Europium(II) Complexes With Benzo-18-Crown-6[‡]

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Two compounds of Eu^{II} with benzo-18-crown-6, triaqua(benzo-18-crown-6)europium(II) diperchlorate (**1**) and triaqua(benzo-18-crown-6)europium(II) perchlorate hydrate benzo-18-crown-6 solvate (**2**), were synthesized by electrochemical reduction. The coordination environment of the metal cation in both cases contains six O atoms of the crown ligand and three water molecules. The first complex display strong blue luminescence with a maximum at 425 nm. The excitation spectra do not show any significant energy transfer from the benzo rings to europium.
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Introduction

Crown ethers have attracted much attention owing to their specific and selective coordination of metal ions. Encapsulation of the metal by the ligand provides at least partial protection from the influence of other reagents that may be present in the system. Therefore crown ethers seem to be a promising class of ligands that may stabilize otherwise unstable entities such as divalent lanthanides. Compounds of divalent lanthanides (mainly Eu^{2+}) with crown ethers have therefore attracted much attention; the present state of the investigations on such complexes was excellently reviewed by Adachi et al.[1] The interest in these compounds arises both due to the luminescent properties of the Eu^{2+} cation in the macrocyclic coordination environment and by the ability of the ligand to stabilize the divalent oxidation state of the lanthanide. The encapsulation effected by the crown ethers leads to an increase of the luminescence quantum yield in comparison with noncyclic polyethers. The other interesting feature of the discussed complexes is their ability to shift the reduction potential of the Eu^{III}/Eu^{II} couple towards more positive values,[2] which may eventually open a way to the application of these compounds or their derivatives as redox-sensitive shift agents in MRI tomography. It is therefore important and very interesting to collect information about the structures and properties of macrocyclic complexes of Eu^{II} both in solution and in the solid state. In previous work[3] we have described the structure of bis(benzo-15-crown-5)europium(II) diperchlorate. This work, which is a continuation of our investigations on the structure and spectroscopy of Eu^{II} complexes with crown ethers in the solid state, deals with two other complexes: triaqua(benzo-18-crown-6)europium(II) diperchlorate (**1**) and triaqua(benzo-18-crown-6)europium(II) perchlorate hydrate benzo-18-crown-6 solvate (**2**).

Results and Discussion

Structures

Crystals of **1** are composed of complex trisaqua(benzo-18-crown-6)europium(II) cations and perchlorate anions, and they are isomorphic with the analogous compound of Sr.[4] Crystals of **2**, apart from the same constituents as in **1**, also contain other, uncoordinated, benzo-18-crown-6 molecules and water of crystallization. The coordination environment of europium is essentially the same in both crystals and consists of three water molecules and six oxygen atoms from the macrocycle ring. The coordination figure in either case is rather irregular. The roughly equatorial positions are occupied by the crown oxygen atoms, whereas two water molecules (OW2 and OW3) are located in axial positions on one side of the equatorial plane, and the third water molecule (OW1) is located in an axial position at the opposite side. A similar coordination geometry is also typical for nine-coordinate compounds of Ln^{III} with 18-crown-6 derivatives, for example triiodo(dibenzo-18-crown-6)samarium,[5] trichloro(18-crown-6)lanthanum(III),[6] and numerous dichloro(18-crown-6)lanthanide(III) solvates (e.g. water or an alcohol)[6−10] or chloro(18-crown-6)lanthanide(III) disolvates.[6,9,11−13] The Eu−O distances, presented

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Table 1. The Eu−O distances (Å) for **1** and **2**

1		2	
Eu−OW1	2.584(3)	Eu−OW2	2.576(3)
Eu−OW2	2.592(3)	Eu−OW1	2.584(3)
Eu−OW3	2.596(3)	Eu−OW3	2.624(3)
Eu−O(4)	2.660(3)	Eu−O(3)	2.633(3)
Eu−O(2)	2.671(3)	Eu−O(2)	2.651(3)
Eu−O(3)	2.682(3)	Eu−O(5)	2.656(3)
Eu−O(6)	2.693(3)	Eu−O(6)	2.663(3)
Eu−O(5)	2.695(3)	Eu−O(4)	2.698(3)
Eu−O(1)	2.741(3)	Eu−O(1)	2.757(3)

