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Contribution from the Dipartimento di Chimica Generale dell'Università di Pavia,
and Dipartimento di Chimica Organica dell'Università di Pavia, Via Taramelli 12, Pavia, Italy

Fluorescent Lanthanide Complexes. 1. Reaction between Tb^{3+} and 4-Oxo-4*H*-1-benzopyran-3-carboxaldehyde in Alcoholic Medium

Carla Bisi Castellani,*,† Oliviero Carugo,† Carlo Tomba,† and Anna Invernizzi Gamba‡

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When 4-oxo-4*H*-1-benzopyran-3-carboxaldehyde (bpa) is reacted with Ln^{3+} ions in alcoholic medium, several different products are obtained, depending on the experimental conditions. At low temperature the following are formed: (i) acetals and hemiacetals in the presence of catalytic amounts of Ln^{3+} (among the acetals, 3-chromonyldimethoxymethane has been obtained as a solid); (ii) a Tb^{3+} complex of the ethyl hemiacetal (i.e. tris(3-chromonylethoxymethanol)terbium(III) perchlorate) in the presence of Tb^{3+} in a stoichiometric amount. This complex strongly fluoresces both in the solid state and in solution. When the complex is refluxed in ethanol, the highly fluorescent bis(di-3-chromonylmethanol)terbium(III) perchlorate trihydrate is obtained. The novel tridentate ligand di-3-chromonylmethanol (dcm) has been isolated and characterized by NMR, vibrational, electronic, and mass spectra and by X-ray crystal structure determination. The compound, $C_{19}H_{12}O_5$, crystallizes in the monoclinic *C*2/*c* space group with unit cell parameters a = 30.646 (2) Å, b = 6.777 (1) Å, c = 13.699 (1) Å, β = 93.816 (5)°; V = 2838.63 (3) Å^3, Z = 8, and d(calcd) = 1.50 g cm^{-3}. The structure converged to a weighted R factor of 5.1% for 2502 observations and 217 parameters. An intramolecular hydrogen bond is formed between the hydroxyl oxygen and one of the two carbonyl oxygen atoms.

Introduction

Lanthanide ion fluorescence is a subject of increasing interest in bioinorganic chemistry.[1] In fact, many biological substances, proteins, enzymes, nucleic acids, etc., act as ligands toward lanthanides, giving rise to complexes that can be conveniently studied by fluorescence techniques. It is also conceivable that fluorescent lanthanide complexes, bearing functional groups able to couple to biological substrates, can act as fluorescent stains, suitable for immunoassay procedures as well as cytological investigations. The ultimate aim of our research project is to obtain such biological stains; the first phase, reported here, involves the synthesis and the characterization of new fluorescent lanthanide complexes.

In a previous work[2] we observed that Eu^{III} and Tb^{III} complexes of 2,6-dimethyl-4-pyrone (dmp) are highly fluorescent in the solid state, indicating the effectiveness of the 4-pyrone structure in yielding the fluorescence. In order to increase the thermodynamic stability of the complexes, we have now employed 4-oxo-4*H*-1-benzopyran-3-carboxaldehyde (bpa) and have found that its ethyl hemiacetal acts as a ligand toward Tb^{3+}, giving a chelated complex that strongly fluoresces both as a solid and in solution. Moreover, the reaction between bpa and Ln^{3+} in ethanol produced a novel tridentate ligand, i.e. bis(4-oxo-4*H*-1-benzopyranyl)methanol (di-3-chromonylmethanol, dcm), which also gives strongly fluorescent complexes with Tb^{3+} ions; these have been isolated as perchlorates in the solid state. Interest in the dcm molecule, besides its chelating properties and its unusual synthesis, catalyzed by Ln^{3+} ions, derives from the possibility that either itself or its derivatives possess antianaphylactic activity, as do many other bis(chromone) compounds.[3]

Experimental Section

IR spectra were obtained with a Perkin-Elmer 1130 spectrophotometer. Electron absorption spectra were recorded with a Varian Cary 2300 spectrophotometer, NMR spectra on a Bruker WP80SY spectrometer, and mass spectra on a Finnigan-MAT 8222 spectrometer. TGA measurements were carried out by means of the Du Pont 1090 system, under a dry N_2 flow of 4 L h^{-1}.

