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PERGAMON

Polyhedron 22 (2003) 337–345

POLYHEDRON

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Europium(II) complexes with unsubstituted crown ethers

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Received 28 August 2002; accepted 5 November 2002

Abstract

Three Eu(II) complexes with crown ethers were obtained by electrochemical reduction. The complex with 12-crown-4 contains Eu bonded to four O crown atoms, three water molecules and a chloride anion, and shows luminescence at 429 nm at room temperature and at 410 nm at 77 K. The bis(15-crown-5)europium(II) cation has a sandwich structure with 10-coordinate metal ion. Its luminescence has the maximum at 433 nm at room temperature and at 417 nm at 77 K. The weakly luminescing (411.5 nm at 77 K) bisperchlorato(18-crown-6)europium(II) is also 10-coordinate; both perchlorate anions are bonded in a chelating bidentate fashion. The luminescence lifetimes and the excitation spectra are discussed.

Keywords: Divalent europium; Lanthanides; Crown ethers; Structures; Luminescence

1. Introduction

The crown ethers and their complexes with metals have received much attention since the discovery of these ligands by Pedersen [1,2]. They have proved potent and versatile receptors for alkali and alkaline earth metals [3]. Also the compounds with lanthanides have been extensively studied; the interest has ensued both from their spectroscopic behaviour, resulting from the interplay of the luminescent properties of the very Ln^{3+} ions, and the encapsulation provided by the macrocycle, and from general supramolecular regards [4,5]. The structural investigations have led to plethora of results; the Cambridge Structural Database contains more than 100 entries of Ln(III)–crown complexes. Therefore for the needs of this work and for the sake of brevity, this introductory overview must be limited to selected examples of halogenide and pseudohalogenide (isothiocyanate) Ln, Ca, Sr and Ba compounds of unsubstituted 12-crown-4, 15-crown-5 and 18-crown-6. The first macrocycle has the smallest cavity, incapable of hosting a large metal ion. For this reason, in the reported structures, the ligand occupies approximately a coordination hemisphere, the other one being left for anions and/or solvent molecules, with varying ratio between the former and the latter. Thus the first coordination sphere of the metal cation may by completed by four (Ca [6]) or five (Ln [7,8]) water molecules only, by two chloride anions and two water molecules (lanthanides [8,9] the alkaline earth metals [10]), or by three anions and a solvent molecule (lanthanides [11,12]). The sandwich bis(12-crown-4)metal structures are rare (Er [9], Ba [10]). The next ligand, 15-crown-5, offers a larger cavity for the metal binding, what in turn leads to diminishing of the number of other coordinated atoms. The general patterns of coordination are the following: the crown + three (Ca [13]) or four (Sm [14]) water molecules, the crown + two anions + a water molecule (Ca [15]) or the crown + 3 anions (Ln [16–20]). The small Yb^{3+} cation forms a complex with two-coordinated chloride anions located on the opposite sides of the crown ligand [21]. As it seems, the sandwich type complexes have not been reported for lanthanides, but they are quite common for Sr [22,23] or Ba [24,25]. The compounds with 18-crown-6 repeat usually these schemes [26,27]. The difference consists in that the cavity is now large enough to include the metal ion, which in turn becomes reachable for coordination from both poles.

Contrary to rich chemistry of Ln(III)–crown ether compounds, investigations of the divalent lanthanide complexes have been rather limited; this is brought

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PII: S0277-5387(02)01358-X

about by experimental problems connected with great sensitivity of these entities towards oxidation. The information collected so far includes their spectroscopic properties in solution [28], and a few crystal structures (2[(dibenzo-18-crown-6)Br_2Eu]·$EuBr_6$·4[(H_3O)(dibenzo-18-crown-6)]·$2H_2O$ [29,30], europium(II) complexes with benzo-15-crown-5 [31], benzo-18-crown-6 [32], ytterbium complexes with 18-crown-6 [33], samarium(II) and ytterbium(II) complexes with 18-crown-6 and a derivative of cyclopentadienyl [34]), although syntheses of similar compounds in the solid state were reported earlier [35–37]. Our interest in these compounds is motivated both by their spectroscopic properties and by the ability of the macrocycle ligand to stabilize the divalent state of the lanthanide ion [28]. In the present paper, we present three new Eu(II)–crown complexes: triaquachloro(12-crown-4)europium(II) chloride (hereinafter **I**) as a low and a room temperature phases (denoted as $\mathbf{I_{LT}}$ and $\mathbf{I_{HT}}$, respectively), bis(15-crown-5)europium(II)diperchlorate (**II**), and bisperchlorato(18-crown-6)europium(II) (**III**).

2. Experimental

2.1. Preparation

2.1.1. General remarks

All three compounds were synthesized by electolytic reduction of wet (containing small amount of water) methanolic solution of $Eu(ClO_4)_3$, obtained by dissolving appropriate amount of Eu_2O_3 in small excess of aq. $HClO_4$ and then concentrating the resulting solution by heating, and of the respective crown ligand. The reductions were performed at controlled potentials in an H-shaped electrolyzer with a sintered glass diaphragm, the pool Hg cathode and Pt anode. Diluted $HClO_4$ solutions in water–MeOH 1:3 mixture were the anolytes, and a mild stream of N_2 would be passed over the reduced solutions, but no particular precautions against the access of air would be undertaken. In the case of 12-crown-4, as this procedure did not lead to formation of crystals, after a few days, a few millilitres of water solution of HCl and CH_3COOH was added to the catholyte and the process was continued for next few days.

