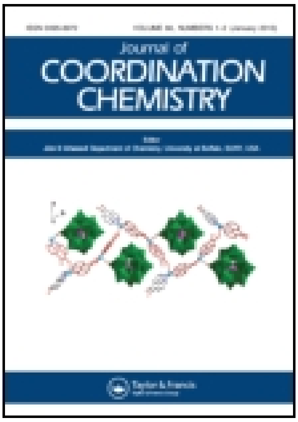

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Tetraaqua-bis(3-hydroxy-4-nitrobenzoato) Co(II) and Ni(II) complexes and diaqua-bis(2-hydroxy-4-methoxybenzoato) Zn(II) complex: crystal structure and thorough metal-coordination investigation

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Reactions of Co(II) and Ni(II) salts with the monosodium salt of 3-hydroxy-4-nitrobenzoic acid (**3**) in aqueous solution resulted in isomorphous covalent complexes **3C** and **3D**, of centrosymmetric geometries. In similar conditions, 2-hydroxy-4-methoxybenzoic acid (**5**) led to the covalent Zn(II) complex **5A**, exhibiting a marked dissymmetric geometry. The present crystallographic data with structural data for a series of closely related metal complexes previously reported allow a tentative rationalization of the solid-state architecture of such complexes. The dissymmetry in **5A** was interpreted on the basis of a mixed (monodentate and bidentate) metal-ligation mode and a pyramidal coordination at the metal.

Keywords: Zn(II), Co(II) and Ni(II) complexes; 3-Hydroxy-4-nitrobenzoic acid; 2-Hydroxy-4-methoxybenzoic acid; Crystal structure; Metal-coordination study

1. Introduction

Before entering into the subject matter, we would like to introduce briefly the crystal structures depicted in figure 1, since they played an important part in the rationalization of the present findings.

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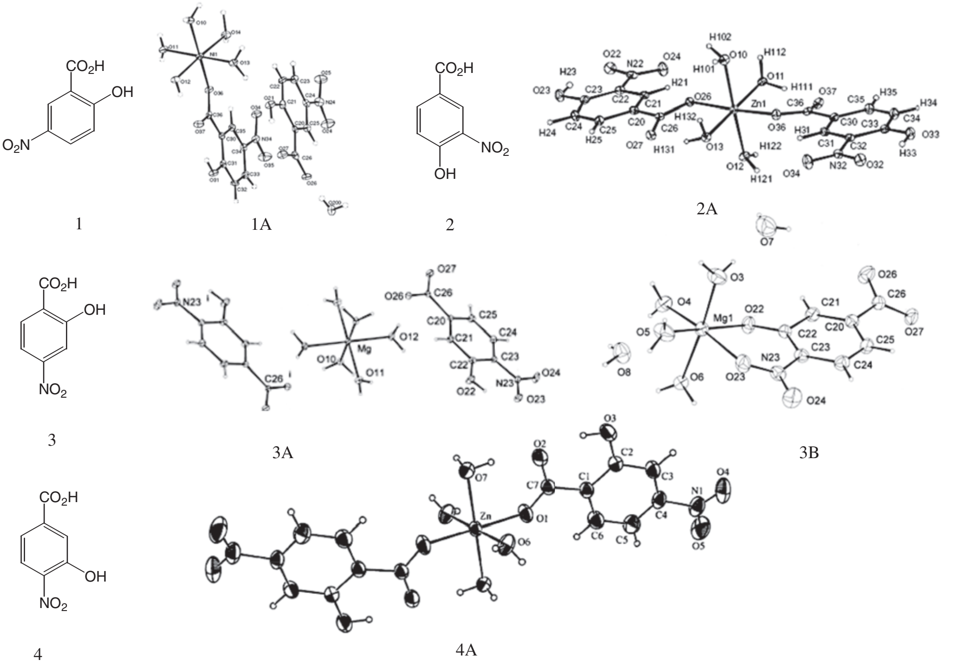

1 1A 2 2A 3 3A 3B 4 4A

Figure 1. Canonical representations of regioisomeric ligands **1**–**4** and crystal structures of their metal complexes.

