Table III. Selected Bond Distances (Å)

Co8–B3	2.070 (7)	B9–B10	1.78 (1)
Co8–B4	2.079 (7)	B1′–B2′	1.75 (1)
Co8–B7	2.257 (7)	B1′–B3′	1.78 (1)
Co8–B9	2.045 (8)	B1′–B4′	1.76 (1)
B1–B2	1.74 (1)	B1′–B5′	1.75 (1)
B1–B3	1.78 (1)	B1′–B10′	1.76 (1)
B1–B4	1.76 (1)	B2′–B3′	1.77 (1)
B1–B5	1.76 (1)	B2′–B5′	1.79 (1)
B1–B10	1.75 (1)	B3′–B4′	1.78 (1)
B2–B3	1.81 (1)	B3′–B8′	1.74 (1)
B2–B5	1.79 (1)	B4′–B8′	1.78 (1)
B2–B6	1.71 (1)	B4′–B9′	1.70 (1)
B2–B7	1.84 (1)	B4′–B10′	1.77 (1)
B3–B4	1.81 (1)	B5′–B10′	1.96 (1)
B3–B7	1.80 (1)	B8′–B9′	1.77 (1)
B4–B9	1.74 (1)	B9′–B10′	1.80 (1)
B4–B10	1.79 (1)	Co8–C11	2.056 (8)
B5–B6	1.78 (1)	Co8–C12	2.062 (8)
B5–B10	1.94 (1)	Co8–C13	2.044 (8)
B6–B7	1.83 (1)	Co8–C14	2.034 (7)
B6–B2′	1.73 (1)	Co8–C15	2.043 (7)
B6–B5′	1.80 (1)	C11–C12	1.37 (1)
B7–B2′	1.83 (1)	C11–C15	1.36 (1)
B7–B3′	1.79 (1)	C12–C13	1.39 (1)
B7–B8′	2.05 (1)	C13–C14	1.39 (1)
		C14–C15	1.44 (1)

resulting in a structure that has a center of symmetry, while *iso*-$B_{18}H_{22}$ has a structure[20] based on the sharing of the 6,6′- and 7,7′-borons,[21] which has 2-fold symmetry but lacks an inversion center. The compound *iso*-8-(η-C_5H_5)$CoB_{17}H_{21}$ clearly has a structure derived from the latter geometry in which the (η-C_5H_5)Co unit has replaced the 8-BH unit in the *iso*-$B_{18}H_{22}$ framework.

Thus, the reaction leading to the formation of the compound involves both the degradative insertion of a cobalt atom and the isomerization of the cage framework from a *n*- to *iso*-B_{18} structure. Fontaine et al.[18a] first noted such a rearrangement of a *n*-$B_{18}H_{22}$ cage during the synthesis of the complex (η-C_5Me_5)$_2Rh_2B_{17}H_{19}$. They proposed that the conversion between structures may occur by a process involving the insertion of a metal vertex at one edge (B7–B8) of a *n*-B_{18} framework followed by elimination of a BH unit (B10) on the opposite side of the same cage. Such a process generates the *iso*-B_{18} framework in a straightforward manner, and our results are consistent with this type of mechanism.

The cobalt atom is coordinated to the four borons B7, B3, B4, and B9 and is 1.343 (1) Å from the plane of these atoms and 1.672 (1) Å from the plane of the cyclopentadienyl ring. The dihedral angle between the B7,B3,B4,B9 plane and that of the cyclopentadienyl ring is only 3.8°. These values as well as the remaining bond distances and angles in the cobaltaborane half of the molecule are similar to those observed in the analogous cage system, 5-(η-C_5H_5)CoB_9H_{13}.[22] The bond parameters in the non-metal half are similar to those found in *iso*-$B_{18}H_{22}$. The substitution of the cobalt atom thus seems to have had little influence on the bonding in the opposite cage.

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Registry No. *iso*-8-(η-C_5H_5)$CoB_{17}H_{21}$, 112139-07-8; *n*-$B_{18}H_{22}$, 21107-45-9; Co, 7440-48-4; cyclopentadiene, 542-92-7.

