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Europium(II) complexes with nitrilotriacetic acid (NTA)

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Abstract

The article presents two complexes of divalent Eu with nitrilotriacetic acid. The first of them, polymeric trisaqua(nitrilotriacetato)sesquieuropium hydrate, $[(C_6H_6NO_6)(H_2O)_3Eu_{3/2}] \cdot H_2O$, precipitates during electrochemical reduction from acidic solution. There are two independent Eu^{2+} cations: one is 8-coordinate (six carboxylic oxygen atoms and two water molecules), whereas the other is nine-coordinate (four carboxylic oxygen atoms, four water molecules, and a nitrogen atom). The other complex, hexacaesium bis(nitrilotriacetato)europate(II) dichloride tetrahydrate, $Cs_6[(C_6H_6NO_6)_2Eu]Cl_2 \cdot 4H_2O$, obtained in basic environment, is monomeric. Europium is eight-coordinate (six carboxylic oxygen and two nitrogen atoms) and its environment has an approximate S_6 symmetry. The latter compound displays very weak luminescence with maximum at 483 nm at 77 K.

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1. Introduction

Previously, structures of several Eu(II) carboxylates have been described by various authors (acetates [1–3], a hydroxyacetate [4], a sulfosalicylate [5], a tartrate [6], an ethylenediaminetetraacetate [7], a diethylenetriaminopentaacetate [8] and a few others). These complexes, with the exception of the last one, are polymeric, and the metal cations are usually connected through various carboxylate bridges. Such crystal arrangement could bring about destructive influence on possible luminescence of Eu(II) centers. In fact, we could not excite emission in any of the reported systems [2–7]. Therefore, it was thought interesting to look for a Eu(II) monomeric complex, with a ligand molecule that could provide effective encapsulation of the metal cation, and the nitrilotriacetate $N(CH_2COO)_3^{3-}$ anion was deemed adequate for this task. Encapsulation is regarded as one of important factors that enhance the luminescence efficiency of Eu(II) [9]. For these reasons we embarked on searching for a system that could contain monomeric bis(nitrilotriacetato)europate(II) anions, and accordingly the goal of this work was to

determine the structure of such a system and then to investigate its luminescent properties. Starting this work we expected to weigh up the role of the encapsulation phenomenon, and to find out the influence of the coordination of the carboxylic oxygen and the tertiary nitrogen atoms on efficiency and the band position of europium luminescence. The obtained results are reported in the present article.

2. Experimental

2.1. Preparation

One gram of Eu_2O_3 dissolved in excess of hydrochloric acid, 5.74 g of CsCl and 2.17 g of nitrilotriacetic acid (NTA) was placed in the cathode compartment of an H-shaped electrolyzer with a frit diaphragm and a pool Hg cathode, and diluted (or suspended in the case of NTA) in a few millilitres of water. The anode compartment was filled with a diluted HCl water solution. The catholyte was reduced at a controlled potential (–1.8 V with respect to the saturated calomel electrode) and a mild stream of dinitrogen was passed over the reduced solution to speed up water evaporation. The solution was initially acidic, then white polymeric deposits

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formed. This was a critical moment of the electrolysis, as the junction between the cathode and anode spaces tended to get clogged. With the progress of the electrolysis, but when the solution still remained acidic, formation of yellow crystalline precipitate of trisaqua(nitrilotriacetato)sesquieuropium hydrate, herein-after denoted as **I**, close to the mercury surface, was observed. Then, as the electrolysis continued further, all the deposits dissolved and the solution became basic. Upon water evaporation intense yellow crystals of hexacaesium bis(nitrilotriacetato)europate(II) dichloride tetrahydrate, labeled here as **II**, were formed. A typical run needed 2–3 weeks to be completed.

