ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2019, Vol. 45, No. 1, pp. 42–46. © Pleiades Publishing, Ltd., 2019.
Russian Text © A.V. Virovets, E.V. Peresypkina, E.V. Cherkasova, T.G. Cherkasova, 2019, published in Koordinatsionnaya Khimiya, 2019, Vol. 45, No. 1, pp. 43–47.

Polymorphism of the Double Octa(ε-Caprolactam)europium(III) Hexa(isothiocyanato)chromate(III) Complex

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Received March 15, 2018; revised May 11, 2018; accepted June 15, 2018

Abstract—A new structural polymorph of the compound $[Eu(\varepsilon\text{-}C_6H_{11}NO)_8][Cr(NCS)_6]$ was isolated from the solid product mixture obtained in the reaction of $EuCl_3$, $K_3[Cr(NCS)_6]$, and ε-caprolactam ($\varepsilon\text{-}C_6H_{11}NO$) in aqueous solution. The crystals were triclinic, space group. $P\bar{1}$, $Z = 2$, $a = 14.2320(4)$ Å, $b = 14.5298(4)$ Å, $c = 17.0014(5)$ Å, $\alpha = 92.4190(10)°$, $\beta = 91.0880(10)°$, $\gamma = 108.4850(10)°$, $V = 3329.39$ Å^3, ρ(calcd.) = 1.454 g/cm^3, $R_1 = 0.0419$ (CIF file CCDC no. 1827162).

Keywords: double complex salt, europium(III), chromium(III), ε-caprolactam, X-ray diffraction, polymorphism

DOI: 10.1134/S1070328419010123

INTRODUCTION

The compound $[Eu(\varepsilon\text{-}C_6H_{11}NO)_8][Cr(NCS)_6]$ (**I**) belongs to the class of double complex salts, which are of interest as precursors for the fabrication of functional, in particular, temperature-sensitive, materials [1–8]. For more than a decade, we have carried out systematic research of double complex salts containing ε-caprolactam (Cpl) as an organic ligand. The structural types of hexa(isothiocyanato)chromates(III) of lanthanide(III) complexes with Cpl were considered in our previous studies [9–11]. Three structural types were found: triclinic, monoclinic, and tetragonal (for the complex $[Eu(\varepsilon\text{-}C_6H_{11}NO)_8][Cr(NCS)_6]$ (**Ia**)). A study of the temperature effect on the crystal structure of complex Ia revealed a phase transition with reversible twinning [11].

The present communication deals with the synthesis and single crystal X-ray diffraction study of the triclinic polymorph of compound **Ib**.

EXPERIMENTAL

The synthesis was carried out according to the general procedure reported in [11] by mixing moderately concentrated aqueous solutions of the complex salt $K_3[Cr(NCS)_6] \cdot 4H_2O$ (0.59 g, 0.001 mol) and europium(III) chloride hexahydrate (0.37 g, 0.001 mol) in the pH range of 4–6 followed by addition of an aqueous solution of Cpl (0.090 g, 0.008 mol). The resulting solution was filtered and subjected to slow crystallization in air under standard conditions. The yield of a mixture of forms **Ia** and **Ib** was 70%.

The chemical analysis data and the IR spectrum of compounds **I** are presented in [11].

X-ray diffraction. Single crystal X-ray diffraction data for **Ib** crystal of 0.206 × 0.112 × 0.025 mm size were obtained at 90 K on a Bruker X8Apex automated four-circle diffractometer equipped with a CCD array detector. The crystals were triclinic, space group $P\bar{1}$, $Z = 2$, $a = 14.2320(4)$, $b = 14.5298(4)$, $c = 17.0014(5)$ Å, $\alpha = 92.4190(10)°$, $\beta = 91.0880(10)°$, $\gamma = 108.4850(10)°$, $V = 3329.39$ Å^3, $F(000) = 1514$, ρ(calcd.) = 1.454 g/cm^3. Altogether 41225 reflections were measured (17876 unique reflections and 13671 reflections with $F_o \geq 4\sigma(F)$) up to $2\theta = 63°$. The absorption corrections were applied by averaging the equivalent reflections by the SADABS program, $T_{\min} = 0.769$, $T_{\max} = 0.967$. The structural model was refined using atom coordinates for the Nd analogue [9]. The refinement was carried out in the full-matrix anisotropic approximation on F^2. The hydrogen atoms were refined geometrically by the riding model. The final R-factors were as follows: $R_1 = 0.0419$ for $F_o \geq 4\sigma(F)$, $wR_2 = 0.0854$, GOOF = 1.043 for all unique reflections (Table 1). The structural data were deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1827162); www.ccdc.cam.ac.uk/data_reguest/cif).

