

Dedicated to O.N. Chupakhin in celebration of his 90th birthday

Samarium(III) Complex Based on 5-Phenyl-2,2'-bipyridine with the Diethylenetriaminotetraacetic Acid Residue in the C6 Position: Synthesis, Crystal Structure, and Photophysical Properties

A. P. Krinochkin^{a, b, *}, S. E. Vatolina^a, V. S. Gaviko^{a, c}, I. A. Litvinov^d, M. I. Valieva^{a, b},
Ya. K. Shtaitz^a, S. S. Rybakova^a, D. S. Kopchuk^{a, b},
G. V. Zyryanov^{a, b}, and V. L. Rusinov^{a, b}

^a Ural Federal University, Yekaterinburg, Russia

^b Postovsky Institute of Organic Synthesis, Ural Branch, Russian Academy of Sciences,
Yekaterinburg, Russia

^c Mikheev Institute of Metal Physics, Ural Branch, Russian Academy of Sciences,
Yekaterinburg, Russia

^d Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences,
Kazan, Russia

*e-mail: a.p.krinochkin@urfu.ru

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Abstract—New samarium complex of 5-phenyl-2,2'-bipyridine with the diethylenetriaminotetraacetic acid (DTTA) residue in the C6 position, $[(L_2)Sm_2Na_5(H_2O)_9(C_2O_4)]_n$ (I), is synthesized. The structure of complex I is studied by XRD (CIF file CCDC no. 2217968). The complex in the crystal is found to be a one-dimensional coordination polymer, and the 2,2'-bipyridine fragments do not chelate the Sm^{3+} cation. The complex is characterized by a luminescence response to the addition of an excess of zinc cations.

Keywords: samarium(III) complexes, 2,2'-bipyridines, diethylenetriaminotetraacetic acid, luminescence, XRD, coordination polymer

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INTRODUCTION

Luminescent water-soluble complexes of lanthanide(III) cations are of interest from the viewpoint of phosphorescence immunoassay [1, 2] as sensors to metal cations [3] and singlet oxygen [4]. 2,2'-Bipyridines with a polyaminocarboxylic acid (DTTA or DO3A) residue in the α position attached via the methylene bridge can be used as ligands for lanthanide(III) cations [5, 6]. The structure of the ligand is caused by the coordination number of the lanthanide(III) cation equal to 9 and by its rigid character. In particular, our research group carried out a number of works on the synthesis of the ligands for lanthanide(III) cations of this type based on (di)aryl-containing bipyridines and studying the photophysical properties of their complexes [7–9]. 5-Aryl-2,2'-

bipyridines with the DTTA residue in the C6 position were used as ligands, since their complexes with the europium(III) cation showed the characteristic luminescence of Eu^{3+} with the quantum yield up to 12.8% [10]. In this work, we present unexpected XRD results for the samarium(III) cation complex $[(L_2)Sm_2Na_5(H_2O)_9(C_2O_4)]_n$ (I) based on one of the ligands of this series, namely, 5-phenyl-2,2'-bipyridine with the DTTA residue in the C6 position (L).

EXPERIMENTAL

UV spectra were recorded on a UV-2600 spectrophotometer (Shimadzu). Luminescence spectra were detected on a Cary Eclipse spectrofluorimeter (Varian) and corrected using the implemented software to the instability of the excitation source and

nonlinearity of the detector. Mass spectra (electrospray ionization) were measured on an Agilent 6545 Q-TOF LC-MS instrument (Agilent Technologies). Elemental analysis was conducted on a PE 2400 II CNH analyzer (Perkin Elmer). Ligand L was synthesized according to a described procedure [10]. Distilled water and methanol (reagent grade) served as solvents.

Synthesis of complex $[(L_2)Sm_2Na_5(H_2O)_9(C_2O_4)]_n$ (I). Ligand L (23 mg, 0.03 mmol) was dissolved in water (8 mL), and NaOH (9.4 mg, 0.24 mmol) was added to the solution. Salt $SmCl_3 \cdot 6H_2O$ (10.9 mg, 0.03 mmol) was added to the resulting solution, and the formed mixture was concentrated at room temperature for 2 h. Then the solvent was removed under reduced pressure. The product was extracted from the residue with hot methanol (3×20 mL). An undissolved moiety was filtered off, and methanol was removed from the filtrate under reduced pressure. The yield was 17 mg (0.020 mmol, 68%). ESI-MS, m/z (I_{rel} , %): found 727.12; calculated 727.12 $[M-Na]^-$.

