Brief Communications

Binuclear zinc naphthoate complex with 1,10-phenanthroline: synthesis, structure, and photoluminescence properties*

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The new binuclear complex [(1,10-phen)$_2$Zn$_2$(μ_2-OOCR)$_2$(η^2-OOCR)$_2$]·4THF (**2**·4THF, RCOO$^-$ is the β-naphthoate anion) was synthesized. According to the single-crystal X-ray diffraction study, a one-dimensional supramolecular structure is formed through intra- and intermolecular π—π interactions between the phenanthroline moieties of complex **2**. Compound **2** exhibits photoluminescence properties at room temperature.

Key words: β-naphthoic acid, zinc(II), phenanthroline, stacking interactions, X-ray diffraction analysis, photoluminescence.

Investigations of the influence of different substituents at the carboxy group on the composition, the structure, and the crystal packing of carboxylate complexes are of great importance for the rational synthesis of coordination compounds. Recently,[1] in the course of studies of the structures and crystal packings of zinc β-naphthoate complexes, we have synthesized complexes, which easily formed in the ZnCl$_2$—L—RCOOK system (L = lutidine, 1,10-phenathroline; RCOO$^-$ is the β-naphthoate anion) in a MeCN—C$_6$H$_6$ mixture. However, only trinuclear compounds of the general composition L$_2$Zn$_3$(μ_2,η^2-OOCR)$_2$(μ_2-OOCR)$_4$ (**1**, L = 2,3-lutidine, 1,10-phen) were isolated at the ratio L : Zn = 1 : 1 in the reaction mixture. According to the X-ray diffraction data, the crystal packing of these molecules is determined by intermolecular stacking interactions between the naphthoate substituents in the carboxylate anions, as well as by their interactions with 1,10-phenathroline. It would be expected that the change in the nuclearity and geometry of the molecules will lead to the formation of intra- and intermolecular π—π interactions between the phenathroline ligands,[2] resulting in a supramolecular assembly, and, as a consequence, to the appearance of enhanced luminescence, which is typical of d^{10} metal complexes with organic fused ligands and is associated with intraligand $\pi^* \rightarrow \pi$ transitions.[3]

In the present study, we report on the synthesis of the new binuclear zinc(II) complex with β-naphthoate anions and 1,10-phenathroline, [(1,10-phen)$_2$Zn$_2$(μ_2-OOCR)$_2$(η^2-OOCR)$_2$]·4THF (**2**·4THF, RCOO$^-$ is the β-naphthoate anion) and the investigation of its photoluminescence properties.

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* Dedicated to Academician V. N. Charushin on the occasion of his 60th birthday.

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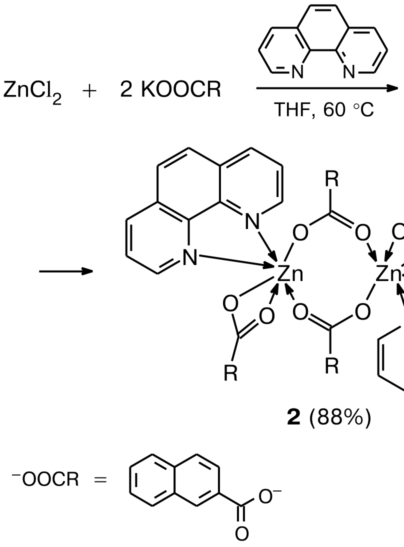
Results and Discussion

We found that the reaction of the product, which was synthesized by the reaction of potassium β-naphthoate with zinc(II) chloride, with 1,10-phenathroline in THF (Zn : L = 1 : 1) at 60 °C afforded binuclear complex **2**•4THF in 88% yield (Scheme 1).

