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Syntheses and Crystal Structures of Zinc(II) Complexes with Two Kinds of Benzoate Derivatives

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Two novel zinc(II) complexes of $[Zn(L_1)_2(phen)]\cdot 5H_2O$ **1** (L_1 = 4-aminobenzoic acid, phen = 1,10-phenanthroline) and $[Zn(L_2)_2(en)]$ **2** (L_2 = 4-methoxybenzoic acid, en = ethylenediamine) have been prepared and characterized by X-ray single crystal structural analysis. Complex **1** crystallizes in the tetragonal system, space group $I4_1/a$. The zinc atom of the central ZnO_3N_2 system is pentahedral coordinated by two N atoms of phen and three O atoms of 4-aminobenzoic acid. Complex **2** belongs to orthorhombic system, space group *Pbcn*. The zinc atom of the central ZnO_2N_2 system lies on a twofold symmetry axis and is tetrahedrally coordinated by two N atoms of en and two O atoms of 4-methoxybenzoic acid.

Key words: zinc(II) complexes, crystal structure, benzoate derivatives

Studies of the coordination chemistry of zinc(II) with carboxylate ligands have aroused more and more interest in the last decade due to their biological modeling applications [1,2] and photoluminescent properties [3,4]. Like most d^{10} metal ions, zinc has the ability to adopt different modes of coordination determined by considerations of size, as well as electrostatic and covalent bonding forces. Furthermore, when complexed with N- and O-donor ligands, its derivatives have additional importance. Zinc(II) is a relatively abundant microelement in biological organisms and plays an essential role in many enzymatic reactions [5].

The number of reports on monomeric zinc complexes containing carboxylate and basic ligands are limited [6]. Zinc(II) is usually tetra-coordinated. Pentacoordinated complexes of zinc are known but are relatively rare [7,8]. As a part of our study on the synthesis, crystal chemistry, properties and biological activity of zinc carboxylates, two novel zinc(II) complexes of $[Zn(L_1)_2(phen)]\cdot 5H_2O$ **1** (L_1 = 4-aminobenzoic acid, phen = 1,10-phenanthroline) and $[Zn(L_2)_2(en)]$ **2** (L_2 = 4-methoxybenzoic acid, en = ethylenediamine) were isolated and their crystal structures were determined.

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EXPERIMENTAL

Materials and physical measurements: All chemical reagents were analytical and used without further purification. Elemental analyses (C, H, N) were carried out with an Elementar EL elemental analyzer. Infrared spectroscopy (KBr pellets) was performed on a Nicolet 7199B spectrophotometer in the 4000–400 cm^{-1} region.

Synthesis of the complexes: Synthesis of complex **1** was carried out by mixing an aqueous solution of $Zn(OAc)_2·2H_2O$ (0.5 mmol, 10 ml) with an ethanol/aqueous (1:1) solution of 4-aminobenzoic acid (0.5 mmol, 5 ml). After stirring for 20 min. an ethanol solution of phen (0.5 mmol, 5 ml) was added. The mixture was stirred for 20 min. and then filtered. The filtrate was allowed to stand at room temperature. After one month, yellow block crystals were obtained (yield 30%).

Synthesis of complex **2** was carried out under similar conditions except that 4-aminobenzoic acid and phen were substituted for 4-methoxybenzoic acid and en dissolved in ethanol/aqueous (1:1) solution. The filtrate was allowed to stand at room temperature for several days over which time colorless prismatic crystals formed on slow evaporation of the solvent (yield 40%).

X-ray measurements and structure determination: Intensity data from the complex **1** (crystal size 0.80×0.70×0.55 mm) were collected at 293(2) K on a Rigaku RAXIS RAPID IP diffractometer; the ω-scan mode was used. Intensity data from complex **2** (crystal size 0.90×0.85×0.60mm) collected at 293(2) K on an Enraf-Nonius CAD-4 diffractometer; the ω-scan mode was used. Absorption corrections were made. Structure solution and full-matrix least-squares refinement were performed with SHELXL-97 and SHELXL-94 program packages, respectively [9,10]. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from molecular geometry and included in the final refinement. The crystal data and details of the data collections and refinements are summarized in Table 1.

Table 1. Summary of the crystallographic data for complexes **1** and **2**.

