

Table II. Populations of CO, NO, and NS σ -Donor and π -Acceptor Orbitals and Atomic Charges

CpMn(CO) ₃		CpCr(CO) ₂ NO		CpCr(CO) ₂ NS	
Orbital Populations					
CO 5 σ	1.42	CO 5 σ	1.49	CO 5 σ	1.51
CO 2 π	0.62	CO 2 π	0.57	CO 2 π	0.52
		NO 5 σ	1.58	NS 7 σ	1.61
		NO 2 π	1.50	NS 3 π	1.69
Atomic Charges					
Mn	+0.42	Cr	+0.80	Cr	+0.87
C(CO)	+0.02	C(CO)	-0.10	C(CO)	-0.09
O(CO)	-0.06	O(CO)	+0.02	O(CO)	+0.05
		N(NO)	+0.03	N(NS)	-0.25
		O(NO)	-0.09	S(NS)	+0.04

of the intense metal band at 8 eV.

The significance of the metal ionizations of these (η^5 -C₅H₅)M(CO)₂L systems can be appreciated if the basic orbital structures of the (η^5 -C₅H₅)M(CO)₂ and L fragments are understood. We recently presented the analysis of (η^5 -C₅H₅)M(CO)₂ in detail.⁶ Briefly, the three occupied metal orbitals in the d⁶ (η^5 -C₅H₅)M(CO)₂ fragment are labeled 1a', 2a', and a''. The 1a' and a'' are effective π donors to the ligand (L), a'' being the best donor. The 2a' orbital is largely δ symmetry with respect to the ligand and will mostly reflect the effects of total charge distribution around the metal.

It is observed (and calculated) that the ionization energy of 2a' decreases dramatically in going from the Mn to the Cr compounds, consistent with going from formally Mn⁺ to Cr⁰. As mentioned, the relationship between the Mn and Cr complexes can be thought of as the transfer of a proton from the metal to the ligand, while a d⁶ configuration is retained around the metal. The electrons in the immediate vicinity of the chromium lose some of the stabilizing influence of the proton.¹³ The 1a' and a'' also experience this effect but in addition are stabilized by the better π -accepting ability of NO (and NS). The calculated Mulliken populations of the π^* -acceptor orbitals of CO, NO, and NS in these three molecules are given in Table II. The a'' orbital is influenced slightly more than the 1a' by changes in π bonding because of its greater π interaction. It is interesting that, for the corresponding orbitals of (η^5 -C₅H₅)Mn(CO)₃, the a'' is less stable than the 1a', while the calculations indicate that these orbitals are essentially degenerate for the nitrosyl complex, as is observed in the ionizations. In a sense the electronic symmetry axis for the metal has shifted from the direction of the cyclopentadienyl ring centroid in the manganese complex to the direction of the nitrosyl ligand in the chromium complex.

The comparison of NO and NS orbital interactions with the metal is shown in the molecular orbital diagram in Figure 3. The differences in electronic structure between the two complexes are influenced more substantially by the ligand-orbital energies than by orbital overlaps. Just as in our previous comparison of CS with CO, the π^* orbital of NS is lower in energy than the π^* of NO (weaker p_x-p_x bonding for sulfur compared to oxygen) and accepts more electron density from the metal. A surprising feature of Figure 2 is that, even though the electronic interactions of NS and NO are appreciably different, the ionization associated with the 2a' orbital does not significantly shift from the nitrosyl to the thionitrosyl complex. The calculations agree with this observation and indicate that stabilization caused by removal of metal electron density by π back-bonding to NS is offset by the greater electron density on nitrogen (sulfur is less electronegative than oxygen) and decreased metal back-bonding to the carbonyls.

(13) This is reflected in the diagonal Fock matrix elements for the metal orbitals but not necessarily in the metal charges in Table II because of the accompanying interflow of electron density with neighboring atoms.