Besides their relevance to solid-state structure and supramolecular design [1–3], diversely substituted benzoato–metal complexes have promising anti-inflammatory and anticonvulsant activities [4–8]. As part of a systematic program devoted to the study of structure–activity relationships of such complexes, we recently reported the crystal structures of metal complexes of 2-hydroxy-5-nitrobenzoic acid (**1**, figure 1) [9]. The structures of Mg(II), Zn(II), Co(II), and Ni(II) complexes show that they are all isomorphous. The crystallographic units can be represented in all cases by the general ionic asymmetric formula $[M(H_2O)_5$ (2-hydroxy-5-nitrobenzoato)$]^+$ [2-hydroxy-5-nitrobenzoato$]^-$ (Ni complex, **1A**, given as an example), in which the carboxylato group of the cationic subunit is covalently linked to the metal center. Detrimental to the cohesion of these structural units was the lack of close contacts (<3.4 Å) involving anionic and cationic moieties. However, the 3-D structure is stabilized through intra-unit aromatic π–π stacking interactions and extensive inter-unit H-bonding associations. Stimulated by the unusual coordination behavior of **1** in metal complex **1A**, we decided to extend the study by moving groups attached to the aromatic ring of **1**. By shifting the hydroxyl group from C(2) to C(4) and the nitro group from C(5) to C(3), a regioisomeric ligand (3-nitro-4-hydroxybenzoic acid, **2**, figure 1) was designed. The corresponding Zn(II) and Co(II) complexes show centrosymmetric structures, in which the carboxylato groups of **2** are covalently linked to the metals (Zn complex, **2A**, given as an example) [8]. Zn complex **2A** is not strictly centrosymmetric, on account of the discrete dissimilarity exhibited by the metal–$O_{\text{carboxylato}}$ bond lengths: 2.059(2) Å and 2.074(2) Å. The 3-hydroxy-4-nitrobenzoic acid (**3**, figure 1) was tailored by permuting the hydroxyl and nitro groups in **2**. Depending on the experimental conditions, two interconvertible Mg(II) complexes of **3** can be obtained (**3A** and **3B**). Complex **3A** exhibits an ionic centrosymmetric structure, in which the two 3-hydroxy-4-nitrobenzoato anionic moieties are not directly linked to $[Mg(H_2O)_6]^{2+}$ cation. Complex **3B** exhibits an unusual *zwitterionic* structure, in which the *phenoxo* group at C(3) of a *single* molecule of **3** is covalently linked to Mg. In that structure, both Mg and the carboxylato group are ionized (Mg^+ and COO^-) [10]. Crystal structures of Co(II) and Zn(II) complexes of 2-hydroxy-4-nitrobenzoic acid [**4**, figure 1, a regioisomer of **1–3**, resulting from the formal displacement of the nitro group from C(5) to C(4) in **1**] have been reported [11]. The two isomorphous structures are centrosymmetric (Zn complex, **4A**, given as an example) in which the two 2-hydroxy-4-nitrobenzoato ligands are covalently linked to the metal.

In this study, we first address the question as to whether ionic structures exhibited by magnesium complexes **3A** and **3B** would also be characteristic for complexes of "softer" metals cobalt and nickel. Our second objective involved the evaluation of the electronic effects of ligand substituents to determine the architecture of corresponding metal complexes. Specifically, we turned to the replacement of the electron-withdrawing nitro group, present in **1–4**, by the electron-donating methoxy group. This was illustrated through the structure elucidation of the Zn(II) complex of 2-hydroxy-4-methoxybenzoic acid (**5**).

2. Experimental

2.1. *Materials and physical measurements*

Commercially available 3-hydroxy-4-nitrobenzoic acid, 2-hydroxy-4-methoxybenzoic acid, zinc sulfate heptahydrate, cobalt sulfate heptahydrate, and nickel chloride hexahydrate were used without purification. Syntheses of metal complexes were performed at room temperature. Characterization of the complexes: elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 analyzer. The IR spectra were recorded with a Bruker Vector 22 spectrometer. Thermogravimetric analysis (TGA) was carried out on a TA Instruments TGA Q500 apparatus. Calibration was performed at different temperatures using Curie magnetic transitions for the recommended materials: alumel (163°C), nickel (354°C); calibration (mass) was carried out using a standard mass of 100 mg, calibration of the furnace was carried out between 100°C and 900°C to verify the thermocouple operation. All the experiments were performed under dry nitrogen with a flow rate of $6\times10^{-2}\,L\,min^{-1}$. Analysis of the compounds without nitrogen purging was conducted at a heating rate of $20^{\circ}C\,min^{-1}$ in order to determine the percentage of mass loss with the highest possible precision. A differential scanning calorimetry (DSC) experiment was carried out with a TA Instruments Universal V4.2E apparatus under nitrogen flow. The samples were introduced in aluminum pans and covered with holed caps in order to avoid any uncontrolled variation of pressure. Calibration of the temperature was performed with indium (156.6°C) and tin (231.9°C) of quality 5 N at a heating rate of $10^{\circ}C\,min^{-1}$.

