

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.

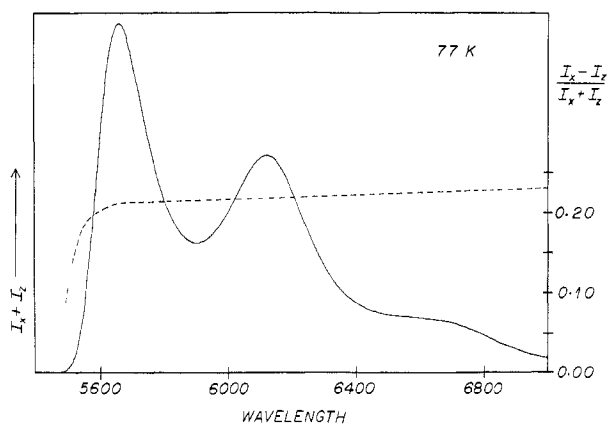


Figure 2. Total luminescence (—) and polarization ratio (---) of the luminescence of $\text{Ru}(\text{bpy})_3^{2+}$ doped in $\text{Zn}(\text{bpy})_3\text{SO}_4 \cdot 7\text{H}_2\text{O}$ at 77 K.

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 $\text{Ru}(\text{bpy})_3$ -

$(\text{PF}_6)_2$, 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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Table I. Geometric Factors for Proximal ($H_{1,2,3}$) and Distal ($H_{4,5,6}$) Protons in $W_2(NMe_2)_6$

	r , Å	θ , deg	G	$10^{-30}G_{av}$
H_1	2.89	85.0	0.013 50	
$H_{2,3}$	3.97	70.0	0.003 46	0.006 81
H_4	3.85	20.1	-0.009 61	
$H_{5,6}$	4.42	39.6	-0.003 02	-0.005 22

We now show that the early ideas of San Filippo, in conjunction with recent experimental data, allow the evaluation of the diamagnetic anisotropies of some metal-metal multiply bonded systems.

Results and Discussion

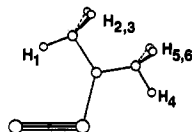
Diamagnetic anisotropy is conveniently monitored by siting otherwise equivalent nuclei in a variety of geometric positions relative to the moiety under investigation.³ A classic example is the use of cyclophanes to position protons directly above the π cloud of benzene.⁴ In the semiclassical free-electron model, circulation of delocalized π electrons induces a field which opposes the applied field, thus shielding the monitor protons; the induced field reinforces the applied field in the plane of the ring and so deshields the aromatic protons.⁵ Similarly, one can rationalize the shielding of acetylenic protons and the deshielding of nuclei in the plane perpendicular to the triple bond.⁶

McConnell's treatment⁷ of this situation allows a quantitative approach in that measurement of the chemical shift of the protons in known positions relative to the triple bond leads directly to the diamagnetic anisotropy (χ); see eq 1, where σ

$$\sigma = \frac{\chi(1 - 3 \cos^2 \theta)}{3r^3} \quad (1)$$

is the chemical shift (in ppm), r is the distance from the electrical center of gravity of the bond to the monitor nucleus (in meters), and θ is the angle made by r with the multiple bond axis.

In order to evaluate the diamagnetic anisotropy of a metal-metal triple bond, it is necessary to have accurate NMR chemical shift data for nuclei whose geometric disposition relative to the center of the bond is known. These criteria are ideally satisfied by the $M_2(NMe_2)_6$ species ($M = Mo, W$) recently studied by Cotton and Chisholm.^{8,9} These molecules adopt a D_{3d} conformation in which the proximal and distal methyl groups are magnetically nonequivalent, and both resonances are observable at low temperatures. Now, for simplicity, with the use of average bond lengths and angles for an idealized D_{3d} molecule, the proton positions are readily obtained.