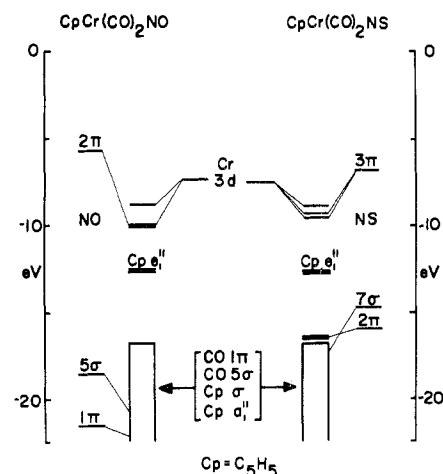


Figure 3. Molecular orbital diagrams (Fenske-Hall method) for (η^5 -C₅H₅)Cr(CO)₂NO and (η^5 -C₅H₅)Cr(CO)₂NS emphasizing relative energy comparisons of NO and NS orbital interactions with the metal orbitals.

Another observation from Figure 2 is that the 1a' and a'' ionizations of the thionitrosyl complexes are actually at lower ionization energy than for nitrosyl complex. This seems surprising on the basis of the better π -acceptor ability of NS compared to that of NO. The explanation is the same as in our comparison of CS and CO. The decreased π interaction between the nitrogen and sulfur greatly destabilizes the NS π bond, which then interacts more strongly with the filled metal 1a' and a'' orbitals. This interaction will tend to again separate the 1a' and a'' ionizations, and, indeed, this separation is partly resolved in the photoelectron spectrum. In terms of the ionizations, the greatest difference between the NS and NO compounds is the interaction of their π bonds with the metal. As in the case of CO and CS, this will also have an important influence on their chemical and physical properties.

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Symmetry of the Lowest Excited States of the Tris(2,2'-bipyridyl)ruthenium(II) Ion

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Solution-phase luminescence and excited-state electron-transfer processes associated with the Ru(bpy)₃²⁺ ion have made it the object of intense electro- and photochemical study. Despite the hundreds of papers in the literature concerning this ion, there is still no universally accepted assignment of the luminescence. This communication will address the assignment of the luminescence from the standpoint of its polarization. We find that our single-crystal polarized emission data are inconsistent with some of the assignments which have been proposed. Further, we find an interesting anomaly in the photoselection spectra of this complex in rigid matrices that suggest an excited-state and/or ground-state molecular symmetry which is lower than D₃. These conclusions are *not based on any choice of model*.

In 1966 Palmer and Piper¹ reported the polarized single-crystal absorption spectra of Ru(bpy)₃²⁺ doped in Zn-(bpy)₃SO₄·7H₂O and in Zn(bpy)₃Br₂·6H₂O. Their studies clearly show that the intense visible charge-transfer absorption band is dominantly *x,y* polarized (*z* is the threefold axis direction). Their results have recently been confirmed by Felix et al.,² who noted the inequivalence of the *x* and *y* polarizations in the bromide host crystal. Felix et al. associate the difference in *x*- and *y*-polarized absorption coefficients with the low site symmetry in the bromide host.

In a series of papers beginning in 1973, Crosby and co-workers³ have extensively studied the luminescence and decay characteristics of this ion incorporated in poly(methyl methacrylate) (PMM) and proposed an electron-ion parent (EIP) coupling model which they use to assign the symmetries of the manifold of states they infer from the experimental data. The salient features of their model are (a) a set of three emitting levels separated by about 10 and 80 cm⁻¹ s, respectively, whose relative populations are described by a Boltzmann distribution throughout the luminescence process, and (b) the symmetries of these levels: A₁, E, and A₂ in order of increasing energy.

In their paper of 1975, Hager and Crosby published a predicted temperature-dependent intensity distribution for the Ru(bpy)₃²⁺ luminescence. Basically, they predict a strongly *z*-polarized luminescence at temperatures above 30 K, *x,y*-polarized luminescence between 6 and 30 K, and an unspecified polarization below 6 K. In contrast, Fujita and Kobayashi⁵ have presented photoselection (of absorption) data which indicate a dominant *x,y* polarization of the emission of Ru(bpy)₃²⁺ in EPA at 77 K. The value they obtain for the limiting polarization ratio $P \equiv (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})$, however, is far in excess of what one would predict for a purely *x,y*-polarized absorption followed by an *x,y*-polarized emission.