2.1.2. Triaquachloro(12-crown-4)europium(II)chloride (*I*)

12-Crown-4 (1 g) and 0.5 g of Eu_2O_3 were processed in the way described above. The reduction potential was −1.5 V with respect to the saturated calomel electrode (SCE). The colourless crystals formed after a few days after adding the HCl–CH_3COOH mixture. Molecular mass: 453.12. *Anal*. Calc for $C_8H_{22}Cl_2EuO_7$: C, 21.2; H, 4.9; Eu, 33.5. Found: C, 20.3; H, 4.6; Eu, 32.7%.

2.1.3. Bis(15-crown-5)europium(II)diperchlorate (*II*)

The synthesis started from 1 g of 15-crown-5 and 0.4 g of Eu_2O_3; the potential was set at −1 V against SCE. The colourless, with a light violet hue in full daylight, crystals were collected after a few hours. Molecular mass: 791.38. *Anal*. Calc. for $C_{20}H_{40}Cl_2EuO_{18}$: C, 30.4; H, 5.1; Eu, 19.2. Found: C, 29.3; H, 5.2; Eu, 18.3%.

2.1.4. Bisperchlorato(18-crown-6)europium(II) (*III*)

18-Crown-6 (1 g) and 0.67 g of Eu_2O_3 were used; the potential was set at −1 V against SCE. The colourless crystals formed after a few hours. Molecular mass: 615.17. *Anal*. Calc. C, 23.4; H, 3.9; Eu, 24.7. Found: C, 22.3; H, 3.8; Eu, 23.6%.

2.2. X-ray experiment

Appropriate crystals were cut from larger ones and mounted on a Kuma KM4 diffractometer equipped with a CCD counter. All the crystals were measured at 100 K, and apart from that **I** was also measured at room temperature (r.t.). The collected data were corrected for polarization, Lorentz and absorption, the lattest calculated from the crystal habits captured from photo scans. (**I**) The positions of Eu were found from Patterson maps, the rest of non-H atoms from difference Fourier maps. The positions of the C-bonded hydrogen atoms were calculated geometrically. No attempt was taken to localize the O-bonded H atoms. For $\mathbf{I_{LT}}$ the refinement was full-matrix with all non-H atoms anisotropic, whereas in the case of $\mathbf{I_{HT}}$ anisotropic refinement was applied to the ordered atoms and to those disordered Cl atoms which had their site occupancy factors close to 3/4. The $\mathbf{I_{HT}}$ refinement suffered from severe correlation problems and the influence of partial overlapping of closely located satellite reflections (see Section 3), therefore, it was decided to remove 43 most affected data and to use restraints for the anisotropic factors of O21, O22, O23, O31, O32, OW32, C11, C16, C17, C18, C24, C27, C31, C34, C35, C36, C37 and C38. Also, the C–C and C–O distances involving the disordered atoms were restrained. The temperature factors of H atoms were constrained to 1.2 of the factors of the relevant C atoms. The data collection and refinement details are presented in Table 1. (**II**) This structure was solved with direct methods, and its refinement presented no particular problems. All non-H atoms were refined anisotropically; the positions of the C-bonded hydrogen atoms were calculated geometrically and their temperature factors were constrained to 1.2 of the factors of the relevant C atoms. The majority of C atoms and the perchlorate O atoms showed high temperature factors during the refinement, what may indicate a certain degree of disorder. This was not, however included in the refined model. (**III**) The crystals were of bad quality, and despite several attempts a strictly monocrystalline sam-

Table 1
Crystal data and structure refinement details for **I_{LT}** and **I_{HT}**

Crystal	**I_{LT}**	**I_{HT}**
Empirical formula	$C_8H_{22}Cl_2EuO_7$	
Formula weight	453.12	
Temperature (K)	100(2)	299(2)
Wavelength (Å)	0.71073	
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1$
Unit cell dimensions		
a (Å)	17.972(9)	14.909(3)
b (Å)	8.531(5)	8.570(2)
c (Å)	20.134(10)	18.134(4)
β (°)	101.68(4)	95.22(3)
V (Å^3)	3023(3)	2307.4(8)
Z	8	6
D_{calc} (Mg m^{-3})	1.991	1.957
Absorption coefficient (mm^{-1})	4.522	4.444
F(000)	1784	1338
Crystal size (mm)	0.35 × 0.25 × 0.1	0.25 × 0.17 × 0.1
Theta range for data collection (°)	3.2–28.4	3.3–28.4
Index ranges	$22 \leq h \leq 24$, $-11 \leq k \leq 11$, $-25 \leq l \leq 23$	$-16 \leq h \leq 19$, $-11 \leq k \leq 10$, $-24 \leq l \leq 23$
Reflections collected	18 954	15 354
Reflections unique	7113 [$R_{int} = 0.0371$]	9696 [$R_{int} = 0.0335$]
Completeness to $2\theta = 28.4$ (%)	87.8	92.5
Absorption correction	analytical, from crystal shape	
Max./min. transmission	0.673/0.341	0.781/0.433
Refinement method	full-matrix least-squares on F^2	
Data/restraints/parameters	7113/0/325	9696/163/484
Final R indices [$I > 2\sigma(I)$]	$R(F) = 0.0396$, $R_w(F^2) = 0.0603$	$R(F) = 0.0355$, $R_w(F^2) = 0.0671$
R indices (all data)	$R(F) = 0.0583$, $R_w(F^2) = 0.0621$	$R(F) = 0.0781$, $R_w(F^2) = 0.0812$
Goodness-of-fit on F^2	2.066	0.968
Largest difference peak and hole (e A^{-3})	1.617 and −1.196	1.002 and −0.714

