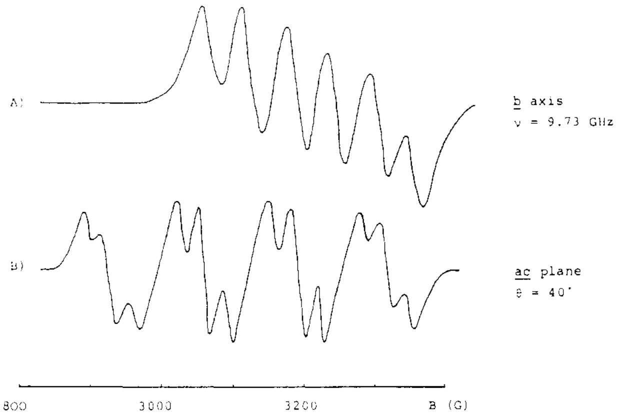

Figure 3. Room-temperature single-crystal X-band spectra of $[Cu(hfac)_2]_3(NITEt)_2$ with the static magnetic field (A) along *b* and (B) on the *ac* plane making an angle of 40° with a^*.

tensors of $[Cu(hfac)_2]_3(NITEt)_2$ correspond to those of the central copper atom. In order to verify this, we recorded both polycrystalline powder and single-crystal EPR spectra.

The polycrystalline powder EPR spectrum recorded at room temperature and Q-band frequency is shown in Figure 2. This is indeed typical of a copper(II) ion[16] with $g_{\parallel} = 2.29$, $g_{\perp} = 2.05$, and $A_{\parallel} = 145$ G. The values compare well with those of elongated-octahedral copper complexes, thus confirming the model.

In order to check if the principal directions correspond to the central copper atom, we recorded X-band-frequency single-crystal spectra at room temperature and 4.2 K rotating around the a^*, *b*, *c* crystal axes. The high- and low-temperature spectra are substantially similar. The signals of two magnetically nonequivalent sites are resolved in the a^*b and *bc* planes as expected for a monoclinic cell. This fact shows that the $[Cu(hfac)_2]_3(NITEt)_2$ intermolecular exchange interactions are smaller than the smaller hyperfine resolved, i.e. 0.0040 cm^{-1}. This result is not unexpected since the shortest distances between the paramagnetic Cu1 centers are 9.070 Å, and no obvious exchange pathway is present.

Copper hyperfine structure is resolved in many orientations, but also additional splittings are observed in some crystal settings. The presence of the fine splitting of the lines and their broadness makes the analysis of the spectra not straightforward. However, in the a^*c plane an extreme close to that observed in the powder spectra is found parallel to a^*, with $a_1 = 2.29$ and copper hyperfine $A_1 = 145$ G. The other extreme in this rotation corresponds to $g_2 = 2.07$ and $A_2 = 35$ G.

Comparing these data with the crystal structure, we see that the direction g_1 is almost parallel to the Cu1–O7 direction, making an angle of about 18° with it, confirming that we are indeed observing the resonance of the central copper ion.

In Figure 3 we show two typical spectra, recorded with the static magnetic field parallel to the crystal *b* axis and in the *ac* plane at 40° from a^*. The latter spectrum clearly shows a hyperfine quartet, with each line further split by ca. 30 G into triplets with intensity ratios 1:2:1 on each hyperfine line as showed by a simple simulation of the spectrum. The *b* spectrum shows six lines equally split by 60 G. Our interpretation of this splitting is that it is due to the fine interaction of the central copper with two copper ions translated by ±1 along the *b* axis. Similar effects were previously observed in other undiluted copper systems.[17-19] These two ions are 9.07 Å apart from the central one, and the simple point dipolar approximation suggests a splitting of 52 G of the lines in the spectrum along *b* and 26 G for the other spectrum. Therefore, the calculated values immediately allow us to assign the latter spectrum. In the *b* spectrum we suggest that the six lines are due to similar fine and hyperfine splitting of 60 G. The intensity ratio calculated from the assumption of simply additive fine and hyperfine splittings is 1:3:4:4:3:1. The experimental value does not agree with this, but a similar case was previously reported, and it was shown[18] that when fine and hyperfine splitting are comparable, the simple additive model does not work; spectra very similar to ours were simulated by using a more accurate model, which takes into account various combinations of hyperfine states of interacting ions.

