Studies on Fluorescent Lanthanide Complexes. New Complexes of Lanthanides(III) with Coumarinic-3-carboxylic Acid

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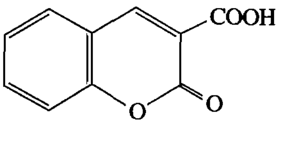
Abstract

The complexes of the types $Ln(cca)_2X \cdot n$solvent and $Ln(cca)X_2 \cdot n$solvent [where Ln = Sm, Eu, Gd, Tb, Dy; cca = coumarinic-3-carboxylate; X = Cl^-, ClO_4^-, NO_3^-] were synthesized by reaction of coumarinic-3-carboxylic acid and the appropriate lanthanide salt in various stoichiometric ratios. The new complexes were characterized by their elemental and thermogravimetric analysis, conductivities, IR and electronic spectral data; their luminescence properties were studied.

Introduction

Lanthanide ion fluorescence is a subject of increasing interest in bioinorganic and coordination chemistry [1]. Recently we described the synthesis and the characterization of new fluorescent terbium(III) complexes derived from 4-oxo-4H-benzopyran-3-carboxyaldehyde, bpa, and from the novel ligand di(3-chromonyl)methanol, dcm, both containing the structure of γ-pyrone [2].

In order to investigate whether ligands derived from α-pyrone would also be effective in yielding ionic luminescence, we prepared several lanthanide(III) complexes derived from coumarinic-3-carboxylic acid, Hcca, and studied their luminescence properties.



Hcca

Experimental

Physico-chemical Measurements

IR spectra were recorded with a 1130 Perkin-Elmer spectrophotometer, as nujol mulls or KBr pellets. Electronic absorption spectra were obtained with a Varian Cary spectrophotometer; the solid state spectra were obtained by pasting the samples with nujol and spreading them on strips of filter paper. TGA measurements were performed by means of the DuPont 1090 System, under a dry N_2 flow of 4 l/h. Conductometric measurements were carried out at 25 ± 0.1 °C, on $6 \times 10^{-5} - 1 \times 10^{-4}$ M solutions, in dry MeOH, by using a Radiometer CDM 80 conductometer, equipped with a Radiometer CDC 104 conductivity cell. Emission and excitation spectra were recorded with an Aminco-Bauman MPF spectrophotofluorimeter.

Synthesis of the Complexes

Coumarinic-3-carboxylic acid was obtained from Aldrich Chemie. The lanthanide salts were prepared as previously described [3].

All the complexes were obtained with the following general procedure. Hcca (1 mmol) and the appropriate amount of lanthanide salt were boiled for 2 h in n-BuOH (40 cm^3); the obtained products were filtered out, washed successively with H_2O, MeOH and ethyl ether and dried for 3 h at room temperature. The analytical data and the molar conductivities are reported in Table 1.

Thermogravimetric Analysis

The stoichiometry of the complexes was confirmed by TGA. In the case of $Tb(cca)Cl_2 \cdot \frac{1}{2}$n-BuOH and $Dy(cca)Cl_2 \cdot \frac{1}{2}$n-BuOH a weight loss of 7.4% occurred between 80 and 220 °C (calc. for $\frac{1}{2}$n-BuOH, 7.5%). In the case of $Sm(cca)Cl_2 \cdot 2H_2O$, $Eu(cca)Cl_2 \cdot 2H_2O$ and $Gd(cca)Cl_2 \cdot 2H_2O$ we observed weight losses of 8.6, 7.5 and 7.3% respectively, between 60 and 165 °C (calc. for $2H_2O$: 8.1, 8.0 and 7.9% respectively); in every case the total weight loss was the sum of two distinct processes of about equal amplitude, indicating that the two water molecules are not equivalent. For $Sm(cca)_2Cl \cdot 2H_2O$, $Eu(cca)_2Cl \cdot 2H_2O$ and $Gd(cca)_2Cl \cdot 2H_2O$ the weight losses between 60 and 130 °C were 6.1, 5.7 and 5.8% respectively (calc. for $2H_2O$: 6.1, 6.0 and 5.9% respectively); although each process consists of more than one step it is impossible to evidence each sub-

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TABLE 1. Elemental Analyses and Conductometric Data

