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Energy transfer luminescence of Eu(III) complexes

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Eu(III) is characterized by their long lived (millisecond) strongly luminescent electronically excited states, which makes them appealing for analytical purpose. Luminescent complexes of Eu(III) may be useful in medicine as luminescent probes.Eu(III) complexes are able to transfer the energy absorbed by the organic ligand to the lanthanide cation which shows a characteristics luminescence with narrow bands in the green and red spectral range.To exploit this luminescence, the lanthanide ions must be co-ordinated to a suitable multidentate ligand in order to (a)populate the lanthanide emitting level taking advantage of a large ligand absorption cross section, followed by ligand to metal energy transfer, because the lanthanide f-f excited states are not readily accessible by direct excitation;(b) protect the ion co-ordination sphere from solvent interaction, which can deactivate its excited state via non-radiative processes.

It is clearly demonstrated in the literature that a relatively modest change in the ligand structure can give dramatic variations in the luminescence properties of corresponding lanthanide complexes, which in turn suggests that the search for ligands which exactly optimize the useful properties of lanthanide complexes is still a challenging task. We have prepared the Eu complexes with hydrotris(pyrazolyl)borate by using different bridging ligands. Reaction of EuCl₃ with one equivalent of the potassium salt of the tridentate ligand hydrotris(pyrazol-1-yl)borate [K(tp)] and two equivalents of sodium p-X-benzoate (X = H, Cl, Br and NO₂) yielded the complexes of composition [{(tp)Eu(μ -p-X-OBz)₂}]. Synthesized complexes were characterized by belemental analysis, infra-red spectroscopy and ESI mass spectroscopy. Luminescent studies indicate that a deactivation process is competing with energy transfer from the ligand centered level to the Eu centered level.

Key words :Luminescence, MRI agent, Supramolecular complexes

INTRODUCTION

The development of luminescent chemical probes and sensors is the subject of intensive research, both in natural and medicalsciences[1]. The importance of the luminescence of lanthanide ions is related to its peculiar characteristics, e.g. long lifetime and line–like emission bands, which make these ions unique among the species that are known for luminescence. Under favorable conditions, many of the lanthanide (III) ions are able to exhibit long-lived

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luminescence following excitation into higher electronic states. The concept here is that the ligand should incorporate a chromophore (sometimes referred to as an antenna [2]) which absorbs light strongly at a suitable wavelength and transfers its excitation energy to the metal which, in accepting this energy, becomes excited to the emissive state. If the antenna has a high absorption coefficient and the energy transfer process is efficient, then the effective molar absorption coefficient of the metal is highly increased and intense luminescence may result following excitation by conventional light sources. Only for Gd(III), Eu(III) and Tb(III) the lifetimes remain in excess of 0.1 ms in aqueous solution. Most research has focused on the later two since the emission of Gd(III) occurs at an inconvenient wavelength in the UV (312nm) whereas the other two ions emit in the visible range. Even for these ions, however, the deactivation effect of water molecules leads to a reduction in the intensity of emission. Thus, in the design of luminescent lanthanide complexes, a second function of the ligand becomes apparent, namely to shield the metal as efficiently as possible from the solvent water molecules. The problem is the stability of the complex with respect to metal ion dissociation. Since the applications in mind are concerned with the detection of molecules at low concentration, it is clearly essential that metal dissociation is negligible at high dilation, otherwise quantitative measurements will not be possible. In other words, suitable complexes should display very low dissociation constants (high association constants) in water over an appropriate pH range and also offer high kinetic stability. The most luminescent complexes of the lanthanide ions are those formed with certain β -diketone ligands [3]. However, the majority of these neither have sufficient water solubility nor stability for use in aqueous solution.

Probes based on Eu(III) and Tb(III) ions are of special interest because of the particularly suitable spectroscopic properties of these ions [4]. Moreover, it has been realized that trivalent lanthanide ions may be incorporated in supramolecular complexes acting as molecular photonic devices [5,6]. In some of these devices, which work on the nanometric scale, the various steps of the overall process involving absorption of light, transfer and emission at another wavelength are performed separately by distinct parts of the complex [7]. Such supramolecular constructions are termed light-conversion molecular devices. To design a good lanthanide luminescent sensor, a unique combination of features must be realized: (i) protection of the included ion from quenching due to interaction with solvent molecules and/or high-energy vibrations from the ligating groups (ii) presence of multiple absorbing groups suitable for energy transfer (antenna effect) [8] and (iii) high thermodynamic stability and kinetic inertness. Typical examples are lanthanide cryptates based on bipyridylunits or containing N-oxide groups [8,9].

