porates the central metal atom, is not in accordance with voluminous prior structural information on five-coordination. This together with some other unusual properties of the complex raises serious doubts as to its correct identification. The interatomic dimensions, especially bond angles, in the molecule of "$TaBr_3(PMe_2Ph)_2$" are so close to those in $TaCl_4(PMe_2Ph)_2$,[2] that it is reasonable to suspect that both of them are in fact of the same type, viz. $TaX_4(PMe_2Ph)_2$. If instead of two disordered Br atoms (17.5 electrons each) we were to use two nondisordered Cl atoms (17 electrons each) there would be no significant effect on the quality of the refinement. On the other hand it would explain the short (ca. 2.38 Å) Ta–X distance. A Ta–Br bond length of this shortness is not acceptable.

For the above reasons we believe that the compound is in fact a six-coordinate octahedral Ta(IV) complex, $TaCl_xBr_{4-x}(PMe_2Ph)_2$, with x equal to or close to 2. This change eliminates all unusual features of the molecular structure and is also consistent with the reported composition determined by elemental analysis (two Cl atoms instead of one Br diminish the molecular weight by only 9 daltons, less than 2%). The presence of chlorine atoms is readily accounted for by the nature of the reaction medium. The combination of Mg, CH_2Cl_2, and Et_2O is likely to produce a chloro Grignard compound, which can easily cause halide ion exchange.

Other reported properties of the material, especially the solution behavior, are confusing. The interpretation of spectra is somewhat ambiguous, and contradictions can be found. While we shall not offer a detailed reanalysis of the spectral data at this time, here are a few examples of some facts that should have been addressed by the authors.

(a) It is not generally easy to observe an EPR signal for a d^2 species, while it is for a d^1 species.

(b) An agostic H atom interacting with a paramagnetic center is not likely to give a detectable NMR signal.

(c) Sharp and not shifted NMR resonances are not compatible with the observed EPR activity of the compound.

In general the magnetic data (solid-state $\mu = 1.19\ \mu_B$) and both NMR and EPR spectra are consistent with a d^1, rather than a d^2, configuration of the tantalum atom. The spectra can be qualitatively explained by the monomer (paramagnetic)–dimer (diamagnetic) equilibria known to exist for some $MCl_4(PR_3)_2$ species.[3] Our work in that area has shown that the solution chemistry is really very complex. On several occasions we discussed the peculiar green solution–red solid phenomenon that is mentioned by the authors. We also found[4] that in the presence of excess phosphine Nb(III) forms an octahedral $NbBr_3(PMe_2Ph)_3$ complex, and the same can be reasonably expected for tantalum.

The reformulation of the compound as a six-coordinate Ta(IV) complex does not rule out its ability to activate a C–H bond. Octahedral Ta(IV) species readily increase coordination number to seven or eight by the formation of TaX_4L_3 or $Ta_2X_8L_4$. Thus the major feature responsible for the postulated activity, namely availability of an unoccupied coordination site, is not lost even with six ligands around Ta. Clearly, however, more evidence is required to clarify this and other phenomena connected with this compound.

In conclusion, both the results presented in the paper itself and earlier studies[2-4] on related species strongly favor the $TaCl_2Br_2L_2$ alternative over the proposed unusual $TaBr_3L_2$ one.

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Registry No. $TaBr_3(PMe_2Ph)_2$, 99211-55-9; $TaCl_2Br_2(PMe_2P)_2$, 101566-49-8.

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Hexaaza Macrocyclic Complexes of the Lanthanides

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The complexes of the lanthanide(III) ions with unidentate as well as bidentate chelating ligands are known to be extremely labile, their complexation and ligand-exchange equilibria being usually attained almost instantaneously.[1] Thus even very stable complexes of bidentate chelating ligands—e.g. tris(acetylacetonato)lanthanum(III) with $\beta_3 = 14.5$[2] or tris(2-pyridinecarboxylato)lanthanum(III) with $\beta_3 = 10.0$[3] —exist in aqueous solution as a mixture of species, of which the uncomplexed (hydrated) metal ion is an appreciable component. Lanthanide complexes of fused polychelated noncyclic ligands still give relatively fast reactions, but those of cyclic ligands may display considerable inertness: with ethylenediaminetetraacetate (β = 14–18 depending on metal radius[4]) metal exchange is complete within a fraction of a second;[5] complexation of Eu(III) with the tetracarboxylate derived from cyclam ($DOTA^{4-}$, $\beta = 28$) is instead very slow.[6]