Complex	Found (calc.) (%)				Λ_M[a]
	C	H	N	Ln	
$Sm(cca)_2Cl\cdot 2H_2O$	40.12 (40.03)	2.20 (2.35)		25.00 (25.06)	88
$Eu(cca)_2Cl\cdot 2H_2O$	40.05 (39.92)	2.04 (2.35)		25.00 (25.25)	90
$Gd(cca)_2Cl\cdot 2H_2O$	39.35 (39.57)	2.40 (2.32)		25.73 (25.90)	90
$Tb(cca)_2Cl\cdot H_2O$	40.48 (40.67)	2.17 (2.05)		26.71 (26.91)	88
$Dy(cca)_2Cl\cdot H_2O$	40.31 (40.42)	2.25 (2.04)		27.58 (27.35)	91
$Tb(cca)_2NO_3\cdot H_2O$	38.96 (38.92)	2.09 (1.96)	2.20 (2.27)	25.61 (25.75)	101
$Tb(cca)_2ClO_4$	37.68 (37.73)	2.02 (1.58)		24.00 (24.96)	114
$Sm(cca)Cl_2\cdot 2H_2O$	26.81 (26.90)	2.15 (2.03)		33.84 (33.69)	100
$Eu(cca)Cl_2\cdot 2H_2O$	27.04 (26.81)	2.14 (2.02)		33.67 (33.92)	98
$Gd(cca)Cl_2\cdot 2H_2O$	27.06 (26.49)	2.08 (2.00)		34.51 (34.69)	96
$Tb(cca)Cl_2\cdot \frac{1}{2}(nBuOH)$	32.09 (31.60)	2.40 (2.21)		34.70 (34.85)	100
$Dy(cca)Cl_2\cdot \frac{1}{2}(nBuOH)$	30.98 (31.36)	2.40 (2.19		35.80 (35.36)	101

[a] Ohm^{-1} cm^2 M^{-1}, in methanol.

process. $Tb(cca)_2Cl\cdot H_2O$, $Tb(cca)_2\cdot NO_3\cdot H_2O$ and $Dy(cca)_2Cl\cdot H_2O$ suddenly decompose at about 210 °C; $Tb(cca)_2ClO_4$ collapses at 150 °C.

Results and Discussion

The composition of the obtained complexes depends on the molar ratio Hcca:Ln and on the nature of the lanthanide used. In order to obtain complexes of general formula $Ln(cca)_2X\cdot n$solvent, the molar ratio Hcca:Ln = 3:1 is sufficient for Ln = Tb, Dy, while for Ln = Sm, Eu and Gd a molar ratio as high as 10:1 is necessary. Analogously, the complexes of the type $Ln(cca)X_2\cdot n$solvent are obtained using a molar ratio Hcca: Ln = 1:1 for Ln = Tb, Dy, while for Ln = Sm, Eu and Gd a ratio = 3:1 is necessary. This might indicate that the stability of the complexes slightly increases as the atomic number of the cation increases. As far as the thermogravimetric analysis are concerned, it is possible to distinguish the hydrated complexes into two groups: the dihydrated complexes of Eu^{3+}, Sm^{3+} and Gd^{3+} lose their water below 165 °C without decomposition; the monohydrated complexes of Tb^{3+} and Dy^{3+} suddenly decompose at about 210 °C. Unfortunately the products do not give crystals suitable for X-ray molecular structure determination, therefore it is not possible to establish with certainty whether the water (or the solvent) is coordinated. However it seems reasonable to assume that the coordination number is six at least in all the complexes and thus at least one water molecule is coordinated. In the cases in which the coordination number is apparently lower than six, it is probable that the molecular structure is polymeric, with some ligand behaving as a bridge and thus increasing the coordination number. A similar feature has often been observed in lanthanide complexes [4].

The molar conductivities indicate that all the complexes behave as 1:1 electrolytes [5]. Anyway, the dissociation is more pronounced for the complexes $Ln(cca)X_2$ than for those of the type $Ln(cca)_2X$.