For $C_{60}H_{76}N_{10}O_{29}Na_5Sm_2 \cdot 18H_2O$

Anal. calcd., %	C, 33.66	H, 5.27	N, 6.54
Found, %	C, 33.51	H, 5.45	N, 6.35

The crystals of complex I suitable for XRD were prepared by the slow evaporation of the solution in H_2O .

XRD of complex I was carried out using the equipment of the Center for Collective Use "Testing Center of Nanotechnology and Advanced Materials" at the Mikheev Institute of Metal Physics (Ural Branch of the Russian Academy of Sciences). XRD experiment was carried out for a platy beige-colored crystal $0.280 \times 0.190 \times 0.060$ mm in size on a Rigaku XtaLAB Synergy automated four-circle diffractometer with a CCD detector using a standard procedure (MoK_α radiation, graphite monochromator, ω scan mode with an increment of 1°) at $T = 295(2)$ K. The data of measured reflections were indexed, integrated, and scaled using the CrysAlisPro software. The structure was solved by a direct method using the SHELXT program [11] and refined by least squares for F^2 using the SHELXL program [12]. Non-hydrogen atoms were refined in the anisotropic approximation. The hydrogen atoms at the nitrogen and oxygen atoms were revealed from the difference Fourier synthesis. All other hydrogen atoms were placed in the calculated positions according to the stereochemical criteria and refined by the riding model. The crystal contains large free volumes of $1062.8 \text{ \AA}^3$ (24% per unit cell) in which solvate molecules were not revealed and refined and, hence, the refinement with disordered solvent using

the SQUEEZE procedure in the PLATON program was used [13]. The calculated free volumes of the unit cell were found to contain 27 solvate water molecules.

The main crystallographic parameters of compound I: crystal $C_{60}H_{58}N_{10}Na_5O_{20}Sm_2 \cdot 9(H_2O)$ [+ water], monoclinic crystal system, space group $P2_1/n$, $Z = 2$, at 295 K; $a = 18.6930(4)$; $b = 9.9504(2)$; $c = 24.1619(6) \text{ \AA}$, $\beta = 101.415(2)^\circ$, $V = 4405.28(17) \text{ \AA}^3$, $\rho_{calc} = 1.349 \text{ g/cm}^3$, $\mu = 1.410 \text{ mm}^{-1}$. Detection range $2.3^\circ < \theta < 26.4^\circ$, 638243 measured reflections, 9013 independent reflections ($R_{int} = 0.283$), of them 7073 observed reflections with $I > 2\sigma(I)$. The final R factors: $R_1 = 0.0756$, $wR_2 = 0.1416$ for observed reflections with $I > 2\sigma(I)$, $R_1 = 0.0968$, $wR_2 = 0.1505$ for all reflections, goodness-of-fit $GOOF = 1.13$. The residual electron density peaks: $1.87/-0.67 \text{ e \AA}^{-3}$.

The XRD results were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 2217968; deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

RESULTS AND DISCUSSION

We have previously described the synthesis of ligand L by the modification of its 3-(2-pyridyl)-1,2,4-triazine precursor [10]. Complex I was also synthesized according to a described procedure by the reaction of tetrasodium salt of ligand L prepared in situ with samarium chloride [10]. The crystals of complex I suitable for XRD were prepared by the slow evaporation of its aqueous solution. It is found that the structure of complex I does not correspond to that expected according to earlier published data [7, 9]. In particular, XRD was conducted for one of the complexes based on the DO3A-containing ligand. In this case, the 2,2'-bipyridine and DO3A fragments were simultaneously involved in the chelation of the europium(III) cation [7], namely, complex I represents a complicated polynuclear structure forming one-dimensional coordination polymer (Scheme 1). The "monomeric unit" of this polymer is the centrosymmetric decanuclear fragment formed by three sodium atoms and two samarium(III) atoms. The geometry of the fragment is shown in Figs. 1 and 2.