The time frame of metal-exchange and ligand-exchange kinetics becomes a major consideration when lanthanide complexes are to be used as probes for biological systems. In the dilute aqueous or aqueous–organic solutions required for these systems, which often involve potentially competing ligands, even a highly stable complex, if labile, may not give reliable results. For this reason, the report by Hart and co-workers[7] that La(III) and Ce(III) are capable of forming macrocyclic complexes of the type $[M(C_{22}H_{26}N_6)]^{3+}$ and that these do not undergo metal exchange in solution appeared to be exceptionally interesting. Although these authors reported failure to extend the macrocyclic synthesis to the other members of the lanthanide series, we felt that the unique inertness of such compounds—if indeed they could be obtained—would open new possibilities in the field of lanthanide chemistry and thus warranted further study. We therefore set out to systematically investigate the conditions leading to the metal-templated macrocyclic synthesis and have now successfully obtained, by an appropriate combination of counterions and experimental conditions, two series of complexes of the macrocyclic ligand $L = C_{22}H_{26}N_6$, with every lanthanide(III) ion except radioactive Pm. We describe here their synthesis, characterization, and properties. As our work was nearly completed, a parallel study of lanthanide macrocycles was reported by Fenton and co-workers;[8] their systems differ from ours in having peripheral H atoms instead of $-CH_3$ groups and include cycles with $-CH_2CH(CH_3)-$ and $-(CH_2)_3-$ side chains.

Experimental Section

Template Synthesis of the $LnL(OH)(ClO_4)_2 \cdot mH_2O$ Complexes (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Ho, Er, Yb; m = 0–2). A mixture of lanthanide perchlorate (1.0 mmol in 20 mL of methanol, stored for several days over Linde 4A molecular sieves), 2,6-diacetylpyridine (2.0 mmol in 20 mL of methanol), and 1,2-diaminoethane (2.0 mmol, 5.0 mL

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of a methanol solution containing ca. 0.10 M Cl^-) was refluxed for 6 h. The solution gradually changed from yellow to pale amber, and a cream-colored solid separated on the walls of the flask. The solid product was filtered, washed with cold methanol, and dried at 80 °C in an oven. Yields ranged from 20 to 40%, depending on the metal. No pure products were obtained for Tm and Dy, because their deliquescent perchlorate salts, obtained as solutions from the commercial source, discolored upon drying in vacuo over Drierite. Owing to the recently reported explosive behavior of anhydrous lanthanide perchlorates[9] in the presence of organic substances, further attempts to purify and dehydrate these salts were discontinued.

The compounds of this series were obtained as cream-colored crystalline powders, except for the Ce(III) complex, which was rose red. The derivatives of La, Pr, Nd, Sm, and Er gave correct analyses (C, H, N) for the anhydrous species, and those of Gd and Tb gave analyses corresponding to the dihydrates; the Eu complex was obtained as the monohydrate. Representative values are given for the Eu complex. Anal. Calcd for $Eu(C_{22}H_{26}N_6)(OH)(ClO_4)_2{\cdot}H_2O$: C, 34.78; H, 3.82; N, 11.06; Cl, 4.70. Found: C, 34.97; H, 3.76; N, 11.07; Cl, 4.23. The analyses of the Ho and Yb complexes showed the presence of hydroxo impurities, also confirmed by the presence of broad absorption in the 3500–3200-cm^{-1} region of the infrared spectrum.

The complexes were moderately soluble in dimethyl sulfoxide and slightly soluble in hot water; they were practically insoluble in all other common solvents. The solids were thermally stable and did not appear to be explosive; however, small samples did flare up when heated on an open flame.

