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Synthesis, characterization and spectroscopic studies of a new europium(III) complex of 3-amino-2-carboxypyridine-*N*-oxide

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Abstract

The new ligand, 3-amino-2-carboxypyridine-*N*-oxide **4** has been synthesized as a potential precursor to highly efficient light conversion molecular devices. The synthesis, characterization and some properties of a complex of this ligand, tris(3-aminopyridine-2-carboxylato-*N*-oxide)triaqua europium(III), are described. The complex exhibits a remarkably strong luminescence and a long decay lifetime (615 μs). © 1998 Elsevier Science S.A.

Keywords: 3-Amino-2-carboxypyridine-*N*-oxide; Europium(III) complex; Light-conversion molecular device

1. Introduction

Recently, highly luminescent europium(III) complexes with mixed ligands such as β-diketones and *o*-phenanthroline-*N*-oxide [1] or 3-aminopyrazine-2-carboxylic acid with two herobiaryl ligands (2,2′-bipyridine and 1,10-phenanthroline) [2] have been synthesized and suggested as promising light-conversion molecular devices as described by Lehn [3]. In a previous communication we reported the synthesis, characterization, spectroscopic and photophysical properties of the Eu(III) complex of **1** (3-NH_2pic) : tris(3-aminopyridine-2-carboxylato)diaqua europium(III) [4]. In addition the theoretical and experimental intensities of the $^5D_0 \rightarrow {}^7F_{0,1,2,4}$ transitions of the Eu(III) in this complex have been communicated [5]. These results indicated an efficient ligand-to-metal energy transfer and pointed to this compound as a good light conversion material. However, this compound has limited utility because of its relative insolubility in water. Furthermore, any material that is to be considered in this context, must preferably be easy to synthesize. Toward this end we have chosen to focus on derivatives of pyridine-2-carboxylic acids because not only are they generally highly luminescent, but the synthesis of the appropriate europium(III) complex is more direct and simpler than the synthesis of complexes with cryptands and macrocycles [6]. Past experience suggests that the corresponding pyridine-*N*-oxide complex should have a greater aqueous solubility and, moreover, would have more efficient luminescence because of the ease of population of the lowest triplet level of the ligand [6].

In this paper we report the synthesis of a new ligand, 3-amino-2-carboxypyridine-*N*-oxide **4** (3-NH_2pic-NO) as well as the synthesis and some of the spectroscopic and photophysical properties of its complex with Eu(III), tris(3-aminopyridine-2-carboxylato-*N*-oxide)triaqua europium(III).

2. Experimental

2.1. Reagents and materials

Flash chromatography was carried out using Merck Kieselgel 60, 230–400 mesh. Commercial grade solvents and reagents were used without purification. Europium oxide (99.99% purity, Aldrich) was used to prepare europium(III) perchlorate.

2.2. Synthesis

2.2.1. 3-Amino-2-carbomethoxypyridine (2)

Conc. H_2SO_4 (15 ml, 280 mmol, 2.8 eq) was added dropwise to a suspension of 3-amino-2-carboxypyridine **1** (13.8 g, 100 mmol) in MeOH (300 ml). The resultant

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yellow solution was refluxed for 19 days, concentrated to a small volume in vacuo, cooled in ice and treated dropwise with 2 N NaOH (145 ml) to give a white ppt. The pH of the mixture was adjusted to 12–13 with NaOH before filtering. The filter cake was washed extensively with water and dried to afford a white solid (12 g, 79%), mp=156–159°C. The filtrate was concentrated to a small volume and extracted (4×) with EtOAc:THF (4:1). The combined organic phases were washed with brine, dried (Na_2SO_4), filtered and concentrated to afford more of the pure product (2.14 g, 14%). Both charges could be used directly in the next step. The aqueous phase contained unreacted carboxylate. For characterization, a small sample of the crude filtrate was dissolved in EtOAc to give a cloudy solution which was washed with sat. aq. $NaHCO_3$, water and brine. Drying (Na_2SO_4), filtration and concentration in vacuo gave a white residue which was recrystallised from i-Pr_2O/ i-PrOH to afford off-white needles, mp=156–158°C. ^1H NMR (200 MHz, $CDCl_3$): $\delta=8.06$ (1H, dd, $J=5$, <1 Hz), 7.21 (1H, dd, $J=10$, 5 Hz), 7.03 (1H, dd, $J=10$, <1 Hz), 5.75 (2H, br s), 3.97 (3H, s); IR (KBr): $\nu_{max}=3457$, 3278, 3157, 1614 cm^{-1}; MS (EI): $m/z=152$ (M^+), 122, 94, 93; $C_7H_8N_2O_2$ calc.: C 55.26, H 5.30, N 18.41, found: C 55.24, H 5.30, N 18.15.

