Scheme II

$$\begin{tikzcd}
\mathrm{FeOH(P\text{-}N_4)} \arrow[r, "\mathrm{Me_2SO}", "\mathrm{slow}"'] \arrow[d, "N\text{-}\mathrm{MeIm}"'] & \mathrm{[Fe(Me_2SO)_2(P\text{-}N_4)]^+OH^-} \arrow[d, "N\text{-}\mathrm{MeIm}"] \\
\mathrm{Fe(}N\mathrm{\text{-}MeIm)OH(P\text{-}N_4)} \arrow[r, "N\text{-}\mathrm{MeIm}"] & \mathrm{[Fe(}N\mathrm{\text{-}MeIm)_2(P\text{-}N_4)]^+OH}
\end{tikzcd}$$

in accordance with Scheme II. The aging process in Me_2SO does not produce an overall spin-state change on Fe, as evidenced by the fact that the magnetic moment as measured by the Evans method is unchanged at 6.0 μ_B, and the ESR spectra of fresh and aged solutions at 4.2 K show identical $g \approx 6, 2$ spectra.

Although the μ-oxo oligomer $[Fe(P\text{-}(NO)_2)]_2O$ is insoluble in Me_2SO, solutions in $CHCl_3$ show little affinity for ligands such as *N*-MeIm, with an estimated $\beta_2 < 10^{-10}$ (cf. $\beta_2 = 65$ for the hydroxo complex in this solvent).

Conclusion

The series of compounds $FeX(P\text{-}N_4)$ has been shown to exhibit a diversity of magnetic behavior. Although a crystal structure of the Cl^- complex indicates an essentially high-spin character on Fe, albeit with an unusual axial ligand combination, it is clear that magnetically this series of complexes is finely balanced near the spin-crossover point. Subtle variations in axial ligand and solvation appear to be sufficient to affect the spin state on Fe, at least in the solid state. The solution behavior, on the other hand, is more clearly defined. With a detailed understanding of the magnetic properties of these complexes now established, an interpretation of the behavior of the heteronuclear complexes $Fe(P\text{-}N_4)XCu^{2+}$ is now possible and will be reported subsequently.

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Registry No. $(FeCl(P\text{-}N_4))_n\cdot CHCl_3\cdot H_2O$, 88082-42-2; $FeCl(P\text{-}N_4)$, 88082-44-4; $(FeBr(P\text{-}N_4))_n$, 88035-69-2; $FeBr(P\text{-}N_4)$, 88082-45-5; $(FeOH(P\text{-}N_4))_n$, 88082-43-3; $FeOH(P\text{-}N_4)$, 88082-46-6; $FeN_3(P\text{-}N_4)$, 88035-70-5; $[Fe(P\text{-}(NO)_4)]_2O$, 88035-71-6; $(P\text{-}N_4)$, 66887-83-0; *meso*-$\alpha,\alpha,\alpha,\alpha$-tetrakis(*o*-aminophenyl)porphyrin, 68070-27-9; nicotinic anhydride, 16837-38-0; trimethylamine *N*-oxide, 1184-78-7.

Supplementary Material Available: Tables of observed and calculated structure factors and of least-squares planes and Tables V, VII–IX showing observed susceptibility data (23 pages). Ordering information is given on any current masthead page.

Contribution from the Istituto FRAE—CNR, Bologna, Italy,
Istituto di Scienze Chimiche della Facoltà di Farmacia and Istituto Chimico "G. Ciamician",
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Photophysical Characterization of the Decatungstoeuropate(9–) Anion

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As a part of an investigation on completely inorganic photosensitizers, the photophysical properties of $EuW_{10}O_{36}^{9-}$ have been fully characterized. The absorption spectra, emission spectra (under low and high resolution), and emission decay of $EuW_{10}O_{36}^{9-}$ under a variety of experimental conditions (solid state, H_2O or D_2O solutions of different concentrations with or without the addition of neutral salts, rigid matrix at 77 K) are reported. On the basis of the results obtained concerning the number of $^5D_0 \rightarrow {}^7F_0$ bands under high resolution, the splitting of the $^5D_0 \rightarrow {}^7F_J$ bands, and the decay of the emission intensity, the following is shown: (i) in aqueous solutions $EuW_{10}O_{36}^{9-}$ maintains its integrity, but it is subjected to equilibria involving the coordination of water molecules to europium, the acid dissociation of coordinated water, and the formation of ion pairs with the cations present in solution; (ii) in very diluted solutions the predominant excited-state species contains four coordinated water molecules and possesses C_{4v} symmetry; the lifetime of the $^5D_0$ emitting state is 0.25 ms in H_2O and 3.7 ms in D_2O, showing that the main radiationless deactivation process involves coupling with OH oscillators; (iii) increasing ionic strength causes the appearance of more strongly emitting and longer lived species that contain fewer coordinated H_2O molecules; (iv) in the solid state only one $EuW_{10}O_{36}^{9-}$ species is present, which exhibits D_{4d} symmetry and whose lifetime is 3 ms regardless of whether it has been crystallized from H_2O or D_2O, showing that no water molecule is coordinated to Eu^{3+}; (v) emission can be obtained upon excitation of both the weak f → f bands in the visible and the strong bands in the UV region, which are attributed to O → W charge-transfer transitions within the $W_5O_{18}^{6-}$ "ligands"; (vi) the emission quantum yield in D_2O solution is 0.5 on excitation at 394 nm ($^5L_6$ level) and 0.2 on excitation at 250 nm (O → W charge transfer). The possible use of $EuW_{10}O_{36}^{9-}$ as a photosensitizer is briefly discussed.

