

Emission Photoselection Studies of Transition-Metal Complexes. 2. Tris(diimine) Complexes

M. KEITH DEARMOND,* CLIFFORD M. CARLIN, and WEN LIANG HUANG

Received May 21, 1979

Luminescence photoselection spectra at 77 K have been acquired for metal-diimine complexes of general formula ML_3^{n+} ($M = Ru(II), Rh(III), Ir(III), Zn(II)$; $L = 2,2'$ -bipyridine, 1,10-phenanthroline). Excitation polarization spectra for the five transition-metal complexes ($[Ir(phen)_3]^{3+}$ not available) are similar in the high-energy $\pi\pi^*$ region to the polarization values measured (-10% to +10%), suggesting overlapping electronic bands. The polarization obtained for the Ir(III) and Rh(III) at the low energy end (where absorption band overlap is unlikely) approaches 12%, consistent with a planar emission oscillator. The excitation polarization for the $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ complexes at the low-energy absorption end is structured with a maximum value of 22% occurring at $\sim 21 \times 10^3 \text{ cm}^{-1}$ for both complexes but decreasing to $\sim 16\%$ near the origin of the emission. Our excitation polarization spectrum for $[Ru(bpy)_3]^{2+}$ is identical with that previously reported by Fujita and Kobayashi. The excitation polarization spectrum for the $[Zn(bpy)_3]^{2+}$ complex is extensively depolarized, in particular at the low-energy limit of the absorption. The emission polarization spectra of all complexes are flat and structureless in contrast to those measured for the free ligands. Various models rationalizing the polarization values are discussed.

Introduction

The coordination of a transition-metal ion to an aromatic π -electron molecule introduces a number of new and unique spectroscopic properties not present in the free π -electron system, including additional transitions and deactivation schemes. For example, the transition-metal ion introduces the possibility of charge-transfer transitions involving transfer from metal d to ligand π orbital (or vice versa), transitions in some sense analogous to those involving nonbonding (n) electrons in the isolated aromatic. Moreover, the localized dd^* transition introduced by the metal ion is one which typically has no analogue in the complex aromatic system. Introduction of a first-series metal ion into a complex π -electron system can cause deactivation of $\pi\pi^*$ luminescent states and thus unique photochemistry as observed for Fe(II) and Co(III) porphyrin systems.^{1,2} Similarly, the significant photochemistry³ of cobalt containing B_{12} apparently occurs because the introduction of the Co(III) into the basic π -electron corrin chromophore deactivates luminescent (and photochemically active) $\pi\pi^*$ states.⁴ The less complex but interesting luminescent diimine chelate ligands 2,2'-bipyridyl (bpy) and 1,10-phenanthroline (phen) are also apparently deactivated by the introduction of Co(III) and Fe(II) ions to give $Co(L_3)^{3+}$ and $Fe(L_3)^{2+}$ type complexes. Here charge-transfer states ($d\pi^*$) and dd^* states are introduced at lower energy than the luminescent free ligand $\pi\pi^*$ states.^{5a} Introduction of second- and third-series ions into such π -electron ligands as the porphyrin or the diimine ligand can cause other effects. The large crystal field splitting associated with these heavy ions causes the dd^* states to occur at higher energy;^{5b} thus a delocalized orbital state ($\pi\pi^*$ ligand or charge-transfer type) may occur at lowest energy. For the Rh(III) porphyrin⁶ and $[Rh(bpy)_3]^{3+}$ and $[Rh(phen)_3]^{3+}$ complexes,^{7,8} the emission occurs from an essentially $\pi\pi^*$ ligand state. The large spin-orbit coupling does increase intersystem crossing such that for these d⁶ diimines only phosphorescence

is observed while the ratio of phosphorescence to fluorescence is increased for the porphyrin system. For these π -electron complexes, no charge-transfer or dd^* bands can be identified at low energy so the presumption is usually made that these transitions must be weak and at high energy covered by ligand bands. Such results imply that this molecule in its ground state and lower excited state possesses little metal-ligand π interaction. Indeed spectroscopic results⁹ for the related mixed-ligand complexes $[Rh(bpy)_2(phen)]^{3+}$ and $[Rh(bpy)(phen)_2]^{3+}$ evidence two simultaneous emissions, one characteristic of the bpy and the other of the phen ligand, indicating a single-ring-type state for this system and implying a similar circumstance for the analogous $[Rh(phen)_3]^{3+}$ and $[Rh(bpy)_3]^{3+}$ complexes. Electrochemical results^{10,11} for these complexes and the tris Ir(III) analogues appear to verify this model of these systems.

The $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ complexes show a unique intense charge-transfer emission at lower energy¹²⁻¹⁴ than the ligand $\pi\pi^*$ phosphorescence which in conjunction with the intense charge-transfer absorption bands imply a substantial metal d-ligand π interaction. Indeed, the magnitude of the d-orbital contribution is such that the large spin-orbit coupling associated with this system mixes triplet and singlet states such that spin, S , cannot be considered a good quantum number. Consequently the emission is described¹³⁻¹⁶ as occurring from a manifold of spin-orbit states rather than a spin-triplet electronic state. An interaction of this magnitude implies that the electronic states are delocalized through the entire D_3 chelate system; i.e., the orbitals are multiring orbitals¹⁷ as opposed to the single-chelate-ring orbitals⁹⁻¹¹ postulated for the Rh(III) complex.

A third configuration of states appears to have been identified in which near-degenerate states of distinct orbital origin lie at lowest energy. Among the diimine complexes, $[Ir(bpy)_2Cl_2]^+$, $[Ir(phen)_2Cl_2]^+$, and $[Ir(5,6\text{-phen})_2Cl_2]^+$ each apparently exhibit two emissions,^{18,20} one from a localized dd^*

(1) Eastwood, D.; Gouterman, M. *J. Mol. Spectrosc.* **1970**, *35*, 359.
 (2) Vogler, Arnd; Kunkely, H. *Ber. Bunsenges. Phys. Chem.* **1976**, *80*, 425.
 (3) Pratt, J. M. "Inorganic Chemistry of Vitamin B₁₂"; Academic Press: New York, 1972; Chapter 14.
 (4) Gardiner, M.; Thomson, A. J. *J. Chem. Soc., Dalton Trans.* **1974**, 820.
 (5) (a) Huang, W. L.; DeArmond, M. K., unpublished results. (b) Jørgensen, C. K. "Absorption Spectra and Chemical Bonding in Complexes"; Pergamon Press: London, 1969; p 114.
 (6) Hanson, L. K.; Gouterman, M.; Hanson, J. C. *J. Am. Chem. Soc.* **1973**, *95*, 4822.
 (7) Hillis, J. E.; DeArmond, M. K. *J. Chem. Phys.* **1971**, *54*, 2247.
 (8) Hillis, J. E.; DeArmond, M. K. *Chem. Phys. Lett.* **1971**, *10*, 326.