bpa (**1**) was prepared as described in the literature.[4]

(3-Chromonyl)dimethoxymethane (3) was prepared by combining a concentrated solution of bpa in methanol (2 mmol of bpa in 10 cm^3 of the solvent) with a very small amount (0.01 mmol) of $LnCl_3 \cdot 6H_2O$ (Ln = La, Tb). The flask, equipped with a $CaCl_2$ drying tube, was kept in the refrigerator; small colorless crystals were obtained in a few days; mp 78–79 °C. Anal. Calcd for $C_{12}H_{12}O_4$: C, 65.44; H, 5.50. Found: C, 65.55; H, 5.41. ^{1}H NMR ($CDCl_3$ δ): 3.45 (6 H, –OCH_3); 5.62 (1 H, –OCHO–); 7.50 (3 H, aromatic); 8.12 (1 H, vinyl); 8.25 (1 H, aromatic).

Tris(3-chromonylethoxymethanol)terbium(III) Perchlorate (4). A 2-mmol amount of bpa in ethanol (30 cm^3) was combined with $Tb(ClO_4)_3 \cdot 6H_2O$ (bpa:Tb^{3+} in the range from 2:1 to 4:1, and the mixture was stirred until a clear solution was obtained. The flask, equipped with a $CaCl_2$ drying tube, was kept in the refrigerator. The white product, obtained in 1 or 2 weeks, was dried in vacuo at room temperature; dec pt 220 °C. Anal. Calcd for $C_{36}H_{36}Cl_3O_{24}Tb$: C, 38.67; H, 3.25; Tb, 14.22. Found: C, 39.12; H, 3.30; Tb, 14.18. Terbium was determined as reported elsewhere.[5]

Bis(di-3-chromonylmethanol)terbium(III) perchlorate trihydrate (5) was isolated by a procedure analogous to that outlined above, except that the solution was refluxed for 4 h. On slow evaporation at room temperature, a microcrystalline product was obtained. It was also obtained by pouring the terbium perchlorate and the ligand together in solution, refluxing for a few minutes, and slowly evaporating at room temperature. In this way the Sm^{III} complex (**6**) was also obtained; compounds **5** and **6** are isomorphous, as demonstrated by their X-ray powder diffraction patterns. Anal. Calcd for $C_{38}H_{30}Cl_3O_{25}Tb$ (**5**): C, 39.61; H, 2.63; Tb, 13.80. Found: C, 40.15; H, 2.87; Tb, 14.92. Weight loss for **5** between 20 and 80 °C: found, 4.70%; calcd for 3 H_2O, 4.9%. Anal. Calcd for $C_{38}H_{30}Cl_3O_{25}Sm$ (**6**): C, 39.91; H, 2.65. Found: C, 39.81; H, 2.65.

Di-3-chromonylmethanol (dcm, 7). This was initially obtained by water hydrolysis of complex **5**. It can also be directly isolated, as pale yellow platelets, by refluxing bpa in ethanol in the presence of terbium chloride instead of perchlorate and concentrating the solution; the mother liquor, containing $TbCl_3$, can be used again for a new preparation. Alternatively the concentrated ethanolic solution can be added to water; the powder so obtained can be recrystallized from acetone; mp 230 °C. Anal. Calcd for $C_{19}H_{12}O_5$: C, 71.24; H, 3.78. Found: C, 70.99; H, 3.82. Absorption spectrum (EtOH; λ_{max}, nm (ϵ, dm^3 mol^{-1} cm^{-1})): 297 (13 184), 304 (13 100). Mass spectrum: M$^+$, m/e 320. ^{1}H NMR (DMSO, δ): 5.83 (1 H, –OH, d, J = 5.0 Hz); 5.93 (1 H, –CHO, d, J = 5.0 Hz); 7.38–8.20 (8 H, aromatic); 8.37 (1 H, vinyl).