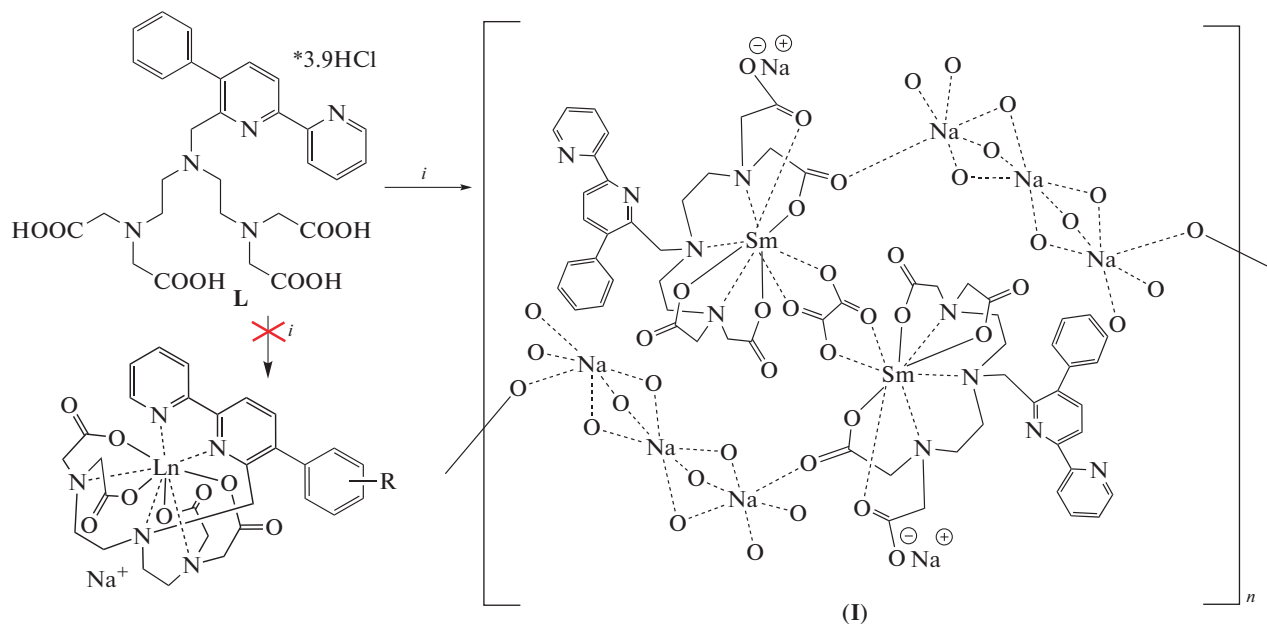
The central moiety of the unit is formed by three sodium cations, one of which is localized at the symmetry center (Fig. 3). The sodium cations are octahedral and surrounded by water molecules. The central ion is coordinated by the water molecules that are bridging between it and terminal sodium ions. The terminal sodium cations are linked with four water molecules (three of which are bridging) and two oxygen

atoms of the amino acid fragments belonging to different samarium complexes.

As for the correspondence of charges in complex **I**, there are nine positive charges (2Sm^{3+} , 3Na^+) and the following negative charges: 2L^{4-} , C_2HO_4^- ; i.e., totally 9^- . The $[\text{Na}_3(\text{H}_2\text{O})_8\text{O}_4]^{3+}$ cation coordinates two deprotonated hydroxyl groups and two carbonyl groups of four ligands (O(2) and O(7) atoms of two different ligands; i.e., this is the fragment joining the complexes into the coordination polymer), whereas the $[\text{Na}_3(\text{H}_2\text{O})_8\text{O}_4]^+$ fragment becomes a single-charge cation, and this charge is neutralized by the single-charge oxalic acid anion. The $[\text{Na}_3(\text{H}_2\text{O})_8\text{O}_4]^+$ cation immediately coordinates four adjacent complexes. Figure 1 shows that the oxalic acid molecule binds two $\{\text{SmL}\}$ fragments, whereas the $[\text{Na}_3(\text{H}_2\text{O})_8\text{O}_4]$ fragment binds four molecules of the complex. Owing to this, the one-dimensional coordination polymer is formed in the crystal. In this case, the hydroxyl group of the oxalic acid molecule is disordered by the symmetry center between two samarium cations. As a result, the positive and negative charges in the structure compensate each other, but two samarium complexes linked via the acid molecules

form a single-charge anion that compensates the charge of the $[\text{Na}_3(\text{H}_2\text{O})_8\text{O}_4]^+$ cation.

