

Contribution from the Departments of Chemistry,
Duke University, Durham, North Carolina 27706,
and North Carolina State University,
Raleigh, North Carolina 27607

**Single-Crystal Magnetic Circular Dichroism Spectrum
and Phase Transition of a Trigonal Cobalt(II)
Complex, $[\text{Co}(\text{OMPA})_3](\text{BF}_4)_2$**

R. S. Evans,¹ A. F. Schreiner,^{*1} M. C.-L. Yang,²
and R. A. Palmer²

Received November 20, 1975

AIC50843T

The literature is devoid of investigations which subject electronic excitations of molecular or ionic complexes containing the cobalt(II) ion in trigonal (D_3) symmetry to the scrutiny of magnetic circular dichroism (MCD) spectroscopy. Substantial reasons for this void are (i) the scarcity of suitable crystals and (ii) the somewhat cumbersome task of employing a Hamiltonian containing trigonality (D_3) and spin-orbit coupling in addition to the other crystal field parameters. The isomorphous series $[\text{M}(\text{OMPA})_3](\text{ClO}_4)_2$ and $[\text{M}(\text{OMPA})_3](\text{BF}_4)_2$, where M is Co and Zn, among others,³ offers an excellent opportunity to fill this void. The complex ion symmetry, as well as the metal site symmetry, is D_3 and the crystal habit of the $P\bar{3}C1$ crystals is hexagonal prismatic. By cocrystallizing varying amounts of the cobalt complex with the zinc complex, crystals of suitable optical density and magnetically induced ellipticity may be obtained in order to study both the optical (electronic absorption) spectra⁴ and MCD of the various bands of the ligand field spectrum. Previously employed computational methods⁵ are also particularly useful for full analysis of the new data provided by MCD. In this paper we report our MCD results on the $[\text{Co}(\text{OMPA})_3](\text{BF}_4)_2$ spectrum between 1.25 and $2.80 \mu\text{m}^{-1}$ with special emphasis on the $2.10\text{-}\mu\text{m}^{-1}$ region and the ${}^2T_{1g}(\text{P})$ transition.

A uniaxial specimen of $[\text{Co}(\text{OMPA})_3](\text{BF}_4)_2$,⁶ doped at the 5% level into $[\text{Zn}(\text{OMPA})_3](\text{BF}_4)_2$ and grown from an acetone solution, was mounted in the variable-temperature bore (4.2 K to room temperature) of a superconducting magnet so as to measure its axial optical and MCD spectra.⁷ With both electric and magnetic dipole vectors of the light perpendicular to the C_3 axis of the complex ions, only $\sigma(x,y)$ -polarized transitions are excited in both optical and MCD spectra (Figure 1). Our original intention of lowering the crystal temperature to ~ 4 K so as to optimize the appearance of fine structure had to be abandoned very early, since an apparent phase transition takes place near 210 K (Figure 2) on cooling the sample. The transition displayed hysteresis under our experimental conditions with the phase change occurring at higher temperature on warming than on cooling. The immense natural ellipticity which suddenly develops as the crystal is cooled below 205 K is reminiscent of that observed for a biaxial crystal in the CD light beam (Figure 2). This experimental observation suggests this procedure as a convenient (measurable *continuously* in most temperature ranges) and sensitive means for detecting the occurrence of phase transitions in even *colorless* uniaxial crystals (in $[\text{Zn}(\text{OMPA})_3](\text{BF}_4)_2$ the probe is the activity of the implanted guest ion, $[\text{Co}(\text{OMPA})_3]^{2+}$).