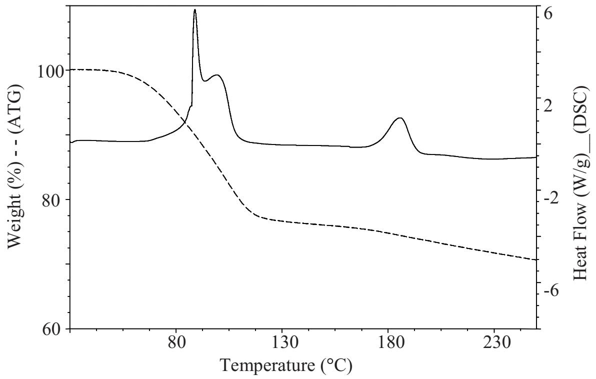

Figure 2. TGA (dotted line) and DSC (solid line) traces for **3C** showing the sequential loss of eight water molecules.

2.2. *Synthesis of complexes*

2.2.1. Complex 3C. The monosodium salt of **3** was prepared by neutralizing **3** (0.915 g, 5.00 mmol) with 5 mL of 1 mol L^{-1} NaOH. To this solution was added $CoSO_4 \cdot 7H_2O$ (0.702 g, 2.50 mmol) in 5 mL of water. After three days **3C** was filtered, crystallized from water, and dried over magnesium sulfate. Yield: 0.990 g (70%). Anal. Calcd for $C_{14}H_{24}N_2O_{18}Co$ (**3C**): C, 29.64; H, 4.26; N, 4.94. Found (%): C, 28.90; H, 3.90; N, 4.78. IR (neat, cm^{-1}): 3419(br, s), 1555(s), 1478(s), 1398(s), 1351(s), 1318(s), 1238(s), 1165(s), 1115(s), 1072(s), 958(s), 916(s), 845(s), 742(s), 658(s), 610(s). The TGA analysis of **3C** revealed a total mass loss of 26.1% on heating from 40°C to 195°C, corresponding to loss of eight water molecules (Calcd 25.3%) (20.0% between 40°C and 110°C (6 H_2O) and 6.1% between 110°C and 195°C (2 H_2O)). The DSC study of **3C** revealed, as the main events, three endotherms centered at 89°C, 109°C, and 195°C, corresponding to loss of water (figure 2).

2.2.2. Complex 3D. The monosodium salt of **3** was prepared by neutralizing **3** (0.915 g, 5.00 mmol) with 5 mL of 1 mol L^{-1} NaOH. To this solution was added $NiCl_2 \cdot 6H_2O$ (0.594 g, 2.5 mmol). After three days **3D** was filtered, crystallized from water, and dried over magnesium sulfate. Yield: 1.044 g (74%). Anal. Calcd for $C_{14}H_{24}N_2O_{18}Ni$ (**3D**): C, 29.64; H, 4.26; N, 4.94. Found (%): C, 30.22; H, 4.27; N, 4.94. IR (neat, cm^{-1}): 3598(m), 3248(br, s), 1555(s), 1472(s), 1432(s), 1399(s), 1320(s), 1237(s), 1074(m), 960(m), 916(s), 846(s), 782(s), 753(s), 654(s). The TGA analysis of **3D** revealed a total mass loss of 26.4% on heating from 40°C to 220°C, corresponding to loss of eight water molecules (Calcd 25.4%) (20.0% between 40°C and 140°C (6 H_2O) and 6.4% between 140°C and 220°C (2 H_2O)). The DSC study of **3D** revealed two endotherms centered at 108°C and 160°C, corresponding to loss of water.