Crystallographic Study of dcm. Crystal data were recorded on a CAD4 diffractometer. Pertinent details are given in Table I. Unit cell dimensions were determined from the θ values for 23 automatically centered reflections. The space group *C*2/*c* was derived from the systematic absences and from intensity statistics. The intensities were corrected for Lorentz and polarization effects and for decay. Semiempirical absorption corrections were applied according to North, Phillips, and Mathews.[6] Only reflections with $I > 3\sigma(I)$ were considered and used in calculations; these were carried out by using the Enraf-Nonius SDP programs.[7] The structure was solved by direct (Multan) and Fourier methods. Refinements were carried out by the full-matrix least-squares technique, by minimizing the sum $\sum w(\Delta F)^2$, with $w = 1/\sigma^2(|F_0|)$.

All the hydrogen atoms were detected in the final ΔF Fourier maps; however, their isotropic thermal parameters were fixed to be 1.3 times those of the non-hydrogen bonded atoms and their coordinates used in the final structure factor calculations were adjusted analytically (C–H

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† Dipartimento di Chimica Generale.
‡ Dipartimento di Chimica Organica.

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0020-1669/88/1327-3965$01.50/0

Table I. Experimental Data for the X-ray Diffraction Studies on dcm

space group	*C*2/*c*
a, Å	30.646 (2)
b, Å	6.777 (1)
c, Å	13.699 (1)
β, deg	93.816 (5)
V, Å^3	2838.81 (3)
mol formula	$C_{19}H_{12}O_5$
mol wt	320.30
color	pale yellow
F(000)	166
Z	8
d(calcd), g cm^{-3}	1.50
radiation used for data collection	Cu Kα (graphite monochromator, λ = 1.5418 Å)
μ, cm^{-1}	9.24
specimen size, mm	0.08 × 0.15 × 0.80
range, deg	$4 \leq \theta \leq 75$
std reflns	4
scan mode	ω/θ
scan speed, deg min^{-1}	5.5
scan width, deg	1.15 + 0.142 tan θ
temp, K	290.0 (3)
reflns measd	*hkl*
range of transmission, %	82.62–98.94
agreement factor (on F_o)	0.036
max decay cor, %	2.9
no. of unique total data	5117
no. of unique refined data [$I \geq 3\sigma(I)$]	2502
no. of refined variables	217
R (referred to F_o)[a]	5.6
R_w (referred to F_o)[b]	5.1

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$.

Table II. Positional (Fractional Coordinates) and Thermal (Å^2) Parameters of Non-Hydrogen Atoms for dcm, with Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*
O(1)	0.14244 (8)	0.5005 (4)	0.7654 (2)	4.68 (5)
O(2)	0.18665 (7)	0.2498 (4)	1.0236 (1)	3.69 (4)
O(3)	0.07538 (7)	1.0510 (3)	0.9204 (2)	3.59 (4)
O(4)	0.01073 (7)	0.5272 (3)	0.8885 (2)	3.70 (5)
O(5)	0.13703 (7)	0.7995 (3)	1.0338 (2)	3.69 (4)
C(1)	0.1642 (1)	0.4218 (5)	1.0206 (2)	3.39 (6)
C(2)	0.14885 (9)	0.5122 (5)	0.9373 (2)	2.88 (5)
C(3)	0.15557 (9)	0.4235 (5)	0.8429 (2)	3.12 (6)
C(4)	0.17954 (9)	0.2363 (5)	0.8474 (2)	2.87 (5)
C(5)	0.1882 (1)	0.1318 (5)	0.7617 (2)	3.50 (6)
C(6)	0.2124 (1)	−0.0389 (6)	0.7678 (2)	4.15 (7)
C(7)	0.2291 (1)	−0.1084 (6)	0.8593 (3)	4.42 (7)
C(8)	0.2206 (1)	−0.0103 (5)	0.9433 (2)	3.96 (7)
C(9)	0.19532 (9)	0.1605 (5)	0.9367 (2)	3.10 (6)
C(10)	0.12648 (9)	0.7095 (5)	0.9394 (2)	2.94 (5)
C(11)	0.0545 (1)	0.5355 (5)	0.9102 (2)	3.26 (6)
C(12)	0.07741 (9)	0.7030 (4)	0.9194 (2)	2.74 (5)
C(13)	0.05538 (9)	0.8934 (4)	0.9083 (2)	2.74 (5)
C(14)	0.00838 (9)	0.8837 (4)	0.8816 (2)	2.73 (5)
C(15)	−0.0169 (1)	1.0519 (5)	0.8618 (2)	3.17 (6)
C(16)	−0.0609 (1)	1.0358 (5)	0.8341 (2)	3.48 (6)
C(17)	−0.0805 (1)	0.8497 (5)	0.8272 (2)	3.64 (7)
C(18)	−0.0566 (1)	0.6811 (5)	0.8467 (2)	3.53 (6)
C(19)	−0.01208 (9)	0.7005 (5)	0.8731 (2)	2.99 (5)

