|)] \tag{5}$$

$$^4(^3LE)(2) = (1/12)^{1/2}[3|d_o\bar{d}_sd_aqq^*| - |\bar{d}_od_sd_aqq^*| - (|d_od_sd_aq\bar{q}^*| + |d_od_sd_a\bar{q}q^*|)] \tag{6}$$

$$^4(^3LE)(3) = (1/20)^{1/2}[4|d_od_s\bar{d}_aqq^*| - |\bar{d}_od_sd_aqq^*| - |d_od_sd_aq\bar{q}^*| - (|d_od_sd_a\bar{q}q^*| + |d_od_sd_aq\bar{q}^*|)] \tag{7}$$

where d_o, d_s, and d_a are d_{xy}, $(1/2)^{1/2}(d_{zx} + d_{yz})$, and $(1/2)^{1/2}(d_{zx} - d_{yz})$, respectively, and q and q^* are HOMO and LUMO of ligand, respectively. The functions $^4(^3LE)(1)$–$^4(^3LE)(3)$ correspond to the final quartet states ($S = {}^3/_2$) in which unpaired electrons of the ligand ($S = 1$) couple with unpaired electrons of the metal center ($S = {}^1/_2$ and ${}^3/_2$). The $^4(^3LE)$ configurations are of the same spin multiplicity as the ground state but optically forbidden in zero order because of their triplet character in the ligand excitation. However, the CT configurations, ^4CTs and ^4CTa, mix with both $^4(^1LE)$ and $^4(^3LE)$ so that the resultant $^4(^3LE)$ states have a $^4(^1LE)$ character. This makes the $^4(^3LE)$ states optically allowed. The second-order perturbation treatment gives a coefficient of $^4(^1LE)$ mixed in $^4(^3LE)(j)$ as

$$(1/12)^{1/2}(\langle d_s|H|q\rangle^2 + \langle d_a|H|q\rangle^2)/(E_3 - E_{CT})(E_3 - E_1)$$

$$(1/24)^{1/2}(4\langle d_s|H|q\rangle^2 + \langle d_a|H|q\rangle^2)/(E_3 - E_{CT})(E_3 - E_1)$$

$$(5/8)^{1/2}(\langle d_a|H|q\rangle)^2/(E_3 - E_{CT})(E_3 - E_1)$$

for j = 1, 2, and 3, respectively, where E_3, E_1, and E_{CT} are the state energies of $^4(^3LE)$, $^4(^1LE)$, and ^4CT, respectively.[7b] Consequently, the electric dipole transition moments for the transitions to $^4(^3LE)(j)$ are expressed by the following equations with disregard of intensity borrowing from the CT transition:

$$\langle G|\mu|^4(^3LE)(1)\rangle \simeq \frac{\langle d_s|H|q\rangle^2 + \langle d_a|H|q\rangle^2}{12^{1/2}(E_3 - E_{CT})(E_3 - E_1)}\langle G|\mu|^4(^1LE)\rangle \tag{8}$$

$$\langle G|\mu|^4(^3LE)(2)\rangle \simeq \frac{4\langle d_s|H|q\rangle^2 + \langle d_a|H|q\rangle^2}{24^{1/2}(E_3 - E_{CT})(E_3 - E_1)}\langle G|\mu|^4(^1LE)\rangle \tag{9}$$

$$\langle G|\mu|^4(^3LE)(3)\rangle \simeq \frac{5\langle d_a|H|q\rangle^2}{8^{1/2}(E_3 - E_{CT})(E_3 - E_1)}\langle G|\mu|^4(^1LE)\rangle \tag{10}$$

It is noticeable that eq 8–10 contain no term due to the spin–orbit interaction. If the three $^4(^3LE)$ states nearly degenerate, the total oscillator strength is expressed as

$$\begin{aligned} f(^4(^3LE)) &\propto E_3\sum_{j=j}^{3}\langle G|\mu|^4(^3LE)(j)\rangle^2 \\ &= {}^1\!/_4[3\langle d_s|H|q\rangle^4 + \langle d_a|H|q\rangle^4 + \\ &\qquad 2\langle d_s|H|q\rangle^2\langle d_a|H|q\rangle^2]\frac{^3E}{(E_3 - E_1)^2(E_3 - E_{CT})^2}\langle G|\mu|^4(^1LE)\rangle^2 \end{aligned}$$

Since q is symmetric for acac, a ratio (ρ) of the oscillator strength for $^4G \rightarrow {}^4(^3LE)$ to $^4G \rightarrow {}^4(^1LE)$ is given by

$$\rho = \frac{f(^4(^3LE))}{f(^4(^1LE))} = \frac{E_3 \times 3\langle d_s|H|q\rangle^4}{E_1 \times 4(E_3 - E_{CT})^2(E_3 - E_1)^2} \tag{11}$$

The ratio (ρ) for bpy, for which q is antisymmetric, is given by the same equation as eq 11 by replacing d_a for d_s. $\langle d_s|H|q\rangle = 2C_O\beta_{dO}$ for $Cr(acac)A_4^{2+}$ and $\langle d_a|H|q\rangle = 2C_N\beta_{dN}$ for $Cr(bpy)A_4^{3+}$, where C_O and C_N are the AO coefficients of MO q on oxygen and nitrogen, respectively, and β_{dO} and β_{dN} are the resonance integrals between a 3d AO and 2p AO's on oxygen and nitrogen, respectively. With use of the previously determined values[7a,b] of C_O (−0.37), β_{dO} (−1.63 eV), E_{CT} (4 eV), E_1 (4.35 eV) and E_3 (2.34 eV), ρ is calculated to be 0.077 for $Cr(acac)A_4^{2+}$. For $Cr(bpy)A_4^{3+}$, $\beta_{dN} = -1.3$ eV from the existent data,[7a,b] $C_N = 0.72$ and $E_1 = 4.2$ eV from the SCF–CI calculation for free bpy, and $E_3 = 2.7$ eV from the phosphorescence origin of $Rh(bpy)_3^{3+}$. An estimation with these parameters gives $\rho = 0.04$, assuming the same value for E_{CT} as for $Cr(acac)A_4^{2+}$.