2.2.3. Complex 5A. The monosodium salt of **5** was prepared by neutralizing **5** (0.840 g, 5.00 mmol) with 5 mL of 1 mol L^{-1} NaOH. To this solution was added $ZnSO_4 \cdot 7H_2O$ (0.720 g, 2.50 mmol). After three days **5A** was filtered, crystallized from water, and dried over magnesium sulfate. Yield: 0.779 g (72%). Anal. Calcd for $C_{16}H_{18}O_{10}Zn$ (**5A**): C, 44.10; H, 4.16. Found (%): C, 43.67; H, 4.23. IR (neat, cm^{-1}): 3246(br, m), 1631(s), 1585(s), 1440(s), 1365(s), 1272(s), 1196(s), 1157(s), 1097(s), 1027(s), 962(s), 835(s), 779(s), 696(s), 632(s). The TGA analysis of **5A** revealed a mass loss of 9.6% on heating from 80°C to 150°C, corresponding to loss of two water molecules (Calcd 8.3%). The DSC study of **5A** revealed, as the main event, one endotherm centered at 147°C, corresponding to loss of water.

2.3. *X-ray diffraction measurements*

Diffraction data were collected with a Bruker-SMART three-axis diffractometer equipped with a SMART 1000 CCD area detector using graphite monochromated Mo-Kα radiation (wavelength $\lambda = 0.71073$ Å) at 298 or 100.0(1) K. The low temperature was reached by an evaporated liquid nitrogen stream over the crystal, provided by the Oxford Cryosystem device. Data collection and processing were performed using Bruker SMART programs [12] and empirical absorption correction was applied using SADABS [12]. The structure was solved by direct methods using SIR97 [13] and refined by full-matrix least-squares based on F^2 using CRYSTALS [14] or SHELXL-97 software [15]. The molecule was drawn using the CAMERON program [16]. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were located in Fourier difference maps and refined isotropically with $U_{iso} = 1.20U_{eq}$, where U_{eq} is the equivalent isotropic atomic displacement parameter of the attached atom. Crystal parameters, data collection, and the refinement details for **3C**, **3D**, and **5A** are reported in table 1.

3. Results and discussion

3.1. *Description of the crystal structures of 3C and 3D*

The structure determinations of **3C** and **3D** indicate that the complexes are isomorphous and crystallize in $P\bar{1}$ triclinic space group. The crystallographic unit can be represented by the general formula $[(C_7H_4NO_5)_2M(H_2O)_4 \cdot 4(H_2O)]$, where M = cobalt or nickel. In sharp contrast to ionic complexes **3A** and **3B**, **3C** and **3D** exhibit covalent structures in which the carboxylato groups of two ligands **3** are directly linked to the metal. Since **3C** and **3D** are isomorphous, no notable differences were observed between their structural parameters. For that reason, only the details of the X-ray structure of the Co(II) complex (**3C**), arbitrarily chosen, are reported and discussed in this article. The CAMERON [16] molecular structure of the Co(II) complex (**3C**) is represented in figure 3, with the atom numbering system used in table 2 which lists the most relevant bond distances and angles. The structure of **3C** consists of *centrosymmetric* monomers with the metal occupying the inversion center at $-x+1$, $-y+1$, $-z+1$ of the triclinic unit cell. This symmetry is revealed by two identical metal–$O_{carboxylato}$ lengths of 2.069(2) Å and two pairs of metal–O(water) distances of 2.112(2) Å and 2.114(2) Å. The monodentate metal ligation by O(26) and $O(26)^{iii}$ carboxylato is highlighted by the significant distance [3.396(2) Å] separating Co center from O(27) atom, which prevents any bonding. The *cis* angles around the Co center

Table 1. Crystal data and structure refinement parameters for **3C**, **3D**, and **5A**.

Compound	**3C**	**3D**	**5A**
Empirical formula	$C_{14}H_{24}N_2O_{18}Co$	$C_{14}H_{24}N_2O_{18}Ni$	$C_{16}H_{18}O_{10}Zn$
Molecular weight	567.28	567.06	435.69
Color	Rust-colored	Olive-greenish	Pale beige
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å, °)			
a	7.313(5)	7.375(5)	5.118(5)
B	7.371(5)	7.429(5)	11.460(5)
c	11.769(5)	11.721(5)	15.823(5)
A	91.241(5)	90.970(5)	69.602(5)
β	96.329(5)	96.435(5)	89.949(5)
γ	118.693(5)	118.386(5)	79.801(5)
Volume ($Å^3$), Z	551.1(6), 1	559.6(6), 1	854.3(9), 2
Calculated density ($g\,cm^{-3}$)	1.709	1.683	1.694
Absorption coefficient (mm^{-1})	0.873	0.960	1.494
$F(000)$	293	294	448
Crystal size (mm^3)	0.15×0.20×0.35	0.17 × 0.22 × 0.30	0.08 × 0.18 × 0.30
θ ranges (°)	1.74–29.95	1.75–27.53	1.376–29.748
$h/k/l$	−10,9/−10,10/0,15	−9,9/−9,9/0,15	−7,6/−15,13/−17,20
Temperature (K)	100	298	100
Reflections collected	4098	3956	6158
Reflections used $\geq 3\sigma(I)$	3332	2008	3474
Parameters	160	160	260
$R\ [F]$	0.0224	0.0268	0.0433
$wR\ [F]$	0.0237	0.0279	0.0981
Goodness-of-fit on F^2	1.1094	1.1212	1.038
Residual density ($e\,Å^{-3}$)	−0.36; 0.54	−0.28; 0.21	−0.769; 3.105
Refine Ls shift/su max	0.000922	0.000093	0.000265

