Trinuclear zinc β-naphthoate complexes: synthesis and structure*

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New trinuclear Zn^{II} β-naphthoate complexes with mono- and bidentate N-donor ligands (2,3-lutidine (lut), 1,10-phenanthroline (phen), and 5,5′-di-*tert*-butyl-2,2′-bipyridine (dtb-bpy)), $(lut)_2Zn_3(\mu_2,\eta^2\text{-}OOCR)_2(\mu_2\text{-}OOCR)_4$ (**1**), $[(phen)_2Zn_3(\mu_2,\eta^2\text{-}OOCR)_2(\mu_2\text{-}OOCR)_4]\cdot 2MeCN\cdot 2C_6H_6$ (**2**), and $(dtb\text{-}bpy)_2Zn_3(\mu_2,\eta^2\text{-}OOCR)_2(\mu_2\text{-}OOCR)_4$ (**3**) ($RCOO^-$ is the anion of β-naphthoic acid $C_{10}H_7COOH$), were synthesized. The structures of compounds **1**—**3** were studied by single-crystal X-ray diffraction. In the crystal structures, molecules **1**—**3** are ordered due to the coplanar arrangement of the aromatic substituents of the acid and the N-donor ligands, as well as through stacking interactions.

Key words: β-naphthoic acid, zinc(II), polynuclear complexes, X-ray diffraction analysis.

Complexes of d^{10} metals with aromatic ligands have attracted interest due to their optical characteristics.[1—6] Since the observed physical effects have a cooperative character, the control over crystal packing by introducing organic donors having particular electronic and geometric features in some cases allows the preparation of crystals with tunable properties. It is important to know which effects influence the molecular ordering and how the local geometric characteristics of molecular fragments (for example, the ligand environment of the metal centers) are changed, particularly, when these fragments and their arrangement determine the properties of the crystal.

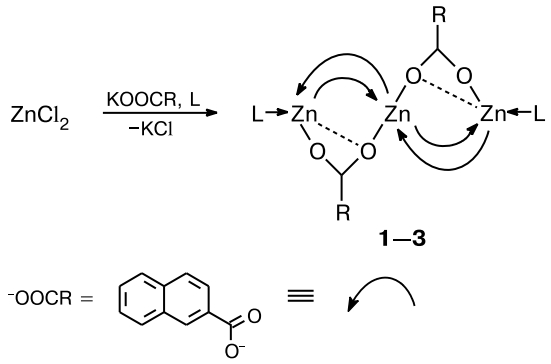
For example, ordered architectures can be formed in the case of molecules based on polyaromatic carboxylic acids and N-donor heteropolycyclic ligands (potentially promising compounds exhibiting photoluminescence properties) through interligand π—π interactions.[2—4,7—10]

The aim of the present study was to synthesize and structurally characterize new trinuclear zinc complexes that were formed in the $ZnCl_2$—L—RCOOK system (L = 2,3-lutidine (lut), 1,10-phenanthroline (phen), or 5,5′-di-*tert*-butyl-2,2′-bipyridine (dtb-bpy); $RCOO^-$ is the β-naphthoate anion). We considered the molecular packings in the crystals and analyzed the dependence of the crystal structure on the nature of the ligands L.

Results and Discussion

The reaction of zinc chloride with potassium β-naphthoate (KOOCR) and 2,3-lutidine or 1,10-phenanthroline in an acetonitrile—benzene mixture at 75 °C afforded the trinuclear complexes $(lut)_2Zn_3(\mu_2,\eta^2\text{-}OOCR)_2(\mu_2\text{-}OOCR)_4$ (**1**) and $[Zn_3(\mu_2,\eta^2\text{-}OOCR)_2(\mu_2\text{-}OOCR)_4(phen)_2]\cdot 2MeCN\cdot 2C_6H_6$ (**2**), respectively (Scheme 1).