Scheme 1



According to the X-ray diffraction data, complex **2** crystallizes as a solvate with four THF molecules (**2**•4THF), and molecules **2** are arranged in the unit cell in such a way that a twofold axis passes between the zinc atoms Zn(1) and Zn(1A) (Zn...Zn, 4.073(1) Å). The metal centers are linked together by two bridging β-naphthoate anions (Zn—O, 2.038(3) and 2.047(3) Å; C—O, 1.251(5) and 1.266(5) Å; the O—C—O angle, 124.1(4)°) (Fig. 1, *a*) and they are in a distorted octahedral environment formed also by the β-naphthoate anion coordinated in a chelating mode (Zn—O, 2.116(3) and 2.380(3) Å; C—O, 1.252(6) and 1.254(7) Å; the O—C—O angle, 121.5(4)°) and the 1,10-phenathroline ligand (Zn—N, 2.157(3) and 2.167(3) Å). There are intramolecular stacking interactions between the coordinated 1,10-phenathroline molecules. The shortest distance (C(23)···C(23A)), the distance between the centers of the interacting moieties, and the angle between the planes are 3.30 Å, 3.69 Å, and 10.2°, respectively (Fig. 1, *a*, *b*).

In addition, there are stacking interactions between the aromatic rings of the N-donor ligands of the adjacent molecules (Fig. 1, *c*). The shortest distance (C(30)···C(32B)), the distance between the centers of the interacting moieties (the dashed line), and the angle between the planes are 3.43 Å, 3.62 Å, and 0°, respectively. Therefore, supramolecular chains are formed through intra- and intermolecular π—π interactions. It should be noted that the naphthoate substituents of the carboxylate anions are not involved in the stacking interactions that occur in the supramolecular architectures of trinuclear complexes **1**, where the naphthoate substituents are involved in intermolecular interactions with each other and with the N-donor ligands.

The binding mode of the metal centers observed in complex **2** is not typical of the isolated binuclear metal fragments $\{M(\mu\text{-}OOCR)_2M\}$. As a rule, binuclear complexes with two bridging carboxylate anions contain the third μ_2-bridging group (for example, H_2O, ^{-}OR, *etc.*).[4–8] In this case, the distances between the metal atoms are substantially shorter. It should be noted that compounds containing the structurally similar metal cores are known for Co^{II},[9,10] Mn^{II},[11,12] Fe^{II},[13,14] Zn^{II}, and Cd^{II}.[2] Earlier, we have shown[10] that the Co...Co distance in the cobalt pivalate complexes is as large as 4.383 Å due to conformational flexibility of the metallocycle.

Compound **2** exhibits relatively bright blue luminescence. The analysis of the photoluminescence spectrum* showed that the experimental curve is approximated by the sum of three Gaussian probability distribution functions and is a superposition of three bands of different intensity with maxima at 368, 389, and 403 nm and half-widths of 17, 16, and 66 nm, respectively (Fig. 2). The emission bands of complex **2** are assigned to π*→π transitions of phenathroline, a slight bathochromic shift of the bands compared with the spectrum of the free ligand (361, 380, and 402 nm) being observed due to the complex formation.[3,15]

An increase in the luminescence intensity can be attributed to the coordination of the ligand to the zinc atoms, which effectively increases its rigidity and reduces radiationless energy losses.[16] Besides, intra- and intermolecular stacking interactions of 1,10-phenathroline can additionally stabilize the structure resulting in the conformational rigidity of the aromatic moieties.

In our opinion, the results of the present study are of certain interest because compounds exhibiting blue luminescence are used as materials for light-emission layers in organic light emitting diodes (OLED). The following requirements should be met: the presence of a narrow emission band, a high luminescence brightness, and the efficient photoluminescence of the active material.[17]

Experimental

The reagents $ZnCl_2$, β-naphthoic acid, 1,10-phenanthroline (Alfa Aesar), and THF (reagent grade) were commercially available and were used as is. The IR spectra were recorded on a Specord M-80 instrument in KBr pellets. The microanalysis was carried out on a Carlo Erba analyzer. The photoluminescence spectra were measured at ~20 °C in the visible region on a Perkin—Elmer LS-55 spectrometer (λ_{ex} = 270 nm).

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* The analysis of the experimental photoluminescence spectrum was performed using the Origin 6.1 software (Model: Gauss, R^2 = 0.99197).

