A Europium(II) Complex with Benzo-15-Crown-5

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Dedicated to the memory of Mikołaj Starynowicz

Keywords: Europium / Crown compounds / X-ray diffraction / Luminescence / Lanthanides

The present paper reports the crystal structure and luminescent properties of bis(benzo-15-crown-5)europium(II) diperchlorate. The structure is composed of complex bis(benzo-15-crown-5)europium(II) cations and perchlorate anions. The complex cation is centrosymmetric, and the metal ion is surrounded by 10 oxygen atoms of two ligand molecules. The compound shows very bright luminescence at 23450 cm^{-1}. The emission parameters (wavelength and the average lifetime of the excited state) are compared to those previously reported for the analogous complex in methanol solutions.

Introduction

Complexes of divalent lanthanides (mainly Eu^{II}) with crown ethers have attracted much attention and the present state of the investigations on these complexes was excellently reviewed by Jiang et al.[1] The interest in these compounds is motivated both by the luminescent properties of the Eu^{2+} cation in the macrocyclic coordination environment and by the ligand's ability to stabilize the divalent state of the lanthanide. The luminescence quantum yield of the Eu^{II}-crown ether complexes in methanol solutions is increased relative to solutions of EuCl$_2$ and noncyclic polyethers because of encapsulation of the central ion, which in turn prevents the solvent OH groups from entering the first coordination sphere of the metal. This effect is particularly pronounced for 15-crown-5 and some of its derivatives. On the other hand the f^{6}d-state splittings in these systems, deduced from absorption and emission spectra, are smaller than for the EuCl$_2$-methanol system. 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 lead 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 gain information about the possible coordination behaviour of the macrocycles in compounds with Eu^{II} both in solution and in the solid state. Unfortunately, to the best of the authors' knowledge, there are no reports on the crystal structures of Ln^{II}-crown ether complexes, or attempts to correlate their spectroscopic properties in the solid state with their properties in solution. This work, which is an extension of our earlier work on Eu^{II} carboxylates, is intended to be such an attempt.

Results and Discussion

Crystal Structure

The crystals are built up from complex bis(benzo-15-crown-5)europium(II) cations and perchlorate anions, which are kept together by weak electrostatic and Van der Waals interactions. The metal ion is located at an inversion centre, between two symmetry-related ligand molecules, thus forming a sandwich-like complex cation. Such a coordination fashion for 15-crown-5-type ligands is common for K,[3] Rb,[4] Cs,[5] Sr[6] or Ba[7] (see also J. W. Steed[8] for a general review), whereas the trivalent lanthanide cations typically form 1:1 complexes.[9] The Eu^{2+} ion is accordingly surrounded by ten oxygen atoms, and the metal coordination environment may be described as a slightly distorted pentagonal antiprism with approximate point symmetry D_{5d}. The θ angles between the idealised C$_5$ axis and the Eu−O vectors are in the range 55.3−61.2°, with the average being 58.4°. The Eu−O distances, given in Table 1, although within the range observed in previously reported organic Eu^{II} compounds,[10] should be considered as rather long.

Table 1. The Eu−O distances (Å)

Eu−O(5)	2.662(3)
Eu−O(1)	2.688(3)
Eu−O(3)	2.694(3)
Eu−O(4)	2.718(4)
Eu−O(2)	2.728(4)

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The shortest Eu−Eu distance is 9.774(2) Å. The whole macrocycle fragment is rather puckered and the aliphatic -CH_2-CH_2- chains in the macrocycle ring are disordered over two sets of positions (see the Exp. Sect.). The high values of the transversal principal components of the thermal ellipsoids may also indicate disorder within the benzo rings; however this could not be resolved during the refinement. The complex cation is drawn in Figure 1.

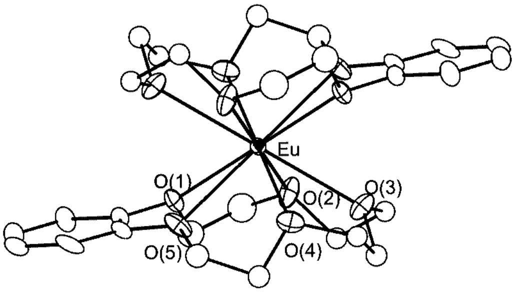

Figure 1. A DIAMOND[20] view of the complex cation; for the sake of clarity only symmetry-independent oxygen atoms have been labelled and the disordered carbon sites with the lower occupancy have been omitted

Spectroscopy

The compound shows very bright luminescence (to the point of gaining a violet hue in full daylight). The emission is observed in the form of a single peak with the maximum at 422 nm (23700 cm^{-1}) at room temperature, and at 426.5 nm (23450 cm^{-1}) at 77 K (see Figure 2). These values are slightly different from those reported for the Eu^{2+}-benzo-15-crown-5 system in methanol solution [417 nm (23980 cm^{-1})],[1,11] which may suggest a larger splitting of the excited $4f^65d^1$ state in the crystal. To identify the emitting level we decided to use the Jγ coupling method as described by Johnson and Sandoe.[12] Thus, it is commonly known that the lowest multiplet of the $4f^6$ core is ^7F, so only splitting of the 5d orbitals merits attention. To simplify our considerations we assumed that the degeneration of the 5d states is lifted by interaction with the ten oxygen atoms belonging to the first coordination sphere only, and the symmetry of the latter is D_{5d}. Following Gołębiewski,[13] the energy shift of the d orbitals in any crystal field is:

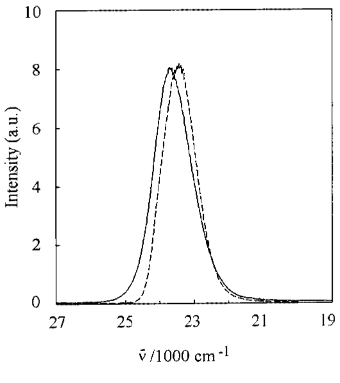

Figure 2. Emission spectrum of the complex at room temperature (solid line) and at 77 K (dashed line)

$$\begin{aligned}
\Delta E(d_{z^2}) &= \tfrac{2}{7}L_{20}G_2+\tfrac{2}{7}L_{40}G_4;\\
\Delta E(d_{xz}) &= \tfrac{1}{7}L_{20}G_2-\tfrac{4}{21}L_{40}G_4+\tfrac{1}{126}(9L_{22}G_2+2L_{42}G_4);\\
\Delta E(d_{yz}) &= \tfrac{1}{7}L_{20}G_2-\tfrac{4}{21}L_{40}G_4-\tfrac{1}{126}(9L_{22}G_2+2L_{42}G_4);\\
\Delta E(d_{x^2-y^2}) &= -\tfrac{2}{7}L_{20}G_2+\tfrac{1}{21}L_{40}G_4+\tfrac{1}{504}L_{44}G_4;\\
\Delta E(d_{xy}) &= -\tfrac{2}{7}L_{20}G_2+\tfrac{1}{21}L_{40}G_4-\tfrac{1}{504}L_{44}G_4;
\end{aligned} \tag{1}$$

where the L terms are angular factors in the form:

$$\begin{aligned}
L_{20} &= \tfrac{1}{2}\Sigma(3\cos^2\theta_i-1);\\
L_{40} &= \tfrac{1}{8}\Sigma(35\cos^4\theta_i-30\cos^2\theta_i+3);\\
L_{22} &= 3\Sigma\sin^2\theta_i\cos2\varphi_i;\\
L_{42} &= 7\Sigma(7\cos^2\theta_i-1)\sin^2\theta_i\cos2\varphi_i;\\
L_{44} &= 105\Sigma\sin^4\theta_i\cos4\varphi_i;
\end{aligned} \tag{2}$$

where θ_i and $_i$ are the angular coordinates of the i-th ligand, and the summation runs over all ligand positions. The G_2 and G_4 are (positive) radial integrals, as defined previously;[13] their detailed forms are not necessary for the reasoning below. Assuming that $\theta_i = \theta$ or $\pi-\theta$, and the φ_i angles span two regular pentagons, the last three L functions disappear. On substituting the previously obtained value of 58.4° for θ into the above equations, one gets:

$$\begin{aligned}
&\Delta E(d_{z^2}) = -0.252G_2-0.928G_4 \quad (A_{1g});\\
&\Delta E(d_{xz}) = \Delta E(d_{yz}) = -0.126G_2+0.619G_4 \quad (E_{1g});\\
&\Delta E(d_{x^2-y^2}) = \Delta E(d_{xy}) = 0.252G_2-0.155G_4 \quad (E_{2g});
\end{aligned} \tag{3}$$

where the symbols of the relevant irreducible representations are given in parentheses.

Thus the d_{z^2} orbital will be the lowest, and the emitting states may be described as $4f^6(^7F)5d_{z^2}$. Furthermore, one may tentatively assume that the energy difference between the e_{1g} and e_{2g} orbitals will not be large because of different signs of the coefficients of G_2 and G_4; the ratio G_2/G_4 lies between 2 and 4.[13] The splitting of the $4f^6$ core must also be taken into consideration, which gives rise to a rather complicated structure of higher lying excited states that can be observed in the excitation spectra (Figure 3). The range in which the bands are observed is similar to the ranges observed in the excitation spectra of Eu^{2+} doped in $BaMg_2Si_2O_7$ [14] or MgF_2 matrices.[15] In our case the spectrum may be roughly divided into two parts: a more intense band between 270 and 400 nm (25000−37000 cm^{-1}; marked as band A in the Figure 3), and a weaker one between 220 and 270 nm (37000−45500 cm^{-1}; band B). The difference between their centres may be estimated as approximately 12000 cm^{-1}, which is similar to the energy difference between the ^7F and ^5D states in Eu^{3+} [16] or Sm^{2+}.[17] Considering this, and the earlier assumption of a small splitting of the e_{1g} and e_{2g} orbitals, one can conclude that the band B must reflect the positions of the $4f^6(^5D)5d$ states. The luminescence decay curves were monoexponen-