The IR spectra of the complexes have been examined in comparison with the spectrum of the free Hcca. For this one the attribution of the bands has been done by comparison with the spectrum of the isomeric benzopyran-3-carboxylic acid [6]. A broad band at 3350–3500 cm^{-1} is assignable to the hydroxyl stretching vibrations; two bands at 1740 and 1680 cm^{-1} can be attributed to the stretching vibrations of the carboxyl and the carbonyl group respectively; two bands at 1605 and 1565 cm^{-1} can be related to the stretching vibrations of the conjugated olefinic system. In all the complexes the ν(C=C) band at 1605 cm^{-1} remains unaltered, while that at 1565 cm^{-1} is split into two maxima at 1550 and 1570 cm^{-1}. As far as the carboxyl and the carbonyl stretching modes are concerned, the spectra can be grouped in two series: (i) in the complexes of the type $Ln(cca)X_2$ both the carboxyl and the carbonyl stretching modes undergo a shift of about 50 cm^{-1} to lower frequencies (1690 and 1630 cm^{-1} respectively); this clearly indicates a quite strong coordination of these groups to the cation; (ii) in the complexes of general formula $Ln(cca)_2X$, the ν(COO) is shifted at 1705 cm^{-1} and the ν(CO) is split into two signals at 1645 and 1665 cm^{-1}. The reasons for this splitting are not clear; in fact it can be attributed either to the solid state effect or to the presence of two non-equivalent ligands [7]. It is worthwhile to note that the shift of ν(COO) and ν(CO) to lower frequencies is more pronounced in the spectra of the complexes $Ln(cca)X_2$ than in those of the complexes $Ln(cca)_2X$. This suggests that the interaction between the coumarin-3-carboxylato ligand and the lanthanide ion is stronger in the former complexes. The IR spectrum of $Tb(cca)_2ClO_4$ shows, besides the signals discussed above, two bands typical of ionic perchlorate in T_d symmetry, *i.e.* a broad band centered at 1100 cm^{-1} and another unsplit band at 620 cm^{-1} [8]. The IR spectrum of $Tb(cca)_2NO_3\cdot H_2O$ shows four bands which can be assigned to vibrational modes of the nitrato group in C_{2v} symmetry: 1505 ($\nu 1$), 1280 ($\nu 4$), 1020 ($\nu 2$) and 810 ($\nu 6$) cm^{-1}. The magnitude of the splitting of the two bands at higher energies is 225 cm^{-1}, suggesting that the nitrato group is bidentate. The other NO_3^- vibrational modes, which should be IR active in this symmetry, are masked by other bands [8].

The electronic spectra of all the obtained complexes are similar (Fig. 1a). In solution they are slightly different from those in the solid state; this indicates a partial dissociation in solution, as already noted on the basis of the conductometric data. In the solid state they are similar to the spectrum of Hcca (Fig. 1b) which shows two intense absorption bands at 315 and 268 nm. All the spectra of the complexes show two similar bands at 320–330 and 240–250 nm, which can be easily related to the signals typical of the ligand. Moreover, in all of them, a new less intense band appears at 200–210 nm, very near to the instrumental cut-off. This band cannot be ascribed to a charge-transfer from the ligand to the metal, because this kind of electronic transition can be expected for europium and samarium compounds but not for the complexes of other lanthanide ions [9]. Moreover this band is too intense to be a charge transfer transition (see Fig. 1). In fact charge transfer bands are not expected to be intense because of the small overlap between the donor ligand orbitals and the acceptor 4f orbitals [10]. Therefore the signal at 200–210 nm is also probably a transition of the ligand, slightly shifted to higher wavelengths owing to the complexation with the metal.

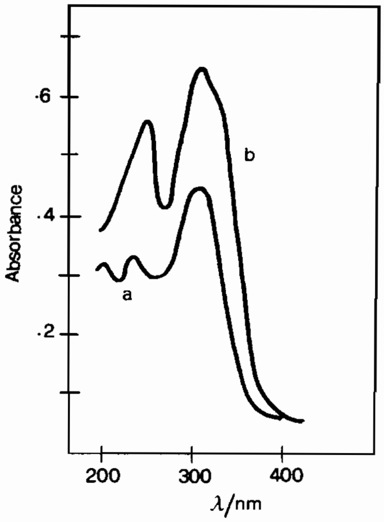

Fig. 1. Solid state absorption spectrum of (a) $Eu(cca)_2Cl\cdot 2H_2O$, (b) Hcca.

Luminescence Properties

Recently we observed that ligands derived from the chromone molecule [2] are very effective in transferring energy to luminescent lanthanides. Now we ascertain that ligands containing the coumarine ring also have this property. We recorded the emission spectra of the complexes of coumarinic-3-carboxylato with Sm^{III}, Eu^{III}, Tb^{III} and Dy^{III} which are lanthanide cations which luminese in the visible region [11]. The results are summarized in Table 2.

No significant variation in quantum yield was noted by changing the excitation wavelength in the range of 300–360 nm. The first conclusion we can reach on the basis of the data of Table 2 is that Eu^{III} complexes luminesce more than those of Sm^{III} and Tb^{III}, while Dy^{III} complexes show the fluorescence of the ligand only. The main reason for this behaviour is the selectivity in the energy transfer to the cation by the ligand. In Fig. 2 the emission spectum of free Hcca (excitation wavelength = 340 nm) at liquid nitrogen temperature in glass of epa (ether, pentane and ethanol) is shown.