The present results are based on the single-ligand wave functions given in eq 2–7. For the complex with more than one ligand, sets of wave functions similar to eq 2–7 should be added. However, this addition does not cause any appreciable modification of the present results. As has been shown in ref 7, the interactions between the CT and ^3LE configurations in the other ligands are negligibly small. Therefore, an addition of the other ligand results in a set of nearly degenerate duplicate states corresponding to eq 2–7 with doubled intensity. The only appreciable interligand interaction is the dipole–dipole type in ^1LE's, which splits the ^1LE states according to the molecular symmetry. However, this interaction is much smaller than the ^1LE–CT or ^1LE–^3LE separation and does not affect much the splitting or intensity of the ^3LE states. Hence the relative intensity, ρ, given above can be applied approximately to any complex, ML_N (n = 1–3), discussed here.

Results

1. $Cr(acac)_3$, $[Cr(acac)(en)_2]Cl_2$, and $Cr(dbm)_3$. $Cr(acac)_3$ exhibits three kinds of absorption bands below 30 × 10^3 cm^{-1} as

---

(9) Baker, B. R.; Mehta, B. D. *Inorg. Chem.* **1965**, *4*, 848–54.
(10) Fernelius, W. C.; Blanch, J. E. *Inorg. Synth.* **1957**, *5*, 130–1.
(11) Elvidge, J. A.; Lever, A. B. P. *J. Chem. Soc.* **1961**, 1257.
(12) Kaizaki, S.; Hidaka, J.; Shimura, Y. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1100–9.
(13) Kaizaki, S.; Hidaka, J.; Shimura, Y. *Inorg. Chem.* **1973**, *12*, 135–42.
(14) Ohno, T.; Kato, S. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1901–7.
(15) Marris, C. M.; McKenzie, E. D. *J. Inorg. Nucl. Chem.* **1963**, *25*, 171.
(16) Ohno, T.; Kato, S. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1528–33.

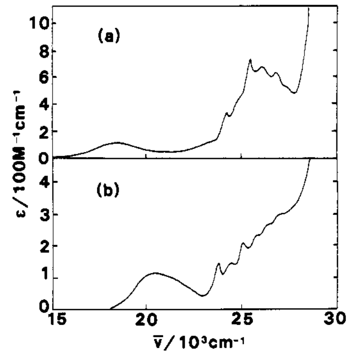

Figure 1. Absorption spectra of Cr(acac)$_3$ (a) and [Cr(acac)(en)$_2$]Cl$_2$ (b) at 77 K.

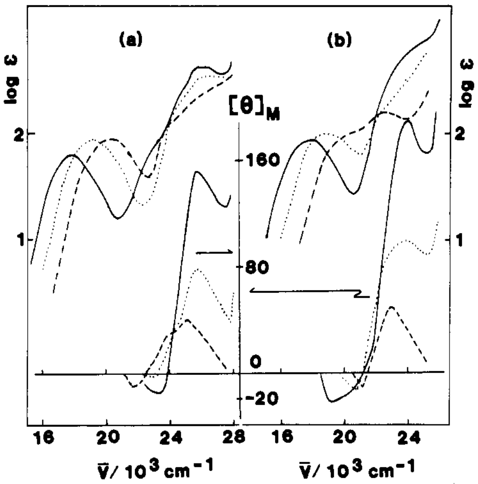

Figure 2. Absorption (upper) and MCD (lower) spectra of acac (a) and acacBr (b) complexes at room temperature: (solid line) [Cr(acacX)$_3$]; (dotted line) [Cr(acacX)$_2$(en)]$^+$; (dashed line) [Cr(acacX)(en)$_2$]$^{2+}$.

Table I. MCD Data of the Acetylacetonato and 3-Halogenoacetylacetonato Complexes of Chromium(III)

complexes	$\bar{\nu}$/cm^{-1} of LE bands ([θ]$_M$/deg M^{-1} cm^{-1} T^{-1})
Cr(acac)$_3$	25 700 (+150.1)
[Cr(acac)$_2$(en)]$^+$	25 700 (+76.9)
[Cr(acac)(en)$_2$]$^{2+}$	25 000 (+39.2)
Cr(acacCl)$_3$	24 000 (+159.5)
[Cr(acacCl)$_2$(en)]$^+$	23 700 (+77.0)
[Cr(acacCl)(en)$_2$]$^{2+}$	22 800 (+51.8)
Cr(acacBr)$_3$	23 300 (+161.8)
[Cr(acacBr)$_2$(en)]$^+$	23 700 (+98.9)
[Cr(acacBr)(en)$_2$]$^{2+}$	22 700 (+47.8)