2.2. X-ray analysis

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, the last calculated from the crystal habits captured from photo scans. 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. In **I** it was possible to localize seven out of eight water hydrogen atoms, whereas no attempt to localize water hydrogen atoms was undertaken in the case of **II**. The refinement was full-matrix with all non-H atoms anisotropic. The temperature factors of C-bonded H atoms were constrained to 1.2 of the factors of the relevant C atoms, while isotropic factors of O-bonded H atoms were refined freely. For both structures the programs used were SHELXS-97 [10] for the solution, SHELXL-97 [11] for the refinement, and DIAMOND [12] for the molecular graphics. The data pertinent to the crystal parameters, data collection and refinement are presented in Table 1.

2.3. Spectroscopy

The luminescence spectra of a polycrystalline sample of **II** were recorded at 77 K only due to very weak emission of the compound at room temperature. The sample was excited by the third harmonic (355 nm) of a Nd³⁺-YAG laser (Continuum Surelite I). The spectrum was recorded using GDM 1000 monochromator and averaged by a Stanford Research Systems 250-boxcar integrator. The luminescence decay curves upon exciting with the same laser radiation were measured (also at 77 K only) with a Tektronix TDS 3052 two channel 500 MHz digital oscilloscope.

Table 1
Crystal data and structure refinement details for **I** and **II**

Compound	I	II
Empirical formula	C ₆ H ₁₄ Eu _{1.5} NO ₁₀	C ₁₂ H ₂₀ Cl ₂ Cs ₆ EuN ₂ O ₁₆
Formula weight	488.12	1468.62
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	C2/c	C2/c
Unit cell dimensions		
<i>a</i> (Å)	17.237(12)	23.92(2)
<i>b</i> (Å)	9.068(6)	8.189(7)
<i>c</i> (Å)	16.216(11)	17.047(14)
β (°)	94.12(6)	94.28(7)
<i>V</i> (Å ³)	2528(3)	3330(5)
<i>Z</i>	8	4
<i>D</i> _{calc} (Mg m ⁻³)	2.565	2.929
Absorption coefficient (mm ⁻¹)	7.444	8.570
<i>F</i> (0 0 0)	1852	2644
Crystal size (mm)	0.2 × 0.2 × 0.1	0.17 × 0.14 × 0.11
θ Range for data collection (°)	3.3–28.4	3.5–28.6
Index ranges	–22 ≤ <i>h</i> ≤ 22, –9 ≤ <i>k</i> ≤ 11, –21 ≤ <i>l</i> ≤ 21	–29 ≤ <i>h</i> ≤ 30, –10 ≤ <i>k</i> ≤ 9, –18 ≤ <i>l</i> ≤ 22
Reflections collected/unique	12 008/2991 (<i>R</i> _{int} = 0.0269)	10 332/3894 (<i>R</i> _{int} = 0.0346)
Completeness of the dataset (%)	44.4	43.0
Absorption correction	analytical, from the shape	analytical, from the shape
Max and min transmission	0.458 and 0.286	0.453 and 0.309
Refinement method	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	2991/0/201	3894/0/177
Goodness-of-fit on <i>F</i> ²	1.283	1.117
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> (<i>F</i>) = 0.0216, <i>R</i> _w (<i>F</i> ²) = 0.0397	<i>R</i> (<i>F</i>) = 0.0435, <i>R</i> _w (<i>F</i> ²) = 0.0767
<i>R</i> indices (all data)	<i>R</i> (<i>F</i>) = 0.0254, <i>R</i> _w (<i>F</i> ²) = 0.0404	<i>R</i> (<i>F</i>) = 0.0740, <i>R</i> _w (<i>F</i> ²) = 0.0856
Largest difference peak and hole (e Å ⁻³)	0.817 and –0.813	2.635 and –1.612

3. Results and discussion

3.1. Structures

In the acidic environment polymeric trisaqua(nitrilotriacetato)sesquieuropium hydrate (**I**) is formed. There are two symmetry independent europium sites in the structure. First of them, Eu1, located in a symmetry center, is eight-coordinate, with six carboxyl and two water oxygen atoms building up the coordination environment of the metal cation. The other europium cation, Eu2, is nine-coordinate, with four carboxyl

oxygen atoms, four water molecules and the nitrogen atom. Eu1 and Eu2 are bridged together by OW1 water molecule and the carboxylic O2 atom, forming thus infinite chains. Water OW3 molecules form bridges between two neighbouring Eu2 atoms, which are in this way linked into di- μ -aqua-europium dimers. The nitrilotriacetate anion is linked to four different Eu cations through its five oxygen atoms and the nitrogen atom; one of the carboxylic oxygen atoms (O6) remains uncoordinated. In such a way a complicated, three-dimensional polymeric network is formed. The crystals are built up from this network and water of hydration (OW4). A fragment of the polymer is shown in Fig. 1.

