Monatshefte für Chemie 125, 647–653 (1994)

Monatshefte für Chemie
Chemical Monthly

Synthesis and Luminescence Studies on Lanthanoid(III) Complexes of a *Schiff* Base Derived from 2-Acetylpyridine and *tris*-(2-Aminoethyl)-amine

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Summary. A potentially heptadentated ligand (*apytren*) was obtained by condensation of 2-acetylpyridine and *tris*-(2-aminoethyl)-amine in the presence of lanthanoid(III) cations. Complexes of the formula $Ln(apytren)(NO_3)_3 \cdot H_2O$ (Ln = La, Eu, Gd, and Tb) have been isolated and characterized, both in the solid state and in solution, by means of vibrational and electronic spectroscopy and of conductometric measurements. Their photophysical properties, including emission quantum yields and lifetimes, were studied and are discussed.

Keywords. Lanthanoid(III) complexes; UV-Vis; Luminescence; *Schiff* Bases; Tripodal ligands.

Synthese und Lumineszenzuntersuchungen an Lanthanoid(III)-Komplexen mit einer aus 2-Acetylpyridin und *tris*-(2-Aminoethyl)-amin hergeleiteten *Schiff*schen Base

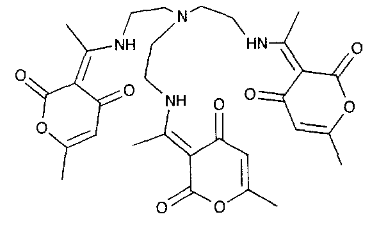
Zusammenfassung. Durch Kondensation von 2-Acetylpyridin und *tris*-(2-Aminoethyl)-amin in der Gegenwart von Lanthanoid(III)-Kationen wurde ein potentiell siebenzähniger Ligand (*apytren*) erhalten. Komplexe der Zusammensetzung $Ln(apytren)(NO_3)_3 \cdot H_2O$ (Ln = La, Eu, Gd und Tb) wurden isoliert und sowohl im festen Zustand als auch in Lösung mittels IR- und UV-Vis-Spektroskopie und Leitfähigkeitsmessungen charakterisiert. Ihre photophysikalischen Eigenschaften, einschließlich Emissionsquantenausbeute und Lebensdauer, wurden untersucht und werden diskutiert.

Introduction

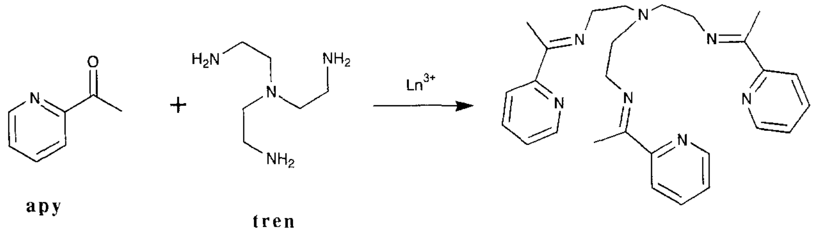
The luminescence of the lanthanoids(III) essentially depends on the 4f electrons; this gives somewhat unique features to the luminescence of the Ln^{3+} compounds, as, for example, long-lived emission or substantial independence of the emission energy on the surrounding [1]. As a consequence of its peculiarity, the luminescence of the lanthanoid(III) compounds found a wide range of applications [2–12]. In particular, the lanthanoid(III) complexes have been exploited in studying the ligands conformation [6, 10], in the analysis of the Ln^{3+} ions [11] and in fluoroimmunoassays [12]. For a Ln^{3+} complex being luminescent, it is necessary that the ligands (*i*) absorb UV radiation with high molecular extinction coefficients in ligand-centered bands and (*ii*) transfer effectively their electronic energy to the Ln^{3+} excited states.

The ligand to metal energy transfer is effective only if the ligands excited states are close in energy to those of the emitting cation.