(9) Halper, W.; DeArmond, M. K. *J. Lumin.* **1972**, *5*, 225.
 (10) Kew, G.; DeArmond, K.; Hanck, K. *J. Phys. Chem.* **1974**, *78*, 727.
 (11) Kew, G.; Hanck, K.; DeArmond, K. *J. Phys. Chem.* **1975**, *79*, 1828.
 (12) Klassen, D. M.; Crosby, G. A. *J. Chem. Phys.* **1968**, *48*, 1853.
 (13) Lytle, F. E.; Hercules, D. M. *J. Am. Chem. Soc.* **1969**, *91*, 253.
 (14) Hager, G. D.; Crosby, G. A. *J. Am. Chem. Soc.* **1975**, *97*, 7031.
 (15) Hager, G. D.; Watts, R. J.; Crosby, G. A. *J. Am. Chem. Soc.* **1975**, *97*, 7037.
 (16) Hipps, K. W.; Crosby, G. A. *J. Am. Chem. Soc.* **1975**, *97*, 7042.
 (17) DeArmond, M. K.; Hanck, K. W., unpublished data.
 (18) DeArmond, M. K.; Huang, W. L.; Carlin, C. M. *Inorg. Chem.* **1979**, in press.

state and the other a delocalized orbital type, i.e., from a charge-transfer $d\pi^*$ or $\pi\pi^*$ state. The apparent lack of communication between these states is quite unusual but not totally unexpected. The extent of the orbital delocalization, i.e., single chelate ring or multiple chelate ring, is not clear.

While luminescence spectral techniques are quite useful in identifying the nature of and interactions of the lowest excited states, room-temperature solution absorption spectra of high-energy ligand-localized transitions are not individually very useful since $\pi \rightarrow \pi^*$ singlet transitions tend to be broad, unstructured, and overlapped. However, for the tris complexes of bpy and phen, Mason^{21,22} has done a series of circular dichroism (CD) and optical rotatory dispersion measurements of these high-energy bands and attempted to measure and calculate the magnitude of the exciton splitting (E to A_2 separation) for these tris π -electron systems.

In a previous paper,¹⁸ we demonstrated the utility of high-resolution emission photoselection instrument and technique in verifying the two-state emission from the C_2 symmetry Ir(III) complexes, characterizing the relaxation mechanism, and in verifying the linear oscillator character of C_2 symmetry complexes (system having no degenerate symmetry representations). An excitation photoselection spectrum²³ has been reported for the D_3 complex $[\text{Ru}(\text{bpy})_3]^{2+}$, while some results²⁴ have been reported for $[\text{Zn}(\text{bpy})_3]^{2+}$ in addition to other lower symmetry complexes. These D_3 complexes possessing a C_3 axis presumably can behave as planar oscillators, i.e., possess E symmetry representations.¹⁸

This work reports emission and photoselection spectra for the D_3 complexes $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Ru}(\text{phen})_3]^{2+}$, $[\text{Rh}(\text{bpy})_3]^{3+}$, $[\text{Rh}(\text{phen})_3]^{3+}$, $[\text{Ir}(\text{bpy})_3]^{3+}$, and $[\text{Zn}(\text{bpy})_3]^{2+}$ with the focus of this research upon (1) the types of polarization spectra possible for these D_3 symmetry systems, (2) the clarification of emission orbital origin, and (3) the determination of the nature and extent of the orbital delocalization for these systems, i.e., single chelate ring or multi chelate rings.

Experimental Section

Solvents. Low-temperature absorption and emission spectra were obtained in ethanol-methanol mixture as described in paper 1 of this series.¹⁸

Metal Complexes. $[\text{Zn}(\text{bpy})_3](\text{NO}_3)_2$ was prepared by the method of Ohno and Kato.²⁴ The prepared complex was recrystallized from water four times.

$[\text{Ir}(\text{bpy})_3](\text{NO}_3)_2$ was prepared by Kahl²⁵ following the method of Flynn and Demas²⁶ except that no attempt was made to convert to the perchlorate salt.

$[\text{Ru}(\text{bpy})_3](\text{ClO}_4)_2$ was prepared by the procedure of Palmer and Piper.²⁷ The complex was recrystallized from H_2O -EtOH mixture four times before use.

$[\text{Ru}(\text{phen})_3](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ was synthesized by using the method of Dwyer et al.²⁹ and was purified by repeated recrystallization from H_2O -EtOH mixture.

$[\text{Rh}(\text{bpy})_3]\text{Cl}_3$ and $[\text{Rh}(\text{phen})_3]\text{Br}_3$ were synthesized by the catalytic procedures of Gillard et al.³¹

- (19) Watts, R. J.; White, T. P.; Griffith, B. G. *J. Am. Chem. Soc.* **1975**, *97*, 6914.
- (20) Watts, R. J.; Missimer, D. *J. Am. Chem. Soc.* **1978**, *100*, 5350.
- (21) McCaffery, A. J.; Mason, S. F.; Norman, B. J. *J. Chem. Soc. A* **1971**, 667.
- (22) Mason, S. F.; Peart, B. J.; Waddell, R. E. *J. Chem. Soc., Dalton Trans.* **1973**, 944.
- (23) Fujita, I.; Kobayashi, H. *Inorg. Chem.* **1973**, *12*, 2758.
- (24) Ohno, T.; Kato, S. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2953.
- (25) Kahl, J. L.; Hanck, K. W.; DeArmond, M. K. *J. Phys. Chem.* **1978**, *82*, 540.
- (26) Flynn, C., Jr.; Demas, J. *J. Am. Chem. Soc.* **1975**, *97*, 1988.
- (27) Palmer, R. A.; Piper, T. S. *Inorg. Chem.* **1966**, *5*, 864.
- (28) Felix, F.; Ferguson, J.; Gudel, H. U.; Ludi, A. *Chem. Phys. Lett.* **1979**, *62*, 153.
- (29) Dwyer, F. P.; Humpoetz, J. E.; Nyholm, R. S. *J. Proc. R. Soc. N. S. W.* **1947**, *80*, 212.
- (30) Rabold, G. P.; Piette, L. H. *Photochem. Photobiol.* **1966**, *5*, 733.
- (31) Gillard, F. D.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc.* **1965**, 1951.