Template Synthesis of $LnL(CH_3COO)_2Cl{\cdot}nH_2O$ (Ln = La–Lu, except Pm; n = 3–6). These complexes were prepared similarly to the hydroxide–perchlorate analogues, with a lanthanide(III) acetate used as the metal ion source. The reaction mixture, after being refluxed for 4–6 h, had a pale yellow color; no precipitate formed even after cooling. Evaporation of the solvent under reduced pressure gave a pale yellow oily residue that solidified upon workup with several 10-mL portions of diethyl ether. The solid was dissolved in a minimum volume of chloroform and filtered over cotton; dilution with diethyl ether gave a crystalline product (needles), which was filtered, washed with ether, and dried at 70 °C for several hours. Yields ranged from 70 to 85%. All compounds gave correct analyses. Anal. Calcd for $Eu(C_{22}H_{26}N_6)(CH_3COO)_2Cl{\cdot}4H_2O$: C, 41.51; H, 5.32; N, 11.17; H_2O, 9.57. Found: C, 41.46; H, 5.50; N, 10.88; H_2O, 9.5 (by mass loss at 100 °C).

The number of water molecules present in other compounds of this series was found to vary between three and six, depending on the metal and the ambient conditions.

The complexes were extremely soluble in methanol, ethanol, acetone, chloroform, dichloromethane, and dimethyl sulfoxide. They were moderately soluble in hot benzene and water and insoluble in petroleum ether or diethyl ether.

Template Synthesis of $[La(NO_3)_3L]$. This compound was prepared according to the method of Hart.[7]

Attempted Synthesis of $[LaL](ClO_4)_3{\cdot}2H_2O$. Attempts to obtain a compound of this formula by the method reported in ref 10 consistently failed, the only product isolated being $LaL(OH)(ClO_4)_2{\cdot}mH_2O$ (m = 0–2).

Physical Measurements. Infrared absorption spectra (4000–200 cm^{-1}) were recorded with use of hexachlorobutadiene and Nujol mulls.

Visible–ultraviolet absorption spectra (700–250 nm) were taken in 1.0 × 10^{-4} M solutions, with use of water as solvent for the hydroxo-perchlorate complexes and both water and chloroform for the acetate–chloride salts.

Magnetic susceptibilities for selected hydroxo–perchlorate complexes were measured at 293 K with a Faraday-Cahn millibalance, using $Hg[Co(NCS)_4]$ as the calibration standard. The calculated values of μ_{eff} (μ_B) were as follows: Ce, 2.3; Pr, 3.3; Nd, 3.2; Sm, 1.7; Gd, 7.2; Dy, 10.3; Er, 9.5.

NMR spectra were measured with a JEOL FX90Q Fourier transform spectrometer, at 44.8 kHz for ^1H and 32.8 kHz for ^{13}C; the samples were dissolved in dimethyl sulfoxide-d_6 or $CDCl_3$ with tetramethylsilane as the internal reference.

Thermograms were obtained with a Perkin-Elmer TGS2 thermogravimetric system, under a He flow of 60 mL/min.

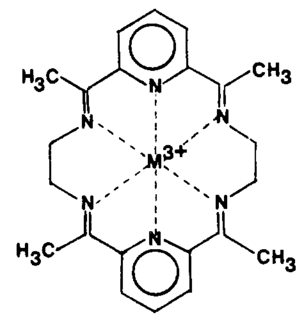

Figure 1. Schematic formula of the macrocyclic complexes considered in this work.

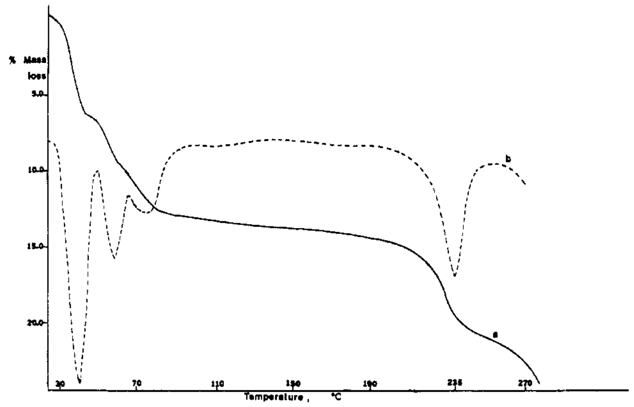

Figure 2. Thermogravimetric behavior of $GdL(CH_3COO)_2Cl{\cdot}6H_2O$: (a) percentage mass loss vs. temperature; (b) first derivative.