in Table 1, are rather long in comparison with other $Eu^{II}-O$ bond lengths. Their average values are the following: $Eu-O_{crown}$ = 2.690(29) Å for **1** and 2.676(45) Å for **2**, $Eu-O_{water}$ = 2.591(7) Å for **I** and 2.595(26) Å for **2**. These quantities compare well with the relevant values for the isomorphic Sr compound: $Sr-O_{crown}$ = 2.683(22) Å, and $Sr-O_{water}$ = 2.568(14) Å.[4] On the other hand it is interesting to see the difference between the analogous Eu^{II} and Eu^{III} complexes. For chlorodiaqua(18-crown-6)europium(III) cations[6,9] the overall mean $Eu-O_{crown}$ distance is 2.536(50) Å, and the $Eu-O_{water}$ distance is 2.424(35) Å. The differences between the values for our Eu^{II} compounds and the Eu^{III} complexes quoted above are in good agreement with the difference between the ionic radii of Eu^{2+} and Eu^{3+} for nine-coordinate compounds (0.18 Å).[14] It is noteworthy that in all the discussed complexes the water molecules are closer to the metal ion than the crown oxygen atoms. The cavity in the unligated crown molecule in **2** remains empty, although OW3 and the uncoordinated OW4 water molecule approach it somewhat (OW3 forms a hydrogen bond with O42, and OW4 interacts in the same way with O43). The coordination of Eu in **1** is shown in Figure 1, and a fragment of **2** is shown in Figure 2. Both crystals are held together by hydrogen bond networks, and electrostatic and Van der Waals interactions.

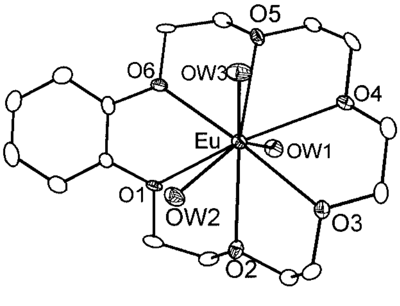

Figure 1. A view of the complex cation in **1**, together with labelling of the metal first coordination sphere

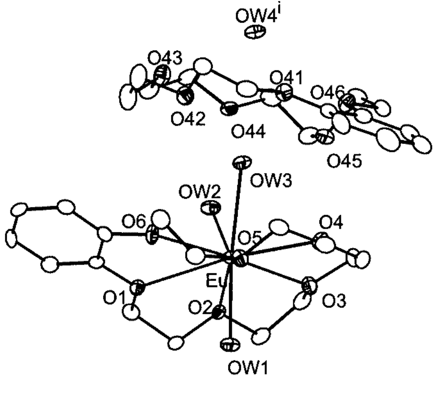

Figure 2. A view of a fragment of **2**; the labels are rendered for Eu and O atoms only for the sake of clarity; ⁱ represents the symmetry operation $-1/2 + x$, $1/2 - y$, $-1/2 + z$

Spectroscopy of 1

The compound displays bright blue luminescence with a maximum at 425 nm (23520 cm^{-1}) at room temperature, and at 430 nm (23260 cm^{-1}) at 77 K (see Figure 3). These values are similar to those reported for bis(benzo-15-crown-5)europium(II) diperchlorate[3] (422 and 426.5 nm, respectively) and remarkably different from the emission maximum observed for the complex formed from $EuCl_2$ and benzo-18-crown-6 in methanol (447 nm[1,15]). This difference may be due to several factors, such as: a) coordination of methanol instead of water, b) the possible coordination of Cl^-, and c) a different coordination number of the metal cation. The discrepancy between the present compound and the quoted complex in solution is manifested even more strikingly in the luminescence lifetimes of both systems. The luminescence lifetime of the $EuCl_2$/benzo-18-crown-6/methanol system was reported to be 0.028 μs. For the present compound the decay curves were measured at 293 and 77 K. At room temperature the decay is bi-exponential, with τ_1 = 8.34(6) μs and τ_2 = 137(11) μs; the decay equation may be expressed as: $I = I_0\cdot\{0.890(3)\exp[-t/8.34(6)] + 0.110(3)\exp[-t/137(11)]\}$ the e.s.d.'s are given in parentheses. At 77 K the decay is a single exponential with a lifetime of 8.01(2) μs. The second, long lived component that appears at room temperature may be due to partial decomposition of the complex brought about by the laser flashes, and, accordingly, can be disregarded. The observed disparity between the τ values for the crystal and the solu-