The refinement of the structure shows that the crystal has large cavities in which no solvate molecules were found: the difference Fourier series of the electron density contain no strong peaks that could be assigned to solvate molecules. The structure was further refined using the SQUEEZE procedure (refinement with disordered solvent). The volume of the cavities in the crystalline cell is $1062 \text{ \AA}^3$ or 24% of the cell volume. Four approximately cylindrical channels with the channel diameter about $6 \text{ \AA}$ falls onto the cell. This free volume can contain up to 27 water molecules (up to seven molecules in the asymmetric part of the crystal), and the calculated density of the crystal and the linear absorption coefficient do not correspond to real parameters. Since the crystal was grown in an aqueous medium, it seems most probable that the cavities mainly contain water molecules that have no fixed positions and do not contribute to the structural amplitudes and intensities of measured reflections (Fig. 4). The cavities are infinite channels along the crystallographic axis b , and in these channels small molecules can migrate rather freely without crystal ordering formation.



Scheme 1. Reagents and conditions: NaOH , H_2O , T_{room} , then $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$, T_{room} , 2 h.

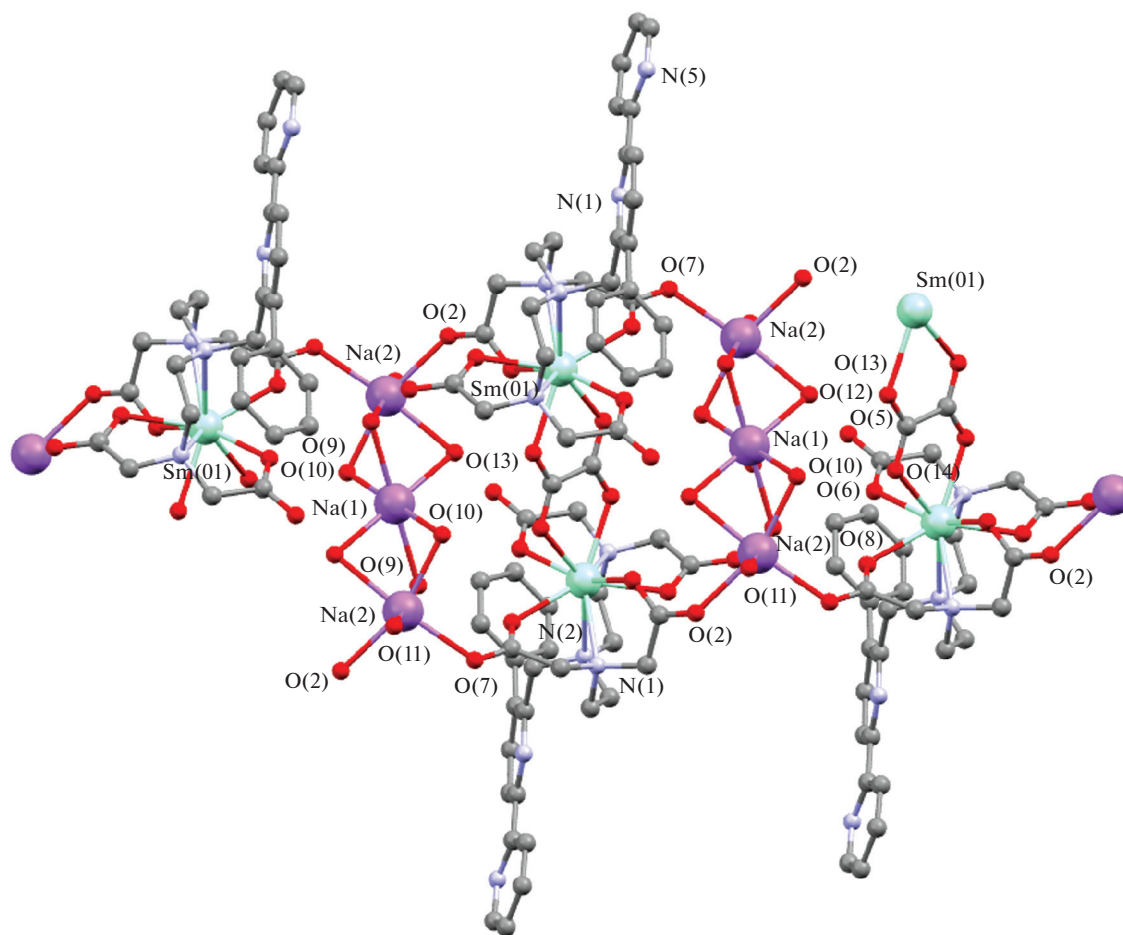


Fig. 1. Fragment of the coordination polymer of complex **I** in the crystal. Sodium atoms are shown by violet, samarium atoms are light green, oxygen atoms are red, nitrogen atoms are shown by blue, and carbon atoms are gray-colored. Hydrogen atoms are omitted for clarity.