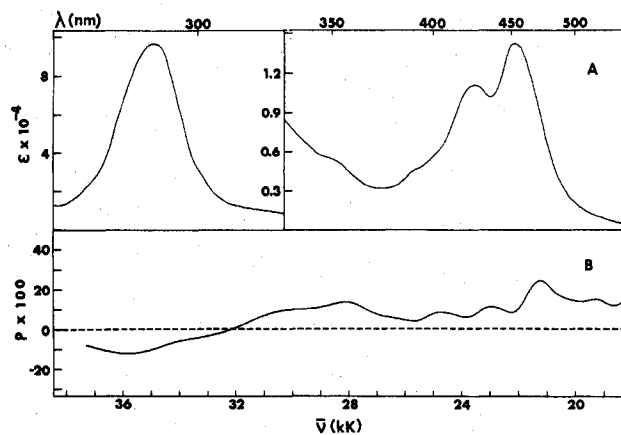


Figure 1. Spectra of $[\text{Ru}(\text{bpy})_3]^{2+}$: (A) absorption spectrum (83 K); (B) excitation polarization spectrum (77 K, 578-nm emission).

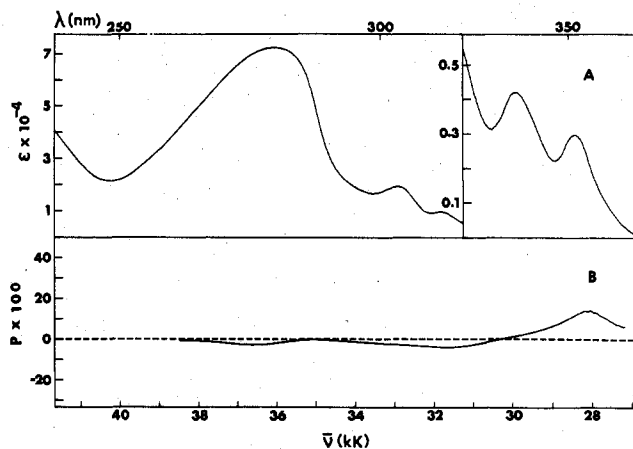


Figure 2. Spectra of $[\text{Rh}(\text{phen})_3]^{3+}$: (A) absorption spectrum (83 K); (B) excitation polarization spectrum (77 K, 478-nm emission).

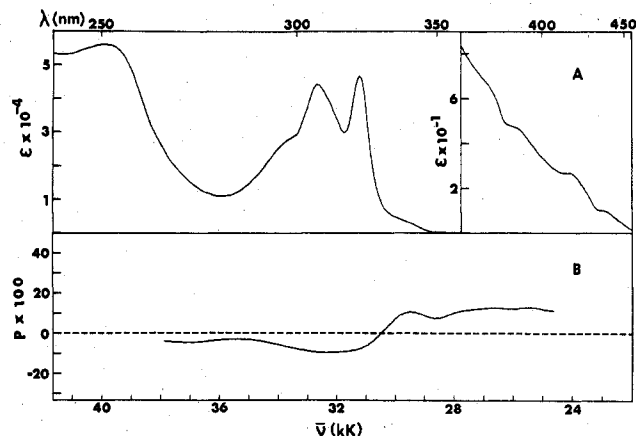


Figure 3. Spectra of $[\text{Ir}(\text{bpy})_3]^{3+}$: (A) absorption spectrum (83 K); (B) excitation polarization spectrum (77 K, 480-nm emission).

Instrumentation. All absorption and emission spectra were obtained with the same instruments as reported in the previous paper.¹⁸ All the polarization spectra were measured with a high-resolution polarizing spectrophotometer.¹⁸

Measurement Technique. Polarization, P , at a particular wavelength is defined by

$$P = (I_{vv} - I_{vh}) / (I_{vv} + I_{vh})$$

where I_{vv} and I_{vh} are the measured emission intensities with the analyzers vertical (v) and horizontal (h), respectively. The excitation source is polarized vertically (v). All polarization values were obtained by using procedures identical with those employed for the bis(diimine) complexes.¹⁸ The lability of the Zn complexes necessitated care to

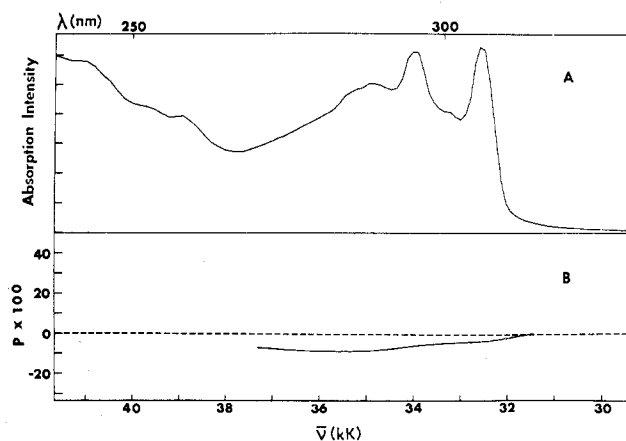


Figure 4. Spectra of $[\text{Zn}(\text{bpy})_3]^{2+}$: (A) absorption spectrum (83 K); (B) excitation polarization spectrum (77 K, 435-nm emission).