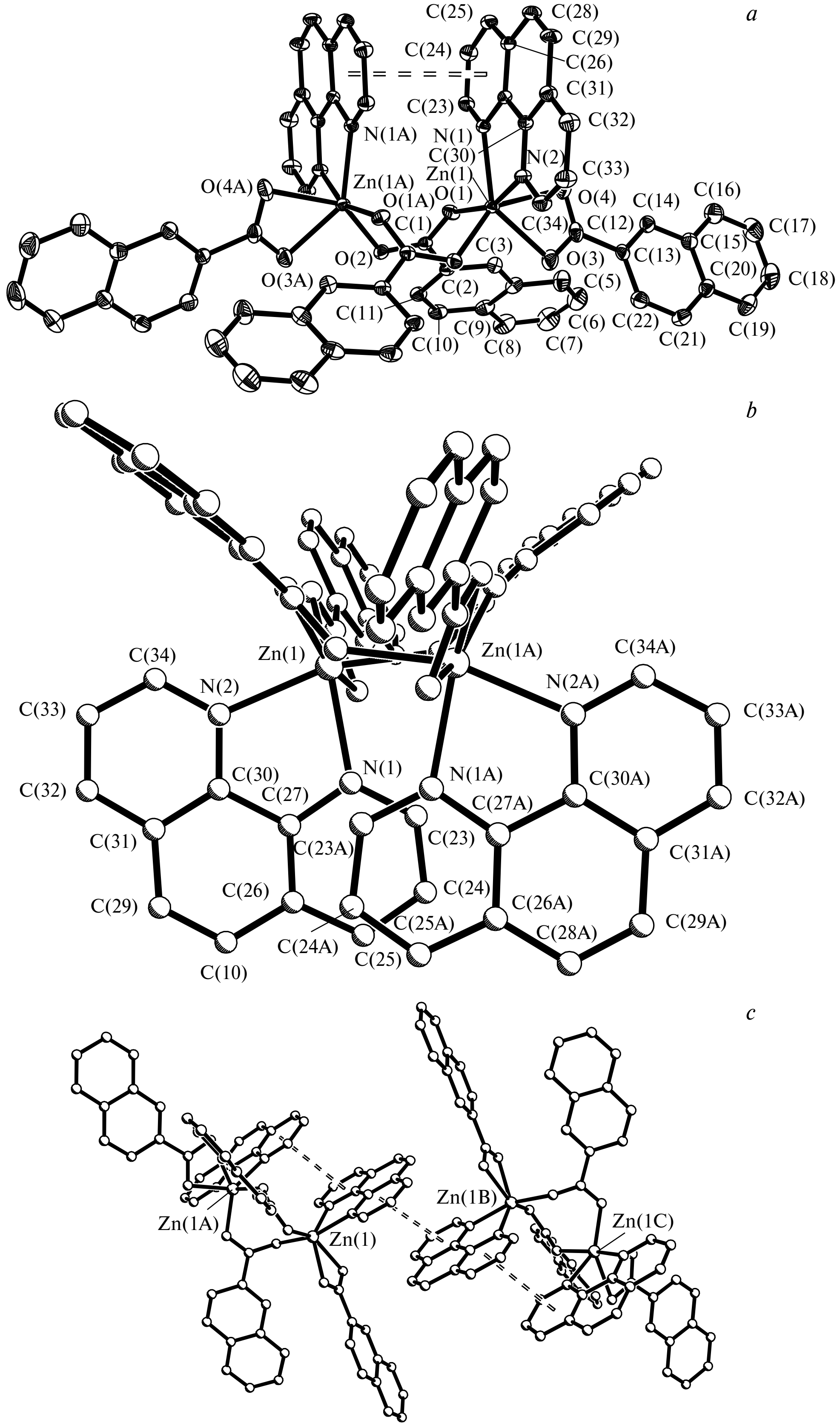

Fig. 1. Molecular structure of complex **2** (hydrogen atoms are not shown, the displacement ellipsoids are drawn at the 30% probability level) (*a*), the mutual arrangement of the coordinated 1,10-phen molecules in complex **2** (the plane of the figure coincides with the planes of the interacting ligands) (*b*), and a fragment of the crystal packing of complex **2** (*c*).