Supplementary Material Available: Tables of general temperature factors, intermolecular angles, bond distances, molecular planes, and hydrogen positions (10 pages); a table of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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Emission Wavelength Independence of the Excitation Polarization of $[Ru(bpy)_3]^{2+}$

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A recent publication by Krausz and Ferguson[1] states that frozen-solution photoselection data[2,3] for $[Ru(bpy)_3]^{2+}$ were the result of solvent heterogeneity, a "red edge" effect.[4,5] The physical basis for this statement was the observation that excitation photoselection (ExP) spectra exhibit a strong dependence upon detection wavelength. This experimental result was in direct conflict with the findings of our own laboratory[2] that variation of the ExP spectra with detection wavelength is negligible, for this complex.

The importance of obtaining the proper ExP spectra must be stressed. Such data[2] are key to the present controversy surrounding the identification and origin of *localization* in the excited states of $[Ru(bpy)_3]^{2+}$ and its analogues. Tazuke and co-workers,[6] as well as Krausz and Ferguson,[1] have argued that the localization is *only* a fluid-solution phenomenon. If the anomalous rigid-solution (77 K) photoselection of these complexes may be discarded as a red edge effect, their case is greatly strengthened, and the converse is also true. Hence, it is necessary to be certain of the ExP dependence observed by Krausz and Ferguson.[1]

Photoselection spectroscopy is an established emission polarization technique used with much success in many areas of research.[7-9] It does, however, require precise experimental methodology to prevent acquisition of erroneous data, and we therefore felt sufficient reason to question the data of ref 1.

The choice, in ref 1, of 110 K as the experimental temperature seems a needless, and in many respects, counterproductive complication for comparison with the original Carlin–DeArmond 77 K experiments.[2] In addition, the 110 K temperature is one at which viscous flow occurs for the EtOH/MeOH system, causing rotational depolarization to be a factor. However, to provide data to compare with ref 1 and 2, we have performed experiments at 110 and 77 K.

Figure 1 illustrates the 110 K result obtained in pure EtOH solution. As shown, we have detected only minor variations of ExP upon detection at the wavelengths used by Krausz and Ferguson.[1] While our experiments were performed in pure EtOH instead of 4:1 EtOH/MeOH, the difference between these solvents is negligible for our purposes. Therefore, this figure may be contrasted with Figure 3 of ref 1, which purports to show the same data. The data obtained at 77 K are identical with those at 110 K, given slight rotational depolarization at the latter temperature, and are also shown in Figure 1.

The reason for the inaccurate results of Krausz and Ferguson is unknown, but several possibilities exist. During the acquisition of the data in Figure 1, we noted that there is significant instability of ethanol glasses at 110 K. At 77 K, ethanol will glass, and the characteristics of that glass are not seen to alter over a period of hours. Major glassy defects, such as cracks or stress-related birefringence, are easily visible to the eye of the observer, and glasses may be obtained that do not contain these defects. Data obtained in these clear glasses are reproducible and give photoselection polarization values (*P*) with accuracies better than

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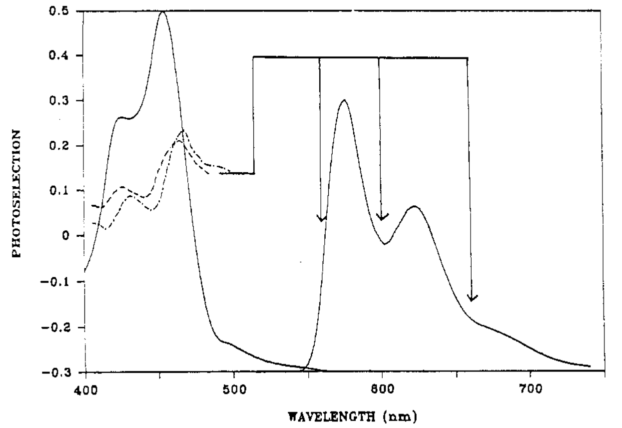

Figure 1. 77 K absorption and emission spectra for $[Ru(bpy)_3]^{2+}$ in ethanol. The 77 (–•–) and 110 K (- - -) photoselection spectra obtained from monitoring at *any* position in the emission are plotted with the absorption spectra. The three emission wavelengths indicated by arrows are 556, 600, and 660 nm.

±0.005. Cracks sometimes appear in these glasses during experimental use, likely due to thermal stress from irradiation, but these cause such a dramatic and immediate effect upon data being recorded that subsequent data may be easily discarded.