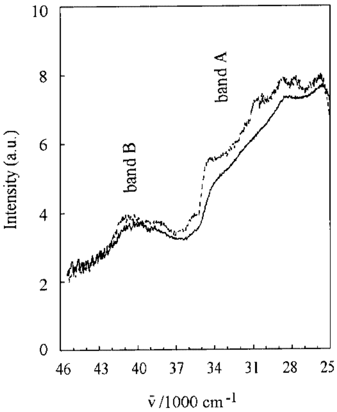

Figure 3. Excitation spectrum of the complex at room temperature (solid line) and at 77 K (dashed line)

tial, with a mean lifetime of the excited state of 0.65(2) μs at room temperature and 0.59(1) μs at 77 K. Comparison of these values with the value observed for methanol solutions (0.14 μs)[11] suggests additional relaxation processes, which could be caused by the presence of methanol OH oscillators in the first coordination sphere of the metal in solution.

Conclusion

A new complex of Eu^{II} with benzo-15-crown-5 has been obtained and characterized by X-ray diffraction and spectroscopic methods. Its properties, namely energy and the luminescence lifetime of the $4f^6 5d \rightarrow 4f^7$ transition, are different from those reported for the $EuCl_2$-benzo-15-crown-5 system in methanol solution. We can therefore conclude that the structure of the complex in the solid state is different from the labile species existing in the solution — in the latter case the solvent molecules probably enter the first coordination sphere of Eu.

Experimental Section

Preparation: Eu_2O_3 (0.663 g, 1.9 mmol) was dissolved in a small excess of 60% $HClO_4$, evaporated until white fumes appeared, cooled down and dissolved in a few millilitres of a 3:1 methanol/water mixture. To this benzo-15-crown-5 (1 g, 3.7 mmol) was added. The resulting mixture was placed in an H-shaped electrolyzer with a pool mercury cathode, platinum anode and a sintered glass diaphragm between the anode and cathode compartments. A dilute solution of $HClO_4$ in a 2:1 methanol/water mixture was the anolyte. Electrolysis was performed at a potential of −1 V with respect to the saturated calomel electrode. The first crystals appeared after half an hour. The compound is colourless, with a light violet hue in full daylight, and is rather stable in air at room temperature. $C_{28}H_{40}Cl_2EuO_{18}$: calcd. C 37.89, H 4.68, Cl 7.99, Eu 17.12; found C 37.21, H 4.54, Cl not analysed due to the explosive properties of the compound, Eu 16.30.

Spectroscopy: The luminescence and excitation spectra were measured on an SCL Aminco 500 spectrofluorimeter. The luminescence was excited with a lamp source with a 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 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 a wavelength of 23460 cm^{-1}. All the measurements (luminescence, excitation and life times) were recorded at room temperature and at 77 K.

X-ray Crystallographic Study: An appropriate crystal was cut from a larger one and mounted on a Kuma KM4 diffractometer equipped with a CCD counter. The collected data were corrected for polarisation, Lorentz and absorption effects; the latter was calculated from the crystal habit captured from a photo scan. The position of Eu was found from a Patterson map, and the rest of the non-H atoms from difference Fourier maps. The positions of the hydrogen atoms were calculated geometrically. The refinement was full-matrix with all ordered atoms anisotropic. The carbon atoms belonging to the aliphatic fragment of the ligand were found to be disordered between two sets of positions [denoted with suffices A and B in the relevant atom names, with occupancies of 0.642(7) and 0.358(2), respectively], and therefore kept isotropic. The temperature factors of the H atoms were constrained to be 1.2-times the factors of the relevant C atoms.

The programs used were SHELXS-97[18] for the solution, and SHELXL-97[19] for the refinement. The data collection and refinement details are presented in Table 2.
CCDC-177469 contains 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].

Table 2. Crystal data and structure refinement details

Empirical formula	$C_{28}H_{40}Cl_2EuO_{18}$
Molecular weight	887.46
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, $P2_1/n$
Unit cell dimensions	a = 9.774(2) Å b = 10.558(2) Å c = 16.989(4) Å β = 102.57(2)°
Volume	1711.1(6) $Å^3$
Z, Calculated density	2, 1.722 $Mg{\cdot}m^{-3}$
Absorption coefficient	2.067 mm^{-1}
F(000)	898
Crystal size	0.25 × 0.2 × 0.1 mm
Theta range for data collection	3.3 to 28.5°
Index ranges	$-12 \leq h \leq 11$, $-13 \leq k \leq 13$, $-22 \leq l \leq 22$
Reflections collected/ unique	11102/4036 (R_{int} = 0.0378)
Completeness to 2θ = 28.5°	88.7%
Absorption correction	calculated from the crystal shape
Max. and min. transmission	0.856 and 0.609
Refinement method	full-matrix least-squares on F^2
Data/ restraints/ parameters	4036/148/216
Goodness-of-fit on F^2	1.901
Final R indices [$I > 2\sigma(I)$]	$R(F) = 0.0459$, $R_w(F^2) = 0.0645$
R indices (all data)	$R(F) = 0.0739$, $R_w(F^2) = 0.0668$
Largest diff. peak and hole	1.000 and −0.903 $e{\cdot}Å^{-3}$

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