In the spectral range of this study the axial optical spectrum of the BF_4^- salt (Figure 1) has, as expected, essentially the same features as the axial spectrum of the ClO_4^- salt,³ e.g., the ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$ transition near $1.80 \mu\text{m}^{-1}$ (the band spread from 1.65 to $1.23 \mu\text{m}^{-1}$ is assigned to ${}^4T_{1g}(\text{P})$, the structure presumably being of vibronic origin) experiences a small decrease in intensity, and the sharp structure of the ${}^2T_{1g}(\text{P})$ band near $2.10 \mu\text{m}^{-1}$ begins to show very distinctly

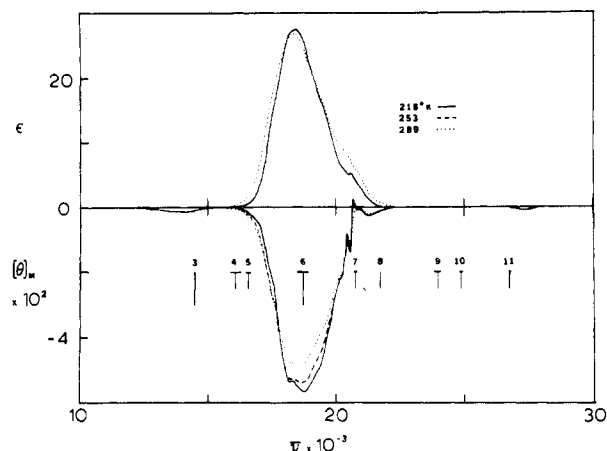


Figure 1. Optical (σ) and MCD spectra of $[\text{Co}(\text{OMPA})_3](\text{BF}_4)_2$ in a single crystal of the Zn(II) analogue. $[\theta]_M$ is the molar ellipticity per gauss.

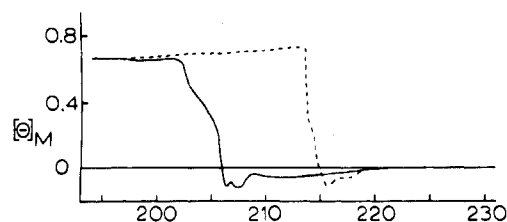


Figure 2. Natural circular dichroism (θ) as a function of temperature (K) of $[\text{Co}(\text{OMPA})_3](\text{BF}_4)_2$ in a single crystal of the Zn(II) analogue. Cool-down (—) and warm-up (---) curves are shown at $1.855 \mu\text{m}^{-1}$.

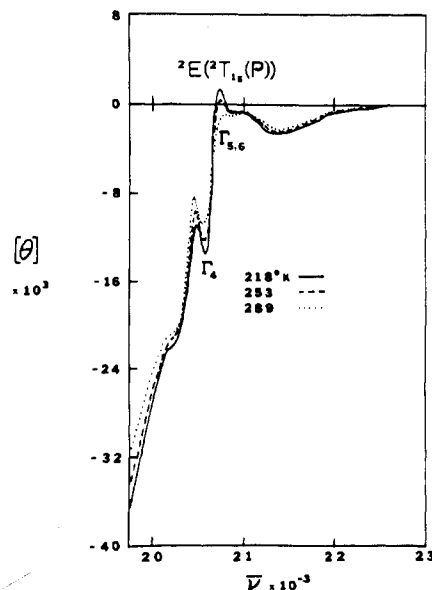


Figure 3. MCD activity of ${}^2E(T_{1g}(\text{P}))$ at three temperatures of the single-crystal specimen of $[(\text{Co}:\text{Zn})(\text{OMPA})_3](\text{BF}_4)_2$.

as the temperature is lowered.

The MCD spectrum in the region of the ${}^2T_{1g}(\text{P})$ band is remarkably sharp even at room temperature (Figure 1), although distinct structure is seen in the optical spectrum only at 80 K and lower.⁴ The MCD structure of this band and its temperature dependence are particularly useful for the detailed understanding of this excited state. As illustrated in Figure 3, the MCD consists of a pair of positive and negative extrema with zero MCD intensity at exactly the energy of the optical band maximum (Table I). The temperature dependence of

Table I. Electronic Transitions of $[\text{Co}(\text{OMPA})_3](\text{BF}_4)_2$ between 1.30 and $2.80 \mu\text{m}^{-1}$