Some lanthanide ions possess strongly emissive and long lived excited states but do not exhibit intense absorption [10,11,12]. Therefore, considerable effort is devoted to the design of lanthanide complexes where light is absorbed by the ligands and the electronic energy is then transferred to the emitting metal ion (antenna effect) [13, 14, 2, 15]. The design of ligands to control the coordination number and coordination geometry of metal ions is one of the most

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fascinating and challenging activities in chemical research. The challenge is the greater for felements since the large size of the ions and the predominantly ionic and hence nondirectional bonding normally result in complexes with high coordination number and variable coordination geometry. A popular approach to impose a low coordination environment is the use of sterically demanding ligands. In this sense the hydrotris(pyrazol-1-yl)-borates (Tp^{R,R'}, where R and R' are substituents at the 3- and 5-positions of the pyrazolyl ring), discovered by Trofimenko [16, 17, 18], offer a unique set of tripodal ligands which by virtue of the wide range of available substituents, allow fine tuning of the steric size of the ligands.

Many types of lanthanide carboxylates have also been reported [19]. The carboxylates show interesting polymeric network and chain structures, few of them fluoresce and only one example of hydrotris(pyrazolyl)borate with yttrium and acetate is available in literature [19a] prior to present work where four benzoate groups are acting as bridging ligands. Also the azido anion serves as a versatile bridging ligand which can coordinate to metal ions giving several kinds of complexes in either end-to-end (EE) or end-on (EO) fashion [20]. The above literature revealed that a relatively modest change in the ligand structure can give dramatic variations in the luminescence properties of the corresponding lanthanide complexes, which in turn suggests that the search for ligands which exactly optimize the useful properties of lanthanide complexes is still a challenging task. There is therefore considerable interest in the development of new lanthanide complexes with suitable photophysical properties for their application.

EXPERIMENTAL

Materials and methods

- All solvents used were purified and predried from appropriate drying agent bypublished methods [20].
- The benzoic acid and p-X-benzoic acid (X = -F, -Cl, -Br or -NO₂) were commercially available and their sodium salts were prepared by reacting with the appropriate amount of sodium hydroxide in water.
- EuCl₃ of highest grade were purchased from Indian Rare Earths Ltd., India.
- The potassium salt of ligand hydrotris(pyrazol-yl)borate [K{HB(pz)₃}] was prepared by published procedures [21].

Physical measurements:

- Carbon, hydrogen and nitrogen were analysed with a Vario EL III elemental analyzer.
- Infrared spectra (400-4000 cm⁻¹) of solid samples were recorded on a Perkin-Elmer model 1600 FT-IR spectrometer as KBr disks.
- Electron Spray Ionisation mass spectra (ESI-MS) in the positive ion mode were recorded on a Hewlett- Packard HP 5989 mass spectrometer.

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Preparation and characterization of complexes