[a] Isotropic equivalent displacement parameters are defined as $^4/_3$-$[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

and O–H distances 1.0 Å). Final ΔF Fourier maps showed no peaks higher than 0.9 e Å^{-3}. Final positional parameters for non-hydrogen atoms and bond distances and angles appear in Tables II and III, respectively.

Results and Discussion

When bpa and Ln^{3+} ions are reacted in alcohols, several different products are obtained, depending on the experimental conditions.

Table III. Bond Distances (Å) and Bond Angles (deg) for dcm, with Their Estimated Standard Deviations

O(1)–C(3)	1.227 (4)	O(3)–C(13)	1.237 (4)
C(3)–C(4)	1.465 (4)	C(13)–C(14)	1.464 (4)
C(4)–C(5)	1.411 (4)	C(14)–C(15)	1.396 (4)
C(4)–C(9)	1.385 (1)	C(14)–C(19)	1.392 (4)
C(5)–C(6)	1.376 (5)	C(15)–C(16)	1.379 (4)
C(6)–C(7)	1.402 (5)	C(16)–C(17)	1.398 (5)
C(7)–C(8)	1.369 (6)	C(17)–C(18)	1.373 (5)
C(8)–C(9)	1.392 (5)	C(18)–C(19)	1.394 (4)
C(9)–O(2)	1.376 (4)	C(19)–O(4)	1.376 (4)
O(2)–C(1)	1.354 (5)	O(4)–C(11)	1.356 (4)
C(1)–C(2)	1.352 (5)	C(11)–C(12)	1.336 (4)
C(2)–C(10)	1.504 (4)	C(12)–C(10)	1.511 (4)
C(10)–O(5)	1.447 (3)	C(12)–C(13)	1.460 (4)
C(2)–C(3)	1.454 (4)		
O(1)–C(3)–C(2)	122.4 (3)	O(3)–C(13)–C(12)	121.9 (3)
O(1)–C(3)–C(4)	122.7 (3)	O(3)–C(13)–C(14)	122.9 (3)
C(2)–C(3)–C(4)	114.9 (2)	C(12)–C(13)–C(14)	115.3 (2)
C(3)–C(4)–C(5)	121.3 (3)	C(13)–C(14)–C(15)	122.5 (3)
C(3)–C(4)–C(9)	120.2 (3)	C(13)–C(14)–C(19)	119.4 (3)
C(9)–C(4)–C(5)	118.4 (3)	C(19)—C(14)–C(15)	118.1 (3)
C(4)–C(5)–C(6)	120.1 (3)	C(14)–C(15)–C(16)	120.6 (3)
C(5)–C(6)–C(7)	120.1 (3)	C(15)–C(16)–C(17)	119.9 (3)
C(6)–C(7)–C(8)	120.6 (3)	C(16)–C(17)–C(18)	121.1 (3)
C(7)–C(8)–C(9)	119.0 (4)	C(17)–C(18)–C(19)	118.1 (3)
C(8)–C(9)–C(4)	121.7 (3)	C(18)–C(19)–C(14)	122.2 (3)
C(8)–C(9)–O(2)	116.6 (3)	C(18)–C(19)–O(4)	115.9 (3)
C(4)–C(9)–O(2)	121.7 (3)	C(14)–C(19)–O(4)	121.9 (3)
C(9)–O(2)–C(1)	118.7 (2)	C(19)–O(4)–C(11)	118.9 (2)
O(2)–C(1)–C(2)	124.3 (3)	O(4)–C(11)–C(12)	124.1 (3)
C(1)–C(2)–C(3)	120.2 (3)	C(11)–C(12)–C(13)	120.3 (3)
C(1)–C(2)–C(10)	121.3 (3)	C(11)–C(12)–C(10)	123.5 (3)
C(3)–C(2)–C(10)	118.5 (2)	C(13)–C(12)–C(10)	116.2 (2)
C(2)–C(10)–O(5)	108.5 (2)	C(12)–C(10)–O(5)	109.6 (2)
C(2)–C(10)–C(12)	114.8 (2)		