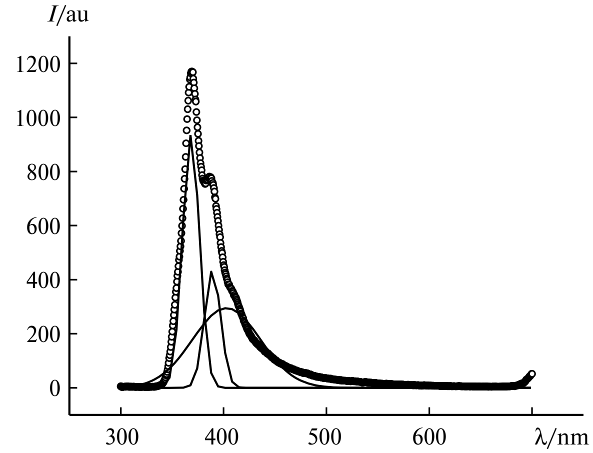

Fig. 2. Photoluminescence spectrum of complex **2**·4THF; the points correspond to the experimental data; the result of the approximation is shown as a line.

Bis(η^2-2-naphthoato-*O*,*O*′)bis(μ_2-2-naphthoato-*O*,*O*′)bis(1,10-phenanthroline)dizinc(II) tetrahydrofuran solvate (2·4THF). 1,10-Phenanthroline (0.022 g, 0.12 mmol) was added to the precipitate, which was prepared by the reaction of potassium hydroxide (0.013 g, 0.24 mmol), β-naphthoic acid (0.042 g, 0.24 mmol), and $ZnCl_2$ (0.016 g, 0.12 mmol) in an aqueous solution, dissolved in THF (30 mL). The reaction mixture was heated (60 °C) with vigorous stirring for 1 h (until the starting reagents were completely dissolved). The resulting solution was cooled to ~20 °C and then kept for 48 h, after which colorless rhombic crystals suitable for X-ray diffraction were obtained. The crystals were separated from the mother liquor by decantation, washed with cold THF, and dried in air. The yield of compound **2**·4THF was 0.16 g (88%). Found (%): C, 68.7; H, 4.7; N, 5.0. $C_{84}H_{76}N_4O_{12}Zn_2$. Calculated (%): C, 69.52; H, 5.24; N, 3.86. IR, ν/cm^{-1}: 3056 m, 3036 w, 2960 m, 2860 m, 1696 m, 1632 s, 1604 v.s, 1560 v.s, 1516 s, 1504 s, 1492 m, 1468 s, 1428 s, 1420 s, 1400 v.s, 1380 v.s, 1368 s, 1352 s, 1340 s, 1260 m, 1240 m, 1224 m, 1204 m, 1144 m, 1104 m, 1064 m, 1016 m, 956 w, 916 w, 892 w, 868 m, 848 s, 792 v.s, 764 s, 724 s, 640 m, 600 m, 548 w, 488 m, 472 m, 424 m, 396 m, 352 w, 324 w.

Single-crystal X-ray diffraction study of compound **2**·4THF was performed on a Bruker SMART APEX II diffractometer equipped with a CCD detector and a monochromatic radiation source (Mo-Kα, $\lambda = 0.71073$ Å) according to a standard procedure.[18] A semiempirical absorption correction was applied.[19] The structure of the complex was solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters for all nonhydrogen atoms. The hydrogen atoms were positioned geometrically and refined using a riding model. All calculations were carried out with the use of the SHELXS-97 and SHELXL-97 program packages.[20] The crystallographic parameters and the structure refinement statistics for complex **2** at $T = 150(2)$ K are as follows: $C_{84}H_{76}N_4O_{12}Zn_2$, $M_w = 1464.23$ g mol^{-1}, colorless rhombic crystals, 0.30×0.30×0.10 mm, space group *C*2/*c*, $a = 34.792(5)$ Å, $b = 9.2943(15)$ Å, $c = 22.649(4)$ Å, $\beta = 106.436(3)°$, $V = 7024.8(19)$ Å^3, $Z = 4$, $\rho_{calc} = 1.384$ g cm^{-3}, $\mu = 0.752$ mm^{-1}, $2.27° \le \theta \le 26.00°$, the segment of the sphere in reciprocal space $-42 \le h \le 42$, $-10 \le k \le 11$, $-26 \le l \le 27$, 18161 measured reflections, 6831 reflections with $I > 2.0\sigma(I)$, $R_{int} = 0.0550$, GOOF = 1.240, R_1 ($I > 2\sigma(I)$) = 0.0708, wR_2 ($I > 2\sigma(I)$) = = 0.1980, R_1 (based on all data) = 0.0872, wR_2 (based on all data) = 0.2082, $T_{min/max} = 0.8059/0.9286$.

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