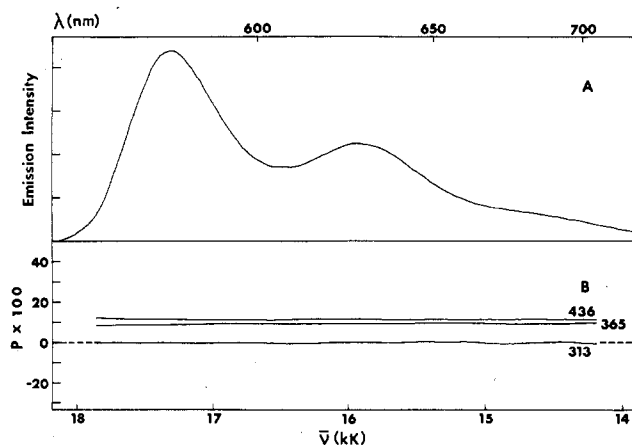


Figure 5. Spectra of $[\text{Ru}(\text{bpy})_3]^{2+}$ (77 K): (A) emission spectrum (313-nm excitation); (B) emission polarization spectra (313-, 365-, 436-nm excitation).

avoid false polarization values from the presence of free bpy ligand. Concentrations were adjusted to minimize this problem.

Results

Absorption spectra (83 K) for the $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Rh}(\text{phen})_3]^{3+}$, $[\text{Ir}(\text{bpy})_3]^{3+}$, and $[\text{Zn}(\text{bpy})_3]^{2+}$ complexes are presented in the top halves of Figures 1–4 with the corresponding 77 K emission spectra given in Figures 5–8. The excitation polarization spectra are given in the bottom halves of Figures 1–4 while the emission spectra are presented with polarizations in Figures 5–8. The spectra for the ligands have previously been presented.¹⁸

The contours of the absorption spectra in the $(31\text{--}40) \times 10^3 \text{ cm}^{-1}$ region for the bpyH^+ , $[\text{Zn}(\text{bpy})_3]^{2+}$, $[\text{Ir}(\text{bpy})_3]^{3+}$, and $[\text{Rh}(\text{bpy})_3]^{3+}$ are generally similar with three intense bands at $\sim(31\text{--}32) \times 10^3$, $(33\text{--}34) \times 10^3$, and $(39\text{--}41) \times 10^3 \text{ cm}^{-1}$. The lowest energy band appears only as a shoulder for bpyH^+ , and the precise position of these $\pi\pi^*$ bands is altered by the charge of the central cation. The $\pi\pi^*$ region of the $[\text{Ru}(\text{bpy})_3]^{2+}$ complex is distinct with only a single band appearing in the $(31\text{--}36) \times 10^3 \text{ cm}^{-1}$ region. The phenH^+ and $[\text{Rh}(\text{phen})_3]^{3+}$ complexes both show bands in the $\pi\pi^*$ region $((31\text{--}40) \times 10^3 \text{ cm}^{-1})$, some of which must be vibronic components. The $[\text{Ru}(\text{phen})_3]^{2+}$ complex also exhibits only a single strong band $(38 \times 10^3 \text{ cm}^{-1})$ with a weak shoulder at $\sim 33 \times 10^3 \text{ cm}^{-1}$ in the $\pi\pi^*$ region. In the lower energy region ($E < 31 \times 10^3 \text{ cm}^{-1}$), the two Ru(II) complexes show intense ($\epsilon_{\text{max}} \sim 10^4\text{--}10^3$) absorption overlapping with the emission and assigned as charge-transfer metal to ligand bands. The magnitude of the absorption in the region of the nominal "phosphorescence" band is indicative of the breakdown of

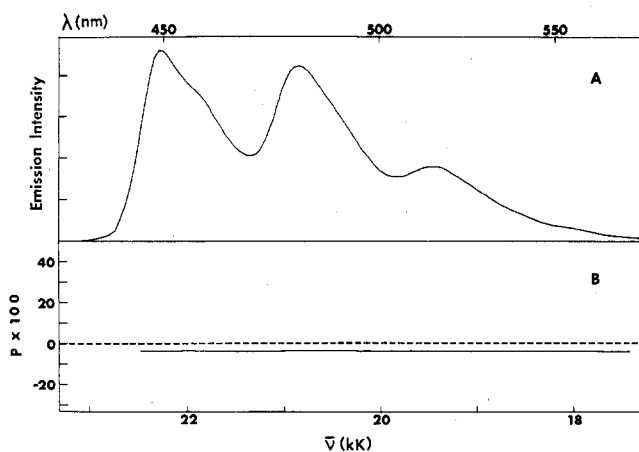


Figure 6. Spectra of $[\text{Rh}(\text{phen})_3]^{3+}$ (77 K): (A) emission spectrum (313-nm excitation); (B) emission polarization spectra (313-nm excitation).

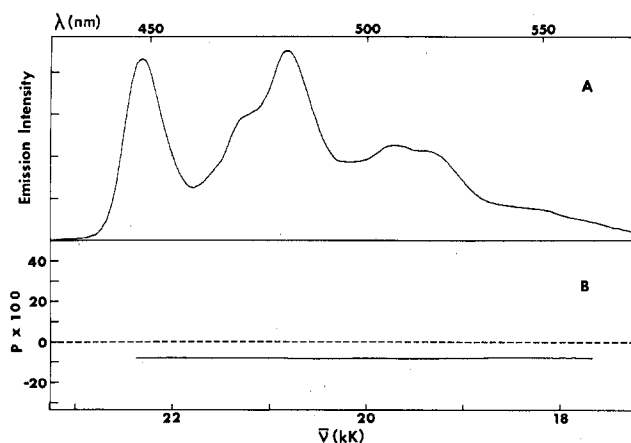


Figure 7. Spectra of $[\text{Ir}(\text{bpy})_3]^{3+}$ (77 K): (A) emission spectrum (313-nm excitation); (B) emission polarization spectrum (313-nm excitation).

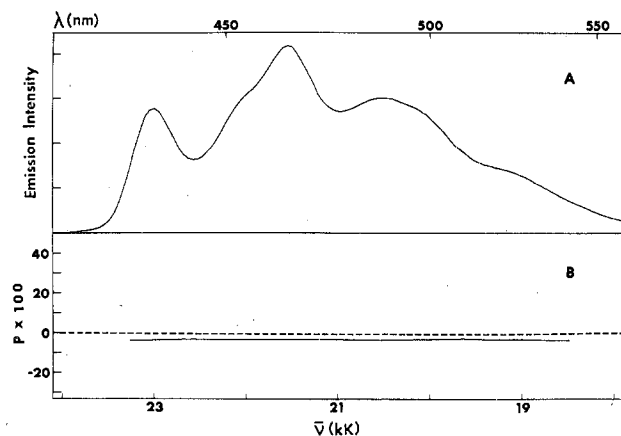


Figure 8. Spectra of $[\text{Zn}(\text{bpy})_3]^{2+}$ (77 K): (A) emission spectrum (313-nm excitation); (B) emission polarization spectrum (313-nm excitation).

validity of the Russell–Saunders angular-momentum model. The tris Ir(III) compounds also evidence absorption in this region, but the intensities of the bands ($\epsilon \sim 10\text{--}10^2$) are much less than those of the Ru(II) complexes. The weak band(s) ($\epsilon \sim 10$) overlapping the emission is (are) likely the spin-orbit enhanced singlet to triplet $\pi\pi^*$ transition rather than a charge-transfer band which is likely at higher energy for the tris(III) chelates. This lower energy region for the Rh(III) complexes contains broad structureless bands (even with

long-path absorption) whose orbital origin is likely $\pi\pi^*$. The $[\text{Zn}(\text{bpy})_3]^{2+}$ complex exhibits a long structureless tail throughout this region.

