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Synthesis and X-ray diffraction study of Zn(II) complexes with o-phthalic acid and aromatic amines^{*}

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Abstract

New zinc (II) complexes [Zn(Pht)A₂], where Pht²⁻ = dianion of *o*-phthalic acid, A = pyridine (1), 3-methylpyridine (2), 4-methylpyridine (3) and [Zn(Pht)A] (A = 4-methylpyridine (4)) have been synthesised and characterised by X-ray crystallography. The compounds have polymeric structures due to 1,6-bridging ability of the *o*-phthalate ligand. Polymeric chains exhibit three types of organisation in the crystal. Complexes 1 and 2 have similar structures, where Zn atom is coordinated by two oxygen atoms of two carboxylate groups and two nitrogen atoms of N-containing ligands. Two independent Zn atoms in 3 have different environments: tetrahedral N₂O₂ and distorted square-pyramidal N₂O₃. One of the acid residues behaves as bidentate 1,6-bridge, while the other acts as tridentate (1,6-bridging and 1,3-chelating) ligand. One of the Zn atoms in 4 has a tetrahedral NO₃ geometry, while the second is characterised by a distorted octahedral NO₅ coordination polyhedron. Both phthalate anions are tetradentate and act as *syn-syn*, *syn-anti* and monoatomic Zn-O-Zn bridging ligands. The IR spectra are discussed in relation to the crystal structures. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Zinc(II) complexes; Zinc(II) carboxylates; Phthalate complexes; Crystal structures

1. Introduction

The versatility of carboxylic acids as ligands and the extraordinary reach binding facilities of carboxylate groups are responsible for the existence of a huge number of metal carboxylates. Carboxylate groups are capable of binding a metal in either a monodentate, bidentate or bridging mode leading to both mono- and polynuclear molecular and polymeric structures [1-3]. Dicarboxylic acids have additional coordination abilities for the formation of new types of polymers and oligomers, which can considerably influence the magnetic, optical or catalytic properties of the ultimate product.

We have recently reported the crystal structures of copper(II) complexes with o-phthalic acid (H₂Pht) [4,5]. These complexes revealed the monodentate as well as chelating and bridging bonding modes. Other metal complexes with phthalate ligands are also available [6–23]. However, data on zinc(II) phthalate complexes containing amines have not been reported yet (CSD version 5.19 [24]).

Herein we report on the synthesis and X-ray diffraction study of zinc(II) complexes [Zn(Pht)A₂] and [Zn-(Pht)A], where A = pyridine, 3-, 4-methylpyridine (β -, γ -Pic).

2. Experimental

2.1. General

Commercial starting materials were used without further purification. The carbon, hydrogen and nitrogen

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contents were determined by standard micro-methods. The zinc content was determined gravimetrically as ZnO. Fourier transform infrared spectroscopy on KBr pellets was performed on a Perkin-Elmer 1725 X FT-IR instrument.

2.2. Synthesis of $[Zn(Pht)Py_2]$ (1)

Zinc(II) carbonate (1.25 g, 10 mmol) was added to a solution of o-phthalic acid (4.98 g, 30 mmol) and pyridine (10 cm³) in water (40 cm³) at 70°C. The resulting mixture was stirred and heated for 30 min. After cooling to room temperature the colourless crystals were filtered off, washed several times with water, ethanol and dried in air. Yield: 71%. Calc. for C₁₈H₁₄N₂O₄Zn: C, 55.75; H, 3.64; N, 7.22; Zn, 16.86. Found: C, 55.87; H, 3.64; N, 7.38; Zn, 16.94%.

2.3. Synthesis of $[Zn(Pht)(\beta-Pic)_2]$ (2)

To a solution of o-phthalic acid (1.7 g, 10 mmol) and 3-methylpyridine (5 cm³) in water (40 cm³) was added a solution of Zn(O₂CMe)₂·2H₂O (2.2 g, 10 mmol) in water (10 cm³). The crystalline product, precipitated after 30 min, was filtered off, washed with water, ethanol, ether and dried in air. Yield: 89%. Calc. for C₂₀H₁₈N₂O₄Zn: C, 57.78; H, 4.36; N, 6.74; Zn, 15.28. Found: C, 57.73; H, 4.36; N, 6.52; Zn, 15.44%.