At warmer temperatures, we have found a different type of glassy failure related to viscous flow. This is an insidious problem and is more difficult to detect, causing "warping" of the glass over a period of 10–20 min, and may be a cause for the inaccuracies of ref 1.

A second possibility is the lack or misuse of an experimental correction factor. These authors do not explain their technique for determining P and make no mention of correcting their data for the polarization response of their detection system.

To determine P experimentally, eq 1 or a variation of it must be used:

$$P = (I_{vv} - CI_{vh})/(I_{vv} + CI_{vh}) \tag{1}$$

I_{vv} = emission intensity polarized vertically following vertically polarized excitation, I_{vh} = emission intensity polarized horizontally following vertically polarized excitation, and C = correction factor.

C is necessary to compensate for reflection and other depolarization mechanisms inherent in any luminescence detection system. Many means of determining C exist, as shown by Azumi and McGlynn,[10] but the most effective means, used in this laboratory, gives C as

$$C = I_{hv}/I_{hh} \tag{2}$$

I_{hv} = emission intensity polarized vertically following horizontally polarized excitation and I_{hh} = emission intensity polarized horizontally following horizontally polarized excitation.

In an L-format instrument, these intensities must be equal, and therefore any variation from $C = 1$ must be due to experimental factors. Hence, CI_{vh} is the intensity of horizontally polarized emission following vertically polarized excitation that would have been measured had the efficiency for the detection of horizontally polarized light equaled that for vertically polarized light.

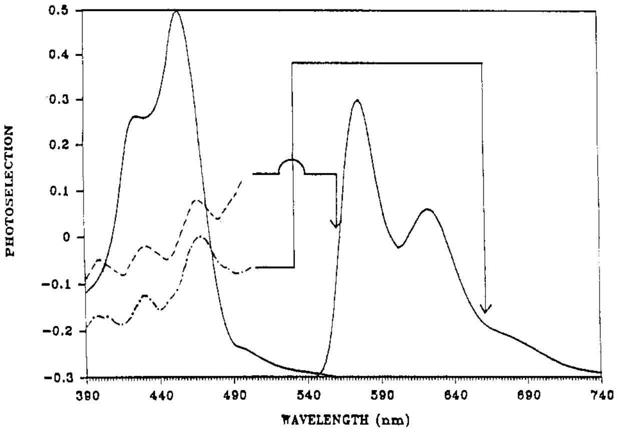

Figure 2. Absorption and emission spectra of $[Ru(bpy)_3]^{2+}$ in 77 K ethanol. Plotted across the absorption are photoselection spectra obtained *without* a correction factor monitored at 556 and 660 nm.

If the procedure is to be done properly, C must be determined for every different wavelength setting of a system. The absence or misuse of C could explain the data of Krausz and Ferguson, as shown here in Figure 2, where we have removed C in our calculation of P at each wavelength. Such misuse of the photoselection equations may result in anomalous data.

In their work Krausz and Ferguson[1] state that *emission* photoselection data from our laboratory[2] support the finding of the strong detection wavelength dependence they find in their *ExP*. In fact, ref 2 demonstrates a small variation of P across the emission envelope, less than ±0.015. This variation is an order of magnitude smaller than would be necessary to corroborate Krausz and Ferguson's result.

In conclusion, results of this laboratory have shown the ExP spectra of $[Ru(bpy)_3]^{2+}$ are insensitive to detection wavelength when appropriate measures are taken to ensure the accuracy of the measurement. This verifies the original Carlin–DeArmond result; hence, the anomalous $P \approx 0.23$ at 21 000 cm^{-1} is diagnostic of reduction of symmetry at 77 K, as originally concluded by Carlin and DeArmond.[11] Since these data in EtOH (or 4:1 EtOH/MeOH) can be identically reproduced in glassy matrices as different as 2:1 CH_2Cl_2/Et_2O,[12] the anomalous photoselection is not due to solvent heterogeneity. The recent observation[13] at 77 K of ExP values approaching the linear absorber–linear emitter limit (0.5) at short observation times offers additional verification that localization of the lowest excited state is intrinsic to this molecule and is not a solvent-driven process.

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Registry No. $[Ru(bpy)_3]^{2+}$, 15158-62-0.

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