2.2.2. 3-Amino-2-carbomethoxypyridine-N-oxide (3)

A solution of 3-amino-2-carbomethoxypyridine **2** (2.14 g, 14.08 mmol) and m-chloroperbenzoic acid (m-CPBA) (4.3 g, ~21.2 mmol, ~1.5 eq) in 1,2-dichloroethane (40 ml) was stirred at 50°C for 4.5 h and at room temperature overnight. Filtration of the precipitated m-CBA and concentration of the filtrate gave a brown solid residue. This was flash-chromatographed to afford a brown gum which was recrystallized from i-PrOH (three crops). The combined crops were treated with decolorizing charcoal in boiling MeOH/i-PrOH, filtered and left to crystallize to give 2 crops of the desired N-oxide **3** as a light brown powder (total yield: 670 mg, 28%). ^1H NMR (200 MHz, $CDCl_3$): $\delta=7.65$ (1H, d, $J=6$ Hz), 6.99 (1H, dd, $J=8$, 6 Hz), 6.63 (1H, d, $J=8$ Hz), 5.00 (2H, br s), 3.98 (3H, s); IR (KBr): $\nu_{max}=3427$, 3133, 1718, 1647, 1584, 1467 cm^{-1}; MS (FAB): $m/z=169$ (MH^+).

2.2.3. 3-Amino-2-carboxypyridine-N-oxide (4)

A solution of 3-amino-2-carbomethoxypyridine-N-oxide **3** (400 mg, 2.38 mmol) in MeOH (30 ml) and 0.1 N NaOH (26 ml, 2.6 mmol, 1.09 eq) was stirred at room temperature for 40 h. The MeOH was removed in vacuo and the residue was acidified with 2N HCl (1.3 ml). The solution was then extensively extracted with 10% THF in EtOAc and the combined organic phases were washed with brine, dried (Na_2SO_4), filtered and concentrated to give an ochre powder (330 mg) which was crystallized from hot EtOAc to give the desired N-oxide in two crops (254 mg, 69%), mp=181–182°C (dec.), (a further recrystallization improved the mp to 186–188°C (dec.)). ^1H NMR (360 MHz, d^6-DMSO): $\delta=18.7$ (1H, br s), 7.92 (1H, d, $J=6$ Hz), 7.69 (2H, br s), 7.43 (1H, dd, $J=9$, 6 Hz), 7.24 (1H, d, $J=9$ Hz); ^{13}C NMR (90 MHz, d^6-DMSO): $\delta=164.85$, 150.47, 127.39, 126.15, 121.32, 116.50; IR (KBr): $\nu_{max}=$ 3418, 3305, 1655, 1608, 1576, 1473, 1377, 1262 cm^{-1}; UV(EtOH): $\lambda_{max}=234$ nm ($\epsilon=6959$ dm^3 mol^{-1} cm^{-1}); MS (CI): $m/z=155$ (MH^+), 111.

2.2.4. Tris(3-aminopyridine-2-carboxylato)diaqua europium(III)

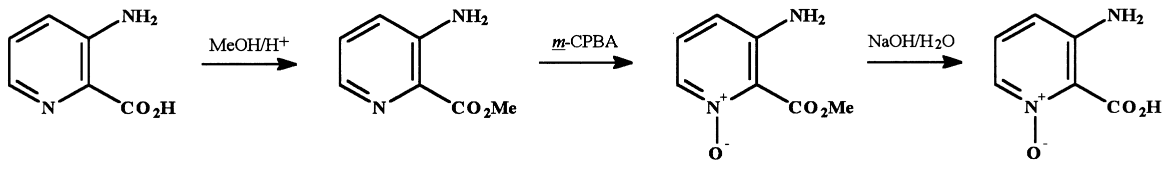
The europium complex was prepared essentially by the method of Ref. [4]. A warm ethanolic solution containing 1.0 mmol of aqueous europium(III) perchlorate (prepared by dissolving europium(III) oxide (99.99%) in perchloric acid) was added gradually, under vigorous stirring, to an ethanolic solution containing the ligand (3.2 mmol). The pH of the mixture was adjusted to 6.5 by addition of aq. NaOH. The resultant ppt was filtered, washed with ethanol, and dried in an Abderhalden apparatus at 80°C over P_2O_5 to give the complex as a brown solid (65%). The composition of the complex was established as Eu(3-NH_2pic-NO$)_3\cdot3H_2O$ by microanalysis: $C_{18}H_{21}EuN_6O_{12}$ calc.: C 32.48, H 3.15, N 12.63, found: C 32.95, H 2.72, N 12.35.

