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Lanthanide Complexes Based on 1,3-Dimethylimidazolium-4-Carboxylate: Syntheses and Structures

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Abstract—The reactions of the norzoanemonine zwitterion, 1,3-dimethylimidazolium-4-carboxylate (L), with praseodymium(III), samarium(III), and europium(III) chlorides afford crystals of two types: the isostructural binuclear complexes $[Ln_2(\mu\text{-}C_6H_8N_2O_2)_4(HOCH_3)_4(H_2O)_4]Cl_6$ (Ln = Pr(III) (**I**) and Eu(III) (**II**)) and the dimeric samarium complex $[Sm_2(\mu\text{-}C_6H_8N_2O_2)_4(C_6H_8N_2O_2)_2(H_2O)_5(OCH_3)]Cl_5$ (**III**), which are characterized by X-ray diffraction analysis and IR spectroscopy. In complexes **I**–**III** (CIF files CCDC nos. 1912829 (**I**), 1912830 (**II**), 1912831 (**III**), the metal atoms are bound by four bridging L molecules without forming the metal–metal bond (the M···M distances are 4.595 Å in **I**, 4.4637 Å in **II**, and 4.584 Å in **III**).

Keywords: lanthanide, samarium, europium, praseodymium, norzoanemonine, X-ray diffraction analysis

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INTRODUCTION

The lanthanide complexes containing a zwitterion as the ligand are widely described in the literature. In particular, many complexes of glycine, betaine, and other amino acids are known: monomeric complexes $Nd_2(Gly)_6(ClO_4) \cdot 9H_2O$ [1], $[Ln(Bet)_2(NO_3)_3\text{-}(H_2O)_2]$ (where Ln = La and Sm) [2], and $[Eu(L\text{-proline})_3(H_2O)_3](ClO_4)_3$ [3]; dimeric complexes with the Chinese lantern structure $[Tb_2(L\text{-alanine})_4\text{-}(H_2O)_8](ClO_4)_6$ [4], $[Ln_2(Bet)_8(H_2O)_4](ClO_4)_6$ (where Ln = Eu and Tb), $[Eu_2(Bet)_4(H_2O)_8]Cl_6 \cdot 6H_2O$ [5], and $[Sm_2(C_6H_{13}NO_2)_4(H_2O)_8](ClO_4)_6$ [6]; and tetranuclear heterometallic complexes Cu(II)–Ln(III) with bridging carboxylates $[Cu_2Ln_2\text{-}(Bet)_{10}\text{-}(H_2O)_8](ClO_4)_{10} \cdot H_2O$ (Ln = La, Ce, and Gd) and $[Cu_2Ln_2(Bet)_{12}(ClO_4)_2](ClO_4)_8$, where Ln = Gd, Sm [7]. The dimeric samarium(III) complexes with short peptides $[Sm_2(Gly\text{-}Val)_4(H_2O)_8](ClO_4)_6$ were also synthesized [8]. The coordination polymers of lanthanides with the zwitterionic ligands are known: {[Ln(N-(4-carboxybenzyl)(3,5-dicarboxyl)Py) $\cdot$ $3H_2O$]Cl $\cdot$ xH_2O} (where Ln = Tb, Eu, and Dy) [9] and {[Eu(1,3-bis(pyridinio-4-carboxylato)propane)-$(NO_3)(H_2O)_3$] $\cdot$ $3.5H_2O$} [10]. The coordination compounds of ^{135}Sm were successfully used as radiotherapeutic remedies, which favored the development of the chemistry of coordination compounds of this element [11]. The complex formation of Sm(III) with peptides (diglycine, triglycine, alanylglycine, propylglycine, and other) was illustrated for the formation of the dimeric complex with glycylvaline (Gly-Val) $[Sm_2(Gly\text{-}Val)_4(H_2O)_8](ClO_4)_6$ [12] in which four molecules of coordinated peptides exist in the form of an inner salt and act as the neutral bridging ligand, whereas other coordination sites are occupied with water molecules. The Sm···Sm distance is 4.04(1) Å. In the case of the neodymium(III) chloride complex with diglycine, each metal atom coordinates one halogen atom instead of one water molecule to form the binuclear tetracation $[Nd_2(HGl)_4(H_2O)_6Cl_2]^{4+}$ [13]. The lanthanide complexes with the amidoxime-containing ligands can be used in the highly selective sorption agents for the sorption of uranyl [14]. The Eu(III) complexes gained significant attention due to several factors: biologically appropriate wavelengths of irradiation in the visible range, long lifetimes in the millisecond range, and higher radiation intensities compared to those of the Sm(III) and Dy(III) complexes [15, 16].