Table 2
Crystal data and structure refinement details for **II** and **III**

Crystal	**II**	**III**
Empirical formula	$C_{20}H_{40}Cl_2EuO_{18}$	$C_{12}H_{24}Cl_2EuO_{14}$
Formula weight	791.38	615.17
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	rhombohedral	triclinic
Space group	$R3c$	$P\bar{1}$
Unit cell dimensions		
a (Å)	17.92(2)	9.1730(18)
b (Å)		9.3920(19)
c (Å)		12.940(3)
α (°)	108.36(6)	74.36(3)
β (°)		77.25(3)
γ (°)		72.31(3)
V (Å^3)	4602(9)	1011.0(3)
Z	6	2
D_{calc} (Mg m^{-3})	1.713	2.021
Absorption coefficient (mm^{-1})	2.294	3.435
F(000)	2406	610
Crystal size (mm)	0.2 × 0.2 × 0.15	0.26 × 0.15 × 0.12
Theta range for data collection (°)	3.5–28.5	3.6–28.5
Index ranges	$-23 \leq h \leq 23$, $-22 \leq k \leq 23$, $-23 \leq l \leq 18$	$-12 \leq h \leq 12$, $-12 \leq k \leq 9$, $-17 \leq l \leq 17$
Reflections collected	31 052	5676
Reflections unique	6764 [$R_{int} = 0.0929$]	3885 [$R_{int} = 0.0574$]
Completeness to $2\theta = 28.5$ (%)	96.3	76.1
Absorption correction	analytical, from the crystal shape	
Max./min. transmission	0.814/0.655	0.684/0.462
Refinement method	full-matrix least-squares on F^2	
Data/restraints/parameters	6764/1/370	3885/0/262
Final R indices [$I > 2\sigma(I)$]	$R(F) = 0.0627$, $R_w(F^2) = 0.0845$	$R(F) = 0.0724$, $R_w(F^2) = 0.1442$
R indices (all data)	$R(F) = 0.0852$, $R_w(F^2) = 0.0874$	$R(F) = 0.0818$, $R_w(F^2) = 0.1472$
Goodness-of-fit on F^2	1.448	2.479
Largest difference peak and hole (e Å^{-3})	1.066 and −0.696	4.671 and −2.113

ple could not be found. The measured crystal was split and showed two component lattices in the reciprocal space. Therefore, it was inevitable to discard a part of the recorded reflections from the data set; on the whole 1235 intensities were purged away. As previously, all non-H atoms were refined anisotropically; the positions of the C-bonded hydrogen atoms were calculated geometrically and their temperature factors were constrained to 1.2 of the factors of the relevant C atoms. The data concerning the data collection and refinement of **II** and **III** are given in Table 2. For all three structures, the programs used were SHELXS-97 [38] for the solution, SHELXL-97 [39] for the refinement, and DIAMOND [40] for the molecular graphics.

2.3. *Spectroscopy*

The luminescence and excitation spectra of the polycrystalline samples were taken on an SCL Aminco 500 spectrofluorimeter. The luminescence was excited with a lamp source with wavelength of 330 nm for **I**, and 350 nm for **II** and **III**. The excitation spectra were recorded for the emission at 429 nm for **I**, 430 nm for **II** at r.t., 420 nm for **II** at 77 K, and 411 nm for **III** at 77 K. All the measurements were recorded at room and 77 K temperatures for **I** and **II**, and at 77 K only for **III**, because of its weak luminescence. The luminescence decay curves for **I** and **II** were detected on a device equipped with Hamamatsu photomultiplier and Tektronix TDS-3052 digital oscilloscope. The samples were excited with the third harmonic of a Nd laser (355 nm).