Introduction

Photochemical conversion of solar energy by redox cycles in homogeneous solution is based on photosensitizer and relay species that must induce and mediate electron-transfer steps of a thermodynamically uphill reaction.[2] For example, the splitting of water by solar energy has been reported to occur when $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) and methylviologen are used as a photosensitizer and relay species, respectively.[3] Most of the molecules proposed so far as photosensitizers and relays for such energy-conversion processes are organic compounds or transition-metal complexes containing aromatic ligands. These molecules usually do not show long-term stability in the reaction medium because they may be involved

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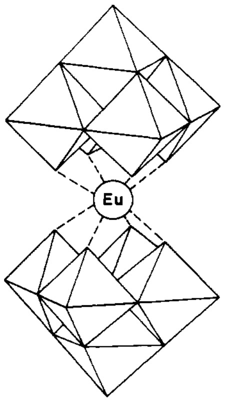

Figure 1. Representation of the structure of the $EuW_{10}O_{36}^{9-}$ anion in the solid state.

in side reactions (e.g., double-bond hydrogenation); as a consequence, their turnover number is too small. As far as the requirement of a high turnover number is concerned, ideal photosensitizer and relay species should be transition-metal ions or transition-metal complexes containing inorganic ligands. Transition-metal ions, however, are useless because they exhibit unsatisfactory spectroscopic properties (e.g., very low extinction coefficients and very short excited-state lifetimes) and also poor kinetic behavior in electron-transfer reactions. On the other hand, the full potential of transition-metal complexes containing inorganic ligands has not yet been explored in depth. Some studies in this direction have been carried out by Gray et al. on binuclear halides,[4a] and reports have also appeared concerning polyoxometalates[4b,c] and a few other systems.[4d,e] We have begun an investigation in the field of completely inorganic photosensitizer and relay systems, focusing our attention on those species where a metal ion is encapsulated into polyoxoanionic structures[7] so as to yield complexes that may be considered inorganic cryptates. In this paper we report the photophysical characterization of $EuW_{10}O_{36}^{9-}$. The redox behavior of the same compound in pulse and steady-state radiolysis experiments will be reported elsewhere.

The decatungstoeuropate(9−) anion, first prepared by Peacock and Weakley[8] in 1971 as a potassium salt and originally formulated as $EuW_{10}O_{35}^{7-}$, is now known[9-13] to have composition $EuW_{10}O_{36}^{9-}$ and to correspond to the coordination of two $W_5O_{18}^{6-}$ fragments (each consisting of five WO_6 octahedra sharing edges) to Eu^{3+}, which is thus eight-coordinated (Figure 1). The luminescence spectrum of this compound was first reported by Stillman and Thomson[14] with the purpose of deriving the site symmetry of Eu^{3+}. More recently, Blasse et al.[9,10] have studied the luminescence spectrum of solid samples of $Na_9EuW_{10}O_{36}\cdot 18H_2O$ and $K_9EuW_{10}O_{36}\cdot 18H_2O$ and Vel'tykova et al.[15] have reported the spectrum of solutions containing $EuCl_3$ and Na_2WO_4 frozen at 77 K.

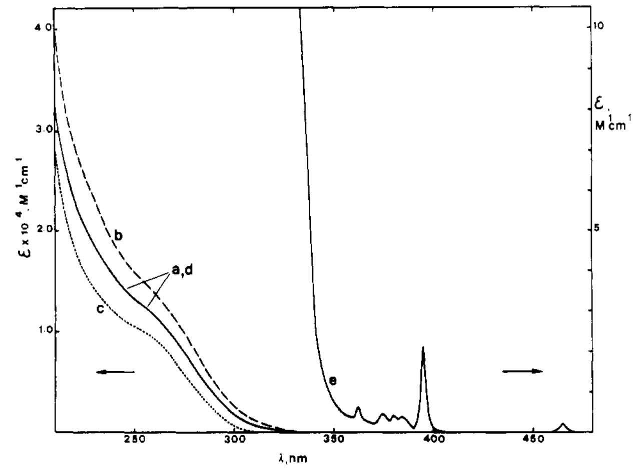

Figure 2. Absorption spectra of $EuW_{10}O_{36}^{9-}$: (a) 5.0×10^{-5} M, natural pH; (b) 5.0×10^{-5} M plus 1.0×10^{-4} M $HClO_4$; (c) 5.0×10^{-5} M plus 1.0×10^{-4} M NaOH; (d) solution b or c after addition of 1.0×10^{-4} M NaOH or $HClO_4$, respectively; (e) 1.0×10^{-2} M, natural pH.