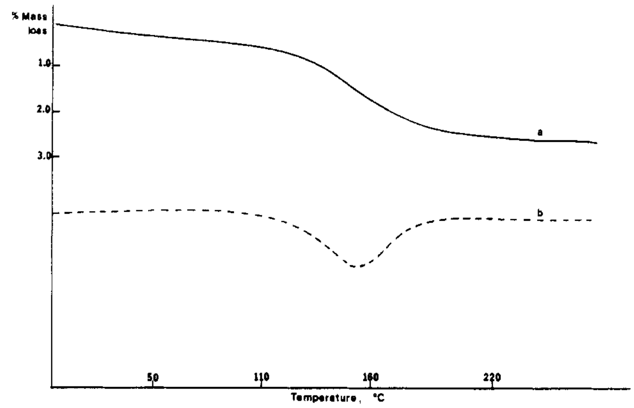

Figure 3. Thermogravimetric behavior of $EuL(OH)(ClO_4)_2{\cdot}H_2O$: (a) percentage mass loss vs. temperatue; (b) first derivative.

Results and Discussion

Formulas and Thermal Behavior. The Schiff-base condensation of 1,2-diaminoethane and 2,6-diacetylpyridine, in the presence of a lanthanide acetate, produced with excellent yields crystalline complexes of the general formula $LnL(CH_3COO)_2Cl{\cdot}nH_2O$, where L was the macrocyclic ligand $C_{22}H_{26}N_6$ and n varied between 3 and 6 depending on the metal and the ambient conditions. The cyclic condensation also took place in the presence of lanthanide perchlorates, but the yields were lower and the products, of formula $LnL(OH)(ClO_4)_2{\cdot}mH_2O$ (m = 0–2), were occasionally contaminated by hydroxo impurities.

All complexes of the acetate–chloride series had the same thermal behavior, illustrated in Figure 2 for the Gd(III) complex: At room temperature the crystalline phase in equilibrium with the atmosphere fell just before, or on the sloping section of, the first dehydration step, which was usually complete at 45–50 °C. Two overlapping steps were then observed, centered at ca. 60 and ca. 80 °C, respectively, and corresponding to the cumulative loss of three molecules of water. The resulting anhydrous products, stil white and crystalline in appearance, immediately rehydrated upon exposure to the atmosphere, returning exactly to their original masses. This lower temperature dehydration–rehydration sequence could be repeated several times with reproducible results. At higher temperature, 220–240 °C, a mass decrease of 8.0% was observed, corresponding to the irreversible loss of one acetate group

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(calculated 7.8%); after this step the sample appeared to be amorphous and slightly charred but still not melted.

For the hydrated hydroxo–perchlorate complexes, e.g. EuL(OH)$(ClO_4)_2$·H_2O, the water loss occurred gradually between 120 and 200 °C (Figure 3) and was again instantly reversible upon exposure to the atmosphere. No further decomposition was observed up to 230 °C.

Infrared Spectra. Within each series of complexes, the infrared spectra were virtually identical for all metal ions; both series showed the typical patterns of the $C_{22}H_{26}N_6$ macrocycle, with its two characteristic strong ν(C=N) absorptions at 1645–1650 and 1585–1595 cm^{-1}.[8] In addition, the acetate–chloride complexes showed the typical major absorptions of the carboxylate group: The antisymmetric COO$^-$ stretching appeared as a strong broad absorption centered at 1540 cm^{-1}, with shoulders at 1550 and 1530 cm^{-1}. The symmetric ν(COO) appeared as a pair of strong bands at 1445 and 1430 cm^{-1}, with shoulders (arising from the deformation modes of the CH_3 groups of the acetate) at 1443 and 1460 cm^{-1}. The δ(OCO) mode appeared as a medium band at 670 cm^{-1}. The spectra also showed a strong absorption in the ν(OH) region, with peaks at 3470, 3400, and 3300 cm^{-1}; a medium, broad absorption centered at 650 cm^{-1} was assigned to the rocking mode of water. The most satisfactory interpretation of these data was achieved by considering the complexes to contain both ionic acetate (ν_a(COO) at 1550 cm^{-1} ν_s(COO) = 1430 cm^{-1}, and $\Delta\nu$ = 120 cm^{-1}) and bidentate chelating acetate (ν_a(COO) = 1540 cm^{-1}, ν_s(COO) = 1455 cm^{-1}, and $\Delta\nu$ = 85 cm^{-1}), in good agreement with values reported in the literature.[11,12] The spectra also suggested the presence of both weakly coordinated and lattice water, in agreement with the observed thermogravimetric behavior. A likely formula for the acetate–chloride complexes is therefore $[LnL(CH_3COO)(H_2O)](CH_3COO)Cl\cdot nH_2O$, in which the central lanthanide ion achieves the often observed nine-coordination.