2.4. Synthesis of $[Zn(Pht)(\gamma-Pic)_2]$ (3)

This compound was synthesised analogously to the complex 2 by using 4-methylpyridine as aromatic amine. Yield: 65%. Calc. for C₂₀H₁₈N₂O₄Zn: C, 57.78; H, 4.36; N, 6.74; Zn, 15.28. Found: C, 57.50; H, 4.39; N, 6.82; Zn, 15.89%.

Table 1						
Crystal	data	and	details	of	data	collection

2.5. Synthesis of $[Zn(Pht)(\gamma-Pic)]$ (4)

To a solution of o-phthalic acid (3.4 g, 20 mmol) and 4-methylpyridine (4 cm³) in water (30 cm³) was added a solution of Zn(O₂CMe)₂·2H₂O (4.4 g, 20 mmol) in water (20 cm³) at 70°C. The mixture was stirred and refluxed for 30 min. After cooling to room temperature the precipitated crystals were collected by filtration, washed with water, ethanol and dried in air. Yield: 54%. Calc. for C₁₄H₁₁NO₄Zn: C, 52.11; H, 3.44; N, 4.34; Zn, 20.27. Found: C, 52.16; H, 3.55; N, 4.31; Zn, 20.19%.

Slow evaporation of the mother liquors of 1-4 afforded colourless crystals suitable for X-ray diffraction analyses.

2.6. X-ray diffraction measurements

Experimental data were collected on a KUMA diffractometer with KM4CCD κ-axis graphite monochromated Mo K α radiation at 293 K for 1 and 3, and at 180 and 150 K for 2 and 4, respectively. The crystals were positioned at 60 mm from the KM4CCD camera. 532 frames (in 4 runs) were measured, each for 45, 40, 20 and 24 s over 0.75 degree scan for 1-4, respectively. The data were processed using the KUMA Diffraction (Wroclaw, Poland) program. Crystal data, details of data collection and refinement of the crystal structures 1-4 are given in Table 1. The structures were solved by direct methods (SHELXS-97 [25]) and refined on F^2 (SHELXL-97 [26]) in anisotropic approach for non-hydrogen atoms. The hydrogen atoms were calculated and allowed to ride with isotropic displacement parameters fixed at $1.2 \times U_{eq}$. The methyl groups in 2 have been found disordered over two positions with the

Crystal data and details of data collection for 1-4							
	1 2		3	4			
Formula	C ₁₈ H ₁₄ N ₂ O ₄ Zn	C ₂₀ H ₁₈ N ₂ O ₄ Zn	C40H36N4O8Zn2	C ₂₈ H ₂₂ N ₂ O ₈ Zn ₂			
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic			
Space group	Pbca	$P2_1/c$	$P2_1$	Cc			
a (Å)	15.730(3)	8.447(2)	10.096(2)	7.4220(10)			
b (Å)	12.380(2)	17.659(4)	15.848(3)	20.462(4)			
c (Å)	17.650(4)	13.498(3)	11.814(2)	17.865(4)			
β (°)	90	104.64(3)	92.61(3)	100.67(3)			
Ζ	8	4	2	4			
Crystal size (mm)	$0.05 \times 0.05 \times 0.4$	$0.1 \times 0.2 \times 0.4$	$0.6 \times 0.35 \times 0.15$	$0.01 \times 0.07 \times 0.035$			
θ Range for data collection (°)	3.12-25.04	2.75-29.71	3.45-29.26	3.37-29.24			
Reflections collected/unique	13365/2285	12812/4992	11644/8658	8574/4203			
Data/restraints/parameters	2285/0/226	4992/0/249	8658/1/487	4203/2/361			
Goodness-of-fit on F^2	1.073	1.120	1.051	0.810			
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0570,$	$R_1 = 0.0443,$	$R_1 = 0.0501,$	$R_1 = 0.0385,$			
	$wR_2 = 0.1345$	$wR_2 = 0.1181$	$wR_2 = 0.1416$	$wR_2 = 0.0904$			
R indices (all data)	$R_1 = 0.1044,$	$R_1 = 0.0585,$	$R_1 = 0.0699,$	$R_1 = 0.0751,$			
	$wR_2 = 0.1547$	$wR_2 = 0.1269$	$wR_2 = 0.1538$	$wR_2 = 0.1024$			
Largest difference peak and hole (e Å $^{-3}$)	0.862 and -0.288	$0.9\overline{69}$ and -0.631	0.792 and -0.595	0.720 and -0.431			