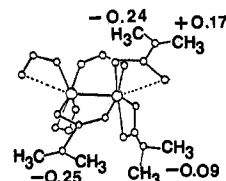
The calculated diamagnetic anisotropic shift difference between the distal and proximal methyl group protons is

merely dependent on χ and the geometric terms G (see Table I). Thus

$$\sigma_{\text{distal}} - \sigma_{\text{proximal}} = \chi(G_{\text{distal}} - G_{\text{proximal}})$$

Now, since the experimentally determined separation of the distal and proximal protons is 1.88 ppm, then $1.88 \times 10^{-6} = (-0.01203 \times 10^{30})\chi$ and $\chi = -156 \times 10^{-36} \text{ m}^3/\text{molecule}$. An analogous calculation for $Mo_2(NMe_2)_6$ gives a value for the diamagnetic anisotropy of the molybdenum-molybdenum triple bond of $\chi_{Mo=Mo} = -142 \times 10^{-36} \text{ m}^3/\text{molecule}$.¹⁰ For comparison, $\chi_{C=C} = -340 \times 10^{-36} \text{ m}^3/\text{molecule}$; thus the anisotropy of the metal-metal triple-bonded systems is roughly half that of the alkyne linkage.

With these values in hand, one should be able to predict chemical shift differences in more complex molecules. Thus, in $W_2(O_2CNMe_2)_6$ one predicts a difference of 0.41 ppm between the pseudoaxial and pseudoequatorial methyl groups of the unsymmetrically bonded carbamate moiety; gratifyingly, the experimentally found¹¹ separation is ≈ 0.35 ppm; the calculated separation of 0.16 ppm for the CH_3 groups of the bridging and nonbridging carbamates is remarkably close to the experimental observed value of ≈ 0.14 ppm.



In principle, this technique is equally applicable to quadruply bonded systems, and indeed San Filippo has pointed out some anomalous shifts in $[(n-C_4H_9)_3P]_2(C_6H_5CO_2)_2Mo_2Br_2$.¹² Typically, the ortho and meta phenyl protons of the bridging benzoate ligand are separated by ≈ 1 ppm. If one were naively to attribute this entire chemical-shift difference to the diamagnetic anisotropy of the multiple bond, one would evaluate $\chi_{Mo-(4)-Mo}$ as $-2040 \times 10^{-36} \text{ m}^3/\text{molecule}$. However, since the ortho and meta protons in benzoates are typically 0.5–0.7 ppm apart, then the $\chi_{Mo-(4)-Mo}$ value is more conservatively estimated as being in the range -600 to $-1000 \times 10^{-36} \text{ m}^3/\text{molecule}$.

It is tempting to compare $\chi_{M-(4)-M}$ values in the complexes $[M_2Me_6]^{n-}$, where $n = 4$ for Cr,¹³ Mo,¹⁴ and W¹⁵ and $n = 2$ for Re,¹⁶ since their geometric factors are rather similar. However, there is a problem in choosing a standard methyl chemical shift for such systems. The methyl protons spend the majority of their time in the deshielding cone of the multiple bond and, since the shifts for the tungsten and rhenium compounds are ~ 0.7 ppm to low field of the molybdenum analogue, the diamagnetic anisotropies of the third-row elements would appear to be considerably larger than those for their second-row partners. In the absence of data for dimethylamido substituents on quadruple bonds, the best probe at present would appear to be the difference in shifts between ortho and meta phenyl protons of bridging benzoate ligands.

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An alternative to the McConnell approximation⁷ would involve a knowledge of the tensor elements of the ¹⁸³W spectra, obtained in a solid-state NMR experiment. This approach has been used to evaluate local anisotropic contributions from carbon atoms in organometallic π systems.¹⁷ In this model, one could regard the situation as being equivalent to having three mutually perpendicular current loops around the tungsten atoms; the local anisotropic contributions to the chemical shifts of nearby protons would therefore be calculable. Such an approach has been successfully tested on alkynes⁶ and, in principle, is more reliable for proximate protons when the dipole approximation often breaks down.

Registry No. $W_2(NMe_2)_6$, 54935-70-5; $Mo_2(NMe_2)_6$, 51956-20-8; $W_2(O_2CNMe_2)_6$, 61091-29-0; $[(n-C_4H_9)_3P]_2(C_6H_5CO_2)_2Mo_2Br_2$, 59493-09-3.

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Structural Assignments and Stereospecificity of the *cis*-Dinitrobis(sarcosinato(1-)-*O,N*)cobaltate(III) Ion

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The stereospecific coordination of chiral ligands manifests itself in the preferred formation of one of the possible diastereoisomers. Frequently the configurations of the ligands produce steric interactions which cause either the Δ or Λ isomer to be preferentially formed. Ligands with donor atoms which become chiral on coordination behave in a similar way. In such cases the configuration of the donor atom for a given isomer is enforced by the remaining part of the chelate ring and vice versa. If the absolute configuration of the donor atom is fixed, the absolute configuration of the complex will be stereoselectively controlled by the donor atom chirality.