In the spectra of the hydroxide–perchlorate complexes, the OH$^-$ group gave rise to a strong, very sharp ν(OH) absorption at ca. 3600 cm^{-u}, together with a strong absorption at ca. 440 cm^{-1} and a weak one at ca. 350 cm^{-1}. These lower energy bands appeared to be somewhat sensitive to the size of the metal ion, as their frequency shifted slightly to higher frequencies in passing from La (418 and 348 cm^{-1}) to Lu (445 and 365 cm^{-1}). The assignment of these bands to the δ(MOH) and ν(MOH) vibrations, respectively, was consistent with the values reported in the literature[12] for metal-coordinated hydroxide; also, a sharp ν(OH) absorption at 3560 cm^{-1} has been observed for non-hydrogen-bonded OH$^-$ coordinated to samarium(III).[8b] Two perchlorate absorptions were observed—one centered at 1100 cm^{-1} and the other at 620 cm^{-1}; both showed considerable splitting and the higher energy band actually had three well-resolved maxima at 1045, 1100, and 1120 cm^{-1}. A similar triple splitting of the antisymmetric ν(Cl–O) has been observed for Ni(II)–ethylenediamine complexes containing bidentate chelating ClO_4^-;[13] this mode of coordination may therefore be considered to exist also in the LnL(OH)$(ClO_4)_2$·mH_2O species. However, the greater intensity of the 1100-cm^{-1} peak, compared to the side peaks at 1120 and 1045 cm^{-1}, suggested the coexistence of ionic perchlorate. A likely formulation for the complexes of this series is therefore $[LnL(OH)(ClO_4)]ClO_4\cdot mH_2O$ (m = 0–2), with the central lanthanide again attaining nine-coordination.

Nuclear Magnetic Resonance Spectra and Ultraviolet Absorption Spectra. The NMR spectra of the La(III) acetate–chloride complex in dimethyl sulfoxide-d_6 gave the following chemical shifts. ^{13}C (32.8 kHz, relative to Me_4Si): δ 182.6 (COO$^-$ of acetate), 169.0 (C=N of Schiff base), 154.4 (α-C of pyridine), 141.3 (δ-C), 126.4 (β-C), 23.8 (CH_3 of acetate), 16.1 (CH_3 of macrocycle). For ^{1}H (44.8 kHz): δ 8.34 (apparent singlet, 6 H, pyridine H), 3.97 (8 H), CH_2), 3.43 (H_2O), 2.5 (12 H, CH_3 of macrocycle), 1.50 (3 H, CH_3 of acetate). Similar spectra were obtained in $CDCl_3$, except that in this solvent the three aromatic protons gave rise to a complex spectrum (8.40–8.05 ppm) typical of symmetrical 2,6-disubstituted pyridines. Almost identical ^{13}C and ^{1}H spectra were obtained for the Lu(III) acetate–chloride complex and, limited to the ^{1}H macrocycle resonances, also for the La–hydroxo–perchlorate species. (The low solubility of this latter complex did not permit the measurement of its ^{13}C spectrum.) In both Me_2SO-d_6 and $CDCl_3$, the proton spectra of both the La(III) and Lu(III) species remained unchanged over a period of weeks.

The ultraviolet absorption spectra of all members of the two complex series were measured over a period of several days in both water and chloroform solutions (1.0 × 10^{-4} M, 25 °C). The spectra were virtually identical for all complexes in both solvents and consisted of a fairly symmterical band (λ_{max} = 300 nm; ϵ_{max} = ca. 9 × 10^3) with a barely detectable shoulder at 315 nm; no appreciable change with time was observed for any of the complexes.

Conclusions

Our results show that the considerable contraction in ionic radius that occurs along the 4f^n series does not appreciably affect the ability of the lanthanide(III) ions to act as templating agents for the formation of the 18-atom macrocycle L. This conclusion contrasts with an earlier report[7] but is consistent with recent results on the lanthanide complexes of a related macrocycle.[8] Indeed, the ease as well as the yield of the metal-templated macrocyclic synthesis appear to depend more on the counterion present than on the metal ion; good O-donor anionic ligands, such as the acetate, favor the reaction much more effectively than do chloride and perchlorate. Once the cationic macrocylic complex is formed, an appropriate combination of coordinating and noncoordinating counterions—e.g. hydroxide with perchlorate or acetate with chloride—facilitates its isolation in crystalline form.