Experimental Section

$Na_9EuW_{10}O_{36}\cdot 18H_2O$ was prepared as described by Peacock and Weakley.[8] Two different preparations gave samples having identical spectroscopic properties. D_2O (C. Erba) was 99.9% pure, and the other chemicals were of reagent grade.

Absorption spectra were recorded with a Cary 219 spectrophotometer and emission spectra (under low resolution) with a Perkin-Elmer MPF 3 spectrofluorimeter equipped with a R 928 phototube. High-resolution emission spectra were obtained by a Jasco R 300 Raman spectrometer using a Spectra-Physics Ar laser for excitation at 457.9, 465.8, or 472.7 nm. Emission lifetimes were measured by a JK system 2000 neodymium Yag DLPY 4 laser, exciting with the fourth harmonic at 266 nm and following the emission at 620 ± 10 nm. The uncertainty on the emission lifetime values reported below is smaller than 5%. The emission quantum yields have been evaluated by the method described by Haas and Stein[5] using as standards $Eu(ClO_4)_3$ ($\Phi_{em} = 0.20$) for 394-nm excitation and $Ru(bpy)_3^{2+}$ ($\Phi_{em} = 0.042$)[6] for 250-nm excitation.

Results

Aqueous solutions of $Na_9EuW_{10}O_{36}$ 10^{-5}–10^{-1} M at their natural pH (~6) are stable. In particular, no change was observed in the absorption and emission spectra over a period of days.

Addition of H^+ or OH^- in a 2:1 ratio with respect to the complex concentration did not appreciably change the pH of the solution and caused small and reversible spectral changes in the UV region (Figure 2).

Upon addition of larger amounts of acids or bases, the complex undergoes decomposition reactions that, judging from the absorption and emission spectra, are at least in part irreversible. All the results described below were obtained with solutions at their natural pH unless otherwise noted.

Absorption Spectra. The absorption spectrum of a diluted (5.0×10^{-5} M) solution of $EuW_{10}O_{36}^{9-}$ (Figure 2) shows the tail of an absorption band in the UV region with a shoulder at 250 nm ($\epsilon \simeq 13\,000$). More concentrated solutions or diluted solutions containing large concentrations of other salts (e.g., 2 M KCl) show a spectrum of the same type but somewhat more intense. The very weak f → f bands of Eu^{3+} in the visible region can only be seen by using concentrated solutions (Figure 2).

Emission Spectra and Quantum Yields. Figure 3 shows the emission spectra under low resolution ($\lambda_{exc} = 270$ nm) and

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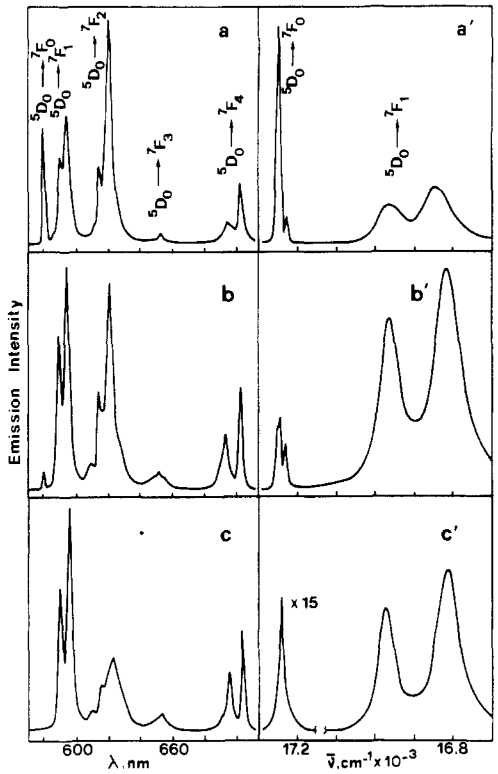

Figure 3. Luminescence spectra of $EuW_{10}O_{36}^{9-}$ solutions under different experimental conditions: (a) 5.0×10^{-5} M solution, low resolution; (a′) 5.0×10^{-5} M solution, high resolution; (b) 1.0×10^{-1} M solution, low resolution; (b′) 1.0×10^{-1} M solution, high resolution (a Gaussian analysis of the $^5D_0 \to {}^7F_0$ band registered under higher sensitivity and resolution shows four components); (c) solid sample, low resolution; (c′) solid sample, high resolution.

under high resolution ($\lambda_{exc} = 465.8$ nm) of $EuW_{10}O_{36}^{9-}$ in different experimental conditions. Parts a and a′ of Figure 3 refer to a 5.0×10^{-5} M solution at room temperature. The assignment of the various bands is given in the figure for identification purpose (see Discussion). As one can see, the most intense bands correspond to the $^5D_0 \to {}^7F_2$ and $^5D_0 \to {}^7F_1$ transitions. The $^5D_0 \to {}^7F_0$ band is also relatively intense, and under high resolution, it is split into a high-intensity peak at 17 254 cm^{-1} and a very small peak (less than 10% of the overall area) at 17 233 cm^{-1}.