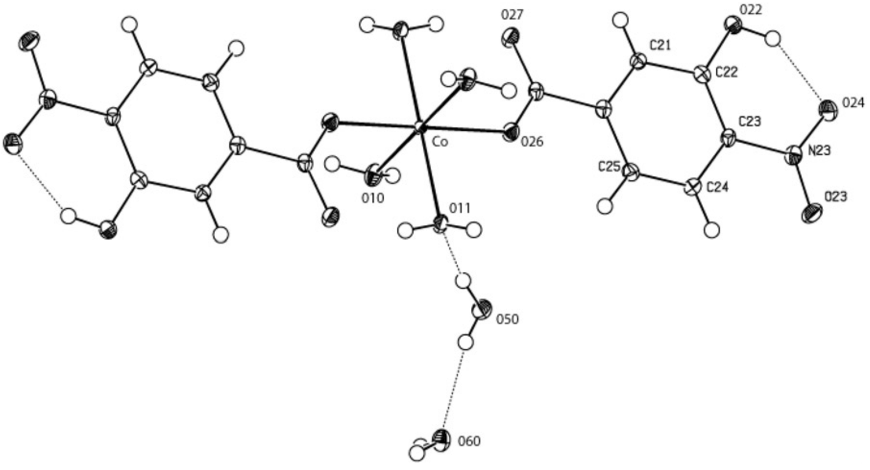

Figure 3. Labeled CAMERON diagram of **3C**. Ellipsoids are drawn at 50% probability level.

consist of three very similar pairs [86.60(3)° and 93.40(8)°, 86.79(3)° and 93.21(3)°, 88.00(6)° and 92.00(6)°], while identical values were observed for the three *trans* angles, 179.99(7)°, resulting in a slightly irregular octahedron around Co. TGA and DSC experiments involving **3C** show the departure of four water molecules of crystallization and two water molecules coordinated to metal between 40°C and 110°C. Removal of

Table 2. Selected bond distances (Å) and angles (°) for **3C**.

Co–O(10)	2.114(2)	O(10)–Co–O(11)	86.60(3)	C(20)–C(26)–O(26)	116.44(9)
Co–O(11)	2.111(2)	O(10)–Co–O(11)^{i}	93.40(8)	C(20)–C(26)–O(27)	117.86(9)
Co–O(26)	2.069(2)	O(10)–Co–O(10)^{i}	179.99(7)	O(26)–C(26)–O(27)	125.69(9)
C(26)–O(27)	1.265(2)	O(11)–Co–O(11)^{i}	179.99(7)	C(23)–N(23)–O(23)	119.04(9)
C(26)–O(26)	1.261(2)	O(11)–Co–O(26)^{i}	93.21(3)	C(23)–N(23)–O(24)	118.56(9)
N(23)–O(23)	1.227(2)	O(11)–Co–O(26)	86.79(3)	O(23)–N(23)–O(24)	122.40(9)
N(23)–O(24)	1.245(2)	O(26)–Co–O(26)^{i}	179.99(7)		
		O(26)–Co–O(10)^{i}	88.00(6)		
		O(26)–Co–O(10)	92.00(6)		

Symmetry code: ^{i} $-x+1$, $-y+1$, $-z+1$.