The compound obtained in basic environment, hexacaesium bis(nitrilotriacetato)europate(II) dichloride tetrahydrate (**II**) is composed of caesium cations, chloride and monomeric bis(nitrilotriacetato)europate(II) anions, and water of hydration. The Eu cation is located in an inversion center and is surrounded by six carboxyl O and two N atoms. The approximate symmetry of the complex anion may be described as S_6 ($\bar{3}$), see Fig. 2 for a view. Analogous bis(nitrilotriacetato) complexes of trivalent lanthanides may be either eight-coordinate (Dy) [13] or nine-coordinate with a water molecule as the ninth ligand (Nd–Ho) [14]. The caesium cations are six- or seven-coordinate (the cut-off criterion for accepting or rejecting a Cs–O separation as a ‘bonding’ was the shortest Cs–C distance,

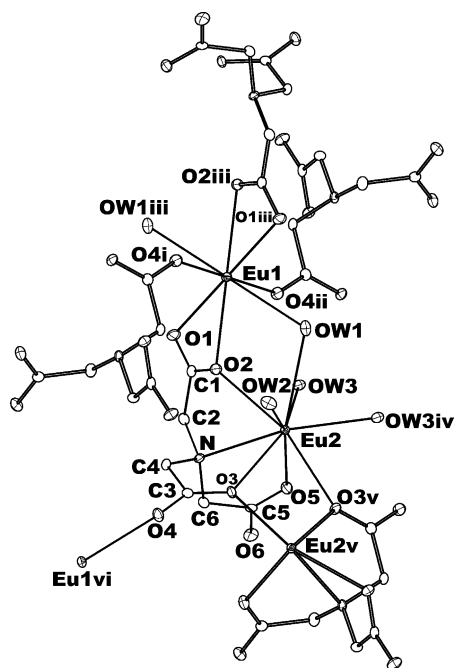


Fig. 1. A fragment of the polymeric network in **I**. The symmetry independent bonds are marked by solid lines and the symmetry generated ones are represented by empty lines. The symmetry codes used are ⁱ $-x+(1/2), y-(1/2), -z+(1/2)$; ⁱⁱ $x, -y+1, z+(1/2)$; ⁱⁱⁱ $-x+(1/2), -y+(1/2), -z+1$; ^{iv} $-x+1, -y+1, -z+1$; ^v $-x+1, y, -z+(1/2)$; ^{vi} $(1/2)-x, (1/2)+y, (1/2)-z$.

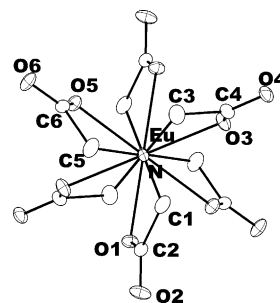


Fig. 2. A view of the complex anion along the N–Eu axis in **II**; Eu and the symmetry related N atom are eclipsed by N. Only symmetry independent atoms have been labeled.

which was 3.45 Å in the present structure). Their nearest surrounding contains three up to five carboxylic oxygen atoms, one or two chloride anions, the rest being water. Half of the water molecules is disordered.

The distances within Eu coordination environments are presented in Table 2 for **I**, and in Table 3 for **II**. They are in general agreement with those reported previously for other Eu(II) complexes with O- and N-donor ligands: trisodium (ethylenediaminetetraacetato)europate(II) chloride heptahydrate [7], two hydrotris(pyrazol-1-yl)borate complexes [15], trisguanidium aqua(diethylenetriaminepentaacetato)europate octahydrate [8] and bis(triethanolamine)europium diperchlorate [16]. However, it is noteworthy to observe elongation of the Eu–O_{water} bonds in **I**, when the water molecules take part in Eu–O–Eu bridges. Formation of bridges also affects the Eu–O_{carboxylic} distances, which are generally longer in **I** than in **II**.