Hemiacetals and Acetals. In methanol, at low temperature, and in the presence of catalytic amounts of Ln^{3+}, 3-chromonyldimethoxymethane (i.e. the bpa dimethyl acetal) was isolated. The compound was characterized, beside in addition to the elemental analysis, by electronic, vibrational, and NMR spectra. The corresponding diethyl acetal, i.e. 3-chromonyldiethoxyethane, could not be isolated. However, its formation in solution, in the presence of La^{3+}, has been demonstrated by NMR measurements. ^{1}H NMR (C_2D_5OD, δ): 5.75 (1 H, –OCHO–); 7.69 (3 H, aromatic); 8.30 (1 H, vinyl); 8.31 (1 H, aromatic).

The catalytic activity of lanthanide(III) ions on acetal formation has been described,[8] and the results obtained by us are in agreement with the reported information. Moreover, the present NMR study of the system bpa/ROH (R = Me, Et)/Ln^{3+} clearly shows the formation of both the hemiacetal and the acetal, indicating an unusual stability of bpa hemiacetals. In C_2D_5OD, even with a La^{3+}:bpa molar ratio as low as 1:200, the signals typical of bpa[4] are missing; instead new signals appear that may be assigned to the hemiacetal and acetal. The –OCHO– hemiacetal signal is deshielded about 0.01 ppm from that of the acetal, and as in the case of the acetal, it shows a very small coupling constant (<1 Hz) with the vinyl H.[9] If the NMR spectrum is recorded immediately after the dissolution of the sample, the ratio hemiacetal:acetal is approximately evaluable as 2:3. The hemiacetal rapidly transforms into the acetal, and when the equilibrium is reached (in about 30 min), the ratio hemiacetal:acetal becomes about 1:10. On addition of a large excess of La^{3+} the equilibrium is shifted again toward the hemiacetal. The behavior of bpa in methanol is similar, except that the stability of the methyl hemiacetal is lower than that of the ethyl hemiacetal. However, the methyl hemiacetal formation can be observed by dissolving bpa in CD_3CN or $(CD_3)_2SO$ and adding CH_3OH. The described behavior can be interpreted in terms of the simultaneous equilibria shown in Scheme I. . Two features can account for the relative

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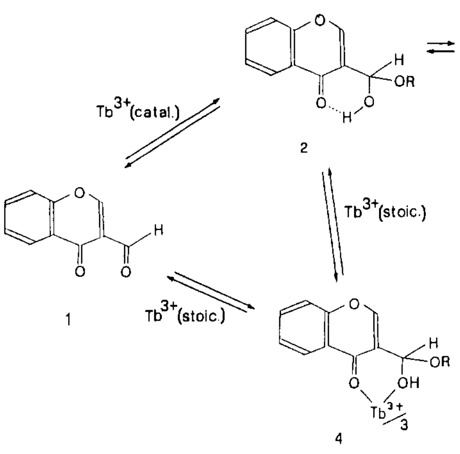
[8] Luche, J. L.; Gemal, A. L. *J. Chem. Soc., Chem. Commun.* **1978**, 976.

[9] The same features also allow identification of the hemiacetal in solvents other than C_2D_5OD.