Band	Symmetry			Calcd ^b energy, μm^{-1}	Optical position, μm^{-1}	MCD position, μm^{-1}	Obsd <i>C</i> parameter		
	<i>O_h</i>	<i>LS</i>	<i>D₃</i>						
3	⁴ A _{2g} (F) (t ₂ ³ e ⁴)	Γ ₈	Γ ₄	1.45	1.45 ^a	1.39			
			Γ _{5,6}	1.45					
4	² T _{1g} (G) (t ₂ ³ e ²)	Γ ₈	Γ ₄	1.59	1.67 ^a				
			Γ _{5,6}	1.59					
			Γ ₄	1.64					
5	² T _{2g} (b) (t ₂ ³ e ²)	Γ ₈	Γ _{5,6}	1.65	(1.762)	(1.749)			
			Γ ₄	1.65					
			Γ ₇	1.67					
6	⁴ T _{1g} (P) (t ₂ ⁴ e ³)	Γ ₈	Γ ₄	1.86	1.850	1.819	+		
			Γ _{5,6}	1.86					
			Γ ₄	1.86					
			Γ ₄	1.87					
			Γ _{5,6}	1.87				(1.936)	+
			Γ ₄	1.91				2.012	+
7	² T _{1g} (P) (t ₂ ³ e ²)	Γ ₈	Γ ₄	2.075	2.060	2.051	+		
			Γ _{5,6}	2.077					
			Γ ₄	2.083					
8	² A _{1g} (b) (t ₂ ⁴ e ³)	Γ ₆	Γ ₄	2.17		2.139	+		
9	² T _{2g} (H) (t ₂ ⁴ e ³)	Γ ₈	Γ ₄	2.37	2.40 ^a				
			Γ ₄	2.40					
			Γ _{5,6}	2.40					
10	² T _{1g} (H) (t ₂ ⁴ e ³)	Γ ₈	Γ _{5,6}	2.48	2.61 ^a				
			Γ ₄	2.48					
			Γ ₄	2.48					
11	² E _g (H) (t ₂ ⁴ e ³)	Γ ₈	Γ _{5,6}	2.66	2.74 ^a	2.74	+		
			Γ ₄	2.66					

^a Values from ref 4. ^b $B = 855 \text{ cm}^{-1}$, $C = 3680 \text{ cm}^{-1}$, $Dq = 745 \text{ cm}^{-1}$, $\nu = 0$, $\nu' = 100 \text{ cm}^{-1}$, $\zeta = 495 \text{ cm}^{-1}$.

the intensity of these extrema (Figure 3) clearly shows them to be Faraday *C* terms.

Arguments based on the Franck-Condon principle indicate that the very sharp and intense $2.060\text{-}\mu\text{m}^{-1}$ optical maximum must be the 0-0 component of the ²T_{1g}(P) band. The extreme clarity and dominant intensity of this peak are especially evident in the 4-K optical spectrum of $[\text{Co}(\text{OMPA})_3](\text{ClO}_4)_2$.⁴ In addition, its nearly complete σ polarization and the established ground state⁴ (⁴A₂) require its specific assignment as ⁴A₂ → ²E(²T_{1g}) or as a transition between two spin-orbit components whose parentage is ⁴A₂ → ²E, in the light of the *D*₃ electric dipole selection rules. The occurrence of the MCD doublet suggests the assignment of this band as a composite envelope of two trigonal electric dipole allowed spin-orbit components of ²E(²T_{1g})

"⁴A₂" → E'(²E) + E''(²E)

where E' is a genuine doublet (Γ₄) and E'' is a Kramers doublet (Γ_{5,6}). Presuming that this origin is correct, the order of the two excited states can then be established from the signs of the Faraday *C* parameters^{5,8}