The reactions of norzoanemonine betaine, 1,3-dimethylimidazolium-4-carboxylate (L), with praseodymium(III), samarium(III), and europium(III) chlorides are studied in this work.

EXPERIMENTAL

Chemical reagents and solvents were commercially available and used as received. Ligand L was synthesized using a known procedure [17]. An EA3000 CHNS analyzer (EuroVector) was used for chemical analysis. IR spectra were recorded on a Bruker Alpha FT-IR spectrometer with the Platinum ATR attach-

ment for recording attenuated total internal reflectance spectra (ATR).

Synthesis of $[Pr_2(\mu\text{-}C_6H_8N_2O_2)_4(HOCH_3)_4(H_2O)_4]Cl_6 \cdot 4HOCH_3$ (I). A solution of L (0.200 g, 1.43 mmol) in MeOH (2 mL) was added to a pale green solution of $PrCl_3 \cdot 7H_2O$ (0.177 g, 0.47 mmol) in MeOH (2 mL). Light green crystals were formed during the slow condensation of Et_2O vapors into the obtained green solution. The yield of complex **I** was 0.116 g (35%).

For $C_{32}H_{72}N_8O_{20}Cl_6Pr_2$ (FW = 1384) solvate with $4CH_3OH$			
Anal. calcd., %	C, 27.78	H, 5.25	N, 8.10
Found, %	C, 28.07	H, 4.83	N, 7.98

IR (ν, cm^{-1}): 3306 m.br, 3077 m.br, 1668 m, 1555 m, 1467 m, 1447 m, 1420 s.br, 1390 m, 1331 vs, 1244 w, 1155 m, 1089 w, 1026 w, 880 w, 827 w, 783 m, 737 w, 616 s, 557 s.br, 432 vs.

Synthesis of $[Sm_2(\mu\text{-}C_6H_8N_2O_2)_4(C_6H_8N_2O_2)_2(H_2O)_5(OCH_3)]Cl_5$ (II). A solution of L (0.200 g, 1.43 mmol) in MeOH (2 mL) was added with stirring to a colorless solution of $SmCl_3 \cdot 6H_2O$ (0.176 g, 0.47 mmol) in MeOH (2 mL). Light yellow crystals were formed during the slow condensation of Et_2O vapors into the obtained colorless solution. The yield of complex **II** was 0.18 g (36%).

For $C_{37}H_{61}N_{12}O_{18}Cl_5Sm_2$ (FW = 1440)			
Anal. calcd., %	C, 30.86	H, 4.26	N, 11.67
Found, %	C, 30.84	H, 4.13	N, 11.53

IR (ν, cm^{-1}): 3294 m.br, 3076 m.br, 1676 m, 1608 m.br, 1555 m, 1447 m, 1420 s.br, 1389 m, 1332 s, 1245 w, 1155 m, 1088 w, 1025 w, 882 w, 827 w, 784 m, 738 m, 613 s, 558 s.br, 433 vs, 407 s.

Synthesis of $[Eu_2(\mu\text{-}C_6H_8N_2O_2)_4(HOCH_3)_4(H_2O)_4]Cl_6 \cdot 4HOCH_3$ (III). A solution of L (0.200 g, 0.143 mmol) in MeOH (2 mL) was added to a pink solution of $EuCl_3 \cdot 6H_2O$ (0.175 g, 0.47 mmol) in MeOH (2 mL), and the mixture was stirred for 30 min. Pale yellow crystals were were formed during the slow condensation of Et_2O vapors into the obtained pink solution. The yield of complex **III** was 0.16 g (52%).