3. Results and discussion

3.1. Lattice geometry of *I*

The lattice parameters of both phases are presented in Table 1. There is not much to say about $\mathbf{I}_{\mathbf{LT}}$, but in the case of $\mathbf{I}_{\mathbf{HT}}$ the data collection and reduction encountered certain difficulties that merit some comment. Examination of the reciprocal spaces of both crystals shows that both lattices may treated as deriving from a basic monoclinic unit cell with the cell parameters $a_B = 7.404$, $b_B = 8.529$, $c_B = 12.059$ Å, $\beta_B = 96.62°$ at 100 K. Both low and high temperature data gave good solutions in this setting and the space group was $P2_1/m$ in either case. However, the Ewald space contains also reflections generated by an additional vector, q^*, which may be treated as a commensurate modulation vector. For $\mathbf{I}_{\mathbf{LT}}$, $q^*_{HT} = 1/4a^*_B - 1/2c^*_B$; for $\mathbf{I}_{\mathbf{HT}}$ $q^*_{HT} = 1/3a^*_B - 2/3c^*_B \approx 4/3q^*_{LT}$. When these reflections are taken into account, one gets the cells presented in Table 1. Namely, $a_{HT} \equiv -q_{HT} = a_B - c_B$; $b_{HT} = b_B$; $c_{HT} = 2a_B + c_B$; and $a_{LT} = 2a_B + c_B$; $b_{LT} = b_B$; $c_{LT} \equiv -q_{LT} = -2a_B + c_B$. The both cells are related as following: $a_{HT} \approx -1/4a_{LT} - 3/4c_{LT}$; $b_{HT} \approx b_{LT}$; $c_{HT} \approx a_{LT}$, and the volume ratio $V_{HT}/V_{LT} \approx 3/4$. However, careful inspection of the reciprocal space diagrams of $\mathbf{I}_{\mathbf{HT}}$ reveals weak satellites that may be regarded as brought about by modulation of the second order with the modulation vector $q'^* = 1/4q^*$. In such a way, a large cell with $a = 4a_{HT}$ and equal to almost 60 Å is formed (the other cell dimensions remain unchanged) and the $\mathbf{I}_{\mathbf{LT}}$ lattice becomes a sublattice of that of $\mathbf{I}_{\mathbf{HT}}$. Unfortunately, for such a large constant the intensities could not be properly retrieved because of extensive overlapping of neighbouring reflections and consequently the structure could not be solved satisfactorily. It was only possible to localize the heavy atoms (Eu and Cl) and to determine the space group ($P2_1/c$). Therefore, a compromise had to be found and ultimately the $\mathbf{I}_{\mathbf{HT}}$ structure was refined in the cell presented in Table 1 and marked here with the **HT** subscripts. It is believed that, due to small intensities of the satellites: (a) the loss of information owing to their omission was not essential; (b) their contribution to the intensities of the main reflections caused by the overlapping was not destructive. The space group chosen was $P2_1$ with twinning, as attempts to refine the structure in $P2_1/m$ led to much worse results (worse R indices, statistics and a larger degree of disorder). It should be mentioned that somewhat similar problems were encountered for structures of 12-crown-4 with Ln(III) [7,8,12]. The following discussion of the $\mathbf{I}_{\mathbf{HT}}$ structure will refer to this simplified unit cell.

3.2. Structure of *I*

The crystals are composed of complex triaquachloro(12-crown-4)europium(1+) cations and chloride anions, some of them disordered in $\mathbf{I}_{\mathbf{HT}}$. Each complex cation consists of a Eu^{2+} ion surrounded by a 12-crown-4 molecule, three water molecules and a chloride anion. The overall figure of the first sphere of coordination may be described as a capped square antiprism with the crown oxygen atoms forming one base, and the three water molecules and the chloride anion spanning the other one. Such a coordination fashion is intermediate between those observed in the compounds of trivalent lanthanides, which form two series of complex cations: nine-coordinate pentaaqua(12-crown-4)lanthanides and eight-coordinate diaquadichloro(12-crown-4)lanthanides [7,8,12], and to the best of the author's knowledge has not been found elsewhere. There are two symmetry independent Eu sites in $\mathbf{I}_{\mathbf{LT}}$ and three in $\mathbf{I}_{\mathbf{HT}}$. At room temperature, the complex cations with Eu1 and Eu2 show disorder of some $-CH_2-CH_2-$ chains. The distances, presented in Table 3, are within the range observed in previously reported structures of Eu(II) crown compounds [31,32]. As before [32], the water molecules generally form shorter bonds to the metal ion, than the macrocycle oxygen atoms; the same can be observed e.g. in 12-crown-4 complexes with Ln(III) [7,8,12], Ca [6,10,41], Sr or Ba, but it is worth to observe the rather large Eu2–OW21 distance. The Eu–Cl bond lengths remain practically the same at both temperatures. The Eu–O_{crown} distances seem to be more uniform at 100 K than at room temperature, although detailed discussion is difficult in the latter case because of rather large estimated standard deviations of the appropriate bond lengths. The macrocycle assumes almost perfect C_4 symmetry at 100 K; such a conformation, being one of the most stable, maximizes the dipole moment of the crown molecule [42] (conformation **6** in the quoted paper). Part of this arrangement is preserved at room temperature, that means that upon rotating the ligand 90° and fitting it to the unrotated molecule the undisordered fragments overlap. The main difference between the molecule 1 and 2 in $\mathbf{I}_{\mathbf{LT}}$ consists in position of water molecules located *trans* to the bonded chloride anion (OW12 and OW22, respectively). In molecule 1, OW12 is turned towards OW13; the twisting measured as the angle between the projections of the vectors Cl1–Eu1 and Eu1–OW12 onto the plane O11–O12–O13–O14 is 7.3°, whereas the OW22 in molecule 2 is rotated towards OW21—the analogous angle is −11.2°. This twisting is accompanied by slight shortening (0.02–0.03 Å) of the Eu–O bond lengths for OW13 and OW21. In $\mathbf{I}_{\mathbf{HT}}$ similar features are preserved, that is the twist of the Eu–*trans* water molecule towards one of the *cis* (with respect to the bonded Cl) H_2O, accompanied by small shortening of the Eu–O bonds formed by these *cis* water