Table 1. Crystal data, X-ray experiment details, and structure refinement details for **Ib**

Parameter	Value
Formula	$C_{48}H_{88}N_8O_8Eu \cdot C_6CrN_6S_6$
M	1457.70
Temperature, K	90.0(2)
Radiation (λ, Å)	MoK_α (0.71073)
System	Triclinic
Space group	$P\bar{1}$
Z	2
a, Å	14.2320(4)
b, Å	14.5298(4)
c, Å	17.0014(5)
α, deg	92.419(1)
β, deg	91.088(1)
γ, deg	108.485(1)
V, Å^3	3329.38(16)
ρ(calcd.), g/cm^3	1.454
μ, mm^{-1}	1.35
F(000)	1514
Crystal size, mm	0.21 × 0.11 × 0.03
Data collection θ range, deg	1.51–31.54
Ranges of reflection indices	$-19 \leq h \leq 20$, $-17 \leq k \leq 20$, $-18 \leq l \leq 24$
Number of measured reflections	41225
Number of unique reflections (R_{int})	17876
Number of reflections with $I > 2\sigma(I)$	13671 (0.042)
Number of refined parameters	757
R_1 ($I > 2\sigma(I)$)	0.042
wR_2 (all reflections)	0.085
GOOF (all reflections)	1.04
Residual electron density (min/max), e/Å^3	−0.72/1.05

RESULTS AND DISCUSSION

Crystallization of mixtures of aqueous solutions of the initial components afforded pale lilac crystals poorly soluble in water, acetone, toluene, and ethanol and readily soluble in DMSO and DMF.

The IR spectroscopic data (cm^{-1}): 2928.8 ν(CN), 825.0 ν(CS), 481.3 σ(NCS) characterize the isothiocyanate group. The shift of the stretching band of the Cpl carbonyl group (1665 cm^{-1}) by 38.3 cm^{-1} to lower frequency attests to formation of the coordination bond between Cpl and europium(III) ions via oxygen [12, 13].

The structure of **Ib** (Fig. 1) was determined by X-ray diffraction. The crystals of **Ib** are isostructural to the crystals of previously studied $[Nd(Cpl)_8]$-$[Cr(NCS)_6]$ [9, 11]. The square antiprism and octahedral coordinations of europium and chromium atoms are retained, as also the crystal packing according to the NaCl motif (Fig. 2). The main difference between structure **Ib** and the tetragonal form of the same compound (**Ia**, [11]) is that in **Ib**, the conformationally flexible Cpl ligands are fully ordered at X-ray diffraction experiment temperature of 90 K. In structure **Ia**, they are markedly disordered, which precludes location of the NH group (Fig. 3). "Freezing" of the disorder in **Ia** by reducing the temperature is impossible, as the crystal undergoes phase transition [11]. Since the chemical compositions of **Ia** and **Ib** are identical, we are dealing with polymorphism, and tetragonal polymorph **Ia** is not transformed to triclinic polymorph **Ib** on cooling. The targeted preparation of a particular polymorph **Ia** or **Ib** is largely a matter of chance, as is often the case with other polymorphs [14,