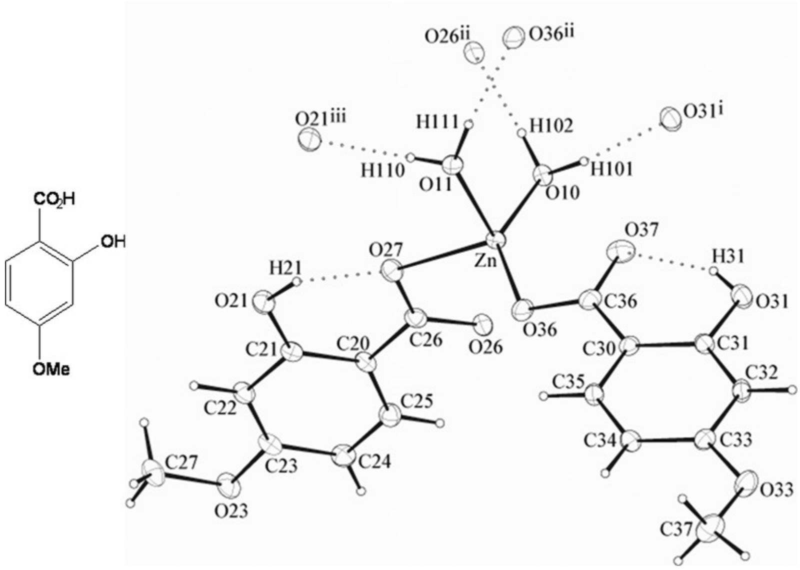

Figure 4. Canonical representation of **5** and labeled CAMERON diagram of corresponding Zn complex **5A**. Ellipsoids are drawn at 50% probability level. For convenience, the metal ligation is depicted in a bis-monodentate mode (see text). Symmetry codes: i, $-x+2$, $-y$, $-z+1$; ii, $x+1$, y, z; iii, $-x+2$, $-y$, $-z$.

the two remaining water molecules required harsher thermal conditions (195°C), giving evidence of a strong anchoring of two water molecules to Co atom (section 2.2.1 and figure 2).

3.2. *Description of the crystal structure of complex 5A*

The CAMERON [16] molecular structure of the Zn(II) complex (**5A**) of **5** is represented in figure 4, with the atom numbering system used in table 3, which lists the most relevant bond distances and angles. The crystallographic unit of $[(C_8H_7O_4)_2Zn(H_2O)_2]$ (**5A**) consists of a *dissymmetric* covalent structure in which the carboxylato groups of two ligands **5** are directly linked to Zn. This dissymmetry is clearly revealed through the dissimilarity between $O(27)_{carboxylato}$–Zn and $O(36)_{carboxylato}$–Zn bond lengths [2.121(2) Å and 1.998(2) Å, respectively] and the nearly orthogonal arrangement of the

Table 3. Selected bond distances (Å) and angles (°) for **5A**.

Zn–O(10)	1.981(2)	O(10)–Zn–O(11)	98.00(11)
Zn–O(11)	2.019(2)	O(10)–Zn–O(27)	112.92(9)
Zn–O(27)	2.119(2)	O(11)–Zn–O(27)	89.44(9)
Zn–O(36)	1.999(2)	O(10)–Zn–O(36)	138.84(9)
C(26)–O(26)	1.269(3)	O(11)–Zn–O(36)	98.07(10)
C(26)–O(27)	1.285(3)	O(27)–Zn–O(36)	104.88(9)
C(36)–O(36)	1.291(4)		
C(36)–O(37)	1.254(4)		

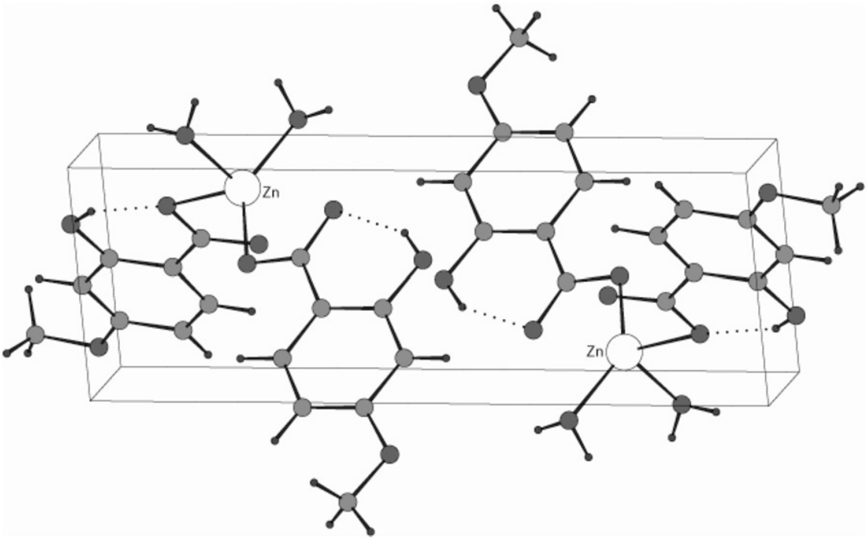

Figure 5. Crystal unit of **5A** (*P*-1 *racemic* centrosymmetric space group, $Z = 2$) showing the presence of a pair of enantiomeric molecules. The crystal packing is mainly governed by stacking interactions (not depicted here) involving the aromatic moieties.