Table 2									
Selected	bond	distances	(Å)	and	bond	angles	(°) f	for	1–4

	1 ^a	2 ^a	3 ^b		4 °	
Bond lengths						
Zn(1)–O(4) #	1.965(5)	1.929(2)	Zn(1)–O(4b) #	1.921(3)	Zn(1)–O(4b) # 1	1.945(3)
Zn(1)-O(1)	1.987(5)	1.970(2)	Zn(1)–O(1a)	1.990(3)	$Zn(1)-O(4a) \neq 1$	1.949(3)
Zn(1)-N(1a)	2.073(5)	2.070(2)	Zn(1)-N(21)	2.046(4)	Zn(1)-N(1a)	2.002(4)
Zn(1)–N(1b)	2.064(6)	2.032(2)	Zn(1)-N(11)	2.072(4)	Zn(1)–O(1a)	2.031(3)
			Zn(2)–O(1b)	1.940(4)	Zn(2)-N(1b)	2.072(4)
			Zn(2)–N(31)	2.044(4)	Zn(2)–O(2b)	2.102(4)
			Zn(2)–O(4a)	2.047(4)	Zn(2)–O(1a)	2.100(3)
			Zn(2)-N(41)	2.075(4)	$Zn(2)-O(3b) \neq 1$	2.121(3)
			Zn(2)–O(3a)	2.405(4)	Zn(2)–O(3a)	2.158(3)
					Zn(2)–O(1b)	2.240(3)
Bond angles						
O(4) # -Zn(1) - O(1)	141.7(2)	109.02(7)	O(4b) # -Zn(1) - O(1a)	110.66(16)	O(4b) # -Zn(1) - O(4a) #	105.46(15)
O(4) # -Zn(1) - N(1b)	108.7(2)	123.78(9)	O(4b) # -Zn(1) - N(21)	124.62(17)	O(4b) # -Zn(1) - N(1a)	103.99(16)
O(1) - Zn(1) - N(1b)	95.5(2)	110.66(9)	O(1a) - Zn(1) - N(21)	110.03(15)	O(4a) # -Zn(1) - N(1a)	119.97(16)
O(4) # -Zn(1) - N(1a)	92.7(2)	110.94(8)	O(4b) # -Zn(1) - N(11)	106.04(15)	O(4b) # -Zn(1) - O(1a)	96.46(15)
O(1) - Zn(1) - N(1a)	110.0(2)	97.54(8)	O(1a) - Zn(1) - N(11)	100.04(16)	O(4a) # -Zn(1) - O(1a)	99.64(14)
N(1b)-Zn(1)-N(1a)	104.3(2)	101.54(9)	N(21)-Zn(1)-N(11)	102.07(16)	N(1a)-Zn(1)-O(1a)	127.27(15)
			O(4a) - Zn(2) - O(3a)	57.11(14)	N(1b)-Zn(2)-O(2b)	147.63(15)
			N(41)-Zn(2)-O(3a)	150.31(15)	N(1b)-Zn(2)-O(1a)	96.75(16)
			O(1b)–Zn(2)–N(31)	127.64(18)	O(2b)–Zn(2)–O(1a)	115.07(14)
			O(1b)–Zn(2)–O(4a)	113.95(18)	N(1b)-Zn(2)-O(3b) #	98.24(15)
			N(31)–Zn(2)–O(4a)	109.19(18)	O(2b)–Zn(2)–O(3b) #	89.37(14)
			O(1b)–Zn(2)–N(41)	102.90(17)	O(1a)–Zn(2)–O(3b) #	87.44(13)
			N(31)–Zn(2)–N(41)	102.72(16)	N(1b)–Zn(2)–O(3a)	87.91(14)
			O(4a) - Zn(2) - N(41)	93.37(16)	O(2b)–Zn(2)–O(3a)	89.88(13)
			O(1b)–Zn(2)–O(3a)	88.30(16)	O(1a)–Zn(2)–O(3a)	83.47(12)
			N(31)–Zn(2)–O(3a)	91.25(16)	O(3b) # -Zn(2) - O(3a)	169.57(13)
					N(1b)-Zn(2)-O(1b)	87.69(14)
					O(2b)-Zn(2)-O(1b)	61.15(13)
					O(1a)–Zn(2)–O(1b)	173.57(13)
					O(3b) # -Zn(2) - O(1b)	87.32(14)
					O(a)–Zn(2)–O(1b)	101.40(12)