Scheme 1



L = lut (**1**), phen (**2**), dtb-bpy (**3**)

Compounds **1** and **2** have a linear structure, the zinc atoms being linked together by six bridging and chelate bridging β-naphthoate anions (Fig. 1, Table 1). The complexes are centrosymmetric; the Zn(2) atom lies on an inversion center. The terminal metal centers coordinate the nitrogen atoms of the lut and phen molecules in complexes **1** and **2**, respectively. In complex **1**, the lut molecules (in complex **2**, phen) lie in a single plane. The corresponding symmetrical naphthalene moieties (three pairs) are parallel.

The reaction of zinc chloride with potassium β-naphthoate in the presence of the substituted bidentate ligand

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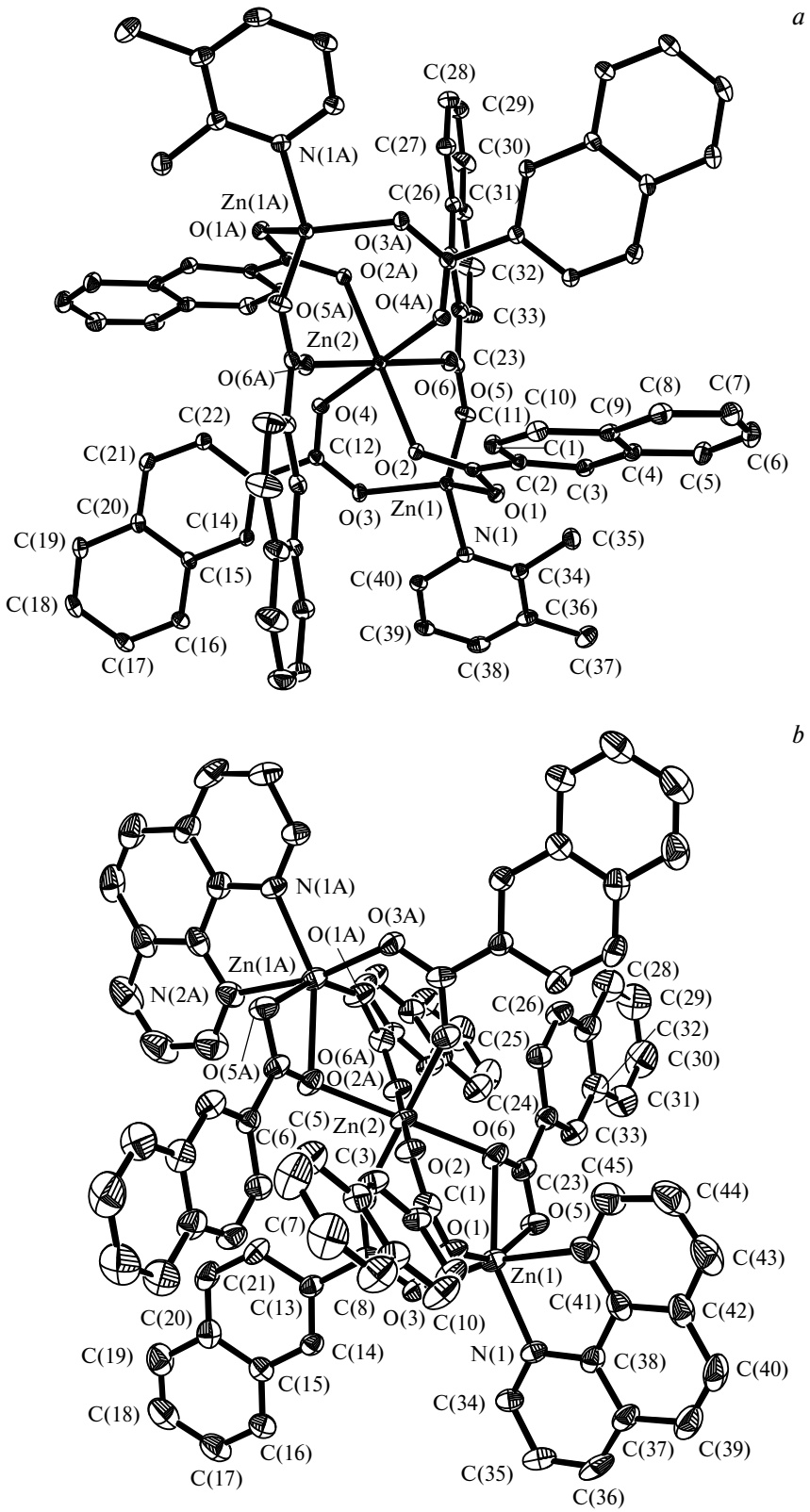