Formula	$C_{26}H_{30}N_4O_9Zn$	$C_{18}H_{22}N_2O_6Zn$
Formula weight	607.91	427.75
Space group	$I4_1/a$	*Pbcn*
Crystal system	Tetragonal	Orthorhombic
a (Å)	30.3052(4)	11.571(2)
b (Å)	30.3052(4)	7.9877(16)
c (Å)	11.8143(1)	19.947(4)
V (Å^3)	10850.3(2)	1843.6(6)
Z	16	4
Density (g/cm^3)	1.489	1.541
θ range	$2.29 \le \theta \le 27.48$	$2.04 \le \theta \le 25.96$
F (000)	5056	888
Ranges of indices h, k, l	–39/39, –39/39, –15/15	–14/0, 0/9, –24/0
μ (mm^{-1})	0.966	1.370
Temperature (K)	293(2)	293(2)
Final R Indices ($I \ge 2\sigma(I)$)	$R_1 = 0.0313$	$R_1 = 0.0575$
	$wR_2 = 0.0698$	$wR_2 = 0.1454$

RESULTS AND DISCUSSION

Infrared absorption spectra: The infrared spectra of complex **1** exhibit characteristic bonds for both 4-aminobenzoate and phen ligands. For **1** the peaks at 1544(s), 1517(s), 1428(s), 1390(vs), 867(m), 848(s), 788(s), 726(s) are attributed to the coordinated phen. The peaks at 3448(m), 3346(m), 3223(m) belong to $–NH_2$ vibration absorptions. In addition, the benzoate ring's characteristic vibration absorptions appear at 1624(s), 1604(vs). The peak at 1175(s) is assigned to $\nu_{C=O}$. The infrared spectrum of **2** is similar to that of complex **1** except that at 3300(s), 3220(s) there are strong and wide peaks for ν_{N-H} of en.

Crystal structure: The X-ray analysis revealed that Zn(II) atom in complex **1** is in a distorted trigonal bipyramidal environment as shown in Fig. 1. The selected bond lengths and angles for complex **1** are presented in Table 2. The Zn(II) atom is coordinated by two N atoms of the phen molecule and two *p*-aminobenzoate molecules. The two *p*-aminobenzoate molecules coordinate the Zn(II) atom by different modes. One carboxylate anion acts as monodentate ligand and the other acts as bidentate ligand. The phen ligand is bidentate ligand and coordinates through N atoms. The Zn–N bond distances 2.0770(16) and 2.0935(17) Å are in agreement with similar distances 2.057(7) and 2.076(7) Å reported in anionic $[Zn(phen)(S_2O_3)_2]^{2-}$ [11], and 2.094(2) and 2.113(2) Å in $[Zn(SC_6H_4NH_2\text{-}4)_2(phen)]$ [12]. Similarly, the N–Zn–N bond angle equal to 80.19(7)° is similar to those in $[Zn(phen)(S_2O_3)_2]^{2-}$ (80.3(3)°) [11] and in $[Zn(SC_6H_4NH_2\text{-}4)_2(phen)]$ (79.26(8)°) [12]. It is worthy to note that the lengths of three Zn–O bonds significantly differ one from the others. The shortest Zn–O bond 1.9847(15) Å is that between Zn and O(1) of the monodentate 4-aminobenzoic anion. The Zn–O(3) and Zn–O(4) distances: 2.3430(15) and 2.0119(15) Å, respectively, show that the chelating carboxylate ligand is bonding in a significantly asymmetric manner. They all can be contrasted to the corresponding Zn–O bond distances of $[Zn(C_4H_5O_2)_2(C_7H_7N)]$ [13], which is also a pentacoordinated complex. A similar chelating mode was also observed in $[Zn(salH)_2(bipy)(MeOH)]$ [14]. The acute O(3)–Zn–O(4) angle (59.97(5)°) is in accord with a similar angle in other zinc carboxylate ring reported, 56.7(2)° in $[Zn(C_4H_5O_2)_2(C_7H_7N)]$ [13] and 59.2(3)° in $[Zn(salH)_2(bipy)(MeOH)]$ [14].

Table 2. Selected bond lengths (Å) and bond angles (°) for complex **1**.

Zn(1)–O(1)	1.9847(15)	Zn(1)–C(20)	2.526(2)
Zn(1)–O(4)	2.0119(15)	O(4)–C(20)	1.286(2)
Zn(1)–O(3)	2.3430(15)	C(20)–O(3)	1.258(3)
Zn(1)–N(2)	2.0770(16)	O(1)–C(13)	1.288(2)
Zn(1)–N(1)	2.0935(17)	O(2)–C(13)	1.254(3)
O(1)–Zn(1)–O(4)	127.26(6)	N(2)–Zn(1)–N(1)	80.19(7)
O(1)–Zn(1)–O(3)	98.71(6)	O(1)–Zn(1)–C(20)	115.10(6)
O(4)–Zn(1)–O(3)	59.97(5)	O(4)–Zn(1)–C(20)	30.33(6)
O(1)–Zn(1)–N(2)	101.10(6)	N(2)–Zn(1)–C(20)	110.67(7)
O(4)–Zn(1)–N(2)	124.97(6)	N(1)–Zn(1)–C(20)	130.79(7)
O(1)–Zn(1)–N(1)	108.93(6)	O(3)–Zn(1)–C(20)	29.66(6)
O(4)–Zn(1)–N(1)	103.41(6)	N(1)–Zn(1)–O(3)	152.16(6)
N(2)–Zn(1)–O(3)	91.54(6)		