^a Symmetry transformations used to generate equivalent atoms: for 1 # -x + 1/2, y - 1/2, z; for 2 # x, -y + 1/2, z - 1/2.

^b Symmetry transformations used to generate equivalent atoms: # x, y, z-1.

^c Symmetry transformations used to generate equivalent atoms: # x+1, y, z.

occupancy factors 0.69 (C(10b)) and 0.31 (C(10c)). Selected bond distances and angles are listed in Table 2.

3. Results and discussion

3.1. Crystal structures

It is worth noting the coordination mode of phthalate ligand, which exhibits a great variety of bonding geometries such as monodentate [27], 1,3-chelating [6] and 1,6-chelating [11,28–30], including various bridging modes [7–12,31–37]. In complexes 1–4 the bridging modes of phthalate coordination have been revealed, which favour the formation of polymeric structures. The compounds differ by the stoichiometric ratio metal: acid: heterocyclic amine, which is 1:1:2 for 1–3 and 1:1:1 for 4, and by geometric peculiarities of substituted pyridines. As a consequence, compounds 1-4 belong to three different structural types.

3.1.1. Compounds 1 and 2

Fig. 1(a) and (b) show a view of the fragment of the polymeric chain $[Zn(Pht)A_2]_{\infty}$. Phtalate ligand acts as 1,6-bridging (I) in both structures. The same picture is seen in the dimer $[Fe_2(TPA)_2O(Pth)](ClO_4)_2$ ·MeOH· H_2O [31], in the *catena*-aqua(1,10-phenanthroline)(µ-phthalato)copper(II) hemihydrate [32], *catena*-(µ-phthalato)bis(oxamideoxime)nickel(II) tetrahydrate [33] and $[Cu_2(Pht)_2(\gamma-Pic)_4H_2O]$ [4]. In both 1 and 2 the phthalate ligand is coordinated by one of the oxygen atoms of each of its carboxylate groups to the neighbouring Zn atom. The Zn···Zn distance is 6.645(1) and 6.896(2) Å, respectively, for 1 and 2. Each Zn atom is in a tetrahedral donor atom environment, which comprises two nitrogen atoms of two pyridine molecules (3-methylpyridine for 2) and two oxygen atoms of two

Pht²⁻ ligands. The Zn-N and Zn-O distances in the coordination polyhedron of **1** and **2** are correspondingly at 2.064(6), 2.073(5) and 1.965(5), 1.987(5) Å, and 2.032(2), 2.070(2) and 1.929(2), 1.970(2) Å.

3.1.2. Compound 3

In 3 the polymeric chain is arranged along the *c*-axis (Fig. 2(a) and (b)). Two adjacent zinc atoms in the polymeric chain differ by their coordination geometry. Zn(1) atom has a tetrahedral environment of N_2O_2 type, while Zn(2) atom is surrounded by the N_2O_3 set of donor atoms, which form a distorted square-pyramid (Table 2). One Pht^{2–} ligand acts as bidentate 1,6-bridging (I), while the other behaves both as 1,6-bridging and 1,3-chelating being coordinated to zinc atoms as is shown by structure representation **II**.