Table II. Fine Structures of Cr(dbm)$_3$ Absorption and Be(dbm)$_2$ Phosphorescence

LE abs of Cr(dbm)$_3$		LE phos of Be(dbm)$_2$	
$\bar{\nu}$/cm^{-1}	$\Delta\bar{\nu}$/cm^{-1}	$\bar{\nu}$/cm^{-1}	$\Delta\bar{\nu}$/cm^{-1}
20 300	1300	20 900	1300
21 600		19 600	1400
		18 200	

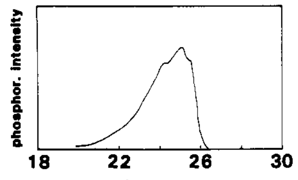

Figure 3. Phosphorescence spectrum of Be(acac)$_2$ (20 μM) at 77 K.

is shown in Figure 1. The bands at 19 × 10^3, (28–31) × 10^3, and (34–40) × 10^3 cm^{-1} have been assigned to LF ($^4A_2 \rightarrow {}^4T_2$), LE, and CT, respectively.[7] An absorption profile in the region of (22–28) × 10^3 cm^{-1} at 77 K presents a close similarity to the low-temperature absorption spectrum of the Cr(acac)$_3$–Al(acac)$_3$ mixed crystal.[17] It consists of some peaks on the broad band, which were observed in the crystal spectrum. The four peaks form a progression of vibronic bands with an origin at 24 150 cm^{-1} and with a spacing of 650 cm^{-1}. A similarly structured band with an origin at 23 730 cm^{-1} was observed for [Cr(acac)(en)$_2$]$^{2+}$ at 77 K as is shown in Figure 1, while the second LF transition ($^4A_2 \rightarrow {}^4T_1$) should be shifted to higher frequency than that of Cr(acac)$_3$ owing to the larger ligand field strength in [Cr(acac)(en)$_2$]$^{2+}$ than that in Cr(acac)$_3$. Therefore, an assignment of the well-structured band to the spin-allowed LF transition ($^4A_2 \rightarrow {}^4T_1$) is eliminated.

A complementary use of CD and MCD spectra for the acac complexes led to another evident discrimination between the LF band ($^4A_2 \rightarrow {}^4T_1$) and the structured band. The negative CD bands with smooth and featureless band envelopes of the acac complexes in this region have been assigned to the second LF transition, because the peak positions of the CD bands vary with the ligand field strength (27 000 cm^{-1} for [Cr(acac)(en)$_2$]$^{2+}$,[13] 25 300 cm^{-1} for [Cr(acac)$_2$en]$^+$,[13] and 23 200 cm^{-1} for Cr(acac)$_3$).[18] A positive MCD band observed in this region for the three comlexes is independent of the ligand field strength (Figure 2 and Table I). The positions of the MCD bands at 25 000–26 000 cm^{-1} are almost the same as the well-structured absorption band observed at low temperature. The MCD intensities ([θ]$_M$ = 39–150° M^{-1} cm^{-1} T^{-1}) are found to be much stronger than those ([θ]$_M$ = 5–10° M^{-1} cm^{-1} T^{-1}) usually observed in the second LF transition ($^4A_2 \rightarrow {}^4T_1$) and approximately proportional to the number of the acac ligands in the mono-, bis-, and tris(acetylacetonate) complexes (Table I). These facts of the spectral shift and the MCD intensity suggest that well-structured absorption components are not due to the LF.

Now, we are able to examine Hanazaki's assignment[7b] of the structured band at 25 000 cm^{-1} to ^{3}LE of acac. Acac coordinating to Be^{2+} emits a poorly resolved phosphorescence with 0″–0 at 25 400 cm^{-1} (Figure 3) as Zn(acac)$_2$ and Al(acac)$_3$ do.[16] The closeness of the lowest absorption peak to the 0″–0 position of the phosphorescence indicates that the S–T transition of acac is responsible for the structured bands of Cr(acac)$_3$ and [Cr(acac)(en)$_2$]$^{2+}$. A similarity in the peak-to-peak spacings (650 cm^{-1}) in the phosphorescence and the absorption spectra is consistent with the assignment. On the other hand, the phosphorescence of Cr(acac)$_3$ at 12 800 cm^{-1},[19] which is identified with the spin-forbidden LF phosphorescence, is useless for assignment of the fine-structured band in the violet region.

The intensities of the resolved bands are too high (150–300 M^{-1} cm^{-1} for [Cr(acac)(en)$_2$]$^{2+}$ and 300–700 M^{-1} cm^{-1} for Cr(acac)$_3$) to be ascribed to the spin–orbit coupling through the exchange interaction between π electrons of acac and d electrons of the chromium ion. The spin–orbit coupling of d electrons brings about the intensity of spin-forbidden LF ($^4A_2 \rightarrow {}^2E$) of less than 1% of that of a spin-allowed LF ($^4A_2 \rightarrow {}^4T_2$).[7b] The spin–orbit coupling of π electrons residing mainly in the ligand must be even smaller than that of d electrons. However, the observed intensity of the ^{3}LE transition of [Cr(acac)(en)$_2$]$^{2+}$ is 4% of the ^{1}LE transition (5700 M^{-1} cm^{-1} at 38 000 cm^{-1}), which is in excellent agreement with the ρ value predicted in the previous section.