Fig. 1. Molecular structures of complexes **1** (*a*) and **2** (*b*) (hydrogen atoms are not shown, the displacement ellipsoids are drawn at the 30% probability level).

Table 1. Selected geometric characteristics of complexes **1**—**3**

Parameter	**1**	**2**	**3**
Bond length		*d*/Å	
Zn—O (μ_2-OOCR)	1.944(1)—2.129(1)	1.986(5)—2.065(4)	2.016(4)—2.087(4)
Zn—O (μ_2,η^2-OOCR)	1.981(1), 2.076(1)	2.153(5), 2.181(5)	2.165(4), 2.471(5)
Zn—N	2.060(1)	2.101(5), 2.187(6)	2.123(7), 2.148(5)
Zn···Zn	3.6700(2)	3.504(1)	3.3760(9)
C—O	1.247(2)—1.280(2)	1.234(7)—1.258(7)	1.228(8)—1.279(8)
Angle		ω/deg	
O—C—O	122.9(2)—126.0(2)	120.8(7)—126.2(7)	122.0(7)—125.6(6)

dtb-bpy in THF at 50 °C afforded the trinuclear complex (dtb-bpy)$_2$Zn$_3$(μ_2,η^2-OOCR)$_2$(μ_2-OOCR)$_4$ (**3**) (see Scheme 1).

Complex **3** is structurally similar to complexes **1** and **2** (Fig. 2, see Table 1). The coordinated dtb-bpy molecules are in parallel planes (but not in a single plane, which is observed in **1** and **2**). Four centrosymmetric naphthalene moieties (two pairs) are coplanar. The other two bridging anions are also in parallel planes.

In the crystal structures, the molecular packing of the zinc complexes with β-naphthoate anions is determined by the ordered arrangement of the aromatic moieties, which are parallel to each other, and, in some cases, is stabilized by intra- and intermolecular stacking interactions. Such molecular packings result in the formation of cavities occupied by solvent molecules.

In the crystal structure of complex **1** with the small lut ligand, there are intermolecular stacking interactions between the naphthoate substituents at the carboxylate group due to their partial overlap (the distance between the planes is 3.38 Å), whereas the donor ligand is not involved in these interactions (Fig. 3, *a*). In complex **2**, the stacking interaction occurs between the phen ligand with the extended conjugated system and the bridging naphthoate anion of the adjacent molecule (3.13—3.74 Å; the dihedral angle between the planes is 12.57°) (Fig. 3, *b*). In the crystal structure of complex **3** with the substituted bpy ligand, there are no intermolecular π—π interactions, and only intramolecular interactions be-