2.3. Spectral measurements

Melting points were recorded on a Büchi melting point apparatus and are corrected. NMR spectra were recorded on a Varian Gemini- (200 MHz–^1H) or Bruker (360 MHz–^1H; 90 MHz–^{13}C) instruments using residual $CDCl_3$ or d^6-DMSO protons as references. Infrared spectra were recorded on Bruker IFS 66 Fourier Transform-, UV spectra on Perkin-Elmer UV-Visible Lambda (6 model 2688-002) and MS spectra on VG TS 250 (EI), VG 70-SE (FAB) or Finnigan TSQ 70 (CI) instruments. The luminescence spectra recorded at 298 and 77 K and were obtained using a Jobin-Yvon Ramanor U1000 double monochromator with a slit width of 0.4 mm. Excitation was effected using a 150-W xenon lamp and a 0.25-m holographic grating monochromator for wavelength selection. Lifetime measurements were made at 298 K using the nitrogen laser system described previously [7].

3. Results and discussion

The 3-NH_2pic-NO bidentate ligand **4** was prepared from 3-amino-2-carboxypyridine **1** via N-oxidation of the methyl ester derivative **2** with *meta*-chloroperbenzoic acid. Saponification of the resultant N-oxide methyl ester **3** gave the desired ligand **4** as shown below.



1 **2** **3** **4**

The ligand was purified by two recrystallizations from hot ethyl acetate and dried in an Abderhalden apparatus at 80°C over P_2O_5. Although satisfactory combustion data of the new ligand (mp=186–188°C (dec.)) could not be obtained, IR and UV-Visible spectra were clearly compatible with structure **4**, whilst MS, ^{1}H and, in particular, ^{13}C NMR *indicated a single pure compound*, fully assignable to the *N*-oxide **4**.

The complex, Eu(3-NH$_2$pic-N0)$_3$·3H$_2$0 is a brown solid decomposing over the range 297–302°C and is sparingly soluble in the polar non-aqueous solvents dimethyl sulfoxide (DMSO) and dioxane, as well as being moderately soluble in water. The IR spectrum of the free ligand has two strong bands at 1655 and 1262 cm^{-1} which are assigned to the antisymmetric carbonyl stretch [8,9] and to the N–O stretch of the *N*-oxide, respectively [7]. In the complex these bands are shifted to 1636 and 1242 cm^{-1}, which is indicative of bidentate O,O chelation by 3-NH$_2$pic-NO. In the 3-NH$_2$pic-NO europium complex the position of the UV absorption maximum is at a longer wavelength (364 vs. 345 nm) and has a molar absorption coefficient some 20% larger (1959 vs. 1632 dm^3 mol^{-1} cm^{-1}) than in the 3-NH$_2$pic complex. These data are shown in Table 1. This, coupled with the increased solubility in polar solvents, including water, suggested that the *N*-oxide ligand would be a better precursor for light-conversion molecular devices, particularly those used as luminescent labels in fluoroimmunoassays [10].

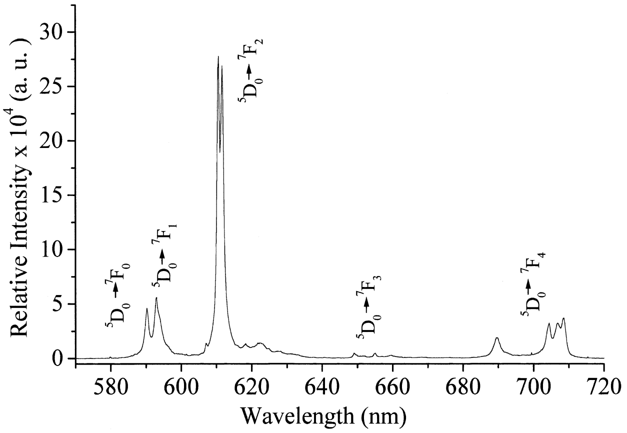


Fig. 1. Luminescence spectrum of solid Eu(3-NH$_2$pic-NO)$_3$·3H$_2$O at 77 K, upon ligand excitation (~388 nm).