Addition of 1.0×10^{-4} M $HClO_4$ caused a decrease in the relative intensity of the 17 233-cm^{-1} peak while addition of 1.0×10^{-4}M NaOH caused an opposite effect. When D_2O instead of H_2O was used as a solvent, the emission spectrum became about 20 times more intense but the relative intensities of the various peaks did not change. Increasing the $EuW_{10}O_{36}^{9-}$ concentration in H_2O solutions up to 1.0×10^{-4} M or addition of small amounts of neutral salts (10^{-3}–10^{-2} M) did not cause substantial changes in the emission spectra. A further increase in the $EuW_{10}O_{36}^{9-}$ concentration or the presence of large amounts of neutral salts caused progressive changes in the relative intensities of the bands under low resolution (see, e.g., Figure 4) and also modified the shape of the $^5D_0 \to {}^7F_0$ emission under high resolution. All these changes are clearly seen on comparing parts a and a′ (which, as we have seen, refer to a 5.0×10^{-5} M solution) to parts b and b′ of Figure 3 (which refer to a 1.0×10^{-1} M solution). The $^5D_0 \to {}^7F_1$, $^5D_0 \to {}^7F_2$, and $^5D_0 \to {}^7F_4$ emissions become much more intense than the $^5D_0 \to {}^7F_0$ emission, which, under high resolution, shows now three peaks at 17 250, 17 245, and 17 232 cm^{-1} and, according to the results of a Gaussian analysis, also a fourth component at ~17 110 cm^{-1}. This spectral behavior of concentrated solutions is in agreement with that reported by Stillman and Thomson.[14] At 77 K, very diluted solutions exhibit a low-resolution spectrum very similar to that of Figure 3a, except for the $^5D_0 \to {}^7F_0$ band, which is much weaker. For more concentrated solutions at 77 K, the $^5D_0 \to {}^7F_0$ emission becomes even smaller, the $^5D_0 \to {}^7F_2$ emission also becomes smaller, and the $^5D_0 \to {}^7F_1$ emission predominates. The emission spectrum of solid (polycrystalline powder) $Na_9EuW_{10}O_{36} \cdot 18H_2O$ at room temperature is shown in Figure 3c,c′. It is quite similar to that reported by other authors[9,14] and closely resembles that of concentrated solutions at 77 K. It is worth noting that the $^5D_0 \to {}^7F_0$ band is much less intense than the $^5D_0 \to {}^7F_{1,2,4}$ bands and that it shows only one peak at 17 237 cm^{-1} under high resolution.

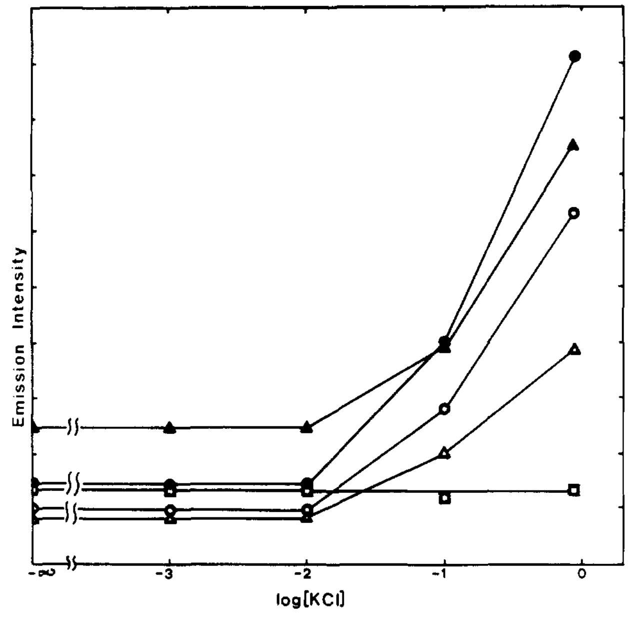

Figure 4. Variations in the intensities of some emission bands of a 1.0×10^{-5} M $EuW_{10}O_{36}^{9-}$ solution upon addition of KCl: $^5D_0 \to {}^7F_0$ (□, 580 nm); $^5D_0 \to {}^7F_1$ (○, 590 nm; ●, 594 nm); $^5D_0 \to {}^7F_2$ (△, 613 nm; ▲, 620 nm).