We are interested in metal complexes with forced configurations of donor atoms. Recently we^{2a} have found that nonbonding interactions between *N*-CH₃ groups of sarcosine exclude the existence of tris(sarcosinato)cobalt(III) *fac* isomers and *mer* isomers with *SSS* and *RRR* configurations at the secondary nitrogen atoms and several other combinations with similar interactions, while very small stereoselectivity is exhibited by the analogous asparaginato chelate. In a cobalt(III) complex with nonequivalent chiral centers, i.e., (sarcosinato)bis((*S*)-(+)-valinato)cobalt(III),^{2b} the stereochemical selection of geometric isomers is determined primarily by the steric requirements of the *N*-CH₃ group of sarcosine, while the degree of stereoselectivity corresponds to the small structural differences arising from the axial or equatorial disposition of the two isopropyl groups of valine. These results prompted us to study the forced configuration of the donor

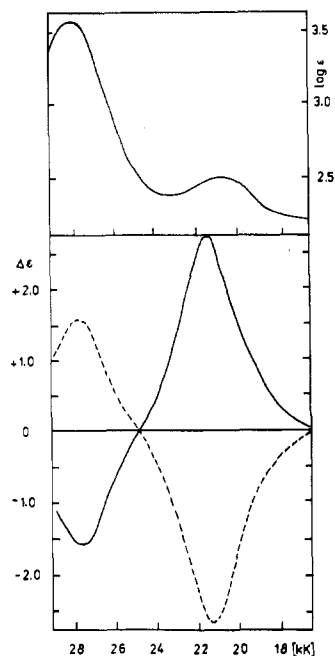


Figure 1. Electronic absorption spectrum of the *cis*(NO₂),*trans*(N),*cis*(O) isomer (—) and circular dichroism spectrum of the Λ (—) and Δ (----) isomers.

atoms in relation to the internal stereoisomerism in bis(chelate) octahedral complexes.

Results and Discussion

Complexes of the type $Co(\widehat{N}O)_2(NO_2)_2^-$, where $\widehat{N}O$ is an unsymmetrical bidentate ligand, can exist in five geometrical isomers: *trans*(NO₂),*trans*(N),*trans*(O); *trans*(NO₂),*cis*(N),*cis*(O); *cis*(NO₂),*cis*(N),*cis*(O); *cis*(NO₂),*trans*(N),*cis*(O); *cis*(NO₂),*cis*(N),*trans*(O). Among these isomers the three *cis*(NO₂) isomers can exhibit enantiomeric (or Δ , Λ) relationships. Accordingly, the number of isomers is up to 8. On the assumption that the secondary nitrogen atom of sarcosine becomes chiral by coordination, the total number of isomers will be 26, excluding conformational isomers. That is, coordination of inert secondary nitrogen atoms can give rise to an *RR* isomer, to an *SS* isomer, and normally to one *RS* isomer—except for the Δ and Λ "all-*cis*" isomers of *C*₁ symmetry for which the two chelate rings are not equivalent and give two *RS* isomers each.

Čelap et al.³ studied a series of the above-mentioned type of complexes and found that the topology of the complexes obtained depended on the temperature, which seems to play an important role in the isomerization. A mixture of isomers has been obtained by a substitution reaction at 60 °C. At higher temperatures only the *cis*(NO₂),*trans*(N),*cis*(O) isomers could be obtained.³ It is evident from a study of models that these isomers exhibit a minimum of nonbonding interactions between the nonpolar amino acid side chains and that the steric volume of the α -amino acid substituents does not influence the geometry of the complexes obtained.

The sarcosine complex was prepared under conditions which lead to several geometrical isomers, but only two isomers were obtained. Their electronic absorption spectra (Figure 1) do not show splitting of the ¹A_{1g} → ¹T_{1g} transition, which suggests that the carboxylate groups are in *cis* positions. The low-energy band located at about 20800 cm⁻¹ is shifted by 600 cm⁻¹ in comparison with other amino acid complexes (see ref 3). This shift may be due to the lower ligand field of the secondary

(1) (a) Prague Institute of Chemical Technology. (b) Ain Shams University. (c) University of Massachusetts.
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