It can be seen that, besides the fluorescence band at about 400 nm (also present in the spectra of the complexes), there is a band with three maxima at 475, 487 and 512 nm, assignable to the phosphorescence emission. Thus the triplet energy of Hcca is evaluable at about 465 nm (21 500 cm^{-1}). Disregarding the possibility of radiative energy transfer

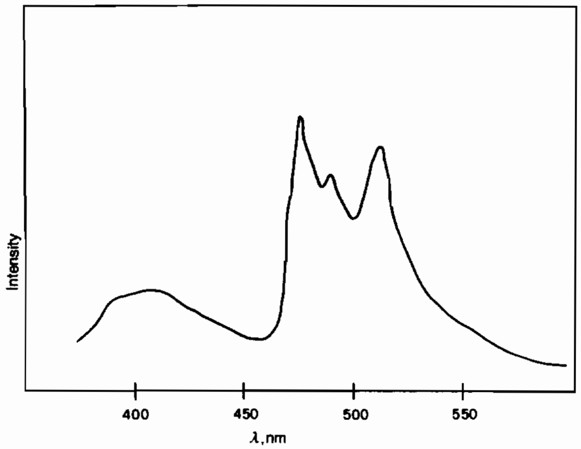

Fig. 2. Emission spectrum of Hcca in epa mixture (ether, pentane and ethanol) at liquid nitrogen temperature (λ_{ex} = 340 nm).

TABLE 2. Emission Data in Methanol Solution

Complex	Bands: assignment/quantum yield (%)					Total cation quantum yield (%)
$Sm(cca)_2Cl\cdot 2H_2O$	ligand 4.20	$^4G_{5/2}-^6H_{5/2}$ 0.03	$^4G_{5/2}-^6H_{7/2}$ 0.06	$^4G_{5/2}-^6H_{11/2}$ 0.25		0.34
$Sm(cca)Cl_2\cdot 2H_2O$	ligand 2.30	$^4G_{5/2}-^6H_{5/2}$ 0.06	$^4G_{5/2}-^6H_{7/2}$ 0.09	$^4G_{5/2}-^6H_{11/2}$ 0.37		0.52
$Eu(cca)_2Cl\cdot 2H_2O$	ligand 3.70	$^5D_0-^7F_0$ 0.15	$^5D_0-^7F_1$ 0.90	$^5D_0-^7F_2$ 1.39	$^5D_0-^7F_4$ 0.26	2.70
$Eu(cca)Cl_2\cdot 2H_2O$	ligand 1.46	$^5D_0-^7F_0$ 0.30	$^5D_0-^7F_1$ 1.92	$^5D_0-^7F_2$ 2.91	$^5D_0-^7F_4$ 0.05	5.18
$Tb(cca)_2Cl\cdot H_2O$	ligand 4.88	$^5D_4-^7F_6$ 0.26	$^5D_4-^7F_5$ 0.17	$^5D_4-^7F_4$ 0.01	$^5D_4-^7F_3$ 0.00	0.44
$Tb(cca)Cl_2\cdot\frac{1}{2}(n\text{-}BuOH)$	ligand 4.40	$^5D_4-^7F_6$ 0.36	$^5D_4-^7F_5$ 0.23	$^5D_4-^7F_4$ 0.01	$^5D_4-^7F_3$ 0.00	0.60
$Tb(cca)_2NO_3\cdot H_2O$	ligand 4.90	$^5D_4-^7F_6$ 0.17	$^5D_4-^7F_5$ 0.11	$^5D_4-^7F_4$ 0.01	$^5D_4-^7F_3$ 0.001	0.29
$Tb(cca)_2ClO_4$	ligand 4.74	$^5D_4-^7F_6$ 0.12	$^5D_4-^7F_5$ 0.07	$^5D_4-^7F_4$ 0.001	$^5D_4-^7F_3$ 0.001	0.19
$Dy(cca)_2Cl\cdot H_2O$	ligand 4.76					
$Dy(cca)Cl_2\cdot\frac{1}{2}(n\text{-}BuOH)$	ligand 4.48					

[9], this value is high enough to allow a good energy transfer from the ligand to the metal, in the cases of Eu^{III} and Sm^{III} complexes; in fact the energies of the first excited state of Eu^{3+} and Sm^{3+} are 17 277 and 17 900 cm^{-1} respectively [12]. Instead, in the cases of Tb^{III} and Dy^{III} compounds, the triplet energy of the ligand is probably too low to allow a good energy transfer; in fact the energies of the first excited state for Tb^{3+} and Dy^{3+} are 20 500 and 21 100 cm^{-1} respectively [12]. Moreover the energy gap between the lowest emitting level and the highest accepting level is 12 300 cm^{-1} for Eu^{3+} and only 7500 cm^{-1} for Sm^{3+} [12]. This implies that non-radiative decays via multiphonon-like processes are more efficient in the case of Sm^{3+} than in the case of Eu^{3+}. Consequently the higher quantum yield of europium complexes compared to that of analogous samarium ones, might depend on a different way of returning to the ground state.