Table I. Emission Lifetimes and Quantum Yields of $EuW_{10}O_{36}^{9-}$ under Different Experimental Conditions[a]

	τ, ms		Φ_{em}
	H_2O	D_2O	D_2O
1.0×10^{-5} M	0.25		
1.0×10^{-4} M	0.24	3.7	0.5,[b] 0.2[c]
1.0×10^{-4} M + 2 M KCl	(0.7),[d] 3.1[e]		
1.0×10^{-3} M	(0.4),[d] 2.1[f]		
1.0×10^{-2} M	(0.7),[d] 2.2[g]	3.7	0.5[b]
solid state (Na^+ salt)	2.9[h]	3.1[i]	0.8[h,j]

[a] All the experiments were carried out at room temperature; the solutions were at their natural pH. [b] 394-nm excitation. [c] 250-nm excitation. [d] Initial decay; see text. [e] Exponential decay after 1 ms. [f] Exponential decay after 1.8 ms. [g] Exponential decay after 0.3 ms. [h] Crystallized from H_2O. [i] Crystallized from D_2O. [j] Reference 10.

For diluted ($<2 \times 10^{-4}$ M) solutions no change was observed in the relative intensities of the various emission band when excitation was carried out at 465 nm instead of at 270 nm (low-resolution spectra). However, for concentrated solutions or for solutions containing large amounts of neutral salts, the relative intensities of the emission bands depended on the excitation wavelength (270 or 465 nm). The major difference concerns the $^5D_0 \to {}^7F_1$ emission, which, compared with the $^5D_0 \to {}^7F_0$ and $^5D_0 \to {}^7F_2$ ones, was much less intense on 465-nm than on 270-nm excitation. Under high resolution, the relative intensities of the three distinct components of the $^5D_0 \to {}^7F_0$ emission (1.0×10^{-1} M solution, Figure 3b′) were slightly different when the excitation was performed with each one of the 457.9-, 465.8-, and 472.7-nm laser lines.

Emission quantum yields were measured in D_2O solution for $EuW_{10}O_{36}^{9-}$ concentrations 1.0×10^{-4} and 1.0×10^{-2} M. The results obtained are shown in Table I.

Emission Lifetimes. In dilute (10^{-4}–10^{-5} M) H_2O solutions the $EuW_{10}O_{36}^{9-}$ luminescence showed excellent first-order decay with lifetime 0.25 ms. Excellent first-order decay was also observed in D_2O solutions where the lifetime was much longer, i.e. 3.7 ms.

Increasing complex concentration or addition of neutral salts did not cause any change in the luminescence decay of D_2O solutions but strongly affected the luminescence decay of H_2O solutions (Table I). In H_2O, the decay was no longer exponential over the entire range and at least a short-lived and long-lived components could be identified. When the solutions were sufficiently concentrated ($\geq 1 \times 10^{-3}$ M) or when large amounts of neutral salts were present, most of the luminescence intensity disappeared according to a slow, good exponential (over 3 lifetimes) decay. Solid samples crystallized from H_2O exhibit an excellent exponential decay with $\tau = 2.9$ ms. Crystallization from D_2O solutions yielded a solid with $\tau = 3.1$ ms.

Discussion

It is well-known that the very peculiar spectroscopic properties of Eu^{3+} can be profitably used to elucidate the composition, structure, and geometry of the coordination environment.[16-20] In particular, from the spectral and decay characteristics of the luminescence emission it is possible to determine the number of different coordination sites, the symmetry of the coordination site, and the number of water molecules directly coordinated to the lanthanide ion. For this reason, Eu^{3+} and other luminescent lanthanide ions are extensively used as probes of the structure of biological macromolecules,[16,19] polymeric materials,[21] and NMR shift reagents.[20,22]

The ^7F free-ion term of Eu^{3+} is split by spin–orbit coupling into seven ^7F_J states ($J = 0, ..., 6$) spaced about 400–1100 cm^{-1} apart.[17,23,24] Each one of these states is split by the local crystal field (Stark splitting) into a maximum of $2J + 1$ states spaced about 50–200 cm^{-1} apart. When $EuW_{10}O_{36}^{9-}$ is excited in the intense UV bands corresponding to oxygen-to-tungsten transitions within the $W_5O_{18}^{6-}$ "ligand" or in the weak visible bands corresponding to f–f excited states of the Eu^{3+} ion, radiationless deactivations lead to the lowest term of the ^5D_J manifold, $^5D_0$, from which virtually all luminescence to the ^7F_J manifold arises.[19,20] The $^5D_0$ level is nondegenerate and therefore remains unsplit in crystal fields of all symmetry types. Thus, the splitting of the visible-region transitions $^5D_0 \rightarrow {}^7F_J$ ($J = 0, 1, 2, 3$ or 4) reflects the crystal field splitting of the ^7F_J term and can yield clear information on the symmetry of the coordination site.[16-20]

Since the $^7F_0$ state is also nondegenerate, the $^5D_0 \rightarrow {}^7F_0$ transition can never be split. On the other hand, it is well-known that even small changes in the coordination arrangement cause shifts of the order of 10 cm^{-1} in the position of the $^7F_0 \rightarrow {}^5D_0$ absorption[25,26] and $^5D_0 \rightarrow {}^7F_0$ emission[14,19,20] bands. Thus, a high-resolution analysis of the $^5D_0 \rightarrow {}^7F_0$ transition can yield information on the presence of species having different coordination arrangements.