3.2. Spectroscopy of **II**

The rather high approximate symmetry of the complex anion (S_6) and small content of water in the structure would render the compound an interesting subject of spectroscopic investigations. Unfortunately the complex shows only very weak luminescence, which could be effectively recorded only upon excitation with

Table 2
Eu–O and Eu–N distances **I** together with the shortest Eu–Eu separation (Å)

Eu1–O4 ⁱ	2.534(2)	Eu2–O5	2.614(3)
Eu1–O2	2.627(2)	Eu2–O2	2.611(3)
Eu1–O1	2.696(3)	Eu2–OW2	2.616(3)
Eu1–OW1	2.756(3)	Eu2–OW3	2.657(3)
		Eu2–O3	2.678(3)
		Eu2–OW3 ^{iv}	2.720(3)
		Eu2–O3 ^v	2.739(3)
		Eu2–N	2.768(3)
		Eu2–OW1	2.966(3)
		Eu2–Eu2 ^v	4.366(3)

Symmetry transformations used to generate equivalent atoms are those used in Fig. 2.

Table 3
Eu–O and Eu–N distances in **II** (Å)

Eu–O5	2.536(5)
Eu–O3	2.563(5)
Eu–O1	2.583(5)
Eu–N	2.763(6)

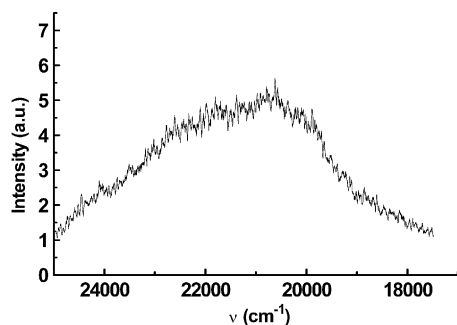


Fig. 3. The luminescence spectrum of **II** at 77 K ($\lambda_{\text{exc}} = 355$ nm).

laser radiation (355 nm) at 77 K. The spectrum (smoothed numerically to get rid of the noise) is presented in Fig. 3. As it may be observed, the emission has the maximum at 20700 cm^{-1} (483 nm) and is shifted towards longer waves as compared with the Eu^{2+} f–d luminescence in halogenide matrices (located approximately in the range 404–445 nm or 24800 – 22500 cm^{-1} (e.g. [17–19])) or in the complexes with such O-donor ligands as crown ethers or polyethylene glycols; (the observed range was 410–467 nm or 24400 – 214000 cm^{-1} [9,20–22]). Presence of the carboxyl group seems to induce slight bathochromic shift of the emission, as it has been demonstrated in the cases of Eu^{2+} -doped Ca carbonate and oxalate (the maxima at approximately 450 nm or 22200 cm^{-1}) [23]. On the other hand, the luminescence peak of the present compound lies well in the range observed for Eu(II) complexes with crown ethers containing tertiary nitrogen atoms (472–488 nm or 21200 – 20500 cm^{-1}) [9]. The shift might be, therefore, at least in part brought about by the donor properties of the ligand N atom, that is by donation of its free electron pair to the unoccupied 5d orbitals of europium. Such a mechanism was recently invoked to explain a large bathochromic shift of Yb(II) emission in alkaline halide matrices doped with cyanide anions [24]. The luminescence lifetime has been estimated as less than $0.1 \mu\text{s}$; this value may be compared with the analogous quantities recorded for crystalline complexes of Eu(II) with crown ethers at 77 K: 0.5 – $8.0 \mu\text{s}$ [20–22]. Such a small value in the present case suggests a dominating role of radiationless processes in the excited state decay. In general, having compared the structural and spectroscopic data for easily luminescing Eu(II) crown ether complexes [20–22] with non- or very weakly-emitting Eu(II) complexes, such as the present