Theoretical Section

Consider an even-electron molecular system which has rigorous *D*₃ symmetry in its ground and relevant excited states. Let the Hamiltonian, *H*, contain all appropriate terms (spin-orbit, vibrational, etc.). Then we must have $[H, R_i] = 0$ for all $R_i \in D_3$. This invariance of *H* to the elements of *D*₃ implies that we may label all states in the following manner

$$H|J, \Gamma_j, \gamma_j\rangle = E_j|J, \Gamma_j, \gamma_j\rangle$$

where Γ_j is one of the irreducible representations of *D*₃ (A₁, A₂, or E) and $\gamma_j = x$ or *y* if $\Gamma_j = E$.

The labeling of states is chosen such that $\{|I, \Gamma_i, \gamma_i\rangle\}$ represents the manifold of ground states, $\{|J, \Gamma_j, \gamma_j\rangle\}$ represents the manifold of final states in absorption, and $\{|K, \Gamma_k, \gamma_k\rangle\}$ represents the (possibly different) manifold of initial states in emission. A transition is said to be partially *x* polarized in absorption if

$$\langle I, \Gamma_i, \gamma_i | x | J, \Gamma_j, \gamma_j \rangle \neq 0$$

Because of the symmetry of the system, it is easy to show that

$$\langle I, \Gamma_i, \gamma_i | x | J, \Gamma_j, \gamma_j \rangle \equiv \langle I, \Gamma_i, \gamma_i' | y | J, \Gamma_j, \gamma_j' \rangle$$

where $C_2^z |J, \Gamma_j, \gamma_j\rangle \equiv |J, \Gamma_j, \gamma_j'\rangle$ and the state $|L, \Gamma_l, \gamma_l\rangle$ is rigorously degenerate with $|L, \Gamma_l, \gamma_l'\rangle$. We therefore have demonstrated that any transition which is partially *x* polarized

is degenerate with one which is equally *y* polarized. So that for an oriented molecular system

$$\epsilon_x(\nu) = \epsilon_y(\nu) \quad (1)$$

Similarly we can show that the probability of emission of *x*-polarized radiation exactly equals that for *y* polarization, provided there was no asymmetry in *x* and *y* excitations. That is

$$\langle K, \Gamma_k, \gamma_k | x | I, \Gamma_i, \gamma_i \rangle \equiv \langle K, \Gamma_k, \gamma_k' | y | I, \Gamma_i, \gamma_i' \rangle$$

and the (γ_k, γ_k') and (γ_i, γ_i') pairs are rigorously degenerate. Therefore

$$I_x(\nu') = I_y(\nu') \quad (2)$$

In the photoselection experiment for an isotropic distribution of frozen molecular orientations, the experimental quantity of interest is $P(\nu, \nu')$ (intensity of emission at ν' polarized parallel to the excitation at ν minus the intensity at ν' polarized perpendicular to the excitation at ν divided by the sum of the two emissions at ν').

In the conventional shorthand

$$P(\nu, \nu') = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp}) \quad (3)$$

Equation 3 specifies $P(\nu, \nu')$ in the laboratory reference system. In order to determine $P(\nu, \nu')$ from the fixed orientation ϵ 's and *I*'s, one must perform averages over all orientations. By the same procedures as given in ref 6 or 7, one obtains

$$P(\nu, \nu') = [I_x(\nu') - I_z(\nu')](\epsilon_x(\nu) - \epsilon_z(\nu)) / \{\epsilon_z(\nu) \times [2I_x(\nu') + 3I_z(\nu')] + \epsilon_x(\nu)[7I_x(\nu') + 3I_z(\nu')]\} \quad (4)$$

This is a perfectly general equation on the basis of the assumption that (a) the molecular symmetry is rigorously *D*₃ for all states connected by the absorption and emission processes and (b) the sample under study is a uniform frozen distribution of molecular orientations on the time scale of the emission processes. As a special case, consider the following:

$$\text{if } I_x > I_z: \quad P(\nu, \nu') \leq \frac{\epsilon_x(\nu) - \epsilon_z(\nu)}{3\epsilon_z(\nu) + 7\epsilon_x(\nu)}$$

$$I_x \geq I_z: \quad -\frac{1}{3} \leq P(\nu, \nu') \leq \frac{1}{7} \quad (5)$$

Experimental Section

The methods of ref 8 have been used to measure the photoselection of emission and absorption [both ν and ν' dependences of *P*] of Ru(bpy)₃Cl₂ dispersed in poly(methyl methacrylate) (PMM) over the 300–2 K temperature range. We have further measured the differential polarized emission of single-crystal Zn(bpy)₃SO₄·7H₂O doped with Ru(bpy)₃²⁺. The *x* and *z* directions used conform to those of ref 1 and 2.