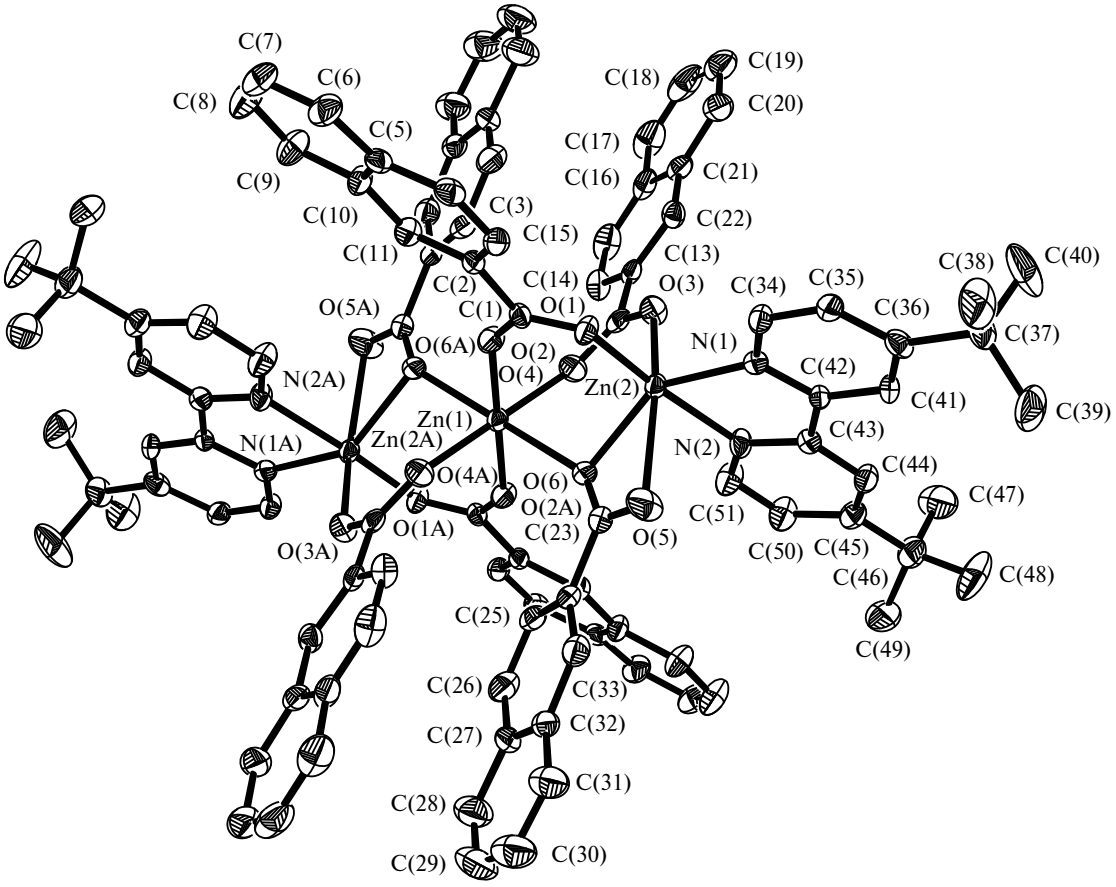

Fig. 2. Molecular structure of complex **3** (hydrogen atoms are not shown, the displacement ellipsoids are drawn at the 30% probability level).