Scheme I



stability of the hemiacetal **2**: (i) the parent carbonyl group is bonded to a strongly attracting group;[10] (ii) the hydrogen bond between the carbonyl and the hydroxyl oxygen atoms involves the formation of a new hexaatomic ring. The shift of the equilibrium toward the hemiacetal, when an excess of Ln^{3+} is added, is explained by the formation of the complex **4**. Such a complex has been actually isolated, as will be described below.

Tb^{3+} Complex of 3-Chromonylethoxymethanol (4). Concentrated solutions of bpa and $Tb(ClO_4)_3$ in ethanol, kept at low temperature, slowly produce tiny, colorless crystals that effloresce as they are removed from the mother liquor, giving a white powder. The composition of the product is consistent with the formula $Tb(bpa)(ClO_4)_3 \cdot 3EtOH$. The extreme instability of the crystals, which presumably contain a higher number of ethanol molecules, precluded, until now, x-ray crystal structure determination. However, the ligand has been identified as 3-chromonylethoxymethanol by means of NMR, vibrational, and electronic spectra. To our knowledge this is the first example of a hemiacetal stabilized by metal complex formation.

The ^1H NMR spectrum in CD_3COCD_3 is consistent with the formation of a Tb^{3+} paramagnetic complex; in fact, all the signals appear as broad singlets in the large range of chemical shifts from −20 to +60 ppm. On addition of D_2O the spectrum of the hemiacetal, above described, appears.

The IR spectra of compounds **3** and **4** have been examined in comparison with the spectrum of bpa. In the spectrum of **3** the –CHO band, located at 1700 cm^{-1} in bpa,[4] is missing. In the acetal group region (1100–1050 cm^{-1})[10b] a very strong band occurs. As far as complex **4** is concerned, we observe a broad band at 3500–3400 cm^{-1}, which may be assigned to the OH stretching vibration, the –CHO band is missing and the pyronic C=O stretching frequency is shifted to lower values (from 1645 cm^{-1} in bpa to 1620 cm^{-1} in **4**), indicating the presence of a carbonyl–Tb^{3+} coordinative bond. Similar shifts have been previously observed in the lanthanide(III) complexes of 2,6-dimethyl-4-pyrone.[2] A very strong band at 1100 cm^{-1}, typical of the uncoordinated perchlorate ion in T_d symmetry,[11] presumably hides the bands of the hemiacetal group.

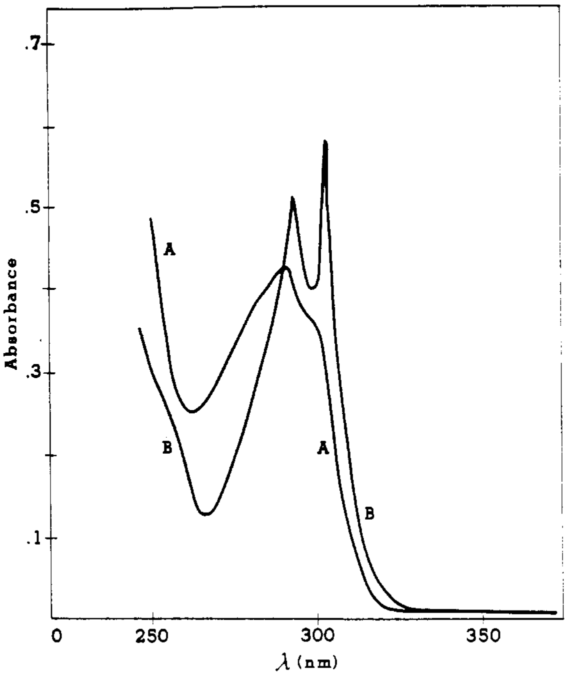


Figure 1. Absorption spectra of (A) bpa and (B) 3-chromonyldimethoxymethane in MeCN.