For $C_{32}H_{72}N_8O_{20}Cl_6Eu_2$ (FW = 1406) solvate with $4CH_3OH$			
Anal. calcd., %	C, 27.34	H, 5.16	N, 7.97
Found, %	C, 27.55	H, 4.72	N, 7.63

IR (ν, cm^{-1}): 3296 m.br, 3076 m.br, 2958 m, 2828 w, 1667 m, 1558 m, 1450 m, 1425 m, 1336 m, 1247 w, 1158 m, 1093 w, 1021 w, 880 w, 829 w, 780 m, 737 m, 620 c, 568 s.br, 422 vs.

X-ray diffraction analysis was carried out on a Bruker APEX II CCD diffractometer. An absorption correction was applied by the method of multiple measurements of equivalent reflections using the SADABS program [18]. The structures of complexes **I**–**III** were determined using the SHELXT program [19] and refined by least squares for F^2 in the anisotropic approximation of non-hydrogen atoms using the SHELX-2014 [19] and OLEX2 [20] program packages. The positions of the hydrogen atoms in the coordinated water molecules were refined with restraints of the O–H distances (0.82 Å) and isotropic thermal parameters $1.5U_{iso}(O)$. Positions of other hydrogen atoms were calculated geometrically. The crystallographic data and refinement parameters for the structures of complexes **I**–**III** are presented in Table 1. Selected bond lengths and bond angles are given in the figure captions to Figs. 1 and 2. The structural contribution of disordered molecules of the solvate solvent in the crystal of complex **I** was removed using the SQUEEZE procedure implemented in the PLATON program [21]. The coordinates of the disordered atoms of the ligand in complex **II** were refined using the restraints for distances and thermal parameters (SAME and DELU instructions).

The coordinates of atoms and other parameters of the structures were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1912829 (**I**), 1912830 (**II**), and 1912831 (**III**); http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The reaction of zwitterion L with praseodymium(III) chloride in methanol affords binuclear complex **I** in which, according to the X-ray diffraction data (Fig. 1), four asymmetric betaine molecules L act as bridging ligands between two lanthanide atoms to form the inversion center in a molecule of complex **I**. The Pr···Pr distance (4.595 Å) indicates that the metal–metal bond is absent. In dimeric praseodymium carboxylates, this value is usually lower due to triply bound carboxylate anions: 3.975 Å in the propionate complex $Pr_2(\mu\text{-}EtCOO)_4(Phen)_2(NO_3)_2$ (Phen is phenanthroline) [22] and 4.023 Å in the cymanthrenecarboxylate complex $Pr_2(\mu\text{-}OOCCym)_4(Glyme)_2(NO_3)_2$ (Glyme is $CH_3OCH_2CH_2OCH_3$) [23]. In the neodymium betaine complex $[Nd_2(Gly)_6](ClO_4)_6 \cdot 9H_2O$ [1], two glycine molecules are monodentate ligands, two molecules are bound to the metal atoms as μ_2-bridging substituents, and two molecules form three Nd–O bonds. The coordination polyhedron of the metal atom is a square antiprism. The lengths of the Pr–O bonds with coordinated L range from 2.3961(16) to 2.5185(17) Å, those of Pr–O(H_2O) are 2.5284(18) and 2.5169(17) Å, and the Pr–O($HOCH_3$) bonds are 2.5102(16) and 2.5185(17) Å. In the IR spectrum of complex **I**, the frequency of the asymmetric vibrations of the coordinated carboxyl group

Table 1. Crystallographic data and structure refinement parameters for complexes **I**–**III**

Parameter	Value		
	I	**II**	**III**
FW	1407.44	1439.92	1405.6
Radiation (λ, Å)		MoK_α (λ = 0.71073)	
Temperature, K	150(2)	150(2)	150(2)
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a, Å	11.4701(3)	10.7250(2)	11.3451(2)
b, Å	14.3642(4)	12.8478(2)	14.2460(3)
c, Å	17.2225(4)	14.2666(2)	17.0971(3)
α, deg	90	114.611(1)	90
β, deg	97.441(1)	91.946(1)	97.631(1)
γ, deg	90	111.207(1)	90
V, Å^3	2813.66(13)	1626.21(5)	2738.80(9)
Z	2	1	2
ρ_{calc}, g/cm^{-3}	1.661	1.470	1.704
μ, mm^{-1}	2.066	2.058	2.635
F(000)	1408.0	720.0	1416.0
Range of θ, deg	4.038–65.59	4.682–65.684	4.606–65.538
Scan mode		ω	
Independent reflections (N_1)	8948 (R_{int} = 0.0381)	9707 (R_{int} = 0.0316)	8484 (R_{int} = 0.0425)
Reflections with $I > 2\sigma(I)$ (N_2)	7992	8816	7439
Number of refined parameters	326	476	340
GOOF (F^2)	1.163	1.067	1.104
R_1 for N_2	0.0311	0.0281	0.0377
wR_2 for N_1	0.0677	0.0627	0.0794
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.89/–0.97	0.84/–0.72	1.50/–1.49