In the last few years, we reported the sensitizer behaviour of some α- and γ-pyrone derivatives towards the lanthanoids(III) [13–18]. In particular, we studied the luminescence properties of Eu^{3+} and Tb^{3+} complexes of a potentially heptadentated ligand derived from the condensation of dehydroacetic acid and *tris*-(2-aminoethyl)-amine (*dhatren*, see Scheme 1). Since many recent studies concern with the luminescence of lanthanoids(III) complexed with ligands containing pyridine or polypyridine ligands [19–25], a comparison between the behaviour of *dhatren* and that of an analogous ligand containing the pyridine ring instead of the pyrone ring seemed advisable. For this reason, we planned the synthesis of the ligand *apytren* by condensation of 2-acetylpyridine (*apy*) and *tris*-(2-aminoethyl)-amine (*tren*) (see Scheme 2). Although the free ligand could not be isolated, its Ln^{3+} complexes were obtained and their properties studied.



dhatren



apy

tren

apytren

Experimental

Syntheses

The lanthanoid(III) nitrates were prepared by routine methods from oxides purchased from Aldrich [26]. 2-Acetylpyridine (*apy*) was purchased from Janssen, *tris*-(2-aminoethyl)-amine (*tren*) from Aldrich.

Ln(*apytren*)$(NO_3)_3 \cdot H_2O$ (*Ln* = La, Eu, Gd, or Tb) were obtained by adding a solution of the hydrated *Ln*$(NO_3)_3$ (1 mmol) in the minimum amount of methanol to a solution of *apy* (1 mmol) and *tren* (0.33 mmol) in 10 cm^3 of methanol. After stirring vigorously for 3 h at room temperature, the light suspension was cooled to -4 °C for 12 h and the resulting white powder was filtered off, washed with methanol and ether, and dried at 1 mm Hg for 5 h at room temperature. *Ln* = La: found: C, 40.8; H, 4.3; N, 17.7; calc. for $C_{27}H_{35}LaN_{10}O_{10}$: C, 40.6; H, 4.4; N, 17.5; m.p. 216–226 °C (dec); IR (cm^{-1}): 1630, 1620, 1585, 1565. *Ln* = Eu: found: C, 40.1; H, 4.4; N, 17.5; calc. for $C_{27}H_{35}EuN_{10}O_{10}$: C, 40.0; H, 4.3; N, 17.3; m.p. 225–232 °C (dec); IR (cm^{-1}): 1630, 1620, 1585, 1565. *Ln* = Gd: found: C, 39.6;

H, 4.3; N, 17.2; calc. for $C_{27}H_{35}GdN_{10}O_{10}$: C, 39.7; H, 4.3; N, 17.1; m.p. 225–232 °C (dec); IR (cm^{-1}): 1635, 1620, 1585, 1565. *Ln* = Tb: found: C, 39.6; H, 4.1; N, 17.2; calc. for $C_{27}H_{35}N_{10}O_{10}Tb$: C, 39.6; H, 4.3; N, 17.1; m.p. 226–237 °C (dec); IR (cm^{-1}): 1636, 1620, 1590, 1565.

Physicochemical measurements

IR spectra were recorded as nujol mulls with a 1130 Perkin-Elmer spectrophotometer. 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. Excitation and emission electronic spectra were obtained with a LS50 Perkin-Elmer spectrophotofluorimeter; the excitation spectra were automatically corrected and the emission ones were corrected according to ref. [27]; the emission quantum yields were determined as the average of three independent measurements by using quinine sulphate solutions in 0.1 *N* H_2SO_4 as standard (estimated error = 10%) [28]. Analytical data were obtained from the Dipartimento di Chimica Organica dell'Università di Pavia. The solvents used in the spectrophotometric studies were of the best grade and obtained from Carlo Erba.