The deactivation of the emitting $^5D_0$ excited state is strongly enhanced by coupling with OH oscillators.[27] According to Horrocks and Sudnick,[19,28] the experimental decay constant (i.e., the reciprocal of the experimental excited-state lifetime) in H_2O solution can be written as

$$k_{H_2O} = k_{rad} + k_{nonrad} + k_{OH} \qquad (1)$$

where k_{rad} is the radiative rate constant, k_{nonrad} is the rate constant for nonradiative deactivation that does not involve OH oscillators, and k_{OH} is the rate constant for nonradiative deactivation via the coupling with OH oscillators in the first coordination sphere. For Eu_{aq}^{3+}, $k_{rad} = 0.19$, $k_{nonrad} = 0.25$, and $k_{OH} = 9.5$ ms^{-1}.[19] In D_2O solution k_{OH} vanishes and k_{D_2O} equals $k_{rad} + k_{nonrad}$, where the latter term includes any small deactivation via OD oscillators. For many Eu(III) complexes in the solid state it has thus been shown[19,28] that the number of coordinated water molecules, q, is related to k_{H_2O} and k_{D_2O} (in ms) by

$$q = 1.05(k_{H_2O} - k_{D_2O}) \qquad (2)$$

with an estimated uncertainty in q of approximately ±0.5 water molecule. Thus, a direct measure of the number of Eu-coordinated water molecules is possible via luminescence decay measurements.

We will now discuss the results obtained in an attempt to elucidate the geometrical and coordination situation of Eu^{3+} in aqueous solutions containing the $EuW_{10}O_{36}^{9-}$ anion. It should be recalled that any information obtained from the analysis of the luminescence spectra and decays pertains to the site symmetry and the coordination arrangement of the emitting excited states. Whether or not this situation reflects the ground-state situation is, of course, a problem to be discussed with great caution.

Solid State. For solid samples, no splitting of the $^5D_0 \rightarrow {}^7F_0$ transition can be observed (Figure 3c′ and ref 14). This indicates that in the solid state there is substantially only one type of $EuW_{10}O_{36}^{9-}$ anion and that these anions occupy substantially equivalent symmetry sites. The X-ray data on the isomorphous Ce(IV)[11] and U(IV)[12] decatungstates show that for the heteroion there is only one crystallographic site of D_{4d} symmetry (Figure 1) if crystal forces are neglected. Under such a symmetry, the $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_2$ transitions are forbidden, the $^5D_0 \rightarrow {}^7F_1$ transition is magnetic dipole allowed and split into two components (A_2 and E_3), and the $^5D_0 \rightarrow {}^7F_4$ transition has two allowed components (B_2 and E_1) for the electric dipole operator.[14] As noted by Blasse et al.,[9,10] the observed emission spectrum (Figure 3c and ref 9) is in fair agreement with the above expectations if one considers that the $^5D_0 \rightarrow {}^7F_2$ transition is hypersensitive[29] (i.e., its transition probability can increase drastically by minor changes in the surroundings) and that the Eu^{3+} site symmetry in the crystal is actually lower than D_{4d}.[11]

The presence of practically only one type of $EuW_{10}O_{36}^{9-}$ anions in the crystal is also in agreement with the strictly exponential decay of the luminescence emission. The values obtained for the emission lifetimes under different conditions (Table I) give other important pieces of information. The

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almost coincident lifetime values found for crystals obtained from H_2O or D_2O solutions show that in the solid state no water molecule is coordinated to Eu^{3+}, in agreement with the previously mentioned X-ray data.[11,12] On the other hand, the fact that the lifetime is shorter in the solid state than in D_2O solution suggests that the interaction between Eu^{3+} and the $W_5O_{18}^{6-}$ ligands is stronger in the solid state.

Solutions at Low Ionic Strength. For diluted solutions of $EuW_{10}O_{36}^{9-}$ in the absence of neutral salt the $^5D_0 \rightarrow {}^7F_0$ transition shows two components (Figure 3a′), indicating that two emitting species are present. The ratio between the intensities of the two $^5D_0 \rightarrow {}^7F_0$ peaks and the relative intensities (under low resolution) of all the emission bands do not change on changing excitation wavelength. This behavior may be explained in two ways: (i) there is only one ground-state species that, during its excited-state lifetime, gives rise to another species in the excited state;[30,31] (ii) there are two ground-state species whose excited states undergo equilibrium during their lifetimes.[19,20,25,26]

The dependence of the relative intensities of the two $^5D_0 \rightarrow {}^7F_0$ peaks on addition of H^+ or OH^- (see Results) shows that the two species are related by an acid-base equilibrium. We have found (Figure 2) that the absorption spectrum also undergoes reversible changes upon addition of H^+ or OH^-. Since the absorption spectrum is a ground-state property, we must conclude that species related by an acid–base equilibrium are certainly present in the ground state. Thus, the second explanation above seems more plausible, and in such a case the area of the two $^5D_0 \rightarrow {}^7F_0$ peaks reflects the relative concentrations of the emitting species,[32] which would be in an approximate 9:1 ratio in solution at natural pH. This ratio would also hold for the ground state if the equilibrium constant is the same in the excited and ground states.