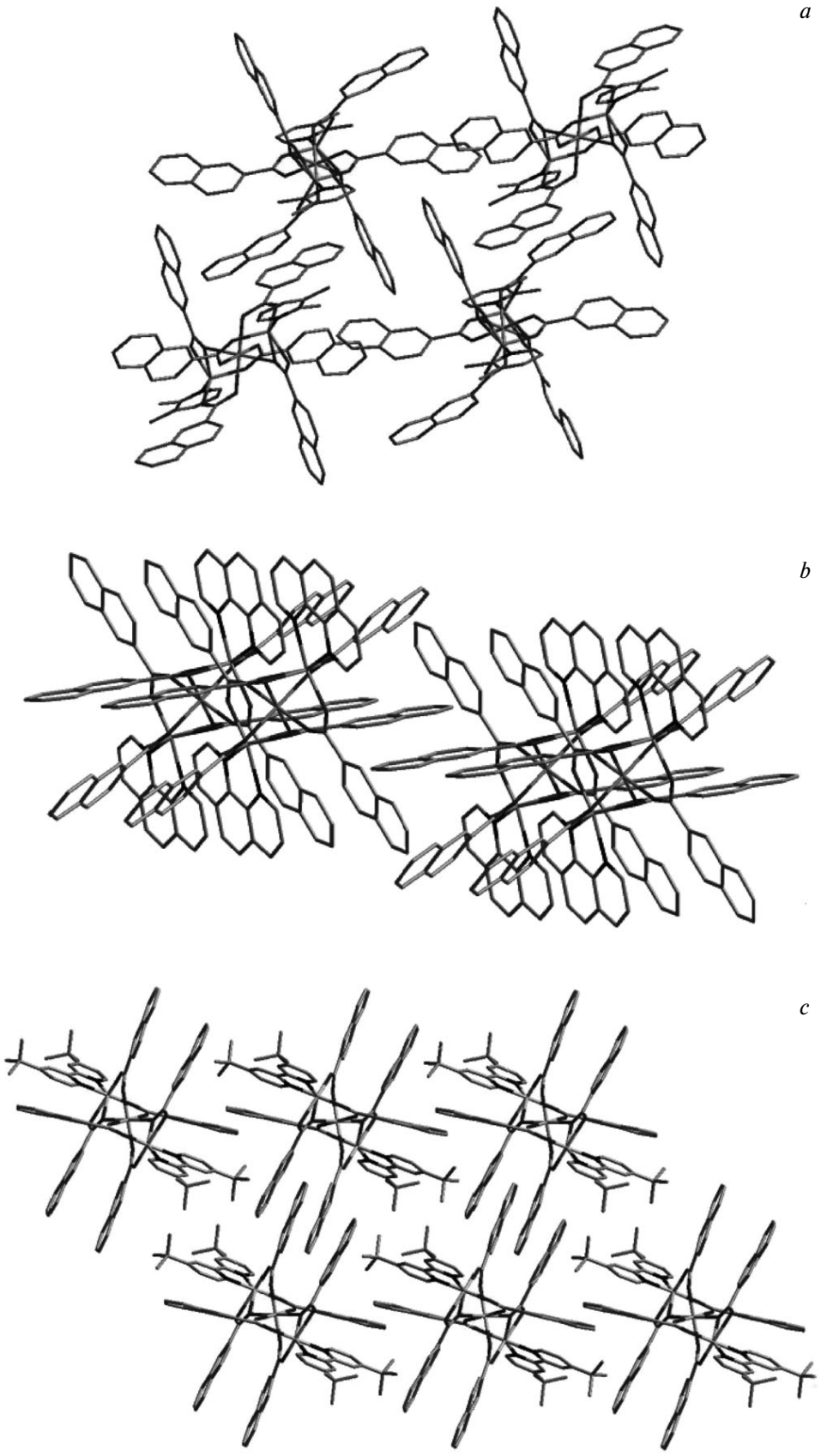

Fig. 3. Crystal packings of complexes **1** (*a*), **2** (*b*), and **3** (*c*) (hydrogen atoms and solvent molecules are not shown).

tween the bridging and chelate bridging anions exist (3.47—4.07 Å) (Fig. 3, *c*).

In summary, we synthesized zinc complexes with β-naphthoate anions, which differ in the nature of the terminal N-donor ligands (mono- and bidentate, including ligands containing bulky alkyl substituents), which enabled us to show that the structure and packing of the complexes depend on the type of the ligand.

Experimental

The reagents THF (reagent grade), MeCN (reagent grade), C_6H_6 (analytical grade), $ZnCl_2$ (Alfa Aesar), KOH (analytical grade), β-naphthoic acid (Alfa Aesar), 2,3-lutidine (Alfa Aesar), 1,10-phenanthroline (Alfa Aesar), and 5,5′-di-*tert*-butyl-2,2′-bipyridine (Alfa Aesar) were commercially available and were used as is. The IR spectra of the complexes were recorded on a Specord M-80 instrument in KBr pellets. The microanalysis was carried out on a Carlo Erba analyzer.