Table 3
Eu–Cl and Eu–O bond lengths (Å) in **I**, **II** and **III**

$\mathbf{I}_{LT}$					
Eu(1)–Cl(1)	2.8750(19)	Eu(2)–Cl(2)	2.8827(19)		
Eu(1)–OW11	2.594(3)	Eu(2)–OW21	2.555(3)		
Eu(1)–OW12	2.590(3)	Eu(2)–OW22	2.598(3)		
Eu(1)–OW13	2.568(3)	Eu(2)–OW23	2.586(3)		
Eu(1)–O(11)	2.658(4)	Eu(2)–O(21)	2.640(3)		
Eu(1)–O(12)	2.657(4)	Eu(2)–O(22)	2.666(3)		
Eu(1)–O(13)	2.692(4)	Eu(2)–O(23)	2.682(3)		
Eu(1)–O(14)	2.650(4)	Eu(2)–O(24)	2.673(3)		
$\mathbf{I}_{HT}$					
Eu(1)–Cl(1)	2.877(3)	Eu(2)–Cl(2)	2.887(3)	Eu(3)–Cl(3)	2.869(3)
Eu(1)–OW11	2.554(10)	Eu(2)–OW21	2.662(11)	Eu(3)–OW31	2.579(11)
Eu(1)–OW12	2.601(10)	Eu(2)–OW22	2.616(7)	Eu(3)–OW32	2.583(6)
Eu(1)–OW13	2.598(10)	Eu(2)–OW23	2.578(12)	Eu(3)–OW33	2.534(12)
Eu(1)–O(11)	2.634(10)	Eu(2)–O(21)	2.625(11)	Eu(3)–O(31)	2.629(9)
Eu(1)–O(12)	2.724(12)	Eu(2)–O(22)	2.680(12)	Eu(3)–O(32)	2.694(9)
Eu(1)–O(13)	2.631(10)	Eu(2)–O(23)	2.666(10)	Eu(3)–O(33)	2.682(10)
Eu(1)–O(14)	2.677(11)	Eu(2)–O(24)	2.699(11)	Eu(3)–O(34)	2.669(9)
II		**III**			
Eu–O(3)	2.676(10)	Eu–O(11)	2.628(7)		
Eu–O(14)	2.693(7)	Eu–O(22)	2.647(8)		
Eu–O(5)	2.707(8)	Eu–O(1)	2.674(6)		
Eu–O(12)	2.705(8)	Eu–O(2)	2.707(6)		
Eu–O(4)	2.717(8)	Eu–O(4)	2.703(6)		
Eu–O(11)	2.732(8)	Eu–O(21)	2.710(7)		
Eu–O(15)	2.741(8)	Eu–O(3)	2.721(7)		
Eu–O(1)	2.738(7)	Eu–O(5)	2.711(6)		
Eu–O(2)	2.746(8)	Eu–O(6)	2.716(6)		
Eu–O(13)	2.760(11)	Eu–O(12)	2.727(8)		

molecules. In molecule 1, OW12 is turned towards OW11, the relevant angle being −5.5°, in molecule 2 OW22 shifts towards OW23, the angle being 13.1°, and in molecule 3 OW32 inclines towards OW33, the angle being 12.9°. Another aspect that merits discussion is the orientation of the Cl*n*–OW*n*1–OW*n*3 system, where *n* is the number of the respective molecule (OW*n*2 is excluded here because of the instability of its position, discussed above) with respect to the crown ligand, or more precisely, to its oxygen atoms. The twisting of both systems may be expressed as a dihedral angle between the planes defined each by a relevant atom from the respective system and the approximate C_4 symmetry axis of the macrocycle. To simplify calculations, the fourfold axis will be substituted by two points, Eu*n*, and X*n*, where X*n* is the gravity center of the four crown O atoms. As the atoms of reference O*n*1 will be used here, and for the sake of brevity only dihedral angles (Eu*n*, X*n*, O*n*1)–(Eu*n*, X*n*, Cl*n*) will be analyzed, once the other ones (with OW*n*1 or OW*n*3) follow the trend. Thus in $\mathbf{I}_{LT}$ the angle (Eu1, X1, O11)–(Eu1, X1, Cl1) is −37.3°, and (Eu2, X2, O21)–(Eu2, X2, Cl2) is −40.4°. In $\mathbf{I}_{HT}$ the relevant angles are −49.4, −41.2 and −47.9° for molecules 1, 2 and 3, respectively. These data indicate that, with the exception of molecule 2, at room temperature the chloride anion turns more towards O*n*4, than at 100 K, and this rotation is followed by analogous clockwise rotation of OW*n*1 and OW*n*3. DIAMOND [40] views of the superimposed complex cations at both temperatures are presented in Fig. 1.

3.3. Structure of II

Crystals of **II** are composed of bis(15-crown-5)europium(II) cations and perchlorate anions. The metal ion

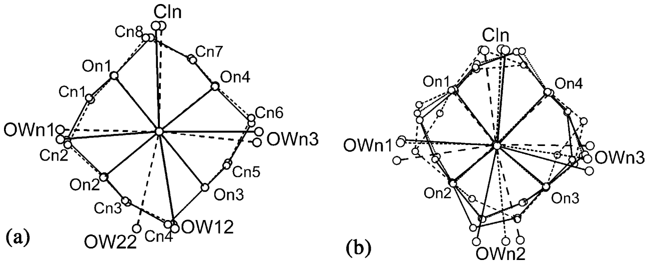

Fig. 1. Views of the superimposed complex cation in $\mathbf{I}_{LT}$ (a) and $\mathbf{I}_{HT}$ (b). The index *n* numbering the respective molecules is 1 (solid bonds), 2 (dashed bonds) or 3 (for $\mathbf{I}_{HT}$ only; dotted bonds). The carbon atom labels not shown in (b) follow the pattern in (a).