Two peaks of moderate intensity (~400 M^{-1} cm^{-1}) in the absorption spectrum of Cr(dbm)$_3$ at 77 K were seen higher than the first LF band ($^4A_2 \rightarrow {}^4T_2$) at 17 500 cm^{-1}. The first band position (20 200 cm^{-1}) and the spacing (1300 cm^{-1}) between the peaks in the absorption of Cr(dbm)$_3$ are in agreement with those (20 900 and 1300 cm^{-1}) of the phosphorescence of Be(dbm)$_2$ as Table II shows. Consequently, the absorption bands in the violet

---

(17) Piper, T. S.; Carlin, R. L. *J. Chem. Phys.* **1962**, *36*, 3330–3.

(18) Norden, B. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 387–94.

(19) Chatterjee, K. K.; Forster, L. S. *Spectrochim. Acta* **1964**, *20*, 1603.

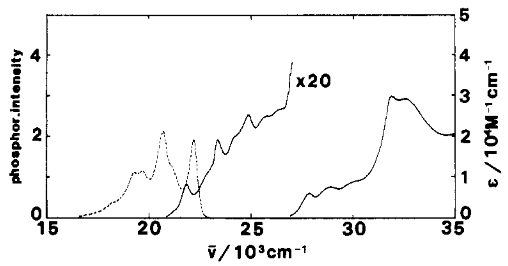

Figure 4. Absorption spectrum of $[Cr(bpy)_3]^{3+}$ (solid line) and phosphorescence spectrum of $[Rh(bpy)_3]^{3+}$ (0.25 mM) (dashed line) at 77 K.

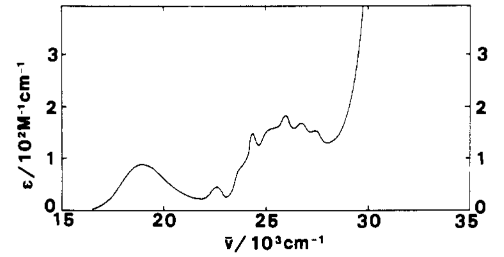

Figure 5. Absorption spectrum of $[Cr(bpy)(mal)_2]^-$ at 77 K.

region are identified as a transition to $^4(^3LE)$. The moderate intensities are well-interpreted in terms of the unpaired electron coupling described above.

As shown in Figure 2 and Table I, the 3-halogenoacetylacetonate chromium complexes give MCD behavior similar in intensity and in band envelope, not in position, to those of the acac complexes, the positive MCD intensities around 23 500 cm^{-1} being proportional to the number of 3-ahlogenoacetylacetonate ligands in the complexes. These MCD positions are shifted to lower frequencies by 1000–2000 cm^{-1} than those of the acac complexes (Table II). Such a lower frequency shift occurs characteristically of the π–π^* LE bands upon 3-halogeno substitution into the acac metal complexes in general as well as that into the acac chromium(III) complexes specifically.[7c] Accordingly, these results confirm that the MCD band at 22 700–24 000 cm^{-1} originates from the S–T LE transition. As for the absorption spectra, they are too diffuse to be decomposed into the LE and LF bands even at 77 K except for $[Cr(acacX)(en)_2]^+$ (X = Cl$^-$ and Br$^-$). The absorption spectrum of the latter exhibits a strange peak at 22 500 cm^{-1} followed by a shoulder near 20 000 cm^{-1} of the first LF band[13] (Figure 2b). Since the position of the absorption peak of $[Cr(acacX)(en)_2]^{2+}$ agrees fairly with that of the positive MCD band (22 700–22 800 cm^{-1}), the observed absorption peak is most likely ascribed to the S–T LE transition of the 3-halogenoacetylacetonate ligands, the intensity of which is enhanced by the above-mentioned mechanism. To our knowledge, this is the first observation of the S–T LE absorption peaks at room temperature, which are well-separated from both the LF and the spin-allowed LE transitions, within such relatively small ligands as acac in complexes.

2. $[Cr(bpy)_3]^{3+}$, $[Cr(bpy)(mal)_2]^-$, $[Cr(terpy)_2]^{3+}$, and $[Cr(dp\text{-}phen)_3]^{3+}$. $[Cr(bpy)_3]^{3+}$ at 77 K exhibits a well-resolved asorption band with an intensity of 300–1000 M^{-1} cm^{-1} in the violet region of (22–27) × 10^3 cm^{-1} in addition to intense bands in the ultraviolet region as Figure 4 shows. The fine structure consists of three peaks and shoulders with an origin at 21 800 cm^{-1}, the peaks of which have been observed even at room temperature.[5,6] $[Cr(bpy)(mal)_2]^-$, whose average ligand field strength is weaker than that of $[Cr(bpy)_3]^{3+}$, displays a similar structured band with an origin at 22 700 cm^{-1} and a LF band ($^4A_2 \rightarrow {}^4T_2$) at 19 000 cm^{-1} as Figure 5 shows. Therefore, the structured bands of the complexes in the violet region are not ascribed to the LF transition. As Figure 4 shows, the phosphorescence of bpy coordinating to the rhodium(III) is a mirror image of the fine-structured absorption band with respect to the band structure and the peak-to-peak separation, while the 0–0 band at 22 200 cm^{-1} for $[Rh(bpy)_3]^{3+}$ is not in complete agreement with the origins of the absorption bands. The intensity of the resolved band (400–1000 M^{-1} cm^{-1}) is in excellent agreement with the predicted value in the previous section. The moderate intensity could not be interpreted in terms of the spin–orbit coupling.[20] Through the direct coupling between the unpaired electrons of the ligand and the chromium(III) ion, an optical tranisition to a quartet excited state mainly constructed from ^3LE of bpy and $^4(d^3)$ and $^2(d^3)$ of the chromium(III) ion becomes allowed to bring about the moderate intensity.