These lanthanide macrocylic complexes are remarkable for two features. In the crystalline state they readily undergo reversible thermal dehydration and even anion loss through hydrolysis, but the macrocyclic moiety is stable up to 240 °C—an exceptionally high temperature for lanthanide-bound N-donor organic ligands. In solution, the macrocyclic moiety remains unaltered even in the presence of excellent oxygen-donor solvents such as water and dimethyl sulfoxide. This inertness is confirmed by the observation that typical precipitating reagents of the lanthanide ions, e.g. F$^-$, OH$^-$, or $C_2O_4^{2-}$, fail to remove the metal ion from the macrocyclic system. Because of this unique inertness and because of their solubility in both water and organic solvents, the complexes of the paramagnetic lanthanides, and in particular those of Pr, Eu, and Yb, should prove to be useful and versatile NMR shift reagents.

All evidence points out that the complexes of each formula type—hydroxide–perchlorates or acetate–chlorides—constitute a closely isostructural series despite minor variations in lattice water content. This close similarity is maintained in solution since the NMR spectra show that all six N-donor atoms of the macrocyclic cavity remain coordinated to the metal ion not only for La(III) but also for the smaller Lu(III) ion. This close similarity along the 14 members of each complex series is somewhat unexpected, since both the stoichiometry and the coordination number of lanthanide complexes of the same ligand usually exhibit at least one marked discontinuity at some intermediate point along the series. Further work will be required to establish whether the structural similarity indicated for these complexes by the infrared and NMR data does indeed extend to the three-dimensional geometry of the macrocyclic entity, thus providing a common rationalization for the observed inertness.

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Registry No. $[LaL(OH)(ClO_4)]ClO_4$, 100205-82-1; $[CeL(OH)(ClO_4)]ClO_4$, 100205-84-3; $[PrL(OH)(ClO_4)]ClO_4$, 100205-86-5; $[NdL(OH)(ClO_4)]ClO_4$, 100205-88-7; $[SmL(OH)(ClO_4)]ClO_4$, 100205-90-1; $[EuL(OH)(ClO_4)]ClO_4\cdot H_2O$, 100205-93-4; $[GdL(OH)(ClO_4)]ClO_4$,

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100205-95-6; [TbL(OH)(ClO$_4$)]ClO$_4$, 100205-97-8; [HoL(OH)(ClO$_4$)]ClO$_4$, 100205-99-0; [ErL(OH)(ClO$_4$)]ClO$_4$, 100206-01-7; [YbL(OH)(ClO$_4$)]ClO$_4$, 100206-03-9; [LaL(CH$_3$COO)(H$_2$O)](CH$_3$COO)Cl·nH$_2$O, 100228-62-4; [CeL(CH$_3$COO)(H$_2$O)](CH$_3$COO)Cl·nH$_2$O, 100206-06-2; [PrL(CH$_3$COO)(H$_2$O)](CH$_3$COO)Cl·nH$_2$O, 100206-09-5; [NdL(CH$_3$COO)(H$_2$O)](CH$_3$COO)Cl·nH$_2$O, 100206-12-0; [SmL(CH$_3$COO)(H$_2$O)](CH$_3$COO)Cl·nH$_2$O, 100206-15-3; [EuL(CH$_3$COO)(H$_2$O)](CH$_3$COO)Cl·nH$_2$O, 100206-18-6; [GdL(CH$_3$COO)(H$_2$O)](CH$_3$COO)Cl·6H$_2$O, 100206-21-1; [TbL(CH$_3$COO)(H$_2$O)](CH$_3$COO)Cl·nH$_2$O, 100206-24-4; [DyL(CH$_3$COO)(H$_2$O)](CH$_3$COO)Cl·nH$_2$O, 100206-27-7; [HoL(CH$_3$COO)(H$_2$O)](CH$_3$COO)Cl·nH$_2$O, 100206-30-2; [ErL(CH$_3$COO)(H$_2$O)](CH$_3$COO)Cl·nH$_2$O, 100206-33-5; [TmL(CH$_3$COO)(H$_2$O)](CH$_3$COO)Cl·nH$_2$O, 100206-36-8; [YbL(CH$_3$COO)(H$_2$O)](CH$_3$COO)Cl·nH$_2$O, 100206-39-1; [LnL(CH$_3$COO)(H$_2$O)](CH$_3$COO)Cl·nH$_2$O, 100206-42-6; 2,6-diacetylpyridine, 1129-30-2; 1,2-diaminoethane, 107-15-3.