The spectrophotometric study of the system $TbCl_3$/Hcca in methanol allowed us to evaluate the formation constants of the Tb^{III} complexes. These were determined by the molar ratio method and refined by successive approximations [13]. The obtained values are: $\log\beta_1 = 5.6 \pm 0.1$; $\log\beta_2 = 10.2 \pm 0.1$. From these values we determined the concentration of each species present at the equilibrium and its molar extinction coefficient at a certain wavelength. Knowing these data we then calculated the quantum yield of the species $Tb(cca)^{2+}$ and $Tb(cca)_2^{+}$. The procedure applies both to the calculation of the emission quantum yield of the cation and to the fluorescence quantum yield of the ligand in the complexes. (In order to carry out this last determination it was necessary to know the quantum yield of the ligand; by exciting it at 350 nm a value of 5.56% was obtained.) In Table 3 the quantum yields of the studied complexes are reported; all the values were obtained by using the values of β_1 and β_2 calculated for Tb^{III} complexes.

TABLE 3. Calculated Emission Data in Methanol Solution

Complex	Quantum yield of ligand fluorescence (%)	Quantum yield of cation luminescence (%)
$Sm(cca)_2Cl\cdot 2H_2O$	5.08	0.32
$Sm(cca)Cl_2\cdot 2H_2O$	0.60	0.67
$Eu(cca)_2Cl\cdot 2H_2O$	4.90	1.80
$Eu(cca)Cl_2\cdot 2H_2O$	0.50	7.36
$Tb(cca)_2Cl\cdot H_2O$	5.08	0.46
$Tb(cca)Cl_2\cdot\frac{1}{2}(n\text{-}BuOH)$	3.93	0.74
$Dy(cca)_2Cl\cdot H_2O$	4.71	0.00
$Dy(cca)Cl_2\cdot\frac{1}{2}(n\text{-}BuOH)$	4.25	0.00

We believe that this approximation is justified since the important point here is the difference between the two stability constants which could effectively be thought of as invariable over the series.

As far as the luminescence of the lanthanide cation is concerned, it is evident from Table 3 that the 1:2 complexes are less luminescent than the 1:1 complexes. The opposite trend is observed for the fluorescence of the ligand. This behaviour might be rationalized as follows. When the ligand bonded to the metal absorbs one photon it can decay either radiatively or non-radiatively, or it can transfer its energy to the metal. Each one of these steps has an intrinsic probability. If the excited ligand is close to another ligand in the ground state, it can transfer its energy to it; in this case the probability of decay processes inside the ligands increases and the efficiency of energy transfer from the ligand to the metal decreases. In fact by passing from the complexes of the type $Ln(cca)X_2$ to those of formula $Ln(cca)_2X$, we observe a decrease of the metal luminescence quantum yield and an increase of the ligand fluorescence quantum yield. Phenomena of this kind are frequently observed in solid luminescent materials and are referred to as 'concentration quenching' [9, 14]. In our case we could speak of 'coordination quenching'.

It is noteworthy that the increase of the ligand quantum yield and the decrease of the lanthanide quantum yield are much more noticeable for Eu^{III} and Sm^{III} complexes than for Tb^{III} and Dy^{III} complexes. This is a consequence of the fact that the efficiency in the energy transfer from the ligand to the metal is much higher in the former than in the latter case.

We can also note that for the solutions of the complexes $Tb(cca)_2Cl \cdot H_2O$, $Tb(cca)_2NO_3 \cdot H_2O$ and $Tb(cca)_2ClO_4$, the ionic luminescence quantum yields are significantly different. This anionic effect can be explained as follows. Methanol is a good quencher, owing to its high ν(OH) energy; the anions which form the more stable adducts with the lanthanide cation protect it better from the solvent, thus improving its luminescence [15]. The conductimetric data reported in Table 1 show that the molar conductivities increase from $Tb(cca)_2Cl \cdot H_2O$ to $Tb(cca)_2NO_3 \cdot H_2O$ to $Tb(cca)_2ClO_4$, indicating an increase in the anion freedom. For this reason the chloride complex luminesces more than the nitrato complex and this one luminesces more than the perchlorato one. However, the data supporting this explanation apparently disagree with those reported by Bünzli and coworkers [16] which indicate that in methanol nitrate binds to Ln^{3+} more strongly than chloride ions. The opposite behaviour observed by us might depend on steric effects due to the presence of cca ligands.

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