Effect of the paramagnetic ion Gd(III) on the molecular triplet state of the organic ligand in complexes

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The effect of the paramagnetic ion Gd(III) on the properties of the molecular triplet state of the ligand 2,2′-bipyridine has been studied by low-temperature phosphorescence and by optical detection of magnetic resonances (ODMR) in a zero field. For the first time, ODMR spectra in zero field are reported for the following two complexes containing the paramagnetic Gd(III) ion: Gd$(acac)_3 \cdot bpy$ and Gd$(NO_3)_3 \cdot 2bpy$. The spectral and kinetic properties of the low-temperature phosphorescence of these compounds have been studied. An energy diagram is proposed for the fine structure of the triplet for Gd$(acac)_3 \cdot bpy$. The effect of the paramagnetic Gd(III) ion in these compounds is linked with exchange Coulomb and spin–spin f–π interactions. The strength of these interactions has been determined experimentally for the first time.

INTRODUCTION

The effect of paramagnetic ions on molecular luminescence has been under study for a long time now.[1–8] The coordination of the rare earth ion Gd^{3+}, which has a first electronic transition $^8S_{7/2} \rightarrow {}^6P_{1/2}$ at 32 200 cm^{-1}, with aromatic molecules, for which the electronic excitation $S_0 \rightarrow T_1$ has a lower energy, results in complexes in which the luminescent state localizes at one ligand. In these complexes one observes an intense molecular phosphorescence, since the paramagnetic ion enhances not only the radiative transition $T_1 \rightarrow S_0$ but also the intercombination transition $S_1 \rightsquigarrow T_1$, as the result of an exchange interaction between the electrons of the central metal and the ligand.

Along with the Coulomb interaction one should also consider the magnetic bonds between the inner $4f$ electrons of the metal and the unpaired π electrons of the ligand. This bonding gives rise to fine structure of the triplet, which cannot be observed by the conventional magnetic-resonance methods. Our purpose in the present study was to use the method of optical detection of magnetic resonances (ODMR) in a zero field to learn about how a paramagnetic metal influences the properties of the molecular triplet state of the ligand.

The compound 2,2′-bipyridine (*bpy*), a typical bidentate ligand, was selected for coordination with acetylacetone and gadolinium (III) nitrate [Gd$(acac)_3$ and Gd$(NO_3)_3$]. We were able to observe a quasiline vibron phosphorescence spectrum of Gd$(acac)_3 \cdot bpy$, which made it possible to estimate the "trip-multiplet" splitting of the $^3\pi,\pi^*$ molecular state. Gouterman's group[2,4] has studied this splitting for complexes of porphyrins with transition metals. Since the exchange interaction of the π electrons of the ligand with the inner f electrons is weaker than that with the d electrons of the metal ion, however, there are no corresponding data for complexes of rare earth elements. In the present paper we are reporting the first ODMR spectra for complexes of paramagnetic ions. Preliminary results were reported in Ref. 9.

EXPERIMENTAL PROCEDURE

The complex Gd$(acac)_3 \cdot bpy$ was synthesized by the procedure of Ref. 10. A similar procedure was used to produce Gd$(NO_3)_3 \cdot 2bpy$ (that there are two *bpy*'s in this complex was proved by x-ray diffraction analysis). Measurements were carried out on crystalline samples in quartz cells. Excitation and luminescence spectra were recorded on an MDR-2 or DFS-24 spectrometer. The microwave source was a HP8620C sweep generator. The optical signal was detected in a photon counting regime with storage in an LP4840 or LP4900B multichannel analyzer. A Decision Mate V personal computer was used for the numerical analysis of the results.

RESULTS

Figure 1 shows phosphorescence emission and excitation spectra of Gd$(acac)_3 \cdot bpy$ at 5 K. The emission spectrum is dominated by the 0,0 band at 432 nm (23 150 cm^{-1}); there are also vibron bands for vibrations at 350, 644, 768, 1014, 1497, and 1601 cm^{-1}. These fundamental frequencies correlate well with the frequencies of completely symmetric vibrations at 330, 612, 763, 993, 1481, and 1601 cm^{-1} which have been observed in the Raman spectra of the *bpy* molecule in a single crystal.[11] In the phosphorescence excitation spectrum these vibrations are seen for the excited state of the complex, in agreement with the interpretation that this state is localized at a ligand and is of the $^3\pi,\pi^*$ type.