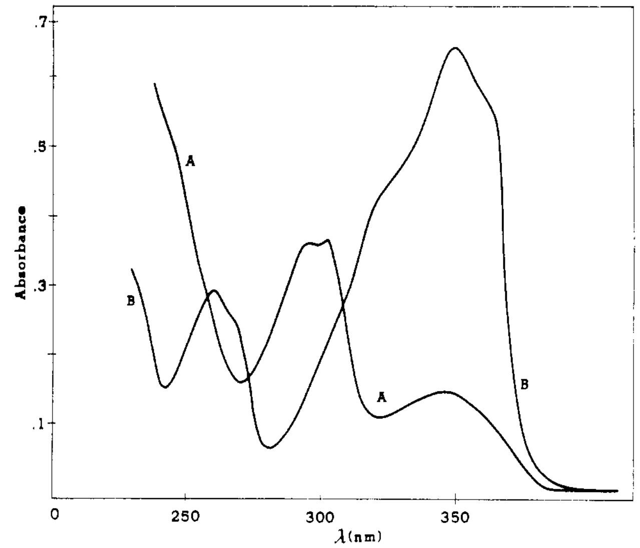


Figure 2. Absorption spectra of (A) bpa in MeOH and (B) the system bpa/Tb^{3+} in MeOH (molar ratio bpa:Tb^{3+} = 1:1).

The electronic spectra of bpa and of 3-chromonyldimethoxymethane in MeCN are reported in spectra A and B, respectively, Figure 1. Figure 2 shows the spectra of bpa in methanol, in the absence (Figure 2A) and in the presence (Figure 2B) of Tb^{3+} in a stoichiometric amount. The spectrum of bpa in methanol is very different from that recorded in MeCN (or other nonalcoholic solvents). In fact instead of one maximum at 290 nm, two maxima are found at the wavelengths typical of the acetal spectrum (295 and 310 nm). This indicates that in diluted alcoholic solution, bpa is present, at least in part, as the methyl acetal. Moreover, a new band appears at higher wavelengths (λ_{max} 340 nm) whose absorbance is not exactly reproducible. In fact the absorbance easily changes with time, with temperature, with dryness of the solvent, or in the presence of traces of acids or bases. A dramatic increase in the molar absorption at 340 nm is produced by the addition of stoichiometric amounts of Tb^{3+} (Figure 2B). The 340-nm band is also present, although with a lower intensity, in aged alcoholic solutions of the acetal; its absorbance increases with time and by addition of traces of bases. On the basis of these observations we believe that this band is due to the formation of the hemiacetal, according to Scheme I; the increase of its molar absorption on addition of increasing amounts of Tb^{3+} can easily be explained by the stabilization of the hemiacetal through chelation. It seems reasonable to suppose that the appearance of this band at relatively high wavelengths is due to a higher delocalization of the electronic density through the new chelated rings in **2** and in **4**. The complexity of the system precludes the determination of the formation constant of complex **4**. Consequently, the quantitative determination of its noticeable ionic fluorescence in solution is also not possible.

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(11) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1986.

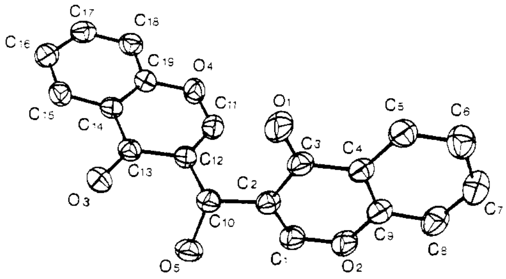

Figure 3. ORTEP view of the dcm molecule.

Although the spectra of the systems bpa/$Tb(ClO_4)_3$ and bpa/$TbCl_3$ in ethanol are quite similar, it has not been possible to isolate a complex analogous to **4**, containing Cl^- as counterion. Perhaps the higher coordinating ability of Cl^- compared to that of ClO_4^- can account for this behavior. Moreover, the ClO_4^- ion is larger and lattice effects might also be important.

Di-3-chromonylmethanol and Its Ln^{3+} Complexes. When bpa and $Tb(ClO_4)_3$ were refluxed in ethanol, the novel highly fluorescent complex bis(di-3-chromonylmethanol)terbium(III) perchlorate trihydrate, ($[Tb(dcm)_2](ClO_4)_3 \cdot 3H_2O$, **5**) and its Sm^{III} analogue **6** were isolated. the ligand (referred to as dcm, **7**) has been separated from the inorganic moiety by water hydrolysis and characterized by elemental analysis, by mass, NMR, and vibrational spectroscopy, and by an X-ray crystal structure determination.