Tetrakis(μ_2-2-naphthoato-*O*,*O*′)bis(μ_2,η^2-2-naphthoato-*O*,*O*′,*O*′)bis(2,3-lutidine)trizinc(II), (lut)$_2$Zn$_3$(μ_2,η^2-OOCR)$_2$(μ_2-OOCR)$_4$ (1). 2,3-Lutidine (0.025 mL, 0.29 mmol) was added with stirring to a suspension of $ZnCl_2$ (0.04 g, 0.29 mmol) in MeCN (20 mL) and C_6H_6 (10 mL). Then a solution of potassium β-naphthoate in MeCN, which was prepared by the addition of a solution of β-naphthoic acid (0.1 g, 0.58 mmol) to KOH (0.033 g, 0.58 mmol), was added to the reaction mixture. The mixture was heated (75 °C) with stirring for 1 h. The solution was filtered off from a flaky precipitate of potassium chloride, and kept at ~20 °C for 3 days. Colorless crystals suitable for X-ray diffraction were obtained. The crystals were separated from the mother liquor by decantation, washed with cold MeCN, and dried in air. The yield of compound **1** was 0.19 g (57% based on $ZnCl_2$). Found (%): C, 66.3; H, 4.1; N, 1.9. $C_{80}H_{60}N_2O_{12}Zn_3$. Calculated (%): C, 66.84; H, 4.22; N, 1.95. IR, ν/cm^{-1}: 3744—3050 m, 3050 w, 1693 s, 1623 v.s, 1573 s, 1506 m, 1464 m, 1434 m, 1390 s, 1367 s, 1352 s, 1332 s, 1271 s, 1239 s, 1204 s, 1153 s, 1137 s, 1103 s, 1017 s, 971 s, 955 s, 924 s, 878 m, 842 m, 791 v.s, 765 v.s, 732 m, 682 v.w, 657 v.w, 633 v.w, 622 v.w, 604 v.w, 537 m, 495 s, 481 s, 454 v.w, 446 v.w, 434 v.w, 411 v.w, 404 v.w.

Tetrakis(μ_2-2-naphthoato-*O*,*O*′)bis(μ_2,η^2-2-naphthoato-*O*,*O*′,*O*′)bis(1,10-phenanthroline)trizinc(II), solvate with two acetonitrile molecules and two benzene molecules, [(phen)$_2$Zn$_3$-(μ_2,η^2-OOCR)$_2$(μ_2-OOCR)$_4$] · 2MeCN · 2C$_6$H$_6$ (2). Compound **2** was synthesized as described for complex **1** (1,10-phenanthroline (0.052 g, 0.29 mmol) was used instead of 2,3-lutidine) in a yield of 0.35 g (77% based on $ZnCl_2$). Found (%): C, 68.5; H, 3.5; N, 4.1. $C_{90}H_{58}N_4O_{12}Zn_3$ (without taking into account the MeCN and C_6H_6 solvent molecules). Calculated (%): C, 68.83; H, 3.70; N, 3.57. IR, ν/cm^{-1}: 3060 m, 1632 s, 1604 v.s, 1572 s, 1556 s, 1548 m, 1540 s, 1504 m, 1492 m, 1472 s, 1464 s, 1424 s, 1396 v.s, 1380 v.s, 1352 v.s, 1344 s, 1264 w, 1236 m, 1204 m, 1140 m, 1100 m, 956 w, 912 w, 896 w, 868 m, 844 m, 808 s, 800 s, 792 v.s, 764 s, 724 s, 672 w, 640 m, 624 w, 596 m, 532 w, 488 m, 472 m, 420 m, 404 m, 376 m.