Results and Discussion

The complexes of *apytren* with Ln^{3+} (*Ln* = La, Eu, Gd and Tb) were obtained as monohydrated nitrates, *Ln*(*apytren*)$(NO_3)_3 \cdot H_2O$, by template condensation of *apy* and *tren* in the presence of the appropriate lanthanoid(III) nitrate. Although it has been impossible to grow single crystals suitable for X-ray diffraction studies, some reasonable hypotheses can be made about their structure. It is in effect reasonable to suppose that the Ln^{3+} cation is coordinated at least by six donor atoms of *apytren*, the three pyridine and the three ketoimine nitrogen atoms, since such arrangement has often been found in complexes containing *Schiff* bases derived from *tren* [29–31], or in other related tripodal polydentated ligands [32]. The coordination of the tertiary amino nitrogen to the cation is very doubtful, since this has been seldom observed [31, 32]. The chelation of the Ln^{3+} cation by the three α-diimine moieties of *apytren* is also supported by the analogy between the vibrational spectra of the complexes *Ln*(*apytren*)$(NO_3)_3 \cdot H_2O$ and those of the Ln^{3+} complexes with 1,2-*bis*-(pyridine-α-aldimino)-ethane (a ligand structurally similar to *apytren*) [33, 34], whose crystal structure actually shows such a chelation [35]. In fact the IR spectra of *Ln*(*apytren*)$(NO_3)_3 \cdot H_2O$ (*Ln* = La, Eu, Gd, and Tb), which are nearly superimposable, exhibit – in addition to a broad band at 3400 cm^{-1} (ν_{OH}) – four strong signals at 1630–1635 ($\nu_{C=N\,\text{side chain}}$), 1620, 1585–1590, and 1565 (ν_{pyridine}) cm^{-1} whose frequencies are close to those of the analogous bands at 1650, 1610, 1593 and 1570 cm^{-1} present in the IR spectra of the Ln^{3+} complexes with 1,2-*bis*-(pyridine-α-aldimine)-ethane. The first coordination sphere of the Ln^{3+} ion in *Ln*(*apytren*) $(NO_3)_3 \cdot H_2O$ is probably completed by the nitrato anions and/or by the water molecule. With regard to this, the vibrational spectra are not very helpful, since in the diagnostic region for the study of the symmetry of the NO_3^- anion, and thus of its type of coordination [36, 37], many bands are present which prevent any sound conclusion. However, just this crowding of bands could actually suggests that the three NO_3^- anions are not equivalent in complexing the metal.

The *Ln*(*apytren*)$(NO_3)_3 \cdot H_2O$ complexes are very insoluble in the most common solvents, with the exception of *DMSO* and *DMF*. In *DMF* solution they decompose at least partially, as it is shown by the differences between the electronic absorption spectra in the solid state and in solution (see Figs. 1 and 2). All the complexes show nearly superimposable spectra (under the same experimental conditions), but the intense ligand-centered band at lowest energy is shifted from 282 nm in the solid state to 268 nm in *DMF* solution. This might be due to the loss of one or more NO_3^- anions in solution which in the solid state are coordinated to Ln^{3+}. In fact the ionic conductivities in *DMF* of all the complexes (140, 142, 137 and 131 $\Omega^{-1}\,cm^2\,mol^{-1}$ for La, Eu, Gd, and Tb, respectively) fall in the accepted range for 1:2 electrolytes (130–170 $\Omega^{-1}\,cm^{-1}\,mol^{-1}$) [38]. The rupture of possible coordinative bonds between Ln^{3+} and NO_3^- in *DMF* diluted solution can be expected since nitrato is known to be quite a weak ligand towards lanthanoids(III) even in methanol [39], whose solvating power towards Ln^{3+} is much smaller than that of *DMF* [40, 41]. A loss of NO_3^- from the first coordination sphere in *DMF* solution could also be indicated by the low symmetry of the metal center in the Eu^{3+} complex, suggested by the electronic emission spectrum of that complex, which present the $^5D_0$–^7F_j emissions at 580.0 ($j = 0$), 590.0, 593.5 and 595.5 (shoulder) ($j = 1$) and 613.6, 614.5 (shoulder), 617.0, 619.0 and 622 ($j = 2$) nm. This band multiplicity is consistent with a non-centrosymmetric metal center of quite low symmetry [6]; the C_s point group could be the most consistent approximation and could reasonably arise from the loss of an initial higher symmetry imposed by the apytren ligand (which is a tripodal pseudo C_{3v}).