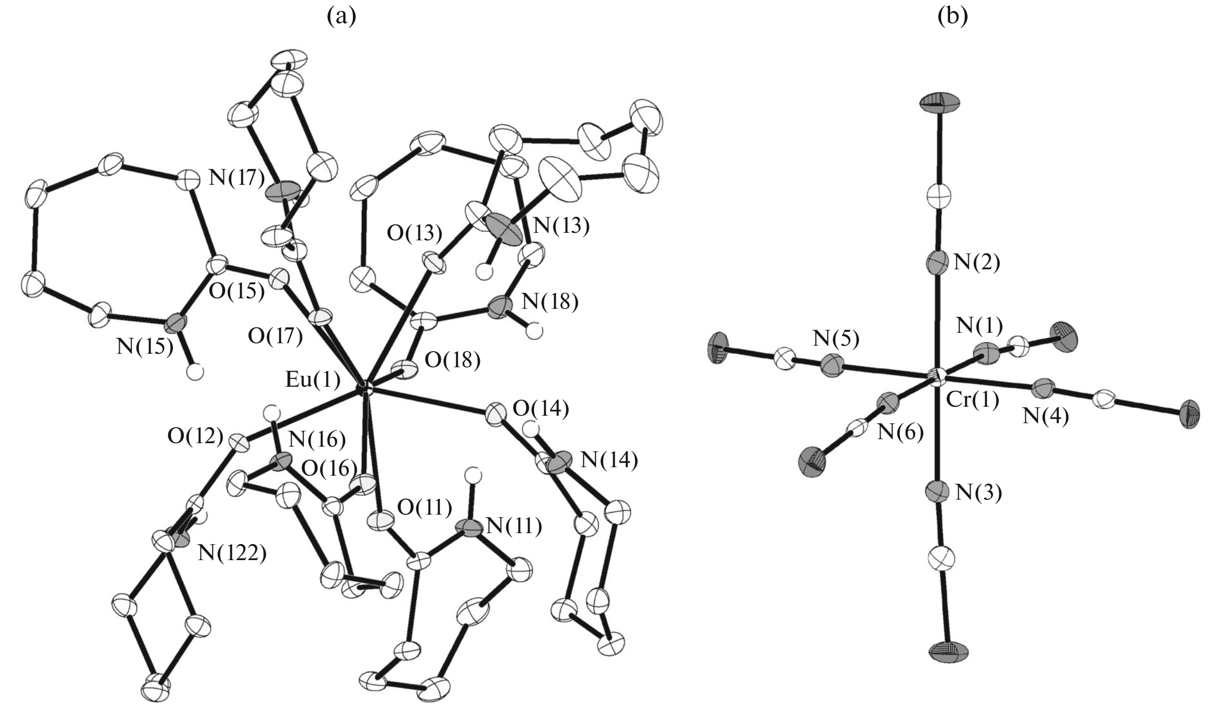

Fig. 1. Structures of (a) cation and (b) anion; atomic displacement ellipsoids are given at 50% probability level. The hydrogen atoms, except for the NH groups, are omitted.

15]. Unfortunately, it is also impossible to find out which polymorph is more stable by comparing their X-ray densities, since the crystallographic data have been obtained at markedly different temperatures (with the difference of almost 200°).

Due to the disorder of the previously determined tetragonal structure, the positions of nitrogen atoms in

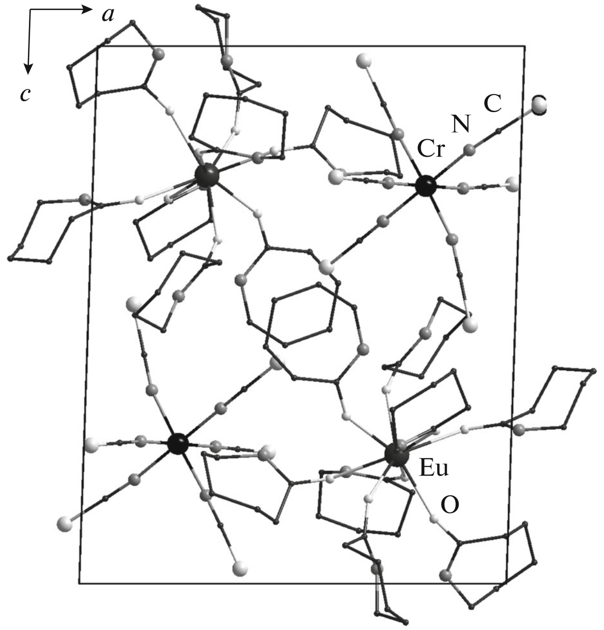

Fig. 2. Packing of ions in the crystal projected along the *b* axis. The hydrogen atoms are omitted.

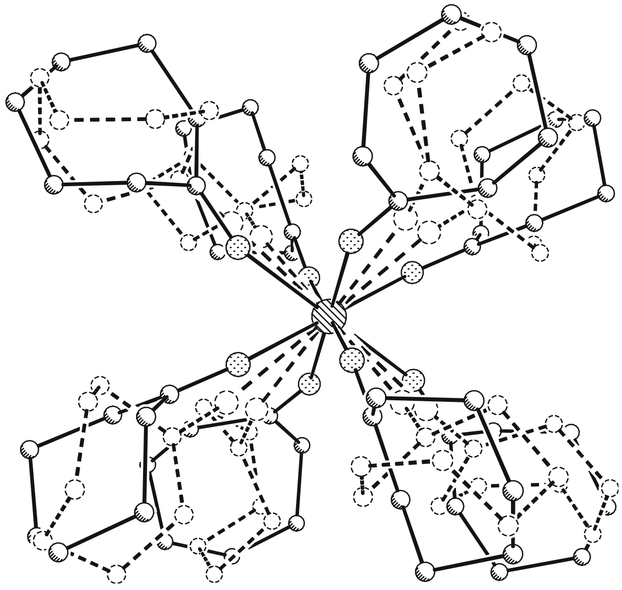

Fig. 3. Cation structure in **Ia** according to data of [11]. The alternative conformations of the Cpl ligands are shown by dashed lines.