The observation of a resonance frequency at 432 nm in the excitation spectrum, on the red wing of the fundamental band at 430 nm, shows that the emission is determined by trapping centers with a depth of 110 cm^{-1}. As the temperature is raised, the phosphorescence intensity falls off, essentially vanishing above 40 K because of thermal deexcitation of the trapping centers. The absorption peak at 390 nm corresponds to an electronic transition to the $^3\pi,\pi^*$ state of acetylacetanate[3] and at 345 nm to the $^1\pi,\pi^*$ state of *cis*-bipyridine.[12]

The A, B, and C lines in the 0,0 band can be ascribed both to various centers and to various electronic states. A detailed analysis of the temperature dependence of the emission intensity in the 0,0 band reveals that, in addition to various centers, there are two electronic states with an energy difference of 11 cm^{-1}. The double phosphorescence observed here was confirmed by a subsequent study of the

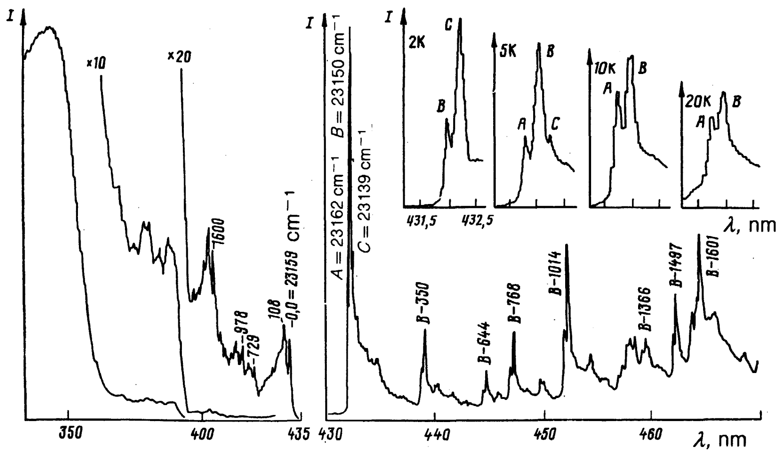

FIG. 1. Excitation spectra (at the left) and emission spectra (at the right) of the phosphorescence of the complex Gd$(acac)_3\cdot bpy$ at 5 K. The insets show spectra of the 0,0 band at various temperatures.

emission kinetics. At a temperature of 20 K, we observe a single-exponential decay for the A and B lines, with a lifetime of 7.8 ms. This lifetime is not altered by a change in temperature. Below 20 K the phosphorescence decays biexponentially, and the lifetime increases noticeably. For line C at 2 K we observe a single-exponential decay with a lifetime of 150 ms. The upper electronic state, with the higher emission capability, thus has a lifetime $\tau_1 = 7.8/2 = 3.9$ ms, while the lower has a lifetime $\tau_2 \geqslant 150$ ms.

Although corresponding spectral and kinetic properties are exhibited by the phosphorescence of the complex Gd$(NO_3)_3\cdot 2bpy$, there are no nonphonon lines in the optical spectra.

Figure 2 shows ODMR spectra for the two complexes. Seven resonances are observed between 2 and 8.5 GHz. A study of the ODMR kinetics shows that the ODMR signal is formed indirectly: When the magnetic transition reaches saturation, the populations of two electronic states which are not coupled by the resonant microwave field are pumped. These electronic states are at thermal equilibrium. When the transition to a new equilibrium occurs, we observe two-stage kinetics: a fast stage with a lifetime of 50 ms, which is typical of phosphorescence decay at 5 K, and a slow stage, with a lifetime of about 500 ms. Either cooling from 5 to 2 K or heating above 50 K reduces the intensity of the ODMR signal.