The much longer emission lifetime in D_2O solution compared with that in H_2O solution (Table I) shows that the europium ion of $EuW_{10}O_{36}^{9-}$ is indeed coordinated to water molecules. From eq 2 a value of 3.9 is obtained for q, indicating that there are four coordinated water molecules. The acid–base equilibrium discussed above concerns most likely those water molecules:

$$EuW_{10}O_{36}(H_2O)_4^{9-} \rightleftarrows EuW_{10}O_{36}(H_2O)_3(OH)^{10-} + H^+ \quad (3)$$

A comparison between parts c and a of Figure 3 shows that there are large changes in the relative intensities of the emission bands in passing from the solid state to diluted solutions. Taking the magnetic dipole $^5D_0 \rightarrow {}^7F_1$ transition as an internal standard,[14] the most prominent variations are the increase in intensity of the $^5D_0 \rightarrow {}^7F_2$ transition, which is forbidden in D_{4d} symmetry, and a strong increase in the intensity of the $^5D_0 \rightarrow {}^7F_0$ transition, which becomes allowed only under C_s, C_n, and C_{nv} symmetry groups.[14,33] Coordination of four water molecules would in fact lower the D_{4d} symmetry of the solid $EuW_{10}O_{36}^{9-}$ anion (Figure 1) to C_{4v} because the water molecules cannot lie exactly in the reflection plane of the alternating S_8 axis. Under the C_{4v} symmetry of the tetraaquo species, the $^5D_0 \rightarrow {}^7F_0$ transition is electric dipole allowed, the $^5D_0 \rightarrow {}^7F_1$ transition is magnetic dipole allowed and splits into A_2 and E components, the $^5D_0 \rightarrow {}^7F_2$ transition has electric dipole allowed A_1 and E components, and the $^5D_0 \rightarrow {}^7F_4$ transition has electric dipole allowed 2 A_1 and 2 E components. The observed spectrum (Figure 3a) is fully consistent with a C_{4v} symmetry for the predominant species of $EuW_{10}O_{36}^{9-}$ in aqueous solution.

Solutions at High Ionic Strength. As we have seen under Results, an increase in the ionic strength causes the appearance of a higher number of species, as is shown by the four components of the $^5D_0 \rightarrow {}^7F_0$ transition (Figure 3b′). Since different species may give rise to transitions at very similar or even coincident wavenumbers,[20,25,26] it is likely that at high ionic strength even more species than the four identified from Figure 3b′ are present. This is also supported by the fact that none of the peaks of Figure 3b′ occur at the same wavenumber as the predominant peak of Figure 3a′.

Increasing ionic strength (i) decreases the number of water molecules available to coordinate or solvate the various ions (e.g., in 2 M KCl there are about 14 H_2O molecules per ion), (ii) affects the acid–base equilibria, and (iii) favors association between cations and the strongly charged $EuW_{10}O_{36}^{9-}$ anions. These three phenomena are, of course, related to one another. Thus, $EuW_{10}O_{36}^{9-}$ in solutions of high ionic strength is expected to give rise to a complicated series of equilibria. This complicated situation is also confirmed by the nonexponential decay of the luminescence emission and by the excitation-wavelength dependence of the emission spectra. These results also show that the equilibria are so complicated that there is not enough time in the excited state to reach complete equilibration among the various species. Under such conditions, predominant but low-emitting species may give small contributions to the emission spectrum. Anyway, the presence of long-lived components of the order of 2–3 ms shows that even in relatively dilute solutions species containing less than one water molecule are already present.

Conclusions. $EuW_{10}O_{36}^{9-}$ is a well-characterized complex, which in the solid state exhibits D_{4d} symmetry (Figure 1). In aqueous solutions the complex mantains its integrity but it is subjected to equilibria involving the coordination of water molecules to europium, the acid dissociation of the coordinated water, and the formation of ion pairs with cations. In very diluted solutions and in the absence of neutral salts there are two excited species; the predominant one (~90%) contains four coordinated water molecules and possesses C_{4v} symmetry, and the other one (~10%) most likely contains three coordinated water molecules and a coordinated OH^- ion. These seem to be the first examples of 12-coordinate Eu^{3+} in solution. Increasing ionic strength causes the formation of species that contain fewer water molecules and/or are associated with cations, and crystallization induces the expulsion of water from the first coordination sphere.