Table 2. Selected bond lengths and bond angles in structure **Ib**

Bond	*d*, Å	Bond	*d*, Å
Cr(1)–N(1)	1.989(3)	Eu(1)–O(12)	2.346(2)
Cr(1)–N(6)	1.993(3)	Eu(1)–O(13)	2.399(2)
Cr(1)–N(4)	1.997(3)	Eu(1)–O(14)	2.328(2)
Cr(1)–N(3)	2.001(3)	Eu(1)–O(15)	2.507(2)
Cr(1)–N(2)	2.005(3)	Eu(1)–O(16)	2.410(2)
Cr(1)–N(5)	2.007(3)	Eu(1)–O(17)	2.435(2)
Eu(1)–O(11)	2.431(2)	Eu(1)–O(18)	2.367(2)
Angle	ω, deg	Angle	ω, deg
N(1)Cr(1)N(2)	90.15(11)	O(12)Eu(1)O(11)	71.41(7)
N(1)Cr(1)N(3)	89.85(11)	O(12)Eu(1)O(15)	72.82(7)
N(1)Cr(1)N(4)	88.94(11)	O(12)Eu(1)O(16)	80.46(7)
N(1)Cr(1)N(5)	88.25(11)	O(12)Eu(1)O(17)	91.62(7)
N(2)Cr(1)N(5)	90.51(11)	O(13)Eu(1)O(15)	68.64(7)
N(3)Cr(1)N(5)	89.94(11)	O(13)Eu(1)O(17)	74.81(7)
N(4)Cr(1)N(2)	90.06(10)	O(14)Eu(1)O(11)	80.26(8)
N(4)Cr(1)N(3)	89.49(10)	O(14)Eu(1)O(16)	72.04(7)
N(6)Cr(1)N(2)	91.20(11)	O(16)Eu(1)O(11)	72.12(7)
N(6)Cr(1)N(3)	88.80(11)	O(16)Eu(1)O(17)	73.54(7)
N(6)Cr(1)N(4)	90.61(11)	O(17)Eu(1)O(15)	75.66(7)
N(6)Cr(1)N(5)	92.19(11)	O(18)Eu(1)O(11)	72.97(7)
		O(18)Eu(1)O(15)	74.01(7)

the seven-membered caprolactam ring, as well as the bond lengths in structure **Ia** have been determined inaccurately. For **Ib**, the nitrogen atom positions were determined from bond lengths, which are shorter than the single C–C bonds. The Eu–O bond lengths in the EuO_8 square antiprism vary in the range of 2.328(2)–2.507(2) Å (Table 2) and are consistent (Fig. 4) with the observed trend of bond length variation in the series of lanthanides [11]. Thus, the existence of the triclinic polymorph for compound **I** solves the issue of abnormal behavior of europium in this series.

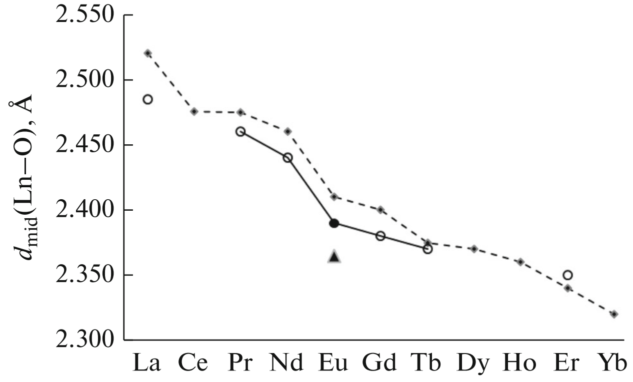

Fig. 4. Dependence of the Ln^{3+} ion radius (for C.N. 8, dashed line) [16], average Ln–O distances (circles) in the complex cations of $[Ln(\varepsilon\text{-}C_6H_{11}NO)_8][Cr(NCS)_6]$ on the lanthanide Ln atomic number. The black triangle designates the value corresponding to **Ia** and the black circle corresponds to the new value for **Ib**.

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Translated by Z. Svitanko