The results of our photoselection studies of Ru(bpy)₃²⁺ in PMM confirm and extend the work of Fujita and Kobayashi, who measured only the ν dependence of *P* above 70 K. Further, by conducting these experiments in the 5–300 K region, we were able to show that the magnitude of *P* is roughly constant throughout that temperature range. In the process of conducting this study however, we noted several troubling aspects about the total and polarized luminescence of this complex in PMM. Of primary importance is the variation of relative polarization from sample to sample (fixed concentration). In one series of three supposedly identically prepared samples, *P* varied from 0.15 to 0.23 at its maximum (excitation wavelength varied). Further, the observed luminescence shifted somewhat as a function of concentration and excitation wavelength. These disturbing variations indicate the existence of very strong ion-matrix interaction and bring the value

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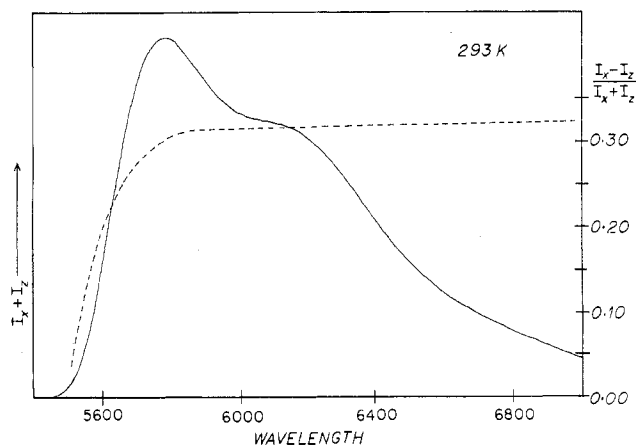


Figure 1. Total luminescence (—) and polarization ratio (---) of the luminescence of $\text{Ru}(\text{bpy})_3^{2+}$ doped in $\text{Zn}(\text{bpy})_3\text{SO}_4 \cdot 7\text{H}_2\text{O}$ at 293 K.

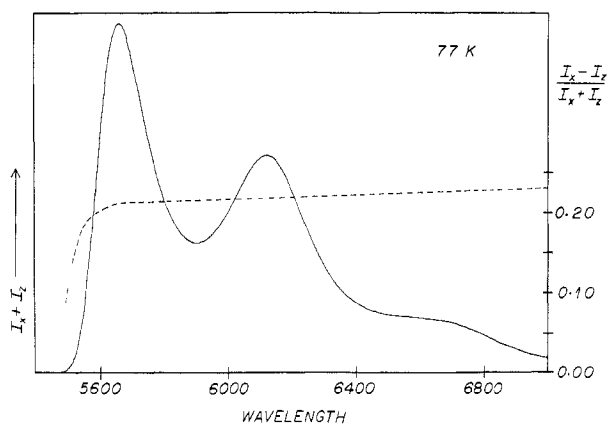


Figure 2. Total luminescence (—) and polarization ratio (---) of the luminescence of $\text{Ru}(\text{bpy})_3^{2+}$ doped in $\text{Zn}(\text{bpy})_3\text{SO}_4 \cdot 7\text{H}_2\text{O}$ at 77 K.

of the polarization results obtained into question.

In order to obtain more definitive results, we have measured the differential luminescence polarization of the $\text{Ru}(\text{bpy})_3^{2+}$ ion doped in $\text{Zn}(\text{bpy})_3\text{SO}_4 \cdot 7\text{H}_2\text{O}$. Figures 1 and 2 depict the luminescence and differential polarized luminescence $(I_x - I_y)/(I_x + I_y)$ obtained at 293 and 77 K by the methods given in ref 6. On the assumption of equivalence in the x and y components of the luminescence, more than 75% of the intensity is carried by x,y polarization. Further, the band shape and relative polarization of emission are essentially wavelength independent throughout the charge-transfer absorption band. At least in one feature, the dominance of x,y polarization, the single-crystal results are in qualitative agreement with the photoselection data.^{5,6} They are in conflict, however, with the quantitative values of P obtained in rigid matrices. This conflict depends only upon the sign of the single-crystal polarization results obtained and not on their magnitude.