DISCUSSION

There are two ways to explain the ODMR spectrum of a complex. First, the magnetic resonances might be linked with the ground state of the complex, in which case the transitions would stem from the spin degrees of freedom of the central ion. The spin state of Gd(III) can split into four sublevels in the field of the ligands;[13] this splitting can in principle give rise to six lines in the ODMR spectrum. Experimentally, on the other hand (Fig. 2), we observe seven resonances, so we need to examine an alternative explanation, which incorporates a direct relationship between the magnetic resonances and features of the optical transitions.

Photoexcitation gives rise to additional paramagnetism in the complex, in the form of a triplet $^3\pi,\pi^*$ state, localized at a ligand. The spin Hamiltonian of the excited complex can thus be written in general as the sum of three terms:

$$H_{spin}=H_S+H_{SI}+H_I, \qquad (1)$$

where H_S is the spin Hamiltonian of the triplet ligand ($S=1$), H_I is the spin Hamiltonian of the paramagnetic ion Gd(III) ($I=7/2$), and H_{SI} is the Hamiltonian of the spin-spin interaction of the f and π electrons.

The experimental data available suggest the following interpretation. Since the excitation in the complex is localized at a ligand, one can ignore H_I in a first approximation.

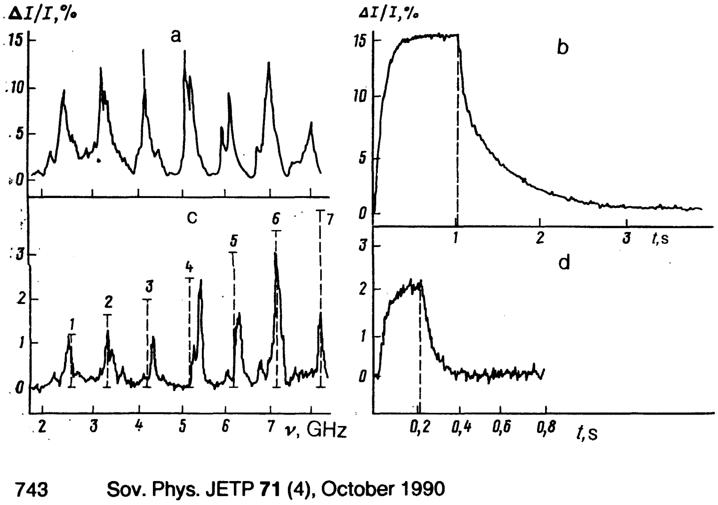

FIG. 2. a,c) ODMR spectra; b,d) kinetic curves of the microwave resonances for (a,b) the complex Gd$(NO_3)_3\cdot 2bpy$ and (c,d) the complex Gd$(acac)_3\cdot bpy$. The vertical dashed lines in Fig. 2c correspond to the calculated transition frequencies.

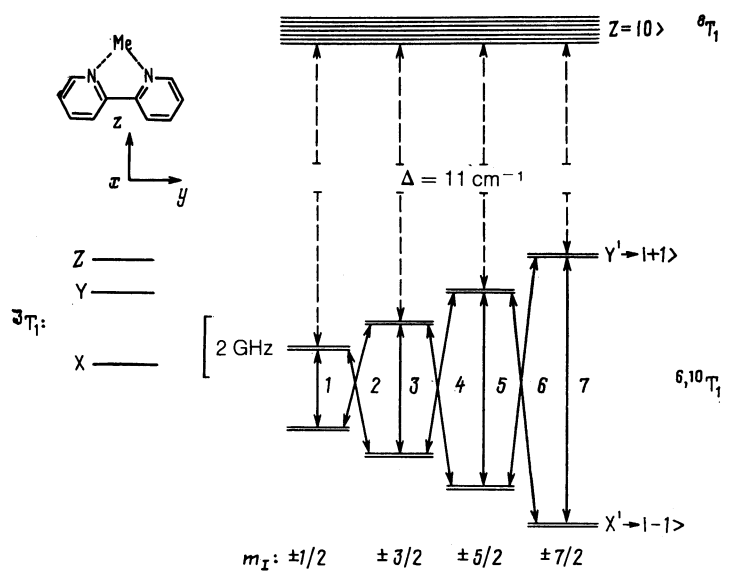

FIG. 3. Scheme of triplet sublevels of 2,2π-*bpy* in Rh(*bpy*)$_3^{3+}$ (at the left)[14] and in Gd(*acac*)$_3\cdot$*bpy* (at the right).