together with two molecules of the macrocycle forms a sandwich-type complex cation thus resulting in the coordination number 10 for Eu. Such a coordination mode has been previously reported for Eu(II) complex with benzo-15-crown-5 [31], and is also known for a Ba compound [25], and for several alkali metal complexes [3]. The Eu–O bonds (see Table 3) are generally longer than in **I**, what is undoubtedly connected with the greater coordination number in **II**. As for $\mathbf{I_{LT}}$, the both macrocycles adopt, from the set of the most stable conformations, one which has maximal dipole moment [43] (conformer **3** in the quoted paper). Molecular mechanics calculation show that this is a preferred conformation for the complexes with medium and heavy metals of the first and second groups of the periodic system [44]. The crown conformers are of low symmetry (C_1) and so is the whole complex cation (see Fig. 2). The whole crystal is held together by electrostatic and van der Waals forces, as there are no hydrogen bonds.

3.4. Structure of *III*

This structure is composed of neutral bisperchlorato(*O*,*O′*)(18-crown-6)europium(II) molecules only. The complex may be seen as one with the crown ligand located roughly in the equatorial plane, and two perchlorate anions reaching the metal ion from the opposite poles; surprisingly, the coordination mode is different from that observed in Eu(II) complexes with a similar ligand, benzo-18-crown-6 [32], where three water molecules enter the environment of Eu. Either perchlorate anion is directly bonded to the metal via two of its oxygen atoms. The ClO_4^- anions are rotated 90° with respect to each other, contrary to what was observed in a Ba complex [45]. The Eu–O_{crown} distances (Table 3) resemble those in **II** and also the Eu–$O_{perchlorate}$ are in the same range. In the published structures with six-dentate crown complexes of Sr [46,47] or Ba [43,48], the metal–perchlorate oxygen bonds tend to be shorter, than the metal–crown oxygen ones when the anion is bonded through one O only, and longer if the perchlorate anions coordinates in a bidentate fashion. The macrocycle ring in **III** adopts a rather flat conformation with rough C_3 symmetry. A view of the complex molecule is given in Fig. 3.

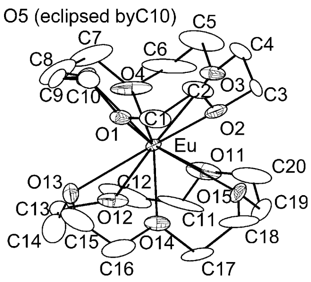

Fig. 2. A view of the complex cation in **II** together with atom numbering scheme.

3.5. Spectroscopy

The emission spectra are shown in Fig. 4. All three compounds are luminescent although at different degrees. Complex **II** is perhaps the most efficient luminophore, whereas **III** shows only a weak emission at 77 K. Complex **I** shows bright blue luminescence which changes into blue–violet on cooling down the sample to 77 K. This change is reversible on warming up. At room temperature, the luminescence shows only one maximum at 429 nm (23 300 cm^{-1}), although at least two Gaussian functions are needed to model reasonably the curve. The maximum is in good agreement with the observed emission maximum for a $EuCl_2$–12-crown-4 system in methanol solution, which was 428 nm [49]. At 77 K, following the phase transition discussed above, the maximum shifts to 410 nm (24 400 cm^{-1}) and, apart from that, a shoulder appears at 422 nm (23 700 cm^{-1}), thus reflecting two crystallographically independent Eu sites. Such a behaviour is contrary to that observed both for the benzo-15-crown [31] complex and for the benzo-18-crown-6 one [32], where the maxima move to longer waves upon cooling the sample. It is difficult to point to any specific structural features which might explain the observed differences between the properties of $\mathbf{I_{LT}}$ and $\mathbf{I_{HT}}$; neither it is possible to associate the particular conformers with the maximum and the shoulder in the luminescence spectrum of $\mathbf{I_{LT}}$. One may tentatively assume that a general reason for the batochromic shift on warming up may be brought about by greater inhomogeneity of the metal coordination environment at room temperature, what in particular includes slightly greater variations of the Eu–O_{water} bond lengths (molecules 2 and 3) and of the Eu–O_{crown} distances (all three molecules). The resulting growth of the inhomogeneity around the metal may increase splitting of the excited $4f^65d$ state with concomitant decrease of the energy of its lowest, emitting level. The excited state may be also sensitive to the subtle molecular rearrangements described above. As it seems the coalescence of

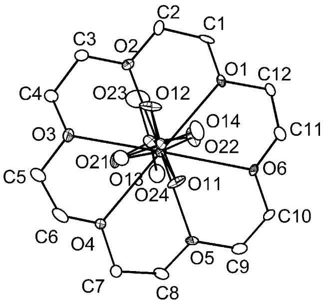

Fig. 3. A view of the molecule in **III** together with atom numbering scheme. The Eu and Cl2 atoms are partially eclipsed by Cl1.