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- [(HB(pz)₃)Eu(μ-OBz)₄Eu(HB(pz)₃)]: A mixture of sodium benzoate (0.288 g, 2.0 mmol) and KHB(pz)₃ (0.504 g, 2.0 mmol) in 20 ml of methanol was added to the methanolic solution of EuCl₃.6H₂O (0.364 g, 1.0 mmol). The suspension was stirred at room temperature for 3-4 hrs.. After removal of solvent under vacuum the resulting solid was extracted three times with CH₂Cl₂ and the solution was filtered to eliminate the salt. The filtrate was dried under vacuum to afford colourless powder solid in 80.0% yield (0.4850 g, 0.40 mmol). Anal.calcd.for C₄₆H₄₀N₁₂B₂O₈Eu₂: C, 45.49; H,3.32; N,13.84. Found: C, 45.90; H,3.50; N,13.97. IR(KBr, cm⁻¹): 2444(vBH), 1605(v_{as}COO), 1505(v_sCOO). MS(ESI⁺, CH₂Cl₂):m/z 1099 (21%) [(tp)₂Eu₂(O₂CPh)₃]⁺, 722(4.2%) [(tp)₂Eu(O₂CPh) + Na]⁺, 579(100.0%) [(tp)₂Eu]⁺.
- [(HB(pz)₃)Eu(μ-p-F-OBz)₄Eu(HB(pz)₃)]: This complex was prepared in 81.0% yield (0.518 g, 0.40 mmol) as outlined above for 1. Anal.calcd.for C₄₆H₄₀N₁₂F₄B₂O₈Eu₂: C, 42.94; H,2.82; N,13.06. Found: C, 43.01; H,2.97; N,13.53. IR(KBr, cm⁻¹): 2453(vBH), 1610(v_{as}COO), 1507(v_sCOO). MS(ESI⁺, CH₂Cl₂):m/z 1187 (1%) [(tp)₂Eu₂(p-F-O₂CPh)₃]⁺, 741(15%) [(tp)₂Eu(p-F-O₂CPh) + Na]⁺, 579(100.0%) [(tp)₂Eu]⁺.
- [(HB(pz)₃)Eu(μ-p-Cl-OBz)₄Eu(HB(pz)₃)]: This complex was prepared in 80.0% yield (0.539 g, 0.40 mmol) as outlined above for 1. Anal.calcd.for C₄₆H₄₀N₁₂Cl₄B₂O₈Eu₂: C, 40.85; H,2.68; N,12.42. Found: C, 40.41; H,2.89; N,12.57. IR(KBr, cm⁻¹): 2444(vBH), 1605(v_{as}COO), 1511(v_sCOO). MS(ESI⁺, CH₂Cl₂):m/z 1203 (1.9%) [(tp)₂Eu₂(p-Cl-O₂CPh)₃]⁺, 757(11.0%) [(tp)₂Eu(p-Cl-O₂CPh) + Na]⁺, 579(100.0%) [(tp)₂Eu]⁺.
- [(HB(pz)₃)Eu(μ-p-Br-OBz)₄Eu(HB(pz)₃)]: This complex was prepared in 85.0% yield (0.648 g, 0.42 mmol) as outlined above for 1. Anal.calcd.for C₄₆H₄₀N₁₂Br₄B₂O₈Eu₂: C, 36.11; H,2.37; N,10.98. Found: C, 37.09; H,2.48; N,11.09. IR(KBr, cm⁻¹): 2444(vBH), 1601(v_{as}COO), 1505(v_sCOO). MS(ESI⁺, CH₂Cl₂):m/z 1336 (1.2%) [(tp)₂Eu₂(p-Br-O₂CPh)₃]⁺, 777(5%) [(tp)₂Eu(p-Br-O₂CPh) + Na]⁺, 579(100.0%) [(tp)₂Eu]^{+.}
- [(HB(pz)₃)Eu(μ-p-NO₂-OBz)₄Eu(HB(pz)₃)]: This complex was prepared in 84.0% yield (0.587 g, 0.42 mmol) as outlined above for 1. Anal.calcd.for C₄₆H₃₆N₁₆B₂O₁₆Eu₂: C, 39.62; H,2.60; N,16.07. Found: C, 40.09; H,2.75; N,16.46. IR(KBr, cm⁻¹): 2455(vBH), 1620(v_{as}COO), 1515(v_sCOO). MS(ESI⁺, CH₂Cl₂):m/z 1329 (3.8%) [(tp)₂Eu₂(p-NO₂-O₂CPh)₃]⁺, 741(15%) [(tp)₂Eu(p-NO₂-O₂CPh) + Na]⁺, 579(100.0%) [(tp)₂Eu]⁺.

RESULTS AND DISCUSSION

The synthesis of the complexes 1-5, were carried out by the stoichiometric combination of EuCl₃ and the appropriate ligand salts in methanol, i.e. EuCl₃(1.0 mmol), [K(tp)] (2.0 mmol) and sodium benzoates/sodium-p-X-benzoate (2.0 mmol).Reaction of tp as its potassium salt with Eu(III)chloride in presence of sodium benzoates/sodium-p-X-

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benzoate resulted in complex of the form $[{(tp)Eu(\mu-p-X-OBz)_2}_2]$.In this case one tp ligand is coordinated to single metal centre, which accounts for seven coordination sites.The remaining sites are occupied by four carboxylate group.All complexes were characterised by ESI mass spectroscopy, elemental analysis and infrared spectroscopy.

- Infrared spectra: IR studies indicate that bands present in the complexes, but not in the free ligand, in the range of 1611-1600 and 1505-1500 cm⁻¹ assigned to asymmetric (v_{as}) and symmetric (v_s) stretching vibrations of the carboxyl group, respectively. The IR spectra are very similar across the series and show only one B-H stretching vibration.Comparison of the IR spectra for benzoate and p-X-benzoate with each other revealed that in all these complexes the carboxyl groups are coordinated in the same fashion, i.e. in bidentate fashion.
- Emission properties: The emission spectrum of the Eu complex 1 in dichloromethane at room temperature exhibit specific maxima at *ca*. 490,545,590 and 620 nm; the peak width at 545 nm is *ca* 300 cm⁻¹ and the intensity ratio is *ca*. 0.5:1.0:1.0:0.5 respectively. The spectral range are due to the ${}^{5}D_{5} \rightarrow 7Fj$ transitions[4-6]. In cyclohexane, acetonitrile or ethanol the maxima intensity ratios are similar. The quantum yield for emission was estimated to be $\Phi_{em} = 0.10$ for 1 in dichloromethane.
- The life time of the first order emission decay of the Eu complexes is typically τ_{em} = 1.2-1.3 ms. Variation of the bridging ligands in dichloromethane or variation of the solvent causes only a small change.

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