$$\frac{C}{D}(E'') = -\frac{1}{2}U$$

$$\frac{C}{D}(E') = \frac{1}{2}U(1/d)$$

where *U* is a component of the ground-state angular momentum, $\langle \bar{E}^+(\text{}^4\text{A}_2) | \bar{L}_z + 2\bar{S}_z | \bar{E}^+(\text{}^4\text{A}_2) \rangle$, *D* is the dipole strength of the band, *d* is a positive quantity, or $1 + M_z^2/M_{x,y}^2$ (approximately equal to unity here because of the *xy* band polarization), *M_z*² is the electric dipole strength of *z* polarization, etc. The computation of the integral *U* is carried out with complete first-order and second-order spin-orbit coupling in the manner previously described,⁵ and the value of the

integral is found to be $2.0 \mu_B$ (parameters of Table I). The energies of pertinent states are given in Table I. The assignment is therefore

$$\frac{C}{D}(E'') = -1.0 \mu_B \text{ (positive MCD peak at higher energy)}$$

$$\frac{C}{D}(E') = 1.0 \mu_B \text{ (negative MCD peak at lower energy)}$$

This order is based on the signs of the *C/D* ratios, which are not sensitive to reasonably large variations of trigonal splitting parameters *v* and *v'*. These MCD signs, then, establish the order of spin-orbit states, E'' > E', of ²E[²T₁(P)].

Following this identification of states, it is also of some interest to reflect, as far as is possible, on the trigonal parameters, *v* and *v'*, and their relationships to these and other data. Two choices of *v* and *v'* correctly predict the MCD-determined order of states: $v = 0$, $v' = +100 \text{ cm}^{-1}$; or $v < 0$, $v' = 0$. With the second parameter set¹⁰ the above *D*₃ spin-orbit/configuration interaction model with $0 > v > -|\zeta|$ predicts ⁴A₂ > ⁴E ($\zeta = 0$) for the ground-state parent ⁴T₁(F), but with the inclusion of spin-orbit coupling the ground state becomes E'(Γ₄) of parentage ⁴A₂(⁴T₁). Therefore, the deduction from polarized crystal spectra that the ground state is "⁴A₂" is consistent with the MCD data and with the calculations using this parameter set. This negative value of *v* implies the presence of axial compression within $[\text{Co}(\text{OMPA})_3]^{2+}$, if Piper's proposed model is applicable. The crystal structures of several other³ $[\text{M}(\text{OMPA})_3]^{2+}$ compounds show this compression, and the positive⁹ zero-field splitting parameter *D* of $[\text{Mn}(\text{OMPA})_3]^{2+}$ is also consistent with trigonal compression. However, assuming this parameter set to be correct, the computed ground-state splitting ⁴A₂ > ⁴E ($\zeta = 0$), mentioned above, means that Piper's model ($v < 0$ for axial compression; expect ⁴A₂ < ⁴E) does not apply or that

axial compression perturbations are absent (or, if present, are of minor influence) in crystalline $[\text{Co}(\text{OMPA})_3](\text{BF}_4)_2$.

Consequences of assuming the alternative (first) parameter set to be the correct one, are as follows. This set ($v = 0$, $v' = +100 \text{ cm}^{-1}$) also predicts the correct order of excited states, $E'' < E'$ of ${}^2E({}^2T_1)$, and the ground state is again $E'(\Gamma_4)$ from ${}^4A_2[{}^4T_1]$. The polarized crystal spectra implication of 4A_2 being the ground state and conclusions reached from the MCD and calculations are all consistent with each other. Obviously it is not now possible to decide unambiguously upon a parameter set. However, the assignment of states remains firm.

The above is a rare, but clear, example of the possibility of assigning the spin-orbit excited states of optically weak, spin-forbidden cobalt(II) transitions using Zeemann or MCD data and ligand field theory. However, the Zeemann experiment is not applicable here, since currently available magnetic field intensities are too low. On the other hand, MCD analysis allows one to identify such transitions.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to the Research Corp., and to the School of Physical and Mathematical Sciences of North Carolina State University for support of this research. R.S.E. held an American Chemical Society-Petroleum Research Fund Fellowship.

Registry No. $[\text{Co}(\text{OMPA})_3](\text{BF}_4)_2$, 60464-13-3; $[\text{Zn}(\text{OMPA})_3](\text{BF}_4)_2$, 60428-13-9.