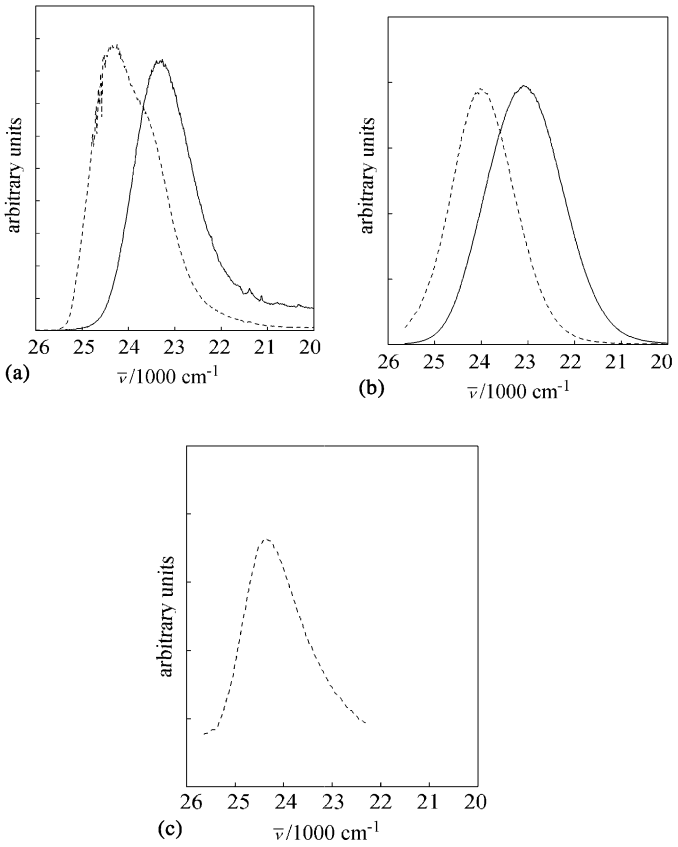

Fig. 4. The emission spectra of polycrystalline samples of **I** (a), **II** (b) and **III** (c). The solid lines represent the room temperature spectra, the dashed ones render those taken at 77 K.

the emission peaks of all Eu sites in $\mathbf{I}_{\mathbf{HT}}$ is fortuitous rather than brought about by a common reason. A similar phenomenon may be observed in **II**: at room temperature, the luminescence maximum was recorded at 433 nm (23 100 cm^{-1}), while on cooling the sample to 77 K it moved to 417 nm (24 000 cm^{-1}). The room temperature emission maximum observed here compares well with the maximum recorded for the EuCl$_2$–15-crown-5 system in a methanolic solution [47,28]; this may suggest close similarity between the complex structure in solution and in crystalline state. It is worth to notice that the temperature shift of the luminescence maximum is more pronounced (and has the opposite direction) in **II** than in related benzo-15-crown-5 complex (422 nm at room temperature, and 426.5 nm at 77 K). This is probably brought about by greater conformational flexibility of the 15-crown-5 molecule, as compared with benzo-15-crown-5, and ensuing from it greater distortions of the metal coordination environment effected by thermal vibrations. The third of the described compounds, **III**, shows only faint luminescence at 77 K. This is a surprise, as the related benzo-18-crown-6 complex is a fairly good luminophore despite the fact that in the latter compound the Eu cation has three water molecules in its first coordination environment. The reason for the quenching is not clear. The maximum of this weak luminescence, located at 411.5 nm (24 300 cm^{-1}), is different from that observed in the quoted benzo-18-crown-6 complex at 77 K (430 nm). The difference of both the coordination and the temperature results in that the emission of the present complex is different from that observed in methanol solutions of EuCl$_2$–18-crown-6 system (446 nm [28,47,50]).

The luminescence decay curves may be regarded as mono-exponential; the respective luminescence lifetimes are presented in Table 4. In **I**, the times are similar to the lifetimes recorded for the crystalline Eu(II)–benzo-15-crown-5 complex (0.65(2) μs at room temperature and 0.59(1) μs at 77 K), and approximately two times longer than the luminescence lifetime found for the methanol solution of the EuCl$_2$–12-crown-4 system (0.3 μs [28,47]). For **II** the times, slightly longer than in the case of **I**, are similar to that recorded for the EuCl$_2$–15-crown-5 system in methanol (0.800 μs [28,47]). This fact, together with the similarity of the respective emission spectra of the solution and the crystals allows to presume that the complex has the same or very similar constitution in both phases, i.e. the sandwich structure.

Curiously enough, the lifetimes of **I** and **II** decrease on lowering the temperature. As no plausible mechanism for increased radiationless decay at low temperatures could be put forward, one may hypothesize that the shortening of the luminescence average lifetime at 77 K is due to growth of the radiative transition probability, which in turn was brought about by rearrangement of the respective coordination environments at that temperature. A clue in favour of such explanation may be found by comparing the low temperature spectrum of **I** ($\mathbf{I}_{\mathbf{LT}}$; see Fig. 4(a)) with the luminescence lifetimes recorded at the above mentioned maximum, and the shoulder. The emission at the maximum (where the radiation from the more intensely luminescing molecules prevails) is shorter lived, than at the shoulder (where the emission from the other conformer contributes more).