(1668 cm^{-1}) is shifted to the high-frequency range over that of the initial betaine (1610 cm^{-1}).

The reaction of L with samarium(III) chloride affords dimeric complex **II** containing the betaine molecules bound via the monodentate mode (one molecule at each samarium atom) along with four bridging betaine molecules. One methanol molecule is deprotonated to form the coordinated alcoholate ligand. The water molecule builds up the coordination polyhedron of lanthanides to a square antiprism (Fig. 2). The Sm···Sm distance (4.584 Å) in complex **II** also indicates the absence of the metal–metal bond. The Sm–O bond lengths with coordinated bridging molecules L range from 2.360 to 2.420(17) Å: for the monodentate ligand, Sm–O is 2.391 Å; Sm–O(H_2O) are 2.446(18) and 2.466(17); and Sm–O($HOCH_3$) is 2.454(16) Å. In the IR spectrum of complex **II**, the frequency of the asymmetric vibration of the coordinated ligand is more strongly shifted to the high-frequency range due to the ligand coordinated via the monodentate mode (to 1676 cm^{-1}).

The reaction of L with europium(III) chloride in methanol affords binuclear complex **III** isostructural to complex **I**. The Eu···Eu distance is 4.4637 Å. In the IR spectrum of complex **III**, the frequency of the asymmetric vibration of the carboxyl group of coordinated betaine is also shifted to the high-frequency range (1667 cm^{-1}).

In all synthesized compounds **I**–**III**, betaine molecule L acts as a neutral bridging ligand between the lanthanide atoms to form the cationic complexes that can be used as frameworks for the formation of heterometallic compounds.