compound (**II**) or other Eu(II) carboxylates [2–7], one may notice a relationship between an average ligand–metal distance and the emission efficiency. Namely shortening of the respective bonds (the Eu–carboxyl O distances being 0.1 – 0.2 \AA shorter than the Eu–crown O distances) seems to favour quenching of the luminescence. Without pretence to offer exhaustive or complete explanation we may suggest that the quenching may take origin both in stronger mixing of the empty 5d metal orbital with matching orbitals of the ligands (in particular the carboxylic oxygen atoms), and by stronger vibronic coupling within the first coordination sphere of europium. The necessary theoretical investigation of the electronic structure of the complex is underway.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC No. 206036 (**I**) and CCDC No. 206035 (**II**). Copies of the data can be obtained free of charge on application to 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>).

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References

- [1] A. Lossin, G. Meyer, *Z. Anorg. Allg. Chem.* 614 (1992) 12.
- [2] P. Starynowicz, *J. Alloys Comp.* 268 (1998) 47.
- [3] P. Starynowicz, *Polyhedron* 14 (1995) 3573.
- [4] P. Starynowicz, *J. Alloys Comp.* 275–277 (1998) 815.
- [5] P. Starynowicz, *J. Alloys Comp.* 305 (2000) 117.
- [6] P. Starynowicz, G. Meyer, *Z. Anorg. Allg. Chem.* 626 (2000) 2441.
- [7] P. Starynowicz, *J. Alloys Comp.* 269 (1998) 67.
- [8] L. Burai, É. Tóth, S. Seibig, R. Scopelliti, A. Merbach, *Chem. Eur. J.* 6 (2000) 3761.
- [9] J. Jiang, N. Higashiyama, K. Machida, G.-y. Adachi, *Coord. Chem. Rev.* 170 (1998) 1.
- [10] G.M. Sheldrick, *SHELXS-97*. Program for Structure Solution, University of Göttingen, 1997.
- [11] G.M. Sheldrick, *SHELXL-97*. Program for Structure Refinement, University of Göttingen, 1997.

- [12] DIAMOND—Visual Crystal Structure Information System, CRYSTAL IMPACT, Postfach 1251, D-53002 Bonn, Germany, 1999.
- [13] Chen Shuying, Liu Zhanliang, Li Du, Wuli Huaxua Xuebao (*Acta Phys.-Chim. Sin.*) 5 (1989) 26.
- [14] P. Starynowicz, *Acta Crystallogr.* C43 (1987) 1509.
- [15] A. Carvalho, Á. Domingos, P.C. Isolani, N. Marques, A. Pires de Matos, G. Vincentini, *Polyhedron* 19 (2000) 1707.
- [16] P. Starynowicz, *J. Alloys Comp.* 323–324 (2001) 159.
- [17] S. Lizzo, A.H. Velders, A. Meijerink, G.J. Dirksen, G. Blasse, *J. Lumin.* 65 (1996) 303.
- [18] C. Wickleder, *J. Alloys Comp.* 300–301 (2000) 193.
- [19] H.J. Seo, W.S. Zhang, T. Tsuboi, S.H. Doh, W.G. Lee, H.D. Kang, K.W. Jang, *J. Alloys Comp.* 344 (2002) 268.
- [20] P. Starynowicz, K. Bukietyńska, *Eur. J. Inorg. Chem.* (2002) 1835.
- [21] P. Starynowicz, K. Bukietyńska, S. Gołąb, W. Ryba-Romanowski, J. Sokolnicki, *Eur. J. Inorg. Chem.* (2002) 2344.
- [22] P. Starynowicz, *Polyhedron* 22 (2003) 337.
- [23] W.-M. Li, T. Hänninen, M. Leskelä, J. Saari, A. Hase, *J. Alloys Comp.* 323–324 (2001) 236.
- [24] C.P. An, V. Dierolf, F. Luty, *Phys. Rev. B* 61 (2000) 6565.