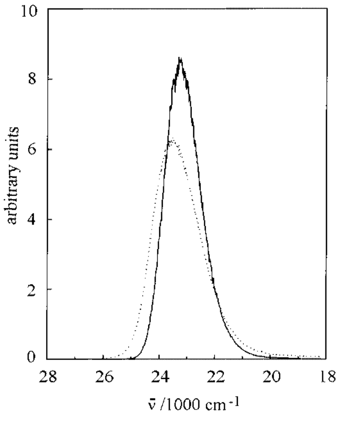

Figure 3. The emission spectrum of **1** at room temperature (dotted line) and at 77 K (solid line)

tion may be caused by several factors. We can safely eliminate the role of OH oscillators in the Eu first-coordination sphere, as they are present in both cases. Therefore the probable reasons for the discussed discrepancy are: a) internal rotations of the macrocycle ring, and b) the exchange dynamics of methanol molecules and possibly chloride anions. Finally, it is noteworthy that the luminescence lifetime for the present compound is an order of magnitude greater than that reported for the benzo-15-crown-5 complex (0.59 μs at 77 K).[3]

The excitation spectrum may be divided into two parts: one, larger, between 275 and 408 nm (24500−38900 cm^{-1}), and the other, smaller, between 230 and 275 nm (38900−43500 cm^{-1}). In the first part three maxima are discernible, at 392 nm (25510 cm^{-1}), 352 nm (28410 cm^{-1}) and 309 nm (32360 cm^{-1}). In the other part only one maximum can be identified at 248 nm (40320 cm^{-1}). The difference in wavenumbers between these and the lowest lying excited (emitting) level are 2250, 5150, 9100 and 17060 cm^{-1}, respectively. Using the simple approach of Johnson and Sandoe[16] we can interpret the first three maxima as being dominated mostly by $4f^6(^7F)5d$ states, whereas the last one, lying 17060 cm^{-1} above the emitting level, should include mainly the $4f^6(^5D)5d$ states, as the respective difference parallels that between the energies of the ^7F_J and ^5D_J levels in Eu^{3+}.

The excitation spectrum of **1**, juxtaposed with the absorption spectrum of the free ligand (Figure 4) shows no evidence for energy transfer from the benzo rings to the metal ion (the so called "antenna effect"), as no correspondence between the peaks in both spectra can be noticed.

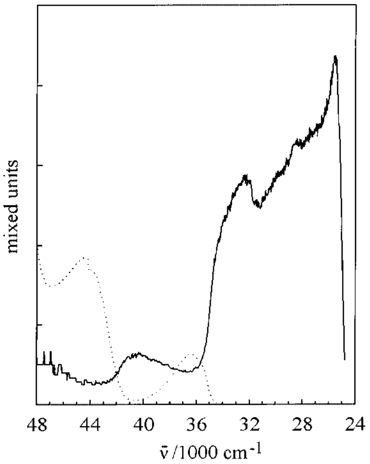

Figure 4. The excitation spectrum of **1** at 77 K (solid line), and the absorption spectrum of benzo-18-crown-6 in water/methanol solution (dotted line)

Conclusion

Two new complexes of Eu^{II} with benzo-18-crown-6 have been obtained in the crystalline state. In both complexes the metal ion is nine-coordinate and the coordination environment is composed of six O atoms belonging to the crown ligand and three water molecules. The spectroscopic properties are similar to those previously reported for a benzo-15-crown-5/Eu^{II} complex, with the exception of the luminescence lifetime, which is an order of magnitude larger in the present case. Both the emission maximum and luminescence lifetime are different from the analogous quantities reported for the $EuCl_2$/benzo-18-crown-6 complex in methanol solution.

Experimental Section

Preparation: a) Compound **1** was obtained by dissolving 0.5 g of Eu_2O_3 in $HClO_4$, evaporating the resulting solution until the evolution of white fumes, cooling down the resulting perchlorate, dissolving it in a 1:2 water/methanol mixture, and then adding 1 g of benzo-18-crown-6. The resulting solution was placed in the cathode compartment of an H-shaped electrolyzer with a sintered glass diaphragm and a pool Hg cathode. A dilute water/methanol (1:2) solution of $HClO_4$ was the anolyte. The reduction was performed at −1.2 V with respect to the saturated calomel electrode, and with a stream of N_2 passing slowly above the reduced solution. Colourless crystals of **1** formed after 1−2 days. The compound is unstable in air and begins to darken after ca. 10−15 min. $C_{16}H_{30}Cl_2EuO_{17}$ (717.26) calcd. C 26.8, H 4.2, Eu 21.2; found C 26.4, H 4.0, Eu 20.3. Compound **2** was the result of an unsuccessful attempt to prepare an acetate salt of the crown complex. The preparation was started from europium acetate, obtained by dissolving 0.5 g of Eu_2O_3 in concentrated acetic acid. The acetate was then dissolved in the water/methanol mixture and a few drops of moderately dilute $HClO_4$ were added to increase the solution conductivity. The synthesis continued similarly as in the case of **1**. The crystals of **2** were also colourless and unstable in air.