Excitation polarizations in the $\pi\pi^*$ region of all five transition-metal complexes are quite similar, showing little structure but having minima ($\sim -10\%$) in the polarization occurring in the $(33-32) \times 10^3 \text{ cm}^{-1}$ range and sharp increases to $\sim +10\%$ occurring in the $(\sim 30-31) \times 10^3 \text{ cm}^{-1}$ region. The $[\text{Zn}(\text{bpy})_3]^{2+}$ excitation polarization is essentially flat and negative (-7%) at $36 \times 10^3 \text{ cm}^{-1}$, increasing gradually to 0% at $31 \times 10^3 \text{ cm}^{-1}$. The tris Ir(III) and Rh(III) complexes give a P value of 12% in the region of emission and absorption overlap ($(25-22) \times 10^3 \text{ cm}^{-1}$). The polarizations for both Ru(II) complexes in the range $(25-19) \times 10^3 \text{ cm}^{-1}$ are structured and approximately similar in contour with a maximum polarization of 22% occurring at $\sim 21 \times 10^3 \text{ cm}^{-1}$ for both complexes, decreasing to $\sim 16\%$ at $19 \times 10^3 \text{ cm}^{-1}$ close to the origin of the emission. Excitation polarization spectra for $[\text{Ru}(\text{bpy})_3]^{2+}$ in the $(20-31) \times 10^3 \text{ cm}^{-1}$ region have been reported by Fujita and Kobayashi,²³ and our data for this region are essentially identical with theirs.

Emission spectra for the $[\text{Zn}(\text{bpy})_3]^{2+}$, $[\text{Ir}(\text{bpy})_3]^{3+}$, and $[\text{Rh}(\text{bpy})_3]^{3+}$ complexes are almost identical and are like the free ligand spectrum with a $\sim 1500\text{-cm}^{-1}$ and a $\sim 900\text{-cm}^{-1}$ vibration prominent in all cases. The $0-1 \text{ } 1500\text{-cm}^{-1}$ vibronic peak is most intense in these cases. Emission polarization spectra are flat (0 slope) and structureless for all complexes, contrasting the situation for the free ligand.

Discussion

The limiting values for the various combinations of emission and excitation oscillators have previously been tabulated.¹⁸ Since for these D_3 molecules E (x,y planar) representations are possible, polarization values of 0.14 can occur for the planar emitter-planar absorber case. Further depolarization due to rotational or intermolecular energy transfer can decrease polarization values below those expected for the limiting cases. For the rigid glassy solvent media used here, rotational depolarization cannot occur. Since, for effective intermolecular energy transfer, the diffusion constant-concentration product must be comparable to the reciprocal of the lifetime of the excited state, no collisional intermolecular energy transfer is expected. The possibility of intramolecular energy transfer between chelate rings of a single species will be considered below.

The transitions in the high-energy region have been examined by various workers^{22,24,27} and classified as $\pi\pi^*$. Primarily on the basis of the mirror-image character of the emission and the constant fluorescence excitation polarizations measured through this region, the structure observed in the $(32-36) \times 10^3 \text{ cm}^{-1}$ region for $[\text{Zn}(\text{bpy})_3]^{2+}$ has been assigned to vibronic transitions²⁴ rather than to an additional electronic transition. Comparable absorption structure is observed for the $[\text{Rh}(\text{bpy})_3]^{3+}$ and $[\text{Ir}(\text{bpy})_3]^{3+}$ complexes and can be assigned to vibronic bands. The excitation polarization spectra for the three compounds in this region may suggest the presence of overlapping transitions of different polarizations since, at both the high-energy and low-energy sides of the band, the polarization becomes more positive. The substantial depolarization in the midportion of this region could then be interpreted as deriving from overlapping E and A states, in general agreement with the circular-dichroism results obtained by Mason and co-workers^{21,22} for a number of bpy complexes including the $[\text{Rh}(\text{bpy})_3]^{3+}$ species.

The absorption spectrum of the $[\text{Ru}(\text{bpy})_3]^{2+}$ complex contrasts with those of the other bpy complexes with a single broad band at approximately $35 \times 10^3 \text{ cm}^{-1}$. The excitation polarization does, however, as for the other bpy complexes, indicate the presence of overlapping transitions consistent with

the circular-dichroism results.

Oriented single-crystal spectra²⁷ for $[\text{Ru}(\text{bpy})_3]^{2+}$ have been interpreted to indicate a weak ${}^1A_2 \leftarrow {}^1A_1$ component at approximately $21\,000 \text{ cm}^{-1}$, overlapped by an intense ${}^1E \leftarrow {}^1A_1$ transition. The excitation polarization spectra measured by Fujita and Kobayashi²³ have been interpreted as indicating that the lowest emitting triplet state is a 3E , rather than a 3A_2 .