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Emission from [Ru(bpy)$_3$]$^{3+}$ in Solids and the Question of Delocalization

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The much studied[1] emitting states of [Ru(bpy)$_3$]$^{2+}$ (I) are now generally assigned, in solution at least, to a ^{3}(MLCT) manifold, with the promoted electron localized on one ligand only,[2] as in the formulation [Ru^{III}(bpy$^-$)(bpy^0)$_2$]$^{2+}$ proposed[3] by us from analogy with the partly reduced species, and closely similar treatments have been applied to the [Ru^{II}(bpy)] chromophore in a range of [Ru^{II}(bpy)] and [Ru^{II}(bpy)$_2$] complexes.[4] However, the situation in condensed phases and at low temperatures may be more complicated.[5]

Recently, Yersin et al. reported the results of elegant experiments on the polarized emission spectra of crystals containing I.[6] We must, however, question any inference that their data provide evidence regarding the degree of delocalization of I in the solid. On the contrary, as we shall show, their experiment is systematically silent on this point, although in principle variants of it could perhaps give more definite information.

Yersin's experiment distinguished between emission polarized along the molecular z axis and that lying in the molecular (xy) plane. The results were interpreted in terms of a D_3' structure for I and in these terms gave a valid distinction between E′ and A$_2'$ levels, with the former giving emission perpendicular, and the latter emission parallel, to the molecular z axis. However, an interpretation in terms of a localized excited state would be equally valid. What is required is a test for *differences* between x- and y-polarized emission intensities when excitation is along, e.g., the molecular x axis, and both these intensities are *combined* in Yersin's experiment. An excited-state distortion, lowering the symmetry to C_2', would split the E′ emission into A′ and B′ components; but unfortunately Yersin's experiment does not give the separate intensities of these components. Thus the central question—whether the x- and y-polarized emissions are concentrated *within* the xy plane along the direction of the electric vector of the exciting light—remains unanswered.

In principle, it may be possible to test for localization in the crystalline phase by irradiating along the z axis with light polarized along the molecular x axis. If the excited state produced is truly of D_3 symmetry, then x and y emissions will be of equal intensity and the 180° scattering will be unpolarized. But if, as our model maintains, I is to be regarded at low exciting energy as three separate, noncommunicating linear parallel absorber–emitters at 120° to each other, then simple geometric considerations show[7] that the ideal intensity ratio $I(\|):I(\perp)$ is 3:1; curiously, this is independent of where the incident light polarization is chosen within the xy plane.[7] It would, of course, be necessary for the exciting light to be of sufficiently long wavelength to provoke the well-known[8] polarization anomaly of I in disordered phases, to which the predicted effect is in our model[2h] directly related. It would also be necessary to avoid loss of polarization through *intermolecular* energy transfer, a goal that might be obtainable with sufficiently dilute crystals. Elementary summation shows, fortunately, that for some structures at least the consequences of inter- and intramolecular energy transfer need not be identical.[9]

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(7) Let the oscillating electric vector of the light lie at angle ϕ to chromophore 1. Then the probability of absorption by chromophore 1 followed by emission is of the form $K\Phi \cos^2 \phi$, and the probability of absorption by chromophore 1 followed by parallel emission is of the form $K\Phi \cos^4 \phi$. Summing over all three chromophores, we have total emission probability of the form $K\Phi[\cos^2 \phi + \cos^2 (\phi + \pi/3) + \cos^2 (\phi + 2\pi/3)]$ and parallel emission probability of the form $K\Phi[\cos^4 \phi + \cos^4 (\phi + \pi/3) + \cos^4 (\phi + 2\pi/3)]$. These expressions reduce to $3K\Phi/2$ and $9K\Phi/8$, respectively, independent of ϕ.

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