The bridging mode of phthalate coordination depicted by structures I and II does not significantly influence the Zn…Zn distances which are at 6.358(2) and 6.405(3) Å in 3. The interatomic distances in Zn(1) tetrahedral core are very close to those found in 1 and

2 (Zn–N 2.046(4) and 2.072(4) Å, Zn–O 1.921(3) and 1.990(3) Å), while bond angles differ significantly (Table 2). In the coordination polyhedron of Zn(2) the Zn–O distances are longer compared to those in Zn(1) tetrahedron (Zn–N 2.044(4) and 2.075(4) Å, Zn–O 1.940(4), 2.047(4) and 2.405(4) Å). The most distorted angle in Zn(2) polyhedron is O(3a)Zn(2)O(4a) at 57.1(1)°, what is common for the carboxylate groups coordinated in a 1,3-chelating manner, as found in a number of 3d metal complexes, as for example, [Cu(HPht)₂Py₂], [Cu(HPht)₂(γ -Pic)₂] [4] and [Cu(Pht)Py₂] [15].

3.1.3. Compound 4

Fig. 3(a) and (b) shows views of crystallographically independent structure fragment and a part of the polymeric chain of **4**. The chain includes two independent Zn atoms with different coordination geometries. Zn(1) is tetrahedral (NO₃), while Zn(2) environment approaches to a distorted tetragonal bipyramid (NO₅). In the Zn(1) coordination core Zn(1)–N bond is at 2.002(4) Å, whereas Zn(1)–O distances are at 1.945(3), 1.949(3) and 2.031(3) Å, bond angles ranging from 96.5(2) to 147.63(2)°. The distances between Zn(2) and surrounding donor atoms are increased dramatically (Zn(2)–N = 2.072(4), Zn(2)–O ranging from 2.100(3) to 2.240(3) Å. Bond angles deviate considerably from 90° (Table 2).

Generally both phthalate ligands behave as 1,6-bridging ones (III and IV) in 4.



Fig. 1. (a) Polymeric chain in compound 1. (b) Polymeric chain in compound 2.



Fig. 2. (a) Crystallographically independent structure fragment in compound 3 with a numbering scheme. (b) Polymeric chain in compound 3.

Note, however, that these bridging phthalate groups link two symmetry related zinc atoms (Zn(1) and $Zn(1)^*$, Zn(2) and $Zn(2)^*$ as displayed in Fig. 3(b). In addition, there are bridges of different type between nonequivalent Zn atoms. Zn(1) and Zn(2) atoms being 3.470(2) Å from each other are bridged by the O(1a) atom of the phthalate ligand a, with the corresponding angle at O(1a) at 114.3(2)°. We also note that both Zn atoms are linked by the bridging bidentate carboxylate group, which adopts a syn-syn arrangement b. Such behaviour is typical for the acetate ion and its derivatives [38-41] and has been established for binuclear copper(II) [42] and zinc(II) compounds [43-45]. The second carboxylate group of the ligand (b) bind the metal in 1,3-chelate manner. Another pair of Zn(1) and Zn(2) atoms being at 3.467(2) Å from each other is bound to the Pht(b) ligand via syn-anti bridge (Fig. 3(b)). The formation of the seven-membered metallocycle on coordination of Pht(a) to Zn(2) has also been found in [11,28-30] and is a distinctive feature of compound 4.

The phthalate ligand shows a high degree of self-organisation upon complex formation. Dihedral angles between the carboxylate groups and aromatic rings range from 12.5(3) to 101.3(3)°. Delocalisation of π electron density over the carboxylate groups is observed, which is typical for the deprotonated RCOO⁻ fragments. The C-O distances range from 1.223(9) to 1.233(8) (1), 1.230(3) to 1.288(3) (2), 1.202(6) to 1.299(6) (3) and 1.225(6) to 1.305(6) Å (4). In 3 and 4 the redistribution of electon density occurs over both chelating and bridging carboxylate groups. The C(sp²)-COO distances ranging from 1.496(6) to 1.528(6) Å can be considered as single bonds. The mean C-C distances in the aromatic rings are 1.382 (1), 1.390 (2), 1.383 (3) and 1.394 Å (4).