Most recently, polarized absorption and CD data obtained for dilute single crystals of $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Os}(\text{bpy})_3]^{2+}$ have been interpreted²⁸ as verifying the Fujita and Kobayashi model.²³ However, Crosby and co-workers,^{14,15} using temperature-dependent lifetime and intensity data, developed an empirical model¹⁶ emphasizing the strong spin-orbit coupling expected for the Ru(II) complexes. The model determines that the emission derives from a manifold of spin-orbit states of A_1 , E, and A_2 symmetries occurring in that order. Moreover, at 77 K , Crosby and co-workers^{14,15} have calculated that the differing radiative rate constants of the E and A_2 levels (emission from A_1 is "forbidden") require that the emission is approximately $\sim 90\%$ from the A_2 level. Utilization of Crosby's spin-orbit model of the emitting manifold with the appropriate symmetry labels along with the polarized crystal data²⁷ of Piper and Palmer does lead to an ambiguity. Piper and Palmer²⁷ determined that the strong band at $23\,000 \text{ cm}^{-1}$ is an E state while a weak A_2 band participates in the absorption at $21\,000 \text{ cm}^{-1}$ of $[\text{Ru}(\text{bpy})_3]^{2+}$. The polarization curve in the $(23-26) \times 10^3 \text{ cm}^{-1}$ region oscillates but has a peak value of $\sim 10\%$ and increases to 22% to $21\,000 \text{ cm}^{-1}$ (the A_2 band). The magnitude ($\sim 10\%$) of the polarization for the E absorption is consistent with a planar emitter, i.e., an E-type emission, 14% . The increased magnitude of the polarization in the region of the A_2 absorption implies a substantial contribution from a linear emitter, i.e., A_2 -type emission. Estimation of the polarization at 77 K , using Crosby's ordering of the states with the appropriate fractional intensities, gives negative polarization values but does correctly predict that the polarization becomes more positive from $23\,000$ to $21\,000 \text{ cm}^{-1}$. Reversal of Crosby's symmetry assignments of the highest and middle levels so that the emission would be 90% E character at 77 K results in the correct magnitude and sign for the polarization at $23\,000 \text{ cm}^{-1}$ but predicts that the $21\,000\text{-cm}^{-1}$ polarization should decrease slightly relative (due to contribution of the linear oscillator) to that at $23\,000 \text{ cm}^{-1}$. The oscillation of the spectra in the $(26-22) \times 10^3 \text{ cm}^{-1}$ region may indicate that a vibronic perturbation (or a spin-orbital perturbation) is participating here, complicating the situation.

Ultimately temperature-dependent polarization spectra may be useful in clarifying the symmetry of the emitting manifold. Lowering the temperature to 10 K should result in population of only the lowest two states with a resultant increase in the $21\,000\text{-cm}^{-1}$ polarization and a substantial decrease at $23\,000 \text{ cm}^{-1}$ if the lowest levels are A_2 and A_1 whereas the Crosby order would cause a reversal in the directions of the polarization change. The possibility that the observed excitation polarization values less than 50% (expected for a linear emission oscillator as A_2) result from overlapping bands or other depolarizing mechanism seems unlikely in view of the experimental results¹⁸ obtained for the bis Ir(III) chelates, necessarily a linear oscillator emission. For these bis complexes, the excitation polarization is $\sim 40\%$ and above in the region of emission and absorption overlap. This contrasts the value of $\sim 14\%$ measured in the overlap region for these tris Ru(II) complexes.

Emission spectra for the bpy complexes here are of essentially two types: the first is a complex vibronic pattern (like that of free bpy) containing more than a single vibration and often having a transition other than $0-0'$ as the most intense band while the second type of emission is less complex con-

taining only a single vibrational interval of $\sim 1400\text{ cm}^{-1}$ and usually having the $0-0'$ band as the most intense band. The former more complex pattern is observed for the $[\text{Zn}(\text{bpy})_3]^{2+}$, $[\text{Rh}(\text{bpy})_3]^{3+}$, and $[\text{Ir}(\text{bpy})_3]^{3+}$ complexes while the simpler second pattern is observed for the $[\text{Ru}(\text{bpy})_3]^{2+}$ complex. The emission of the phen complexes by contrast is generally less complex with only a single vibrational progression (as the phenH^+) of $\sim 1400\text{ cm}^{-1}$. The $[\text{Rh}(\text{phen})_3]^{3+}$ emission does indicate a weak shoulder at approximately $\sim 400\text{ cm}^{-1}$. For all phen complexes here the $0-0'$ band is the most intense band, contrasting the situation for the phenH^+ system. Since the relative intensity pattern reflects the Franck-Condon factor, therefore the relative displacement along some arbitrary coordinate of the excited and ground states, a similar spatial extent is implied for the triplet of free phen and $[\text{Zn}(\text{phen})_3]^{2+}$, i.e., a localized excited state. Ohno and Kato²⁴ have utilized changes in the vibronic intensities to argue that a direct ligand π interaction occurs between the chelate rings, resulting in changes in the fluorescence to phosphorescence yield for the tris relative to mono complexes. The quantitative validity of such arguments is however uncertain in view of other evidence, suggesting a small, almost zero interaction occurs between the rings. For example, the triplet-state ESR spectra²⁹ of the free phen and $[\text{Zn}(\text{phen})_3]^{2+}$ produce identical values for D , the zero-field splitting parameter.

The emission spectra most altered in structure and energy from the spectra of the free ligand are those that are unambiguously assigned as charge-transfer emission ($\pi^* \rightarrow d$) whereas those spectra little changed from the ligand are generally best considered as $\pi\pi^*$ type emission (although charge-transfer absorption bands are apparent in some of these complexes). The emission polarization spectra for all complexes are structureless and with 0 slope although not necessarily completely depolarized ($P \approx 0$). Such polarizations contrast with the vibronic polarization of the free ligand. For the transition-metal complexes, the absence of fluorescence, the short lifetimes, and the flat polarization imply the expected dominance of first-order spin-orbit coupling¹⁸ in the relaxation of the excited states. For the $[\text{Zn}(\text{bpy})_3]^{2+}$ ²⁴ complex, the fluorescence to phosphorescence ratio increases relative to the free ligand while the triplet lifetime of the complex is of comparable magnitude to that of the ligand, thereby implying that spin-orbit coupling is of little significance here. Consequently, the absence of a vibronic structure in the emission polarization here may relate to the substantial depolarization occurring in this system.