References and Notes

- (1) North Carolina State University.
- (2) Duke University.
- (3) OMPA is the neutral ligand octamethylpyrophosphoramide. See M. D. Joesten, M. S. Hussain, and P. G. Lenhart, *Inorg. Chem.*, **9**, 151 (1970), and references therein.
- (4) R. A. Palmer and C. R. Taylor, *Inorg. Chem.*, **10**, 2546 (1971).
- (5) P. J. Hauser, A. F. Schreiner, and R. S. Evan, *Inorg. Chem.*, **13**, 1925 (1974).
- (6) Polarized microscopy viewings revealed the unique optic axis parallel to the sixfold axis of the hexagonal-prismatic habitat. Virtual absence of natural CD activity in this direction also confirmed this axis selection to be correct. Finally, the σ spectra of ClO_4^- and BF_4^- salts are analogous.
- (7) Optical and MCD spectra were measured with light from a Spex 1400 $3/4$ -m double monochromator and the $1/4\lambda$ modulator and electronics of a JASCO ORD/UV/CD-5 (SS-20 modification). Slit narrowing from 300μ produced no improvements in the structured region of ${}^2T_1(\text{P})$.
- (8) A. D. Buckingham and P. J. Stephens, *Annu. Rev. Phys. Chem.*, **13**, 1925 (1964).
- (9) J. C. Hempel, R. A. Palmer, and M. C.-L. Yang, *J. Chem. Phys.*, in press.
- (10) v' is likely not to equal zero. However, for previously studied complexes it has been found that the absolute value of v is larger than that of v' .

Contribution from the Department of Chemistry,
McMurry College, Abilene, Texas 79605

Synthesis and Spectroscopic Characterization of Ruthenium and Osmium Complexes with Sterically Hindering Ligands. 2.¹ Tris Complexes with 2-(2'-Pyridyl)quinoline and 2,2'-Biquinoline

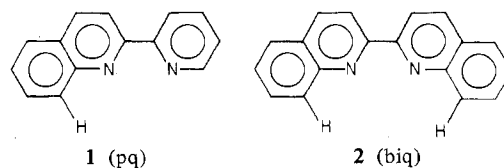
David M. Klassen

Received March 1, 1976

AIC60159U

Recently we reported the synthesis and spectroscopic properties of bis(diquinolylpyridine) complexes of ruthenium(II) and osmium(II).¹ Of further interest are the complexes of these metals with the structurally related bidentate ligands 2-(2'-pyridyl)quinoline (pq) (1) and 2,2'-biquinoline (biq) (2).

The steric crowding caused by the hydrogen atoms on the benzo rings markedly changes the metal chelating properties of biq and pq as compared to 2,2'-bipyridine (bpy).^{2,3} In



particular a single benzo substitution of bpy to form pq changes the tris complex with iron(II) from low spin in $\text{Fe}(\text{bpy})_3^{2+}$ to essentially high spin in $\text{Fe}(\text{pq})_3^{2+}$, while double benzo substitution to form biq so increases the steric hindrance that the tris complex $\text{Fe}(\text{biq})_3^{2+}$ could not be synthesized.⁴ We report here the synthesis of the tris(pyridyl)quinoline and tris(biquinoline) complexes of ruthenium(II) and osmium(II) and the effect of the benzo substituents on the absorption and emission spectra of the complexes.

Experimental Section

Ligands. 2-(2'-Pyridyl)quinoline (pq) was prepared as previously described⁴ in 60% yield; mp 99–100°. 2,2'-Biquinoline (biq) was used as purchased from Columbia Organic Chemicals, Co.