two aromatic planes (dihedral angle: 94.8°). The presence of six strongly dissimilar O–Zn–O bond angles at the metal [ranging from 89.44(9) to 138.84(9)° (table 3)] results in a *markedly* irregular coordination tetrahedron around Zn. This severe steric strain destabilizes the tetrahedral metallic core; the energetically preferred alternative appears to be the sterically less hindered five-coordinate pyramidal geometry depicted in figure 6 (section 4.2). The CAMERON drawing of **5A** suggests that each ligand could be bidentate; however, such coordination proved to be in contradiction with the marked difference observed between O(36)–Zn and O(37)–Zn distances (see below). Consequently, a conventional alternative model was designed, involving bis-monodentate ligation of the metal with the nearest $O_{carboxylato}$ of each ligand, O(27) and O(36) (figure 4). Nevertheless, the involvement of a *mixed* (monodentate *and* bidentate) ligation at Zn needs to be considered for an ultimate adjustment at the metal-coordination pattern of the previous model (see section 4.2). Since the O(37)–Zn distance [2.535(2) Å] is markedly longer (by 0.537 Å) than the O(36)–Zn bond length [1.998(2) Å], O(37) cannot significantly participate in metal ligation. However, the slight difference (0.112 Å) observed between the O(26)–Zn distance [2.233(2) Å] and the

O(27)–Zn bond length [2.121(2) Å] suggests that the O(26) atom could cooperate with O(27) in bidentate coordination of Zn. In accord with this hypothesis, the ORTEP drawing [17] of **5A** (not depicted here) reveals a mixed mode of metal–ligand coordination: monodentate at O(36) and bidentate at O(26) and O(27).

Two *dissimilar* intramolecular H-bonds [*d* H(21) ··· O(27): 1.848(2) Å, *d* H(31) ··· O(37): 1.778(3) Å; ∠O(21)–H(21) ··· O(27): 140.39(7)°, ∠O(31)–H(31) ··· O(37): 146.31(8)°] are found in **5A**, reflecting the dissymmetric coordination of the two ligands. These differences in the intramolecular H-bond patterns are likely caused by dissimilar environments at the two H-bonded O(27) and O(37) carboxylates, respectively, coordinated and *not* coordinated with the metal center. The two methoxy groups ornamenting this complex exhibit, at first sight, dissimilar conformational geometries. In order to identify the factor(s) responsible for such conformational geometries, comparison was made between the unshared electrons pairs at the methoxy oxygen atoms and the carboxylate bonds coordinated with the metal [C(26)–O(27) and C(36)–O(36)], revealing that they are aligned in *antiparallel* orientation, in *both* ligands (figure 4). This suggests that the conformational geometries at the two methoxy group sites are in fact dictated by the dissymmetric environment at the metal. The quasi-perfect coplanarity observed between the three planes defined by adjacent carboxylate, aromatic spacer and methoxy group [$C_{aromatic}$–O–C(H_3) plane] in *para*-position give evidence of electron density delocalization within this triad, consistent with the previous assumption. The most intriguing characteristic displayed by **5A** consists in its *non-symmetric* structure, even though the central metal component is covalently bound to two *identical* ligands. A tentative interpretation of this phenomenon is given in section 4.2. Another manifestation of the dissymmetry in **5A** is its *chirality*, highlighted by the presence of a pair of enantiomeric molecules per unit cell (figure 5). The presence of an intermolecular network of four *dissimilar* H-bonds, in discriminating between the two water molecules bound to Zn, play a critical role in the manifestation of this chirality [interatomic distances (in Å): O(11)-O(21^{iii}): 2.678(4), O(11)-O(36^{ii}): 2.726(4), O(10)-O(26^{ii}): 2.648(4), O(10)-O(31^{i}): 2.715(4)].