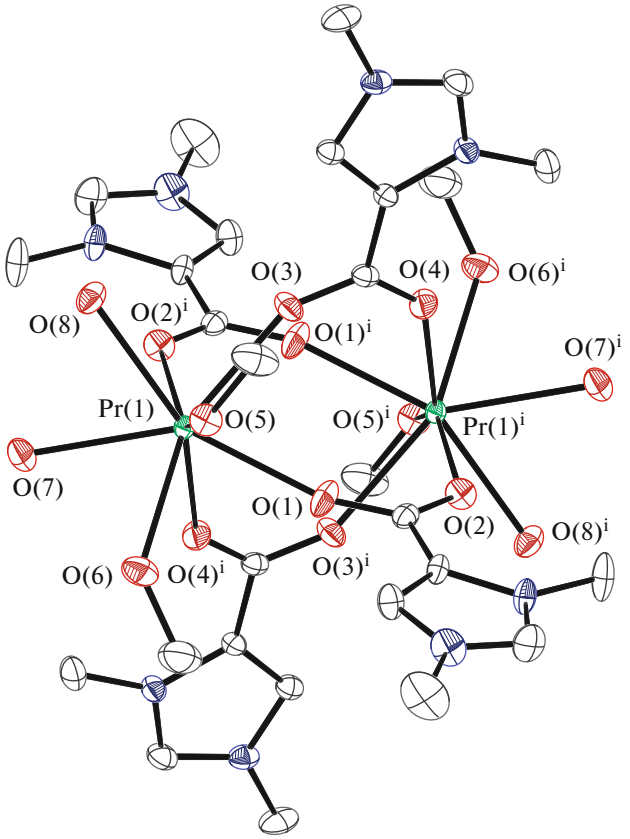

Fig. 1. Molecular structures of cations **I** and **III** (isostructural). Hydrogen atoms are omitted for clarity. Selected bond lengths and bond angles (**I**): Pr(1)–O(1) 2.3961(16), Pr(1)–O(2) 2.4369(16), Pr(1)–O(3) 2.4080(15), Pr(1)–O(4) 2.4295(16), Pr(1)–O(5) 2.5102(16), Pr(1)–O(6) 2.5185(17), Pr(1)–O(7) 2.5284(18), Pr(1)–O(8) 2.5169(17) Å and O(1)Pr(1)O(2) 119.20(6)°, O(1)Pr(1)-O(3) 75.56(6)°, O(1)Pr(1)O(4) 75.08(6)°, O(1)Pr(1)O(5) 76.09(6)°, O(1)Pr(1)O(6) 77.55(6)°, O(1)Pr(1)O(7) 143.88(6)°, O(1)Pr(1)O(8) 142.31(6)°, O(2)Pr(1)O(5) 146.98(5)°, O(2)Pr(1)O(6) 139.89(6)°; (**III**): Eu(1)–O(4) 2.313(3), Eu(1)–O(5) 2.393(3), Eu(1)–O(2) 2.319(2), Eu(1)–O(1) 2.280(3), Eu(1)–O(3) 2.298(2), Eu(1)–O(8) 2.394(3), Eu(1)–O(6) 2.404(3), Eu(1)–O(7) 2.393(3) Å and O(4)Eu(1)Eu(1) 63.69(6)°, O(4)Eu(1)O(5) 139.19(9)°, O(4)Eu(1)O(2) 73.96(9)°, O(4)Eu(1)O(8) 141.49(9)°, O(4)Eu(1)O(6) 76.98(10)°, O(4)Eu(1)O(7) 78.58(10)°, O(4)Eu(1)C(7) 69.58(9)°.

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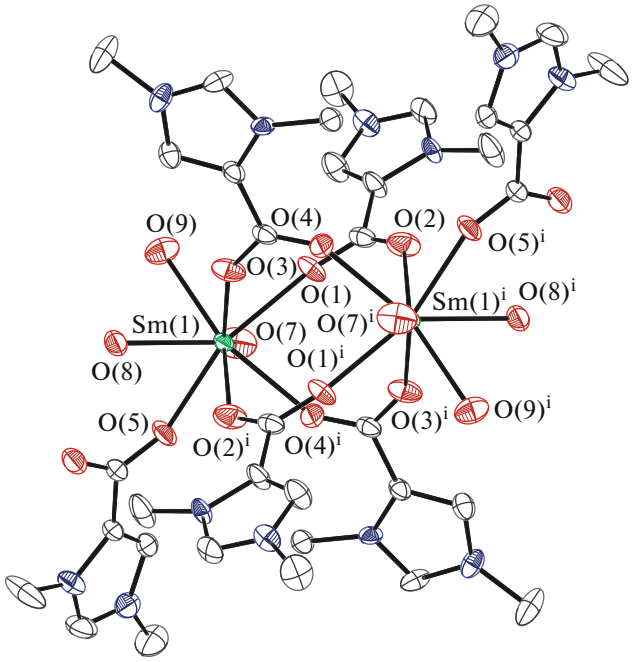

Fig. 2. Molecular structure of complex **II**. Hydrogen atoms are omitted for clarity. Selected bond lengths and bond angles: Sm(1)–O(1) 2.3854(16), Sm(1)–O(2) 2.4201(17), Sm(1)–O(3) 2.3599(16), Sm(1)–O(4) 2.3858(17), Sm(1)–O(5) 2.3912(15), Sm(1)–O(7) 2.4665(19), Sm(1)–O(8) 2.4465(17), Sm(1)–O(9) 2.4544(18) Å and O(1)Sm(1)O(2) 120.15(7)°, O(1)Sm(1)O(4) 77.83(6)°, O(1)Sm(1)O(5) 142.85(6)°, O(1)Sm(1)O(7) 74.30(7)°, O(1)Sm(1)O(8) 140.17(6)°, O(1)Sm(1)O(9) 80.35(7)°, O(2)Sm(1)O(7) 139.59(7)°, O(2)Sm(1)O(8) 73.08(7)°, O(2)Sm(1)O(9) 144.61(7)°.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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