The spectral and kinetic data on the phosphorescence of the complex suggest that there are two distinct electronic states, i.e., that the lifting of the spin degeneracy ($I + S = 5/2, 7/2, 9/2$) is not complete.

On this basis one might suggest that the trip-octet ($I + S = 7/2$) state lies (along the energy scale) above the degenerate trip-sextet ($I + S = 5/2$) and trip-dectet ($I + S = 9/2$) states by an amount Δ which is determined by the *f*–π exchange Coulomb interaction. This quantity was found to be 11 cm^{-1} from the splitting of the 0–0 band in the phosphorescence spectrum of Gd(*acac*)$_3\cdot$*bpy* at 5 K. This figure is significantly lower than the energy of the *d*–π exchange interaction which has been found for porphyrin complexes containing copper (more than 100 cm^{-1}; Refs. 2 and 4).

When the *f*–π exchange interaction, which gives rise to trip-multiplets, is taken into account we find the following expression for the spin Hamiltonian H_S:

$$H_S=(\Delta+D)[S_z^2-{}^1/_3S(S+1)]+E(S_x^2-S_y^2), \qquad (2)$$

where D and E are the parameters of the splitting of the zero field for the free ligand. In this case the spin of the π electrons is quantized along the *z* axis, which bonds the paramagnetic ion Gd(III) with the ligand *bpy*.

Since Δ is substantially greater than D and E, the Hamiltonian of the *f*–π spin–spin interaction is dominated by a term $H_{SI} = A_{zz}S_zI_z$, which mixes the "pure" trip-sextet and trip-dectet states (A_{zz} is the component of the spin–spin interaction tensor along the *z* direction).

The arguments above are illustrated in Fig. 3 with an energy diagram of the excited state of the Gd(*acac*)$_3\cdot$*bpy* complex. The seven transitions observed here can be put in two groups: four transitions with $\Delta m_I = 0$ and frequencies $\nu_{2mI} = 2(E^2 + m_I^2A_{zz}^2)^{1/2}$, and three flip–flop transitions with $|\Delta m_I| = 1$ and frequencies

$$\nu_{2m_{I+1}}=(\nu_{2m_I}+\nu_{2m_{I+2}})/2.$$

From Fig. 2c we see that the transition frequencies in the ODMR spectrum agree satisfactorily with the calculated values with $E = 1.11$ GHz and $A_{zz} = 1.13$ GHz.

According to this scheme, the sublevels coupled by the resonance have identical radiative deexcitation rates. The microwave transitions are detected only when the temperature is raised to 5 K, and a sufficient population is created in the trip-octet, which is at dynamic equilibrium with the lower-lying states and which has a phosphorescence quantum yield which is much higher (the lifetime of the $^6T_1$ and $^{10}T_1$ states is 150 ms, and that of the $^8T_1$ state is 5 ms).

CONCLUSION

In summary, these experimental data show that the effect of the paramagnetic Gd(III) ion in complexes with an excitation localized at a ligand is determined by the exchange Coulomb and spin–spin *f*–π interactions. The magnitude of the *f*–π Coulomb exchange interaction between the paramagnetic Gd(III) ion and triplet 2,2′-bipyridine has been determined experimentally for the first time. The result is 11 cm^{-1}. The strength of the spin–spin *f*–π interaction has been found to be ∼0.038 cm^{-1}.

It can be concluded from these results that ODMR in a zero field can serve as a new approach for studying subtle magnetic interactions in complex compounds with a paramagnetic central ion.

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