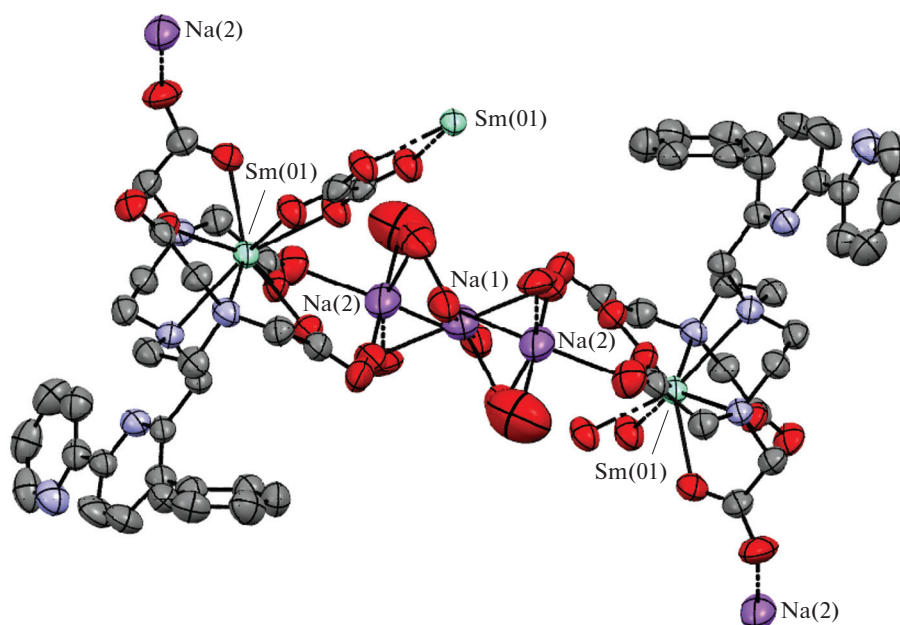


Fig. 2. Geometry of the "monomeric unit" of coordination polymer **I**. Ellipsoids of anisotropic displacements are shown with 50% probability. Sodium atoms are shown by violet, samarium atoms are light green, oxygen atoms are red, nitrogen atoms are shown by blue, and carbon atoms are gray-colored. Hydrogen atoms are omitted for clarity.

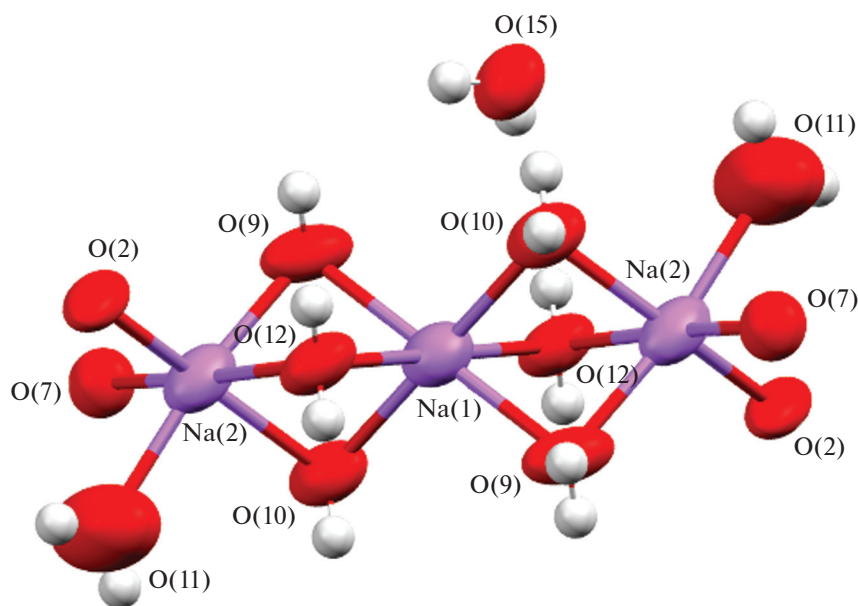


Fig. 3. Coordination of the central fragment (Na_3O_{12}) of complex I: the O(2) and O(7) atoms are in the amino acid ligands, and the remained oxygen atoms belong to the water molecules. Hydrogen atoms are shown as white spheres of arbitrary radii, and the identified and refined molecule of water of crystallization (O(15) atom) is shown.