Registry No. $Cu(hfac)_2$, 14781-45-4; $[Cu(hfac)_2]_3(NITEt)_2$, 114719-66-3.

Supplementary Material Available: Anisotropic thermal parameters for the non-hydrogen atoms (Table SI), complete listings of bond lengths (Table SIII) and angles (Table SIV), atomic positional parameters (Table SV), and experimental parameters of the X-ray data collection (Table SVI) for $[Cu(hfac)_2]_3(NITEt)_2$ (10 pages); observed and calculated structure factors (Table SII) (18 pages). Ordering information is given on any current masthead page.

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Time Dependence of the Excitation Polarization Ratio of $Ru(bpy)_3^{2+}$ in 4:1 Ethanol/Methanol Glass at 77 K

Sir:

Myrick, Blakley, and DeArmond[1] (MBD) have recently reported the luminescence excitation polarization ratio, *P*, of $Ru(bpy)_3^{2+}$ (RBY) to be time dependent on the 0–300-ns time scale in a number of frozen glasses at 77 K, including the most commonly studied glass-forming mixture, 4:1 ethanol/methanol (EM). These results were used to support the idea of *intrinsic* localization in the excited luminescent state of RBY, i.e. that MLCT luminescence arises from excitation of a single ligand. A maximum value for *P* of 0.5 would be allowed by such a process.

The high values observed at short times (0.30 ± 0.01 at 5–10 ns), compared to the long-time value of *P* (0.22 ± 0.02 at ≥300 ns) were used by MBD to propose a hopping model, where excitation, initially localized, would subsequently diffuse around the ligands, giving rise to a gradually reducing value of *P* until a steady-state level was reached.

In view of the unexpected and potentially important nature of these results, we have carefully repeated those in EM using a different and experimentally advantageous procedure over that used by MBD. We have found no observable time dependence for *P* of the magnitude reported by these workers, with effectively constant in time (but different) values being observed for excitation at a number of wavelengths throughout the MLCT region of 400–500 nm.

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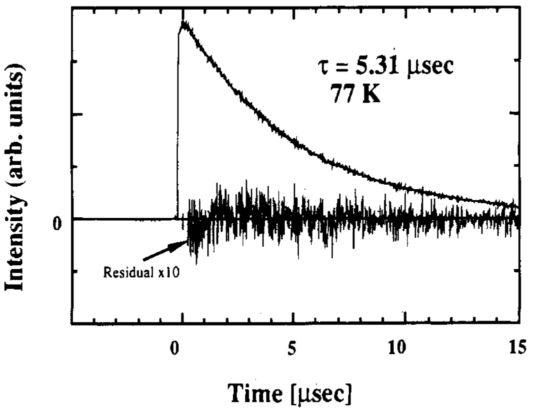

Figure 1. Experimental decay profile of Ru(bpy)$_3$Cl$_2$ 1.6 × 10^{-4} M in 4:1 ethanol/methanol at 77 K, excited at 468 nm and detected at 615 nm, with residuals from a fitted 5.31 ± 0.01-μs lifetime. The decay curve is the average luminescence arising from 1024 laser pulses.

MBD report a number of precautions taken to avoid the possibility of artifacts, including running solvent blanks. They reported a lack of any observable time dependence of P for the related Ru(bpy)(py)$_4^{2+}$ complex. This was used as supporting evidence that the effect was indeed genuine. The experimental procedure used involved a dye laser operating at 468 nm and a boxcar integrator gated for differing times after the laser ≃3-ns pulse. The value of P at any time is then determined by taking the ratio of separate measurements for differing detection polarization conditions, parallel or perpendicular to the exciting polarization. We have chosen to use a Tektronix 2430 high-speed digital scope, which accumulates 1024 time points in parallel and can be used to average many laser pulses more efficiently than the boxcar system. It also reduces problems due to dye/laser power drift. Drift will give errors in the absolute value of P but not introduce a spurious time-dependent P. As a digital scope does not require a pretrigger to record fast events (as do boxcars), it can be triggered by the laser *light* pulse itself (as monitored by a fast diode), effectively eliminating effects due to laser time jitter.