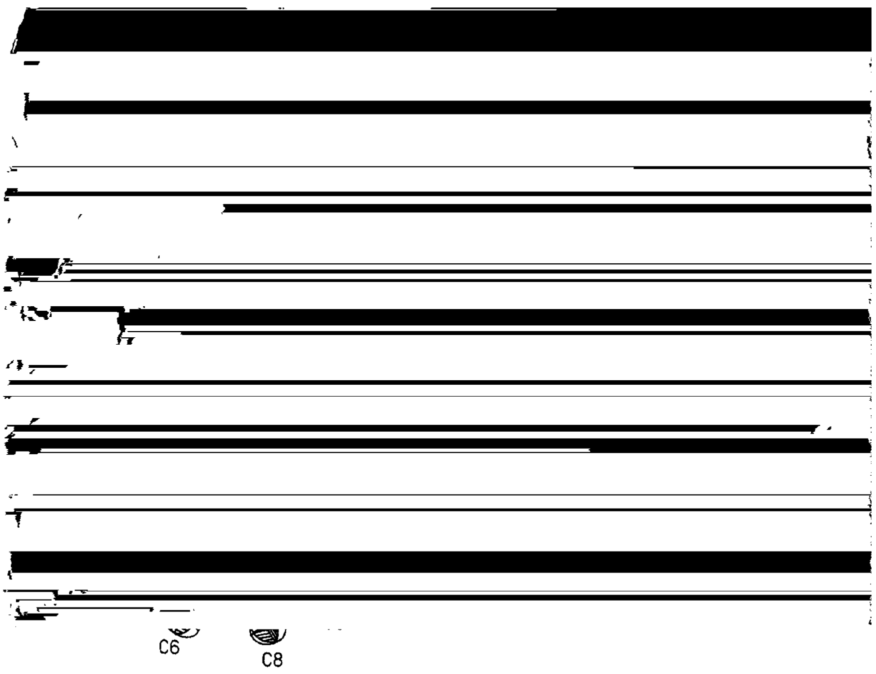

Figure 1. Molecular structure of complex **1**.

Unexpectedly, O(3)–C(20) bond length, 1.258(3) Å, for the coordinating O atom is almost the same as the distance between O(2) and C(20), 1.258(3) Å, but shorter than O(4)–C(20) (1.286(2) Å) and O(1)–C(13) (1.288(2) Å).

As shown in Fig. 2, the Zn(II) atom in complex **2** is in a slightly deformed tetrahedral coordination formed by two 4-methoxybenzoate anions and one en molecule. Table 3 lists selected bond lengths and angles of complex **2**. Both 4-methoxybenzoate anions act as monodentate ligands, which are different from complex **1**. The en ligand is also bidentate and coordinates through N atoms. The bond lengths in the coordination polyhedron are as expected. The Zn–N bond distance, 2.068(2) Å, is in accord with similar distances reported previously, 2.039(8) Å in $[ZnCl_2(C_{17}H_{19}N_3)_2]$ [15], 2.052(4) Å in $[Zn(C_7H_5O_2)_2(C_5H_6N_2)_2]$ [6], and 2.056(4) Å in $[Zn(C_5H_7NO_2)_2]$ [16]. The Zn–O distance, 1.939(3) Å, is a little shorter than corresponding distances: 1.959(3) Å in $[Zn(C_3H_5O_2)(CH_4N_2S)_2]$ [17] and 1.963(2) Å in $[Zn(C_7H_5O_2)(CH_4N_2S)_2]$ [18]. It is almost identical with the corresponding bond in $[ZnCl_2(C_{17}H_{19}N_3)_2]$. The deformation of the coordination polyhedron, which is centered on a twofold axis, involves mainly two angles bisected by that axis, *i.e.* O1–Zn–O1#, which is widened to 129.52(15)°, and N–Zn–N#1, which is narrowed to 85.07(14)°. In addition, O(1)–Zn–N bond angle is 112.64(10)° and O(1)–Zn–N#1 is 104.09(9)°. The C–O bond length, 1.277(3) Å of the coordinated O atom, is somewhat longer than those of non ligating O atoms (1.233(3) Å). The latter suggests a more double-bond character for the C–O bond [19]. The en ligand is planar and coordinates so that the zinc ion lies near the plane. Thus, the carboxylate and its mode of coordination appear to be entirely normal. The packing diagram of the complex **2**, shown in Fig. 3, illustrates an infinite quasi-two-dimensional hydrogen-bonding pattern. The H atom-acceptor distance in the N–H···O bond is 2.910(3) Å.