The most characteristic features of the dcm vibrational spectrum, compared to that of bpa, are (i) the lack of the -CHO stretching mode, located at 1700 cm^{-1} in bpa and (ii) a sharp band at 3500 cm^{-1}, which can be assigned to the intramolecular by bonded OH stretching vibration[12] (a slight shift (10 cm^{-1}) of the pyrone carbonyl stretching toward lower frequencies, compared to the signal for bpa, might also be assigned to this hydrogen bond).

The crystal structure of the dcm molecule is shown in Figure 3. Each chromonyl moiety is planar, and the bond lengths and angles are in agreement with those of other chromone derivatives of known structure.[13] The two chromonyl moieties are twisted, forming a dihedral angle of 75.5°. The hydroxyl oxygen atom O(5) is bonded through the hydrogen atom H(O5) to the carbonyl oxygen O(3) of one of the two chromonyl moieties, thus forming an intramolecular hydrogen bond; the O(3)-H(O5) distance is 2.181 (2) Å, and the O(3)-H(O5)-O(5) angle is 137.0 (1)°. The carbonyl oxygen atom of the other chromonyl moiety does not form any intra- or intermolecular hydrogen bond.

The IR spectra of complexes **5** and **6** are similar to that of dcm except for the following features: (i) a very broad band at 3600-3100 cm^{-1} due to water molecules; (ii) an intense band at 1100 cm^{-1} assignable to the uncoordinated ionic perchlorate group in T_d geometry; (iii) a shift of the C=O pyronic stretching mode to lower frequencies (from 1640 to 1620 cm^{-1}), which indicates a carbonyl-Tb^{3+} coordinative bond. It is noteworthy that the Sm^{III} complex shows a smaller shift (ca. 10 cm^{-1}); this is in agreement with the decreasing stability of the Ln^{III} complexes as the atomic number decreases.

The thermogravimetric analysis shows that the three water molecules are all lost below 80 °C; this indicates that water is presumably noncoordinated. Considering that the perchlorate group is ionic, it is quite reasonalbe to suppose that dcm acts as a tridentate ligand and Ln^{III} ions in complexes **5** and **6** are hexacoordinated; although the coordination number 6 is considered low for lanthanides, some other examples have been reported;[14] moreover, in this case the bulkiness of the ligand can account for this feature. The X-ray structure determination, which would completely clarify this point, has not yet been possible due to the extremely small size of the crystals obtained so far. It is worth mentioning that when the described reaction between bpa and Tb^{3+} is carried out in the presence of Cl^- as counterion, no complexes could be isolated and only free dcm was obtained.

The spectrophotometric study of the system dcm/Tb^{3+} in ethanol in the UV-vis region was carried out with the aim of determining the formation constant and possibly the fluorescence intensity of complex **5**. However, it was impossible to obtain reproducible values for K. In fact, the spectra vary with time and, in a few days, a band at 340 nm appears, which suggests the hypothesis that Tb^{3+} catalyzes the slow decomposition of dcm to complex **4** and chromone. The mechanism of the formation of dcm from bpa in the presence of Ln^{3+} (and that of its decomposition) is at present under study. At the moment we can anticipate that such a reaction does not occur in nonalcoholic solvents; therefore, it is reasonable to suppose that the Tb^{III} complex **4** is an intermediate in the synthesis of dcm.

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Registry No. **1**, 17422-74-1; **2** (R = Me), 116785-27-4; **3** (R = Me), 116785-24-1; **3** (R = Et), 116785-26-3; **4** (R = Et), 116785-29-6; **5**, 116785-31-0; **6**, 116785-33-2; **7**, 116785-25-2; $LaCl_3$, 10099-58-8; $TbCl_3$, 10042-88-3.

Supplementary Material Available: Listings of positional and thermal parameters for hydrogen atoms (Table S1), anisotropic displacement parameters (Table S2), and selected least-squares planes (Table S3) (3 pages); a table of observed and calculated structure factors (Table S4) (17 pages). Ordering information is given on any current masthead page.

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