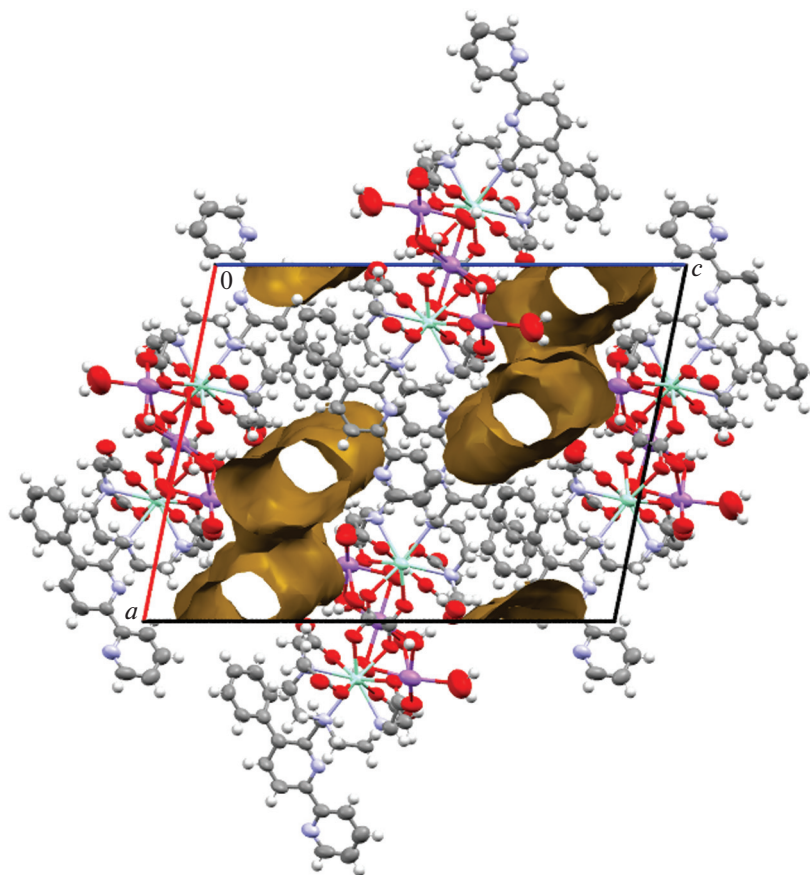


Fig. 4. Packing fragment of complex I in the crystal. Free volumes (VOIDS) (projection along the b axis) are shown.