Table 3. Selected bond lengths (Å) and bond angles (°) for complex **2**.

Zn–O(1)#1	1.939(3)	O(1)–C(1)	1.277(3)
Zn–O(1)	1.939(3)	O(2)–C(1)	1.233(3)
Zn–N	2.068(2)	Zn–N#1	2.068(2)
O(1)#1–Zn–O(1)	129.52(15)	O(1)#1–Zn–N	104.09(9)
O(1)#1–Zn–N#1	112.64(10)	O(1)–Zn–N	112.64(10)
O(1)–Zn–N#1	104.09(9)	N–Zn–N#1	85.07(14)
C(1)–O(1)–Zn	112.25(19)	C(9)–N–Zn	106.55(19)

Symmetry transformations used to generate equivalent atoms: #1 – x, y, –z + 1/2.

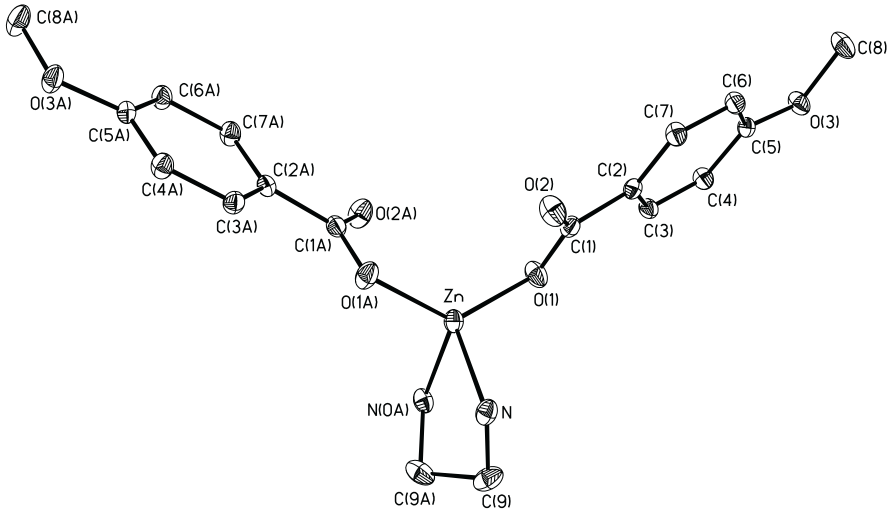

Figure 2. Molecular structure of complex **2**.

Supporting information. Detailed crystallographic data, atomic position parameters, bond lengths and angles in CIF format in this paper have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-166397 for **1**, and CCDC-166396 for **2**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

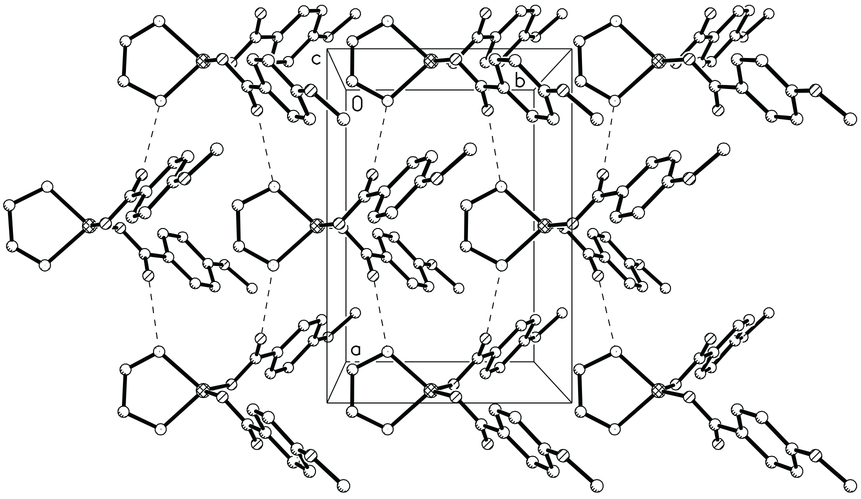

Figure 3. Packing diagram of complex **2.** The hydrogen bonds have been indicated by the dashed lines. The H-atoms have been omitted for clarity.

Acknowledgments

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