$EuW_{10}O_{36}^{9-}$ is a strongly luminescent complex. Its emission quantum yield is 0.5 in D_2O solutions upon 394-nm excitation. The emission quantum yield decreases in H_2O because of the deactivating effect of OH oscillators on the $^5D_0$ emitting state and upon UV excitation presumably because of a relatively low conversion efficiency of the O → W charge-transfer excited states into the europium $^5D_0$ emitting state.

The excited-state energy (2.1 eV) and the excited-state lifetime (ms range) would be very appropriate for the use of $EuW_{10}O_{36}^{9-}$ as a photosensitizer. However, the low absorption in the visible region and the relatively low efficiency of conversion from the allowed charge-transfer excited states of the $W_5O_{18}^{6-}$ ligands to the long-lived $^5D_0$ excited state are severe drawbacks that should be eliminated (or, at least, reduced) in some way. The redox properties of the complex are pres-

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[30] According to Marcantonatos et al.,[31] for Eu_{aq}^{3+} the excited $^5D_0$ level has a different coordination ability than the $^7F_0$ ground state.

[31] Marcantonatos, M. D.; Deschaux, M.; Vuillemuier, J. *J. Chem. Phys. Lett.* **1981**, *82*, 36.

[32] It can be assumed that the two species have the same oscillator strength for the $^7F_0 \rightleftarrows {}^5D_0$ transitions (see ref 25 and 26). Since the rate of equilibration of the two species in the excited state is faster than the excited-state decay[20] (see below), the two species have the same lifetime and thus the same emission quantum yield. It follows that the area of the two emission peaks are proportional to the concentrations of the two emitting species.

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ently the object of investigations in these laboratories.

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Relativistic Calculation of the Electronic Structure and Related Properties of $IrCl_6^{2-}$

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Relativistic MS–Xα calculations have been performed for an $IrCl_6^{2-}$ cluster. Good agreement with experiment is obtained for the photoionization, optical (absorption), and electron spin resonance spectra. The incidence of the relativistic effects is pointed out, and the ability of the numerical wave function is emphasized to describe the magnetic properties. The calculation of these latter properties is based on a corrected ground-state wave function and takes into account admixtures of singly and doubly excited states. Different procedures for the normalization of the wave function (truncated by the scattered-wave method) have been tested in the $\langle r^{-3} \rangle$ integral calculations.

Introduction

The hexachloroiridate complex $IrCl_6^{2-}$ is a well-known outer-sphere oxidant, extensively used in electron-transfer reactions,[1] and both its structure and reactivity have been studied for a long time by many experimental techniques. Photochemical studies[2] have shown that this complex can undergo intramolecular redox reactions after irradiation with a wavelength corresponding to the charge-transfer bands. These electrophilic properties arise from the electronic structure of this d^5 complex. The ground-state (GS) electronic energy levels have been investigated in numerous studies of optical,[3–5] magnetic circular dichroism,[6] and photoelectron spectra[7] of this compound, though uncertainties remain for the assignment of some absorption bands.

The magnetic properties have been largely studied by magnetic susceptibility,[8,9] nuclear quadrupole resonance,[10,11] and electron spin resonance[12–16] measurements. The first observation of superhyperfine coupling (interaction of the unpaired electron spin with ligand nuclear spin) was already reported in 1953,[12] leading to the first unambiguous experimental evidence of the delocalization of the metal d electrons over the whole molecule. Since then, this complex has been of considerable experimental and theoretical interest especially due to the covalent nature of the metal–ligand binding and to the existence of π bonds in addition to the σ bonds.

In spite of this ample experimental information, there is a lack of theoretical studies using molecular orbital (MO) models, except extended Hückel calculations (EH).[5,17] This situation is unfortunate since quantitative theoretical description and interpretations of several properties could be of interest (origin and sign of the Fermi term, main contributions to the hyperfine tensor, etc.).

It is therefore interesting to perform a detailed theoretical investigation of this complex by using the multiple-scattering (MS) Xα–MO method, which has already been shown to give realistic descriptions of various properties of complexes.[18–20] As in the previously reported study of $IrCl_6^{3-}$,[21] the mass–velocity and Darwin relativistic corrections are included self-consistently while the spin–orbit interactions are evaluated by an application of first-order perturbation theory, once self-consistency has been reached.

Table I. Xα Parameters for $IrCl_6^{2-}$

region	sphere radii, au	α exchange parameter
Ir	2.5767	0.69310
Cl	2.5961	0.72325
outer sphere	6.9614	0.71894
intersphere		0.71894

In this paper, we will present the ground-state electronic structure of $IrCl_6^{2-}$ and related properties such as electronic excitations and ionization energies. The quality of the MS–Xα relativistic wave functions will be tested by calculating the hyperfine interaction parameters of both the Ir and Cl atoms in the complex. These parameters are then compared to both experimental values and parameters obtained through nonrelativistic calculations. The great importance of the relativistic corrections, particularly on the Fermi term, which reflects the

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