Some Models. The extent of delocalization of the excited states (the effective symmetry) is a detail that presumably should be partially elaborated by the luminescence photoselection data. In essence, two limiting cases¹⁷ can be identified for these materials: the first in which the wave functions are delocalized through the total tris system, producing an effective D_3 system, and the second in which the interaction between the chelate rings is zero so that the excited state can be considered a localized exciton, producing an effective C_{2v} symmetry. In the latter case, the three identical chromophores within a single moiety would produce an accidental threefold degeneracy (i.e., $3C_{2v}$ systems). A multiring D_3 symmetry can be viewed as a C_{2v} symmetry system in which rapid (compared to vibrational relaxation) intramolecular hopping from ring to ring occurs. Therefore, the continuous decrease of the hopping rate (relative to the time frame of the hopping) would ultimately result in a single-ring system having effective C_{2v} symmetry. The hopping rate is likely determined by vibrational factors. The magnitude of the E-A state splitting is an electronic factor determined by the direct overlap of the nitrogen orbitals from adjacent rings and/or delocalization of π electron through the d orbitals of the metal. The $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{phen})_3]^{2+}$ complexes with the strong charge-transfer band evident obviously are expected to fall into this D_3 (multiring category) category. Indeed, polarization spectra in the low-energy charge-transfer band have been interpreted above as indicating an E-type state consistent with the D_3 point group. $[\text{Zn}(\text{bpy})_3]^{2+}$ would seem to best approach a localized-exciton system (C_{2v}) since only the small overlap of adjacent ring nitrogens should permit delocalization of the wave function. Therefore, the qualitative similarity of the polarization spectra for the $[\text{Zn}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{bpy})_3]^{2+}$ complexes in the $\pi\pi^*$ region is puzzling. Both are substantially depolarized throughout the $\pi\pi^*$ region relative to the free ligand. The overlap of $\pi\pi^*$ bands of opposite polarization could produce the diminished values measured here. The upward curvature of the polarization at low and high energies implies that this is the case for the Ru(II) complexes. The depolarization of $[\text{Zn}(\text{bpy})_3]^{2+}$ presumably can occur from a similar overlap of bands, but the flat polarization observed at higher energy for $[\text{Zn}(\text{bpy})_3]^{2+}$ implies that this may not be the entire explanation. Certainly a small exciton interaction (approximate C_{2v} symmetry) could produce depolarization by a hopping mechanism. Such a depolarization is consistent with the depolarization²⁹ observed for the photoselection ESR of the analogous $[\text{Zn}(\text{phen})_3]^{2+}$ complex. The zero polarization value observed for $[\text{Zn}(\text{bpy})_3]^{2+}$ in the overlap region (absorption and emission spectral overlap) could indicate that the emitting manifold contains planar oscillator character (i.e., E-type representation) or could result from single-ring C_{2v} symmetry with hopping. In any case a model in which both E and A states emit, as suggested earlier, seems unlikely. Finally, the presence of vibronic structure in this $\pi\pi^*$ region of $[\text{Zn}(\text{bpy})_3]^{2+}$ contrasts the broad structureless $\pi\pi^*$ absorption measured for the $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{phen})_3]^{2+}$ complexes and is likely indicative of the weak (small) exciton coupling of the $[\text{Zn}(\text{bpy})_3]^{2+}$ and the strong exciton coupling present in the $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{phen})_3]^{2+}$ species.²²

The polarization data for the $[\text{Rh}(\text{L}_3)]^{3+}$ and $[\text{Ir}(\text{L}_3)]^{3+}$ species are somewhat different from those observed for $[\text{Zn}(\text{bpy})_3]^{2+}$ ($P \approx 12\%$ in the overlap region and $P \approx 0$ in the singlet $\pi\pi^*$ region); therefore the possibility that the emitting manifold is here a planar oscillator, E type, seems even more likely than for the Zn^{2+} case.

In either case (localized C_{2v} with hopping or D_3) the splitting of the states would be small. For the D_3 case, ΔE must be only slightly greater than kT while for the C_{2v} limit, the magnitude of the splitting is ~ 0 . The hopping that would have to occur for the single-ring C_{2v} situation would likely have to be energy dependent to explain the variation in excitation polarization from 0 to 12%.

Therefore, we suggest that the emitting electronic state for the Rh(III) and Ir(III) complexes, at this temperature and to the resolution of these measurements, involves a planar oscillator. Consequently the effective system symmetry is D_3 , implying a multiring orbital. However, the splitting between the emitting E and A levels should be quite small. Moreover, the magnitude of the interaction between the rings (hopping) can be small, approaching the single-ring C_{2v} limit. The hopping process likely is a vibrationally determined process while the magnitude of the E and A split is an electronic interaction. Thus at lower temperatures or at 77 K with small structural perturbations as in mixed-ligand complexes as $[\text{Rh}(\text{bpy})_2(\text{bpy})_D]^{3+}$ (one ligand ring perdeuterated), the polarization spectra would probably indicate that the system has moved closer to the C_{2v} single-ring limit.

Conclusions

Polarization (emission and excitation) spectra have been measured for tris(diimine) complexes of Ru(II), Rh(III), Ir(III), and Zn(II). The polarization spectra of the two

charge-transfer emitting Ru(II) complexes indicate an E-type emission, apparently verifying the effective D_3 symmetry of these complexes and the delocalization of the excited state. Polarization spectra can, for the Zn(II) species, be interpreted as indicating single-ring C_{2v} symmetry with hopping consistent with vibronic $\pi\pi^*$ absorption spectra and published ESR triplet and ESR photoselection data. The excitation depolarization measured in the $\pi\pi^*$ singlet and overlap region for the Ir(III)

and Rh(III) complexes leads to an ambiguous interpretation. The best present interpretation may be that the emitting chromophore is a multiring D_3 species but that small perturbations (structural or temperature) may result in the single-ring circumstance (C_{2v} with hopping).

Registry No. [Zn(bpy)₃](NO₃)₂, 29881-78-5; [Ir(bpy)₃](NO₃)₂, 71818-71-8; [Ru(bpy)₃](ClO₄)₂, 15635-95-7; [Ru(phen)₃](ClO₄)₂, 14767-24-9; [Rh(bpy)₃]Cl₃, 32680-72-1; [Rh(phen)₃]Br₃, 15378-54-8.