Fig. 3. (a) Crystallographically independent structure fragment in compound 4 with a numbering scheme. (b) Polymeric chain in compound 4.

The composition of 1-4 and full deprotonation of both carboxylate groups in o-phthalic acid makes impossible the formation of hydrogen bonds. Van der Waals and weak C-H···O contacts are the only interactions between the chains. The latter is also a source of an additional binding within the polymeric chains. The C-H···O contacts resemble those reported in Ref. [46]. In 1 (Fig. 1(a)) we mention the $C(9a)-H\cdots O(2)$ contact with $C \cdots O = 3.298$ and $O \cdots H = 2.59$ Å. Between the chains two similar interactions were found: C(35)- $H \cdots O(3) = 3.346$, $H \cdots O(3) = 2.52$ Å and C(6a)- $H \cdots O(3) = 3.472, H \cdots O(3) = 2.54$ Å. In 2 a contact of the same type has also been found $(C(8a)-H\cdots O(1) =$ 3.341 and $H \cdots O(1) = 2.39$ Å). Intermolecular contacts H…O ranging from 2.23 to 2.54 Å are also present in 3 and **4**.

3.2. Spectroscopic properties

Complexes 1 and 2 have similar structures and their spectra show broad $v_{asym}(CO_2)$ absorptions at 1618 and 1567 cm⁻¹ (with shoulders at 1590 and 1539 cm⁻¹) and 1622 and 1590 cm⁻¹, respectively, which can be attributed to monodentate phthalate bridges [2,3,47]. The $v_{asym}(CO_2)$ bands in 3 are slightly red shifted relative to those in 1 and 2 (1610 and 1560 cm⁻¹). The symmetric CO₂ stretching vibrations appear as a strong band correspondingly at 1390, 1372 and 1388 cm⁻¹ in the spectra of 1-3. The IR spectrum of 4 shows several bands in the $v_{asym}(CO_2)$ and $v_{sym}(CO_2)$ region at 1636, 1610, 1584, 1556 cm⁻¹ and 1409, 1374 cm⁻¹, respectively. The absorptions at lower frequencies (1610-1556 cm^{-1}) can be attributed to deformation vibrations of the chelating and bridging carboxylate groups. Such absorptions have already been reported for copper(II) complexes with o-phthalic acid and aromatic amines $(1620-1520 \text{ cm}^{-1})$ [4.5] and a number of other carboxylate bridged compounds [3]. The Δv values related to the frequency differences between each $v_{asym}(CO_2)$ and $v_{sym}(CO_2)$ at 1409 cm⁻¹, range from 201 to 147 cm^{-1} . The band at 1636 cm^{-1} can be assigned to $v_{asym}(CO_2)$ of the monodentate phthalate bridge (Zn-O-Zn). Analogous assignment has been proposed for other zinc carboxylate complexes containing the same bridge (1630-1620 cm⁻¹) [48]. Because of the nonequivalence of the two oxygen atoms, a large Δv value at 296 cm⁻¹ is observed.

4. Conclusion

New Zn(II) compounds with o-phthalic acid and aromatic amines of 1:1:2 and 1:1:1 stoichiometries have been obtained and characterised by X-ray crystallography. All compounds have a polymeric structure with Zn atoms linked by 1,6-bridging Pht²⁻ ligands. In the case of amine deficient (1:1:1) complex the phthalate ligand coordination capacity increases up to 4, displaying additional bridging facilities. Carboxylate groups adopt different arrangements: syn-syn, syn-anti, monoatomic Zn–O–Zn bridging. We consider the 1,6-bridging mode as the most favoured for the transition metal coordination with *o*-phthalic acid.

5. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 140711 (1), 140712 (2), 140713 (3), 140714 (4). Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http:/ /www.ccdc.cam.ac.uk). Structure factors for 1-4 are available from the authors on request.

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