As far as the luminescence properties of the *apytren* complexes are concerned, a comparison with the corresponding *dhatren* complexes is possible only from a qualitative point of view, due to the instability of both kind of complexes in solution. In the case of *dhatren*, the problem was overcome by designing a procedure – different from the conventional methods – which allows the quantum yields deter-

Fig. 1. Electronic absorption spectrum of La(*apytren*)$(NO_3)_3 \cdot H_2O$ in *DMF* solution

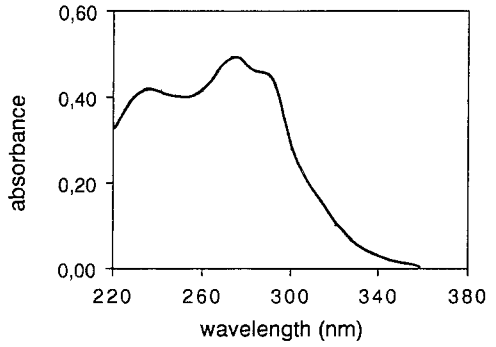


Fig. 2. Electronic absorption spectrum of La(*apytren*)$(NO_3)_3 \cdot H_2O$ in the solid state

minations once the formation constants for the complexes are known [18]. Such a procedure cannot be applied in the case of the *apytren* complexes, since a sample of the free ligand would be necessary in order to determine the complexation constants. Unfortunately, it has been impossible to obtain the free *apytren* ligand, either by direct interaction of *apy* and *tren* (in methanol, benzene, *iso*-propanol, *n*-butanol and chloroform; at room temperature or refluxing) or by demetallating the *Ln*(*apytren*)$(NO_3)_3 \cdot H_2O$ complexes (numerous insoluble compounds – fluorides, sulphates, hydroxides – can be separated from the complexes, but the *apytren* ligand decomposes).

By exciting *DMF* solutions of the Eu^{3+} or Tb^{3+} complexes with *apytren* in the ligand-centered bands, the well known structured emission of Eu^{3+} or Tb^{3+} is observed. In both cases the nephelauxetic ratio parameter $\bar{\beta}$ (0.997 for Tb^{3+} and 0.991 for Eu^{3+}) indicates a very small participation of the 4f orbitals in bonding [42]. Both the Eu^{3+} and the Tb^{3+} emission quantum yields are quite low (0.017% and 0.009% respectively at a concentration of $2 \times 10^{-4} M$; at concentration of $2 \times 10^{-5} M$ the quantum yields are reduced to 0.009% for Eu^{3+} and to 0.004% for Tb^{3+}); their emission lifetimes are 0.78 ± 0.06 and 1.13 ± 0.03 ms respectively and are statistically independent of the complex concentration. In both the emission spectra of the Eu^{3+} and the Tb^{3+} complexes, a quite strong ligand fluorescence band is present with maximum at 378.5 nm, but with an intensity about 50% lower than that presented by the emission spectra of the La^{3+} or Gd^{3+} complexes, which has a quantum yield of about 4.10%. The phosphorescence emission spectra of the La^{3+} and Gd^{3+} complexes at 77 K in glass of ether-pentane-ethanol, which are superimposable and show a structured band with maxima at 435, 486, 509 and 548 nm (see Fig. 3), indicate that the lowest energy ligand triplet excited state is at about 27400cm^{-1}. The singlet-triplet splitting, which is about 24kJ mol^{-1}, indicates that the lowest excited state of *apytren* has a certain π^*-n character [43]. The excitation spectra of both the Eu^{3+} and the Tb^{3+} complexes fit their absorption spectra, which are superimposable.