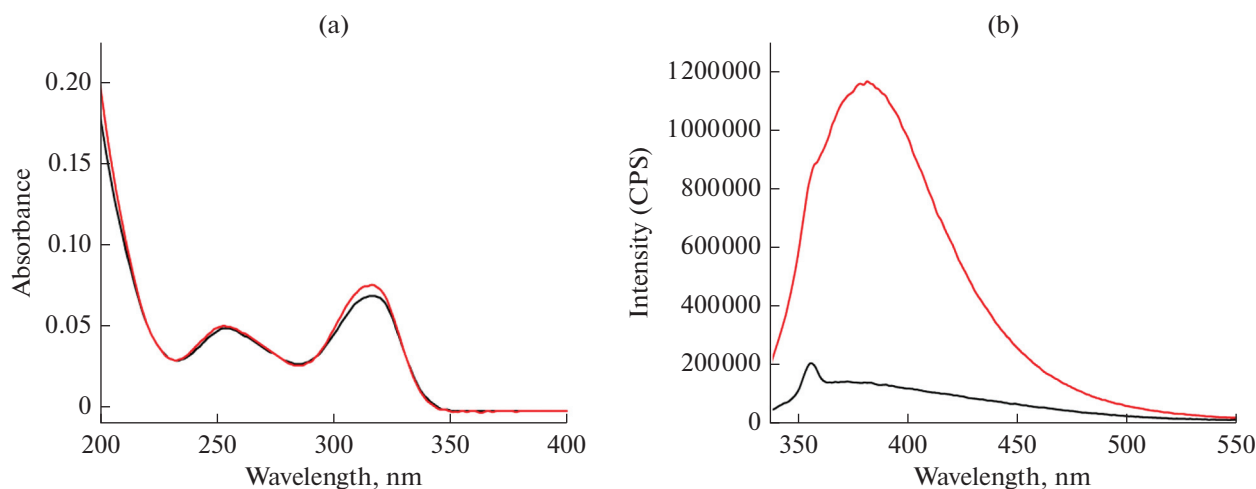


Fig. 5. (a) Absorption and (b) emission spectra of complex **I** before (black lines) and after (red lines) the addition of an excess of Zn^{2+} cations in water at room temperature.

Concerning the question about the origin of the oxalate anion in the crystals, its formation involving carbon dioxide from air can be assumed. Similar transformations catalyzed by the samarium compounds were described [14, 15].

We also studied the response of complex **I** to the addition of an excess of zinc cations to an aqueous solution of the complex. An appreciable increase in the emission intensity with a slight bathochromic shift of the maximum was observed (the spectra are presented in Fig. 5). This behavior for zinc cation chelation was described for unsubstituted 5-aryl-2,2'-bipyridine [16]. Thus, this fact indirectly confirms the presence of the free 2,2'-bipyridine fragment in complex **I**.

To conclude, we pioneered in synthesizing the samarium complex of 5-phenyl-2,2'-bipyridine with the DTTA residue in the C6 position, and its structure was studied by XRD. The result was unexpected: this complex in the crystal represents a complicated polynuclear structure forming the one-dimensional coordination polymer, and the 2,2'-bipyridine fragments do not chelate the Sm^{3+} cation. The luminescence response to the addition of a zinc cation excess was shown for the complex, which also indirectly confirms the presence of free 2,2'-bipyridines in complex **I**.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

REFERENCES

1. Hovinen, J. and Guy, P.M., *Bioconjugate Chem.*, 2009, vol. 20, p. 404.
2. Hagan, A.K. and Zuchner, T., *Anal. Bioanal. Chem.*, 2011, vol. 400, p. 2847.
3. Hanaoka, K., Kikuchi, K., Kojima, H., et al., *J. Am. Chem. Soc.*, 2004, vol. 126, p. 12470.
4. Song, B., Wang, G., Tan, M., et al., *J. Am. Chem. Soc.*, 2006, vol. 128, p. 13442.
5. Cross, J.P., Dadabhoy, A., and Sammes, P.G., *J. Lumin.*, 2004, vol. 110, p. 113.
6. Quici, S., Cavazzini, M., Marzanni, G., et al., *Inorg. Chem.*, 2005, vol. 44, p. 529.
7. Prokhorov, A.M., Kozhevnikov, V.N., Kopchuk, D.S., et al., *Tetrahedron*, 2011, vol. 67, p. 597.
8. Krinochkin, A.P., Kopchuk, D.S., Kim, G.A., et al., *Polyhedron*, 2017, vol. 134, p. 59.

9. Krinochkin, A.P., Kopchuk, D.S., Kim, G.A., et al., *ChemistrySelect*, 2019, vol. 4, p. 6377.
10. Krinochkin, A.P., Kopchuk, D.S., Kim, G.A., et al., *Polyhedron*, 2020, vol. 181, p. 114473.
11. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Cryst. Adv.*, 2015, vol. 71, p. 3.
12. Sheldrick, G.M., *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, vol. 71, p. 3.
13. Spek, A.L., *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, vol. 71, p. 9.
14. Evans, W.J., Perotti, J.M., Brady, J.C., et al., *J. Am. Chem. Soc.*, 2003, vol. 125, p. 5204.
15. Evans, W.J., Seibel, C.A., Ziller, J.W., et al., *Inorg. Chem.*, 1998, vol. 37, p. 770.
16. Kozhevnikov, V.N., Shabunina, O.V., Kopchuk, D.S., et al., *Tetrahedron*, 2008, vol. 64, p. 8963.

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