A Hamamatsu 943-02 photomultiplier with 3-ns risetime was used, terminated into the 50-Ω input of the scope which itself has a "risetime" of 2.8 ns (in 150-MHz BW mode), providing a good match of performances. The photomultiplier base was fitted with 0.2-μF capacitors in the last three stages, and signal levels were kept to below about 5 mV. Reasonably good (3%) linearity was observed in the range 0.5–5 mV. Luminescence was observed through a 615-nm interference filter with a 10-nm band-pass. This has the advantage of strongly rejecting laser light but not fluorescing as most glass filters do, as well as providing wavelength selection. Checks were made by using both an interference filter and a sharp-cut filter. It has been shown that there is a small wavelength dependence of the luminescence lifetime with detected wavelength,[2] so, in general, detection at a specific wavelength is preferred. A small segment of an unfocused Molectron nitrogen laser/dye laser attenuated with a neutral density filter and then polarized with a Glan-Taylor prism, having a duration of ≃3 ns, was used at powers much less than 10 μJ/pulse absorbed energy. The maximum absorbance of the sample, thickness 1 mm, was 0.1.

The sample, as the chloride salt, was freshly prepared from AR grade solvents and purged with argon for 20 min. It formed a clear glass without cracks when immersed in liquid nitrogen. Figure 1 shows the decay and residuals to a 5.31 ± 0.01 μs fitted lifetime. This value is in excellent agreement with other values in the literature.[2,3] Identical values (±0.01) were obtained by excitation at 337, 440, 468, and 514 nm. A very recent value of 4.44 μs[4] is in marked disagreement with all others.

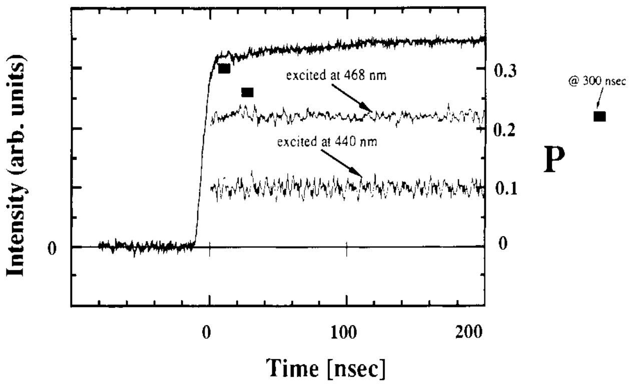

Figure 2. Luminescence of the sample (thick curve) in Figure 1 in the 0–200-ns range and the observed polarization ratio, $P = (I_\parallel - I_\perp)/(I_\parallel + I_\perp)$ as a function of time. Rectangles relate to values reported in ref 1.

Figure 2 shows the luminescence in the first 200 ns and the experimentally measured time-dependent polarization ratio excited at 468 nm and at 440 nm. These measurements were made under conditions identical with those for the total decay displayed in Figure 1. No significant variation of P with time is seen, and the average values are in good agreement with those obtained previously in the steady state.[2,5,6] This good agreement with average values is an internal check of the efficiencies of polarization optics and drift of the laser power. Some original (time-dependent) P values reported by MBD are also presented in Figure 2 for comparison.

Clearly, no time variations of P of the magnitude reported are present in our data. We have repeated measurements on a number of samples and have had similar results. As MBD have taken a number of precautions and would be aware of the potential of artifacts in this work, we can only report that we have found it imperative to make measurements at the lowest possible power in order to avoid artifacts due to laser heating. Transients with 10–100-ns time dependence were observed when much higher laser power was used but were not quantified.

The higher value of P near 468 nm can be clearly associated with a distinct (E symmetry) electronic electronic state in this region, as identified by its characteristic (*A* term) MCD spectrum.[7] The value of P observed (0.22), is much closer to $^1/_7$ (0.14) than to $^1/_2$ (0.5), values predicted by planar and linear oscillators, respectively. This is consistent with the E state developing a small degree of in-plane anisotropy due to environmental effects. Some corroborative evidence is supplied by the observation that the maximal P value is slightly smaller (0.20), in the highly dielectric medium 9 M LiCl.[2b]

Acknowledgment. I gratefully acknowledge the guidance of Dr. H. Riesen in his insistence on the need for low-power excitation in luminescence spectra. I also thank Dr. G. Moran for her assistance.

Registry No. Ru(bpy)$_3^{2+}$, 15158-62-0; ethanol, 64-17-5; methanol, 67-56-1.

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