Tris[2-(2'-pyridyl)quinoline]ruthenium(II) Perchlorate, $[\text{Ru}(\text{pq})_3](\text{ClO}_4)_2$. A blue solution of ruthenium(II) chloride in methanol was prepared by the hydrogen (2 atm) reduction⁵ of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (Engelhard Industries). Twenty milliliters of this solution containing 2 mmol of Ru(II) was added slowly under a nitrogen atmosphere to a hot ($\sim 80^\circ\text{C}$) solution of 1.3 g (6.3 mmol) of pq dissolved in 25 ml of ethylene glycol. After distillation of the methanol solvent the reaction mixture was refluxed for 3 h and then heated for another 5 h while the volume was reduced to 10 ml. The cooled dark red solution was diluted with 20 ml of water and filtered. The filtrate was heated almost to boiling and NaClO_4 solution (10%) was added slowly. The reddish brown precipitate which formed was collected, washed with water, and air-dried. The solid was recrystallized from $\text{EtOH-H}_2\text{O}$ and dried to yield 1.6 g (87% yield). The complex was purified by saturating 10 ml of absolute methanol and passing it through a column (2.8 \times 59 cm) of Sephadex LH-20 (Pharmacia Fine Chemicals). The main band was collected and the methanol allowed to evaporate slowly to produce reddish brown crystals which were then vacuum-dried for 24 h over P_2O_5 . Anal. Calcd for $[\text{Ru}(\text{C}_{14}\text{H}_{10}\text{N}_2)_3](\text{ClO}_4)_2$: C, 54.91; H, 3.29; N, 9.15; Cl, 7.72. Found: C, 54.48; H, 3.05; N, 9.08; Cl, 7.80.

Tris(2,2'-biquinoline)ruthenium(II) Perchlorate, $[\text{Ru}(\text{biq})_3](\text{ClO}_4)_2$. Essentially the same procedure was used for the synthesis of this complex as described above for the $[\text{Ru}(\text{pq})_3](\text{ClO}_4)_2$ complex. Glycerol was used as the solvent and the reaction mixture was heated for only 1 h. Attempts to purify the product on a Sephadex LH-20 column produced a pale blue decomposition product all the way down the column. The complex was recrystallized twice from methanol to produce a 43% yield of brown crystals. Anal. Calcd for $[\text{Ru}(\text{C}_{18}\text{H}_{12}\text{N}_2)_3](\text{ClO}_4)_2$: C, 60.68; H, 3.40; N, 7.86. Found: C, 60.48; H, 3.47; N, 7.74.

Tris[2-(2'-pyridyl)quinoline]osmium(II) Perchlorate Hydrate, $[\text{Os}(\text{pq})_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$. A mixture of 0.26 g (0.5 mmol) of $\text{K}_2\text{OsCl}_6 \cdot 2\text{H}_2\text{O}$ (Research Organic/Inorganic Chemical Corp.) and 0.40 g (1.9 mmol) of pq in 15 ml of glycerol were refluxed for 3 h under a nitrogen atmosphere. The dark solution was cooled, diluted with 20 ml of water, and filtered. Two 5-ml washings of the unreacted ligand were added to the filtrate. The filtrate was heated to 80–90 $^\circ\text{C}$ and 8 ml of a 10% solution of NaClO_4 added dropwise. The hot solution was cooled overnight in the refrigerator. The black precipitate which formed was collected, washed twice with cold water, and dried to give 0.30 g of product. An additional 0.09 g was obtained by evaporating the filtrate to dryness, dissolving the residue in hot water, and precipitating the product with aqueous sodium perchlorate. The complex was purified on a column (2.8 \times 59 cm) of Sephadex LH-20 using methanol as the solvent. The methanol was evaporated and the residue dissolved in hot water and precipitated with NaClO_4 . The black crystals were collected, washed with cold water, and vacuum-dried for 24 h over P_2O_5 to give 0.25 g (49% yield). Anal. Calcd for $[\text{Os}(\text{C}_{14}\text{H}_{10}\text{N}_2)_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$: C, 49.17; H, 3.14; N, 8.19; Cl, 6.91. Found: C, 49.09; H, 2.97; N, 8.10; Cl, 7.34.

Tris(2,2'-biquinoline)osmium(II) Perchlorate Hydrate, $[\text{Os}(\text{biq})_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$. The same procedure was used for the synthesis and purification of this complex as described above for the $[\text{Os}$