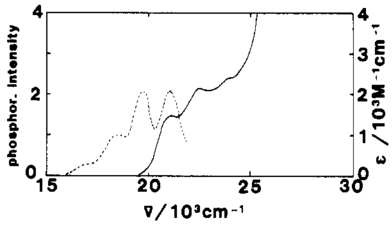

Figure 6. Absorption spectrum of $[Cr(bp\text{-}phen)_3]^{3+}$ (solid line) and phosphorescence spectrum of $[Zn(dp\text{-}phen)]^{2+}$ (0.2 mM) (dashed line).

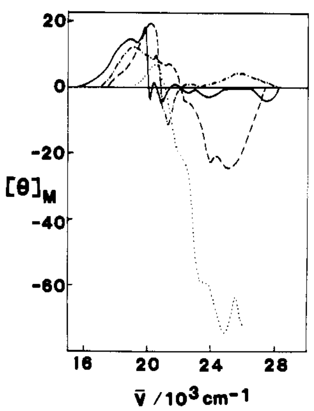

Figure 7. MCD spectra of bpy complexes at room temperature: (dotted line) $[Cr(bpy)_3]^{3+}$; (dashed line) $[Cr(ox)(bpy)_2]^+$; (solid line) $[Cr(ox)_2(bpy)]^-$; (dashed–dotted line) $[Cr(ox)_2en]^-$.

Table III. Fine Structures of $[Cr(terpy)_2]^{3+}$ Absorption and $[Zn(terpy)]^{2+}$ Phosphorescence

LE abs of $[Cr(terpy)_2]^{3+}$		LE phos of $[Zn(terpy)]^{2+}$	
$\bar{\nu}$/cm^{-1}	$\Delta\bar{\nu}$/cm^{-1}	$\bar{\nu}$/cm^{-1}	$\Delta\bar{\nu}$/cm^{-1}
21 140	1430	23 000	1500
22 570	1130	21 500	1100
23 700		20 400	500
		19 900	

An absorption band group of $[Cr(bp\text{-}phen)_3]^{3+}$ in the violet region becomes distinct to display two peaks (21 900–22 500 cm^{-1}) and one shoulder (23 800 cm^{-1}) at 77 K. The first and second peaks are moderately intense (1500–2000 M^{-1} cm^{-1}) and should again be assigned to $^4G \rightarrow {}^4(^3LE)$. As Figure 6 shows, the first peak at 21 000 cm^{-1} is in agreement with the 0–0 band of phosphorescence of dp-phen coordinating to a zinc(II) ion and the peak-to-peak spacing of absorption progression (1400 cm^{-1}) is very close to that of phosphorescence. This result suggests that the excited state is of ^3LE character.

König and Herzog hesitated to assign the structured band of $[Cr(bpy)_3]^{3+}$ to the LF transition ($^4A_2 \rightarrow {}^4T_2$) because of its moderate intensity and fine structure.[5] Serpone et al. observed similar bands for chromium(III) compounds having substituted bpy and phen as ligands.[6] Since the origins and the intensities of the fine-structured bands were affected by substituents (methyl, phenyl, or pyridyl), they supposed that an LMCT transition was involved. An intense band group of $[Cr(terpy)_2]^{3+}$ observed by

---

(20) The spin–orbit coupling has been known to bring about a low-intensity (10 M^{-1} cm^{-1}) S–T absorption of bpy coordinating to the third-row metals such as the iridium(III) ion (Z = 77).[21]

(21) Flynn, C. M.; Demas, J. N., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 1959–60.

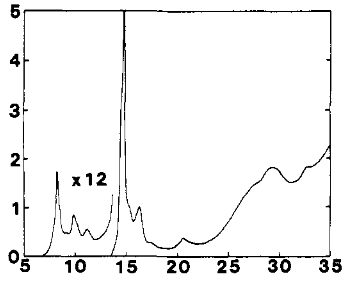

Figure 8. Absorption spectrum of Cr(PC)(OH) in DMA at room temperature.

Serpone et al.[6] as well as the resolved bands of $[Cr(bpy)_3]^{3+}$ and $[Cr(dp\text{-}phen)_3]^{3+}$ is assigned to the transition to $^4(^3LE)$ by means of a mirror-image relation between the absorption of $[Cr(terpy)_2]^{3+}$ and the phosphorescence of $[Zn(terpy)]^{2+}$ as Table III shows.