The emission spectrum of solid Eu(3-NH$_2$pic-NO)$_3$·3H$_2$O at 77 K is shown in Fig. 1. In complexes of this type excitation in the absorption bands belonging primarily to the ligands, results in emission from the lowest excited state of Eu(III), $^5D_0$, to the components of the ^7F ground state. The complex is highly luminescent with the majority of the emission concentrated in the red $^5D_0 \rightarrow {}^7F_2$ transition. Theoretical calculations have in fact shown that other complexes containing *N*-oxides have ligand triplet levels which are nearly in resonance with the excited levels of the lanthanide ion and should therefore lead to increased luminescence efficiency [11]. Transitions to $^7F_1$ and $^7F_4$ are also present but are only about 20% as intense. The $^5D_0 \rightarrow {}^7F_0$ transition is observed but is very weak. Although normally the splitting of the peaks is definitive for identification purposes, for complexes such as this, which have a ion symmetry, no conclusions can be drawn with respect to the symmetry in this case.

The lifetimes of the $^5D_0$ state were obtained by monitoring the $^5D_0 \rightarrow {}^7F_2$ emission line and are given in Table 1. The value obtained for the lifetime of Eu^{3+} in the Eu(3-NH$_2$pic-NO)$_3$. 3H$_2$O complex is shorter at 298 K. This can be ascribed to a less-efficient non-radiative $^5D_0$ relaxation processes at lower temperature [12]. Furthermore, the value obtained for the lifetime at 298 K is about

Table 1
Photophysical data for Eu(3-NH$_2$pic)$_3$·2H$_2$O and Eu(3-NH$_2$pic-NO)$_3$·3H$_2$O in the solid state[a] and solution[b]

Complex	Absorption[b]		Luminescence[a]		Lifetimes[a], τ (10^6 s)	
	λ_{max} (nm^{-1})	ϵ (10^3 mol dm^3 cm^{-1})	λ_{exc} (nm)	λ_{emis} (nm)		
Eu(3-NH$_2$pic)$_3$·2H$_2$O[c]	345	1.632	340	617	652*	552**
Eu(3-NH$_2$pic-NO)$_3$·3H$_2$O	364	1.959	388	610	615*	1004**

[a] Experimental errors: ±10% on lifetimes at 298 (*) and 77 K (**).

[b] $^5D_0 \rightarrow {}^7F_2$ emission band.

[c] From Ref. [4].

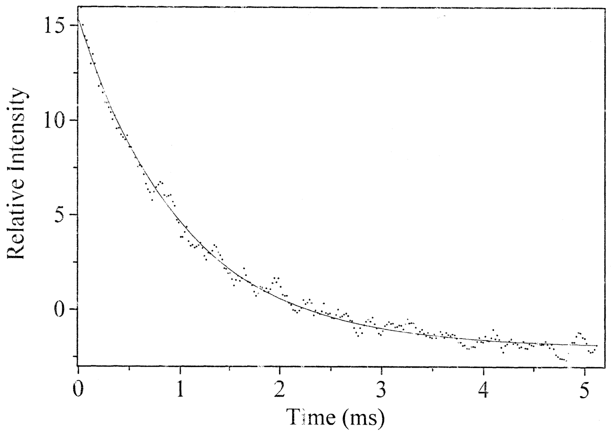


Fig. 2. Decay lifetime of the $^5D_0$ luminescence for complex Eu(3-NH_2pic-NO)$_3$·$3H_2O$ at 77 K.

50 μs shorter than that found for Eu(3-NH_2pic)$_3$·$2H_20$. This shorter value is not surprising because there is most likely an additional coordinated water molecule in the *N*-oxide complex and it is well known that luminescence from the $^5D_0$ level of Eu(III) is strongly quenched by coupling with OH vibration [13] (Fig. 2).

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