Contribution from the Institut für Strahlenchemie im Max-Planck-Institut für Kohlenforschung, D-4330 Mülheim, West Germany

Low-Temperature Matrix Photochemistry of (1,3-Diene)tricarbonyliron Complexes

GABRIELE ELLERHORST, WOLFGANG GERHARTZ,* and FRIEDRICH-WILHELM GREVELS

Received January 5, 1979

UV photolysis of (η^4 -2,3-dimethylbutadiene)Fe(CO)₃ and (η^4 -butadiene)Fe(CO)₃ in inert matrices at 10 K was monitored by IR and UV spectroscopy. Elimination of CO is the predominant photoreaction. In the latter case we also observed the decomplexation of the butadiene ligand and hence the formation of (η^2 -butadiene)Fe(CO)₃. This product is also obtained during the photolysis of (η^2 -butadiene)Fe(CO)₄ which is subsequently transformed to (η^4 -butadiene)Fe(CO)₃. For comparison, (η^2 -ethylene)Fe(CO)₄ and (η^2 -1,3-cyclohexadiene)Fe(CO)₄ were photolyzed under analogous conditions. Photolysis of (η^4 -1,3-diene)Fe(CO)₃ complexes in nitrogen matrices gives (η^4 -1,3-diene)Fe(CO)₂N₂; formation of (η^2 -butadiene)Fe(CO)₃N₂ from (η^2 -butadiene)Fe(CO)₄ requires annealing of the nitrogen matrix subsequent to irradiation.

Introduction

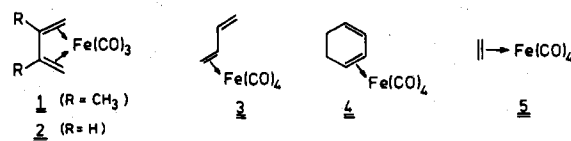
Photolysis of binary carbonylmetal complexes in low-temperature matrices and the structures of the resulting carbonyl-metal fragments have been thoroughly investigated.¹ Recent studies on a series of carbonylnitrosylmetal² and organotricarbonylmetal³ complexes under analogous conditions revealed a clear-cut discrimination between the different ligands in favor of photoelimination of carbon monoxide. With the provision of such detailed knowledge about primary photoproducts and reactive intermediates, the matrix isolation technique is widely considered as a useful tool with regard to mechanistic problems despite certain limitations and occasional disagreements⁴ with reactions in solution.

Our interest in optimizing and controlling the photoreactions of (1,3-diene)tricarbonyliron complexes with, e.g., excess 1,3-diene to produce bis(1,3-diene)carbonyliron⁵ or with olefins to form C-C coupling products,^{6,7} led us to investigate the mechanisms of such processes, in particular the primary photoreactions of (η^4 -1,3-diene)tricarbonyliron complexes.

The primary photochemical reactions of (η^4 -cyclohexadiene)tricarbonyliron have been thoroughly discussed. From flash photolysis experiments in the gas phase C₄H₄ detachment was concluded to be the major primary photolytic step,⁸ however, irradiation in frozen gas matrices^{3,9} clearly

demonstrates the loss of carbon monoxide, in agreement with the photoreactions in solution.^{10,11} Carbonyliron complexes of open chain 1,3-dienes, on the other hand, undergo photo-substitution of both the diene and CO when irradiated in solution in the presence of, e.g., phosphorus ligands.¹²

In this paper we report the IR and UV spectroscopic characterization of various species formed upon irradiation of (η^4 -2,3-dimethylbutadiene)tricarbonyliron (**1**) and (η^4 -butadiene)tricarbonyliron (**2**) in argon and nitrogen matrices at 10 K.¹³ For comparison, the tetracarbonyliron complexes of η^2 -coordinated butadiene (**3**, in argon and nitrogen), 1,3-cyclohexadiene (**4**, in argon), and ethylene (**5**, in argon) were similarly photolyzed.



Experimental Section

Low temperatures were achieved by means of a Displex CSW-202 closed-cycle helium cryostat (Air Products) equipped with an APD-IC-1 temperature controller. The target window (NaCl or CaF₂) was attached to the cold end by a copper sample holder and indium gaskets. The brass vacuum mantle (ca. 10⁻⁶ mbar) allows matrix deposition and simultaneous monitoring of the deposition rate by means of a He-Ne laser,¹⁴ as well as irradiation normal to the direction of deposition. Infrared spectra were recorded by using a Grubb-Parson

- (1) J. K. Burdett and J. J. Turner in "Cryochemistry", M. Moskovits and G. A. Ozin, Eds., Wiley-Interscience, New York, 1976, p 493 ff, and references cited therein.
- (2) O. Crichton and A. J. Rest, *J. Chem. Soc., Dalton Trans.*, 536, 656 (1977); 202 (1978).
- (3) A. J. Rest, J. R. Sodeau, and D. J. Taylor, *J. Chem. Soc., Dalton Trans.*, 651 (1978).
- (4) J. D. Black, M. J. Boylan, P. S. Braterman, and W. J. Wallace, *J. Organomet. Chem.*, **63**, C21 (1973).
- (5) E. Koerner von Gustorf, J. Buchkremer, Z. Pfajfer, and F.-W. Grevels, *Angew. Chem.*, **83**, 249 (1971); *Angew. Chem., Int. Ed. Engl.*, **10**, 260 (1971).
- (6) R. C. Kerber and E. A. Koerner von Gustorf, *J. Organomet. Chem.*, **110**, 345 (1976).
- (7) F.-W. Grevels, U. Feldhoff, J. Leitich, and C. Krüger, *J. Organomet. Chem.*, **118**, 79 (1976).
- (8) W. J. R. Tverman, M. Kato, P. K. Bebarle, S. Masamune, O. P. Strausz, and H. E. Gunning, *Chem. Commun.*, 497 (1967).

- (9) O. L. Chapman, J. Pacansky, and P. W. Wojtkowski, *J. Chem. Soc., Chem. Commun.*, 681 (1973).
- (10) P. Reeves, J. Henery, and R. Pettit, *J. Am. Chem. Soc.*, **91**, 5888 (1969).
- (11) I. Fischer, K. Hildenbrand, and E. Koerner von Gustorf, *Angew. Chem.*, **87**, 35 (1975); *Angew. Chem., Int. Ed. Engl.*, **14**, 54 (1975).
- (12) O. Jaenicke, R. C. Kerber, P. Kirsch, E. A. Koerner von Gustorf, and R. Rumin, to be submitted for publication.
- (13) Due to the temperature gradient from the cold end of the cryostat ($T_c = 10$ K) to the sample, the actual temperature of the sample (T_s) is estimated to be 13-14 K.
- (14) P. Groner, I. Stolkin, and Hs. H. Günthard, *J. Phys. E*, **6**, 122 (1973).