MCD spectra of chromium(III)–bpy complexes exhibit a fine structure in the region of 22 000–28 000 cm^{-1} corresponding to the S–T transition of the bpy ligand as shown in Figure 7. While $[Cr(ox)_2bpy]^-$ exhibits a weak and complicated MCD spectrum in this region, the bis- and tris(2,2′-bipyridine) Cr(III) complexes give a distinct MCD band with a negative sign. The components of the MCD spectrum in the region of 22 500–25 000 cm^{-1} agree with the absorption peaks of $[Cr(mal)_2bpy]^-$ and $[Cr(bpy)_3]^{3+}$ and do not change in position with the ligand field strength in the complexes (Figures 5 and 7). Moreover, the MCD intensities increase with, but not proportionally to, the number of the coordinated bpy ligands. Accordingly, some of the fine structure of $[Cr(ox)_2bpy]^-$ in the region of 22 500–25 000 cm^{-1} are ascribed to the ^3LE transition, while the other in the region of 18 500–23 000 cm^{-1} may belong to the progression due to the spin-forbidden $^4A_2 \rightarrow {}^2T_2$ transition, which was seen in the MCD spectrum of $[Cr(ox)_2en]^-$ (Figure 7). A similar MCD spectrum was also observed for $[Cr(mal)_2(bpy)]^-$, but the resolution of the fine structure is much lower than that of the oxalato complex. Only one CD band ($\Delta\epsilon$ = +0.53 M^{-1} cm^{-1} at 25 300 cm^{-1}) with the smooth band envelope observed for $(-)_{546}$-$[Cr(ox)_2(bpy)]^-$ is similar in position and intensity to that of the corresponding en complex ($\Delta\epsilon$ = +0.35 M^{-1} cm^{-1} at 25 300 cm^{-1}), the CD being due to $^4A_2 \rightarrow {}^4T_1$.[12] Therefore, these chiroptical facts strongly support that the vibronic structured MCD bands of the bpy complexes in the violet region (22 500–28 000 cm^{-1}) are due to the S–T LE transition, similarly as observed for the acac complexes mentioned above.

3. Cr(PC)(OH). The green compound Cr(PC)(OH) in DMA exhibits two strong LE bands, which are common to most of metallophthalocyanines.[22] In addition to these bands, two extra bands, one consisting of four peaks beginning at 8300 cm^{-1} and the other at 20600 cm^{-1}, were found as is shown in Figure 8. Inspection of Figure 8 reveals that a definite progression of the lowest band is not so different from the LE (Q-band) in the red region in spite of the much lower intensity (1400 M^{-1} cm^{-1}). Therefore, the π electrons of the ligand must be participating in the band group in the near-infrared region. As a matter of fact, the singlet–triplet bands of Cu(PC) (9150 cm^{-1})[22] and Pb(PC) (8160 cm^{-1})[23] are similar to the lowest band of Cr(PC)(OH) with respect to the 0–0 position and the spacing between the 0–0 and the next small peak. An excited-state absorption (ESA) must be a diagnosis in this case. ESA of Cr(PC)(OH) similar to those of the lowest triplet excited states of a phthalocyaninate ion coordinating to Pb^{2+} and Al^{3+}[24] and Zn^{2+}[25] indicates that the lowest excited state of Cr(PC)(OH) is of ^3LE character (see Figure 9). Since the ^3LE transition in the PC coordinating to the paramagnetic chromium(III) ion must be visible unlike the S-T transitions of free aromatic compounds, the band group at the lowest energy is assigned to the $^4G \rightarrow {}^4(^3LE)$ transition. On the other hand, a similarly resolved band of $[Cr(TSPC)]^{3-}$ with an origin at 7900 cm^{-1} was assigned to spin-allowed LMCT by Lever et al.,[22] on the basis of the LMCT energy (9030 cm^{-1}) estimated from redox potentials of $[Cr^{III}TSPC]^{3-}/[Cr^{II}TSPC]^{4-}$ and $[Cr^{II}TSPc]^{3-}/[Cr^{II}TSPC]^{4-}$.

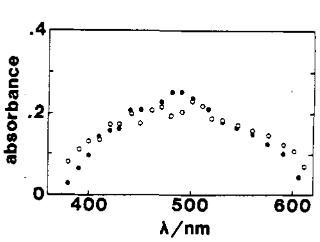

Figure 9. Transient absorption spectra of Cr(PC)(OH) in DMA and Pb(PC) in Me_2SO on laser excitation in DMA at room temperature: (open circles) Cr(PC)(OH); (closed circles) Pb(PC).

The lifetime of the ESA (35 ns) is shorter than that of Pb(PC) (160 ns) and is the shortest of triplet excited states of metallophthalocyanines ever studied.[24-26] This seems to be reasonable because the absorption intensity of Cr(PC)(OH) in the near-infrared region is much higher than that of Pb(PC). However, the situation may be more complicated; the lowest excited state is not $^4(^3LE)$ but $^6(^3LE)$, whose transition to the ground state is spin-forbidden so that the rate of thermal excitation to $^4(^3LE)$ determines the lifetime of $^6(^3LE)$.

Discussion

Studies of optical spectra of the first-row transition-metal compounds are mostly limited to spin-allowed transitions of LF, LE, and CT. As for spin-forbidden transitions, those that have been observed are low-intensity LF transitions with a fine structure. As one goes to the second- and third-row transition-metal compounds, the multiplicity-restricted transitions of LE and CT become detectable in the fortunate cases such as $[Ir(bpy)_3]^{3+}$[21] and $[Os(bpy)_3]^{2+}$.[27] The partial breakdown of the multiplicity restriction on the optical transitions reveals that spin–orbit interaction is still weak for at least the first-row transition-metal compounds. The moderate-intensity optical transitions to ^3LE of the chromium(III) compounds, which were also observed by means of magnetic circular dichroism, are brought about by a totally different mechanism. The formal description of the quartet excited state with a configuration of ^3LE (eq 5–7) is effective when unpaired electron coupling among the triplet excited ligand and the quartet and doublet chromium(III) is caused by a mixing with the CT state. Both the d-resonance integral and the energy difference between ^3LE and CT affect the optical transition intensity. From this point of view, ligands with large π-electron systems coordinating to a paramagnetic metal ion are expected to exhibit a moderate-intensity absorption band below the spin-allowed LE, since in these compounds E_{CT} is expected to be low enough to cause an effective mixing. Actually, the ligands in the chromium(III) compounds studied here belong to this category. A band group of the tetraphenylporphyrinate ion coordinating to the chromium(III) ion has been assigned to $^4(^3LE)$ in terms of an unpaired electron coupling model by Gouterman et al.,[4] who also interpreted weak S–T transitions of the porphyrinate ion coordinating to copper(II) and vanadyl(III) ions[27] on a basis different from that of Hanazaki.[7] The moderate-intensity band of tris(salicylideneamine)chromium at 22 000 cm^{-1}[29] may be