Tetrakis(μ_2-2-naphthoato-*O*,*O*′)bis(μ_2,η^2-2-naphthoato-*O*,*O*′,*O*′)bis(5,5′-di-*tert*-butyl-2,2′-bipyridyl)trizinc(II), (dtbbpy)$_2$Zn$_3$(μ_2,η^2-OOCR)$_2$(μ_2-OOCR)$_4$ (3). 5,5′-di-*tert*-Butyl-2,2′-bipyridine (0.032 g, 0.12 mmol) was added to the dried 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

Table 2. Crystallographic characteristics for complexes **1**—**3**

Parameter	**1**	**2**	**3**
Molecular formula	$C_{80}H_{60}N_2O_{12}Zn_3$	$C_{106}H_{76}N_6O_{12}Zn_3$	$C_{102}H_{90}N_4O_{12}Zn_3$
Temperature/K	150(2)	296(2)	296(2)
Space group	$P2_1/n$	P-1	$P2_1/n$
a/Å	13.2724(6)	10.905(4)	16.3334(15)
b/Å	13.4960(6)	13.071(5)	11.9290(12)
c/Å	18.8317(8)	15.220(6)	22.2263(19)
α/deg	90	92.790(12)	90
β/deg	104.1740(10)	97.987(12)	91.738(3)
γ/deg	90	94.000(13)	90
V/Å^3	3270.5(2)	2139.4(14)	4328.6(7)
Z	2	1	2
ρ_{calc}/g cm^{-3}	1.460	1.414	1.350
μ/mm^{-1}	1.160	0.905	0.891
θ_{max}/deg	30.58	26.37	26.37
Number of measured reflections	25768	13244	26511
Number of reflections with $I > 2\sigma(I)$	7581	3748	3888
GOF	1.053	1.028	0.987
R_1 ($I > 2\sigma(I)$)	0.0352	0.0731	0.0719
wR_2 ($I > 2\sigma(I)$)	0.0887	0.1416	0.1375
R_1 (based on all data)	0.0529	0.1798	0.1935
wR_2 (based on all data)	0.0991	0.2008	0.1944
$T_{max/min}$	0.8452/0.7223	0.8762/0.8398	0.8780/0.8420

reagents were completely dissolved). The resulting solution was cooled to ~20 °C and kept for 48 h. The colorless rhombic crystals suitable for X-ray diffraction were separated from the mother liquor by decantation, washed with cold THF, and dried in air. The yield of compound **3** was 0.15 g (69% based on $ZnCl_2$). Found (%): C, 70.3; H, 2.8; N, 4.8. $C_{102}H_{90}N_4O_{12}Zn_3$. Calculated (%): C, 70.14; H, 3.21; N, 5.16. IR, ν/cm^{-1}: 3704—3300 m, 3056 m, 2968 s, 2940 m, 2904 m, 2868 m, 1700 w, 1668 w, 1632 s, 1608 v.s, 1552 v.s, 1536 s, 1504 s, 1488 s, 1476 v.s, 1436 s, 1404 v.s, 1380 v.s, 1352 s, 1304 s, 1268 m, 1240 s, 1204 s, 1152 m, 1136 m, 1120 m, 1110 m, 1080 w, 1028 s, 1020 s, 988 w, 956 m, 916 m, 892 m, 876 m, 856 s, 836 m, 804 v.s, 792 v.s, 768 s, 740 m, 720 m, 684 w, 668 m, 640 m, 608 s, 544 m, 524 w, 472 s, 436 m, 420 m, 396 m, 356 w, 324 w.

Single-crystal X-ray diffraction study. X-ray diffraction data sets for complexes **1—3** were collected on a Bruker SMART APEX II diffractometer equipped with a CCD detector and a monochromatic radiation source (Mo-Kα, λ = 0.71073 Å) according to a standard procedure.[11] For all complexes, semiempirical absorption corrections were applied.[12] The structures of the complexes were 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.[13] Crystallographic parameters and the structure refinement statistics are given in Table 2.

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