It is not easy to rationalize these data. From one point of view, the fact that the Eu^{3+} quantum yield is significantly higher than that of Tb^{3+} could indicate that the radiationless deactivation pathways due to multiphonon-like processes [1, 44], or to a ligand-to-metal *charge-transfer* level [2, 19], which would be more effective in the case of Eu^{3+} than in that of Tb^{3+}, are not important in deactivation the cation excited states. Although this hypothesis can be supported by the fact that *DMF* has a solvating character towards Ln^{3+} greater than water [40, 41] (and therefore *DMF*

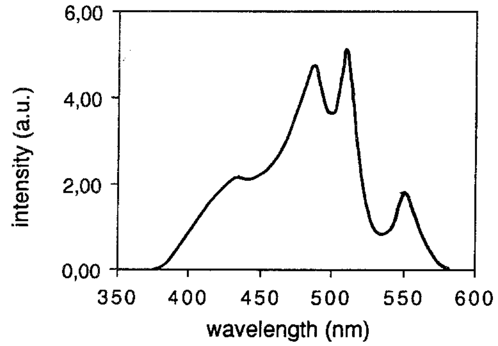


Fig. 3. Phosphorescence spectrum of La(*apytren*)$(NO_3)_3 \cdot H_2O$ at 77 K in glass of ether-pentane-ethanol

would substitute the *Ln*$^{3+}$ coordinated water, which is the major responsible of the multiphonon-like radiationless deactivations), it disagrees with the fact that the lifetime of the Tb^{3+} complex is significantly greater than that of the Eu^{3+} complex. From the other point of view, looking at the quantum yields, it would be possible that the triplet quenching of Tb^{3+} is effective, but looking at the lifetimes, the contrary would be expected. Sound points are that (*i*) owing to the similarity between the excitation spectra, the Eu^{3+} and Tb^{3+} excited states are populated by the same ligand excited states and that (*ii*) the ligand-to-metal energy transfer is not effective, since the quantum yields are quite low and a considerable ligand fluorescence is kept even after complexation. It is not clear, on the basis of our results, why a ligand triplet level as high as 27400 cm^{-1} can not populate at least the $^5D_3$ Tb^{3+} level or the $^5L_7$ Eu^{3+} level [45]. It is possible to suppose, for example, a triplet quenching of both the Tb^{3+} $^5D_3$ and Eu^{3+} $^5L_7$ levels, or a triplet quenching of the $^5D_3$ level in the case of Tb^{3+} parallel to a ligand-to-metal *charge-transfer* quenching in the case of Eu^{3+}.

Similar problems have been encountered in studying the mechanism of the ligand-to-metal energy transfer process in the case of the complexes between Eu^{3+} or Tb^{3+} and *dhatren* [18], but some important differences clearly appear between the *apytren* and the *dhatren* complexes. While the lowest energy triplet excited state of *dhatren* and *apytren* have similar energy (26650 and 27400 cm^{-1} respectively), these two ligands show an opposite sensitizer behaviour towards Eu^{3+} and Tb^{3+}. The ratio between the Tb^{3+} and Eu^{3+} emission quantum yields is 33 in the case of *dhatren* and 0.5 in that of *apytren*, and the ratio between the Tb^{3+} and Eu^{3+} lifetimes is 1.0 for *dhatren* and 1.4 for *apytren*. This implies that the overall ligand-to-metal energy transfer process and the decay pathways of the metal excited states are very different for the *dhatren* and the *apytren* complexes. Although further studies would be necessary to reach a deeper understanding of the reasons of the differences between the sensitizer behaviours of *dhatren* and *apytren*, the data obtained so far suggest that ligands derived from *dhatren* and *apytren* could find interesting applications owing to their opposite selectivity in sensitizing the Eu^{3+} and Tb^{3+} luminescence.

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Received July 6, 1993. Accepted September 20, 1993