---

(22) Lever, A. B. P.; Pickens, S. R.; Minor, P. C.; Licoccia, S.; Ramaswamy, B. S.; Magnell, K. *J. Am. Chem. Soc.* **1981**, *103*, 6800–6.

(23) Katayama, Y.; Yasunaga, H.; Takeya, K. *Rep. Univ. Electro-Commun.* **1972**, *23*, 25–8.

(24) Ohno, T.; Kato, S.; Yamada, A.; Tanno, T. *J. Phys. Chem.* **1983**, *87*, 775–81.

(25) Ohno, T.; Kato, S.; Lichtin, N. N. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2753–9.

(26) Ohtani, H.; Kobayashi, T.; Ohno, T.; Kato, S.; Tanno, T.; Yamada, A. *J. Phys. Chem.* **1984**, *88*, 4431–5.

(27) Felix, F.; Ferguson, J.; Gudel, H. U.; Lude, A. *J. Am. Chem. Soc.* **1980**, *102*, 4096–102.

(28) Ake, R.; Gouterman, M. *Theor. Chim. Acta* **1969**, *15*, 20–42.

(29) Yamada, S.; Iwasaki, K. *Inorg. Chim. Acta* **1971**, *5*, 3.

assigned to the ^{3}LE transition, because the phosphorescence of salicylideneamine coordinating to the zinc(II) ion has the 0–0 band at 22 200 cm^{-1}.[30]

Registry No. $Cr(acac)_3$, 21679-31-2; $[Cr(acac)_2(en)]^+$, 59220-43-8; $[Cr(acac)(en)_2]^{2+}$, 71723-96-1; $Cr(acacCl)_3$, 13963-55-8; $[Cr(acacCl)_2(en)]^+$, 104111-08-2; $[Cr(acacCl)(en)_2]^{2+}$, 104111-09-3; $Cr(acacBr)_3$, 15025-13-5; $[Cr(acacBr)_2(en)]^+$, 104111-10-6; $[Cr(acacBr)(en)_2]^{2+}$, 104111-11-7; $Cr(dbm)_3$, 21679-35-6; $Be(dbm)_2$, 19368-60-6; $[Cr(terpy)_2]^{3+}$, 54984-99-5; $[Zn(terpy)]^{2+}$, 104035-35-0; $Be(acac)_2$, 10210-64-7; $[Cr(bpy)_3]^{3+}$, 15276-15-0; $[Rh(bpy)_3]^{3+}$, 47780-17-6; $[Rh(bpy)(mal)_2]^-$, 104035-36-1; $[Cr(dp\text{-}phen)_3]^{3+}$, 69178-81-0; $[Zn(dp\text{-}phen)]^{2+}$, 16561-57-2; $[Cr(ox)(bpy)_2]^+$, 32629-19-9; $[Cr(ox)_2(bpy)]^-$, 21748-32-3; $[Cr(ox)_2(en)]^-$, 46752-51-6; Cr(PC)(OH), 15053-50-6; Pb(PC), 15187-16-3.

---

(30) Ohno, T.; Kato, S.; Takeuchi, A.; Yamada, S. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 6–9.

Contribution from Istituto FRAE-CNR, 40100 Bologna, Italy, and Dipartimento di Chimica dell'Università
and Centro di Studio sulla Fotochimica e Reattività degli Stati Eccitati dei Composti di Coordinazione del CNR, 44100 Ferrara, Italy

Phosphorescent 8-Quinolinol Metal Chelates. Excited-State Properties and Redox Behavior

Roberto Ballardini,† Graziano Varani,‡ Maria Teresa Indelli,‡ and Franco Scandola*‡

Received November 13, 1985

A number of metal complexes of 8-quinolinol (QOH) of general formula $M(QO)_n$ ($n = 3$, M = Al(III), Bi(III), Rh(III), Ir(III); $n = 2$, M = Pt(II), Pb(II)) have been synthesized and characterized. The heavy-metal complexes (M = Pt(II), Pb(II), Bi(III), Ir(III)) exhibit long-lived ($\tau \simeq$ 2–4 μs) phosphorescence and excited-state absorption (ESA) in fluid solution. The photophysics of these complexes (emission spectra and lifetimes, ESA spectra and lifetimes, emission quantum yields, efficiencies of formation of the long-lived state) has been studied in some detail. The long-lived emitting state is assigned as a metal-perturbed triplet state of the 8-quinolinol ligand. On the basis of their ground-state redox potentials and on their excited-state properties, the heavy-metal 8-quinolinol complexes are predicted to behave as powerful excited-state reductants (potentials in the −0.8 to −1.3 V range vs. SCE). Quenching studies verify these expectations.