The excitation spectra of all the three compounds (Fig. 5) have rather weakly developed structure. In the case of **I** at room temperature, one may found only two distinct features, namely a peak at 28 300 (353 nm) and a flat shoulder at 35 000 cm^{-1} (286 nm), whereas at 77 K

Table 4
Observed luminescence lifetimes in **I** and **II**

Crystals	Temperature	τ (μs)	Emission at (cm^{-1})
$\mathbf{I}_{\mathbf{HT}}$	Room	0.763(9)	23 250
$\mathbf{I}_{\mathbf{LT}}$	77 K	0.576(5)	23 400
$\mathbf{I}_{\mathbf{LT}}$	77 K	0.506(5)	24 400
II	Room	0.922(24)	23 000
II	77 K	0.745(18)	24 000

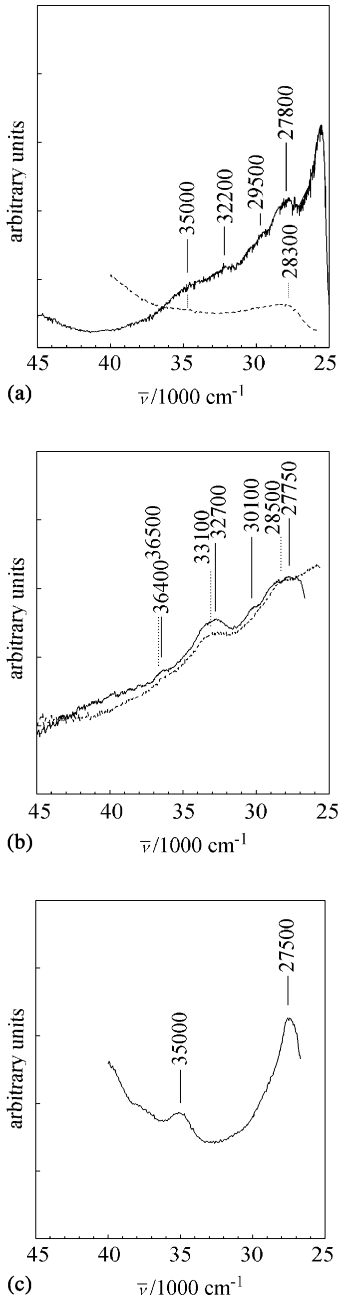

Fig. 5. The excitation spectra of polycrystalline samples of **I** (a), **II** (b) and **III** (c). The solid lines represent the spectra recorded at 77 K, the dashed ones show the room temperature spectra.

a peak at 27 800 cm^{-1} (360 nm), and three shoulders (at 29 500, 32 200 and 35 000 cm^{-1}, or 339, 311 and 286 nm) can be distinguished. For **II** two distinct shoulders at 28 500 and 33 100 cm^{-1} (351 and 302 nm) and a weak one at 36 500 cm^{-1} (274 nm) may be observed at room temperature, and four principal features: a peak at 27 750 cm^{-1} (360.4 nm), a shoulder at 30 100 cm^{-1} (332 nm), a peak at 32 700 (306 nm) and a weak shoulder 36 400 cm^{-1} (275 nm). The peaks at 27 750 and 32 700 cm^{-1} seem to have a composite structure, but perhaps spectra taken at helium temperatures might be helpful to resolve them into their components. The spectrum of **III** is poor—only two peaks at 27 500 (363.6 nm) and at 35 100 cm^{-1} (285 nm) can be identified. Contrary to previously reported Eu(II)–crown complexes there are no minimum at approximately 35 000 cm^{-1}, and the excitation bands start at longer wavelengths (approximately at 250 nm or 40 000 cm^{-1}), than in the case of the benzo-15-crown-5 complex (220 nm or 45 500 cm^{-1}), or for the benzo-18-crown-6 complex (230 nm or 43 500 cm^{-1}). The absence of the minimum, observed in the benzo-crown complexes, suggests that the minimum was brought about by radiation reabsorption effected by the benzo rings. On the whole, the bands in the excitation spectrum lie in the range observed also for Eu^{2+} cations embedded in various inorganic matrices, viz. fluorides and some oxygen containing hosts The 4f^{6}5d states, as seen in the excitation spectra, are somewhat less split in comparison to these states in BaMg$_2$Si$_2$O$_7$ [51] or BaMgAl$_{10}$O$_{17}$ [52] matrices, and experience the crystal field of the strength similar to that observed in MgF$_2$ [53], KMgF$_3$ [54], CaC$_2$O$_4$ or CaCO$_3$ [55]. Generally saying both the emission and excitation spectra imply rather weak ligand fields exercised by the metal ions.

4. Conclusions

1) The f^{6}d configuration is sensitive to subtle rearrangements of the Eu(II) coordination sphere, as it has been demonstrated for trisaquachloro(12-crown-4)europium(II) complex.
2) The sandwich structure of bis(15-crown-5)europium(II) efficiently shields the molecule from the influence of external environment and gives rise to pronounced luminescent properties of this complex.
3) Contrary to the case of the Eu(II)–benzo-18-crown-6 complex, the perchlorate anions enter the first coordination sphere in bisperchlorato(18-crown-6)europium(II), exerting deleterious effect on its luminescent properties.
4) Electrochemical reduction may be useful and convenient synthetic route to Eu(II) compounds.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 188082–188084 and 188140 for compounds **I**$_{\mathbf{HT}}$, **I**$_{\mathbf{LT}}$, **II** and **III**, respectively. Copies of the data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

The author thanks Professor K. Bukietyńska for discussion, Dr Sci. Z Ciunik, for help in X-ray data collection, Dr J. Sokolnicki and MSc. Z Marchewka for luminescence measurements, and Professor W. Ryba-Romanowski and Dr P. Solarz for recording the luminescence decay curves.

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