X-ray Crystallographic Study: Appropriate crystals were cut from larger ones and mounted on a Kuma KM4 diffractometer equipped with a CCD counter. The collected data were corrected for polarization, Lorentz and absorption effects; the latter were calculated from the crystal habits captured from photo scans. The positions of Eu were found from Patterson maps, and the rest of the non-H atoms from difference Fourier maps. The positions of the C-bonded hydrogen atoms were calculated geometrically. No attempt was made to localize the O-bonded H atoms The refinement was full-matrix with all non-H atoms anisotropic. The temperature factors of the H-atoms were constrained to 1.2 times the factors of the relevant C atoms. A peak with height of 2.0 $e\cdot Å^{-3}$ (see Table 2) located 2.8 Å away from Eu and placed between OW2 and OW3, that appeared on the final residual difference Fourier map of **2**, was unrefinable, and therefore was not included in the model. The programs used were SHELXS-97[17] for the solution, SHELXL-97[18] for the refinement, and DIAMOND[19] for the molecular graphics. The data collection and refinement details are presented in Table 2.

Spectroscopy: The spectroscopic investigations for **1** only will be presented here. The luminescence and excitation spectra were taken on an SCL Aminco 500 spectrofluorimeter. The luminescence was excited with a lamp source with wavelength of 330 nm, and the excitation spectra were recorded for the emission at 425 nm. The luminescence decay curves were detected on a device equipped with a Hamamatsu photomultiplier and a Tektronix TDS-3052 digital oscilloscope. The sample was excited with the third harmonic of a neodymium laser (355 nm), and the registered output signal had

Table 2. Crystal data and structure refinement details

	1	**2**
Empirical formula	$C_{16}H_{30}Cl_2EuO_{17}$	$C_{32}H_{56}Cl_2EuO_{24}$
Molecular weight	717.26	1047.63
Temperature	100(2) K	100(2) K
Wave length	0.71073 Å	0.71073 Å
Crystal system, space group	monoclinic, $P2_1/n$	monoclinic, $P2_1/n$
Unit cell dimensions	a = 10.794(9) Å b = 21.397(16) Å c = 11.019(9) Å β = 94.74(6)°	a = 13.050(3) Å b = 17.633(3) Å c = 18.281(3) Å β = 93.97(2)°
Volume	2536(4) $Å^3$	4196.6(14) $Å^3$
Z, calculated density	4, 1.878 $Mg{\cdot}m^{-3}$	4, 1.658 $Mg{\cdot}m^{-3}$
Absorption coefficient	2.762 mm^{-1}	1.710 mm^{-1}
F(000)	1436	2148
Crystal size	0.3 × 0.1 × 0.07 mm	0.3 × 0.15 × 0.1 mm
Theta range for data collection	3 to 28.5°	3 to 28°
Index ranges	$-14 \le h \le 12, -28 \le k \le 27, -14 \le l \le 13$	$-17 \le h \le 16, -20 \le k \le 23, -22 \le l \le 24$
Reflections collected/unique	16685/5885 (R_{int} = 0.0398)	27320/9774 (R_{int} = 0.0540)
Completeness to 2θ = 28.5°	89.2%	89.5%
Absorption correction		calculated from the crystal shape
Max. and min. transmission	0.804 and 0.550	0.874 and 0.674
Refinement method		full-matrix least-squares on F^2
Data/restraints/parameters	5885/ 0/ 325	9774/ 0/ 532
Goodness-of-fit on F^2	1.530	1.291
Final R indices [$I > 2\sigma(I)$]	$R(F) = 0.0451$, $R_w(F^2) = 0.0534$	$R(F) = 0.0595$, $R_w(F^2) = 0.0570$
R indices (all data)	$R(F) = 0.0637$, $R_w(F^2) = 0.0552$	$R(F) = 0.1015$, $R_w(F^2) = 0.0628$
Largest diff. peak and hole	1.091 and −0.666 $e{\cdot}Å^{-3}$	2.178 and −2.000 $e{\cdot}Å^{-3}$

23550 cm^{-1}. All the measurements (luminescence, excitation and life times) were recorded at room and 77 K temperatures. The absorption spectrum of a 2×10^{-4} M water/methanol (1:1) solution of the free ligand was recorded on a Cary 50 spectrophotometer.

CCDC-181112 (**1**) and CCDC-181113 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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