Introduction

The photophysics of metal chelates has been studied quite extensively in the last two decades, following the pioneering work of Crosby and his associates.[1,2] By far, the best studied class of metal chelates is that of transition-metal polypyridine complexes, for which a variety of long-lived, often emitting, lowest excited states have been observed.[3-13] Depending on the type of metal and of polypyridine ligand, metal-centered states (also indicated as MC or d–d), metal-to-ligand charge-transfer states (also indicated as MLCT or d–π^*), or ligand-centered states (also indicated as LC or π–π^*) can be the lowest spin-forbidden state in these systems. In particular cases, even very subtle changes in the periphery of the bipyridine ligand can be sufficient to bring about a change in the type of lowest excited state ("fine tuning").[1,2,10] Aside from these intrinsic points of interest, studies on metal polypyridine complexes have received additional momentum from the discovery that some of these compounds behave as effective photosensitizers for hydrogen or oxygen generation from water.[10,14-20] A remarkable amount of work has thus been devoted to the characterization of the excited-state redox properties and of the kinetics of excited-state electron-transfer reactions of these complexes.[21-23] In all these studies, phosphorescent emission in fluid solution has been the main handle for investigating the excited-state behavior of the complexes. In some instances, excited-state absorption (ESA) has also been used for this purpose.[24-26]

Looking for new classes of redox photosensitizers, we have undertaken an investigation of the photophysical and excited-state redox behavior of 8-quinolinol (QOH) metal chelates. Many chelates of this type, of general formula $M(QO)_n$ (where n equals the oxidation state of the metal M) have been known for a long time in the analytical literature (under the name of metal oxinates).[27-30] Notably, a number of analytical methods for the determination of group III (13)[89] metals are based on the formation of such species.[31] On the other hand, little attention seems to have been devoted to the synthesis and characterization of specific metal chelates, in particular of the 8-quinolinol complexes of the heaviest non transition (6s, 6p) and transition (5d, 6d)

---

† Istituto FRAE-CNR.

‡ Dipartimento di Chimica and Centro CNR.

(1) Crosby, G. A.; Watts, R. J.; Carstens, D. H. W. *Science (Washington, D.C.)* **1970**, *170*, 1195.
(2) Crosby, G. A. *Acc. Chem. Res.* **1975**, *8*, 231; *J. Chem. Educ.* **1983**, *60*, 791.
(3) Demas, J. N. *J. Chem. Educ.* **1983**, *60*, 803.
(4) Kemp, T. J. *Prog. React. Kinet.* **1980**, *10*, 301.
(5) DeArmond, M. K. *Coord. Chem. Rev.* **1981**, *36*, 325.
(6) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159.
(7) Watts, R. J. *J. Chem. Educ.* **1983**, *60*, 834.
(8) Jamieson, M. A.; Serpone, N.; Hoffman, M. Z. *Coord. Chem. Rev.* **1981**, *39*, 121.
(9) Serpone, N.; Hoffman, M. Z. *J. Chem. Educ.* **1983**, *60*, 853.
(10) Balzani, V.; Bolletta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1.
(11) Balzani, V.; Juris, A.; Barigelletti, F.; Belser, P.; Von Zelewsky, A. *Sci. Pap. Inst. Phys. Chem. Res. (Jpn.)* **1984**, *78*, 78.
(12) Juris, A.; Barigelletti, F.; Balzani, V.; Belser, P.; Von Zelewsky, A. *Inorg. Chem.* **1985**, *24*, 202.
(13) Allen, G. H.; White, R. P.; Rillema, D. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2613.
(14) Connolly, J. S., Ed. *Photochemical Conversion and Storage of Solar Energy*; Academic: London, 1981.
(15) Rabani, J., Ed. *Photochemical Conversion and Storage of Solar Energy 1982*; Weizman: Jerusalem, 1982.
(16) Grätzel, M., Ed. *Energy Resources through Photochemistry and Catalysis*; Academic: London, 1983.
(17) Sutin, N.; Creutz, C. *Pure Appl. Chem.* **1980**, *52*, 2717.
(18) Whitten, D. G. *Acc. Chem. Res.* **1980**, *13*, 83.
(19) Grätzel, M. *Acc. Chem. Res.* **1981**, *14*, 376.
(20) Meyer, T. J. *Isr. J. Chem.* **1977**, *15*, 200.
(21) Sutin, N.; Creutz, C. *J. Chem. Educ.* **1983**, *60*, 809 and references therein.
(22) Balzani, V.; Scandola, F. In *Energy Resources through Photochemistry and Catalysis*; Grätzel, M., Ed.; Academic: London, 1983; and references therein.
(23) Meyer, T. J. *Prog. Inorg. Chem.* **1983**, *30*, 389 and references therein.
(24) Indelli, M. T.; Carioli, A.; Scandola, F. *J. Phys. Chem.* **1984**, *88*, 2685.
(25) Indelli, M. T.; Ballardini, R.; Scandola, F. *J. Phys. Chem.* **1984**, *88*, 2547.
(26) Ohno, T.; Kato, S. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1528.
(27) Hillebrand, W. F.; Lundell, G. E. F.; Bright, H. A.; Hofman, J. I. *Applied Inorganic Analysis*, 2nd ed.; Wiley: New York, 1953; p 122.

0020-1669/86/1325-3858$01.50/0