Discussion

The results depicted in Figures 1 and 2 clearly indicate that $I_x(\nu') > I_y(\nu')$ for all ν' . Equation 5 is therefore appropriate, and we have

$$P(\nu, \nu') \leq 1/7 \quad (6)$$

Equation 6 and the available photoselection data are incompatible. The observed values of $P > 1/7$ cannot be obtained from a D_3 symmetry molecule whose emission is principally x,y polarized irrespective of the absorption polarization. We are led to the conclusion that (a) the $\text{Ru}(\text{bpy})_3^{2+}$ ion, including its immediate environment, is not D_3 in symmetry in its ground and/or excited state when incorporated in PMM or EPA or (b) all previous assignments of the $\text{Ru}(\text{bpy})_3^{2+}$ orientation within a single crystal are incorrect. Alternate b is highly unlikely. Conclusion a is somewhat surprising in light of recent X-ray crystallographic work which shows that, in $\text{Ru}(\text{bpy})_3^{2+}$

(PF_6)₂, the $\text{Ru}(\text{bpy})_3^{2+}$ ion is D_3 in symmetry.⁹ On the other hand, the low-symmetry environment of the $\text{Zn}(\text{bpy})_3\text{Br}_2 \cdot 6\text{H}_2\text{O}$ crystal is known to cause a pronounced splitting of the x and y polarized components of the $18 \times 10^3 \text{ cm}^{-1}$ absorption band.² If, in the rigid matrices studied, the x and y directions are inequivalent, then P may be as large as $1/2$.

The inequivalence between the x and y axes of $\text{Ru}(\text{bpy})_3^{2+}$ in PMM and EPA may arise from either of two sources: (a) the ground state ion may have less than D_3 symmetry due to the asymmetric potential field of the surrounding environment and especially the anions which will be strongly paired with $\text{Ru}(\text{bpy})_3^{2+}$ in the low dielectric constant matrices studied or (b) the ion may distort in the excited state with the excited electron localized on one of the three ligands. These two possibilities cannot be distinguished with the available data, and, in fact, they are not necessarily separable. A small local distortion due to the surroundings can induce a preferential excitation of an electron to one or more of the ligands. A comparison of the Raman spectra obtained from a $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ crystal to that obtained from the same system dispersed in PMM would be most helpful.

In conclusion, we have shown that the available data on the luminescence of the $\text{Ru}(\text{bpy})_3^{2+}$ ion in PMM and EPA below ca. 90 K is not consistent with the molecule having D_3 symmetry throughout the absorption-emission process. This conclusion is independent of any choice of model for the states of the ion. It brings into question the assignments made on the basis of rigid-matrix experimental results. In particular, the IEP model is in conflict with the available linear polarization data.

Note Added in Proof. Subsequent to submission of this note, Dallinger and Woodruff¹⁰ presented convincing evidence that in aqueous solution the luminescent state symmetry of $\text{Ru}(\text{bpy})_3^{2+}$ is not D_3 .

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Registry No. $\text{Ru}(\text{bpy})_3^{2+}$, 15158-62-0; $\text{Zn}(\text{bpy})_3\text{SO}_4$, 15406-72-1.

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Diamagnetic Anisotropy of Metal-Metal Triple Bonds

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The delineation of the chemistry of metal-metal bonded species has been one of the more exciting branches of inorganic chemistry in recent years.¹ In particular, the collaborative efforts of the Cotton and Chisholm groups have produced a rich harvest of triple-bonded species which have been structurally characterized and spectroscopically studied. Of special interest are the low-temperature NMR spectra of such species in which the predominant forms in solution apparently closely resemble the structures found by X-ray crystallography. Indeed, the low-temperature NMR spectra show evidence of a diamagnetic anisotropic effect attributable to the metal-metal multiple bond; this possibility was suggested by San Filippo in 1972.²

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