4. Concluding remarks

4.1. *Tentative interpretation of the solid-state architecture of metal complexes*

Whilst it would be premature to draw definite conclusions on the factors which govern the solid-state architecture of substituted benzoate-metal complexes, some general observations can be made. Three main factors can *a priori* affect the structure of such complexes: the nature of starting ligand and metal, and the type of protocol used to elaborate these complexes. With the exception of **3B**, all other complexes reported in this article have been synthesized in the *same* operating conditions, namely the addition at room temperature of a divalent metal salt to an aqueous solution of two equivalents of ligand monosodium salt, the variance being so restricted to only the nature of the ligand and metal. Ligand **1** led invariably to ionic stacked structures of type **1A**, *irrespective of the nature of the metal* (Mg, Zn, Co, and Ni), a surprising reactivity which probably originates from the strong acidity of **1** (pKa_{COOH}: *ca* 2.1 [9]). This marked acidity clearly reflects on the presence of a hydroxyl group in the *ortho*-position to the carboxylate [compare the pKa_{COOH} of salicylic acid (*ca* 2.8) with that of benzoic acid (*ca* 4.2)] and, on the other hand, the presence of an electron-withdrawing nitro group at the C(5) position. This substituent indeed matches with the C(2) hydroxyl, in that this (*para*) regiochemical relationship is favorable to a mesomeric electron density delocalization, thus reinforcing the acidity at the salicylic site. Assuming that the "acidifying effect" attributed to the hydroxyl group in **1** is essentially due to H-bonding between the *ortho*-positioned COOH and OH groups, this effect is necessarily restricted to only salicylic-type ligands **1**, **4**, and **5**. Consequently, a significant decrease in the acidity was expected for **2** and **3** compared with that of **1**, considering that their hydroxyl groups, occupying, respectively, the C(4) and C(3) positions, are less potent in terms of acidity strengthening. In fact, **2** led to covalent complexes of type **2A** with Zn and Co metals. Ligand **3** (pKa_{COOH}: *ca* 3.1 [10]) led to *ionic* complex **3A** with the "hard" Mg^{2+} and *covalent* structures **3C** and **3D** with the "softer" Co and Ni. Though being a member of the salicylic family, a substantial acidy weakening was expected for **4** compared with that of regioisomer **1**, considering that its nitro group, at C(4), does not electronically match with the C(2) hydroxyl owing to their unfavorable *meta*-relationship. This ligand led to covalent complexes of type **4A** with Zn and Co metals. The presence at C(4) of an electron-donating methoxy group in **5** results in a slight decrease in its acidity [pKa_{COOH}: *ca* 3.0 (this work)] compared with that of parent salicylic acid (pKa_{COOH}: *ca* 2.8). This ligand led to the *dissymmetric* covalent structure **5A** with Zn.

4.2. *Rationalization of the dissymmetry in complex 5A*

The marked structural dissymmetry in **5A** can be tentatively rationalized by referring to the well-known propensity of certain four-coordinate metal centers to accommodate an additional ligand, resulting in five-coordinate pyramidal geometry (a relevant example of tetrahedral/pentahedral dual coordination behavior of Cu^{2+} has been reported [18]). Because of **5A**'s putative involvement in bidendate ligation of Zn, the $O(26)_{carboxylato}$ could play the role of *internal* fifth coordinating center, giving a Zn coordination sphere of five oxygen atoms. Remarkably, the spatial arrangement at zinc of **5A** fulfills the geometrical criteria inherent in this alternative model, in that the five oxygen atoms occupy the vertices of a square pyramid (figure 6). Apart from O(26)–O(27) distance (2.19 Å), the three other interatomic distances separating the basal atoms are rather similar (2.91, 3.03, and 3.06 Å) and satisfy the geometric requirements for a square base. This structure is also characterized by a relatively high *index of trigonality*, defined as the pathway of distortion, along the metal-apex axis, from square pyramidal toward trigonal-bipyramidal. In fact, by making use of the "Addison τ parameter" criterion [19], the present index of trigonality is conveniently described as being 63%. Being *a priori* sterically less constrained, and therefore more stable than the tetrahedron of highly irregular geometry, this alternative pyramidal structure appears to be the model with a mixed ligation [monodentate at O(36) and bidentate at O(26) and O(27)]. The metal then dictates the dissymmetry at two other sites: the nearby intramolecular hydrogen bonds and the remote methoxy groups. In the latter case, the unshared electron pairs at the methoxy oxygen atoms and the carboxylates participating in metal ligation [C(26)–O(27) and C(36)–O(36), see below] are *antiperiplanar*, a conformational geometry which minimizes the repulsive dipole–dipole interactions at these sites.

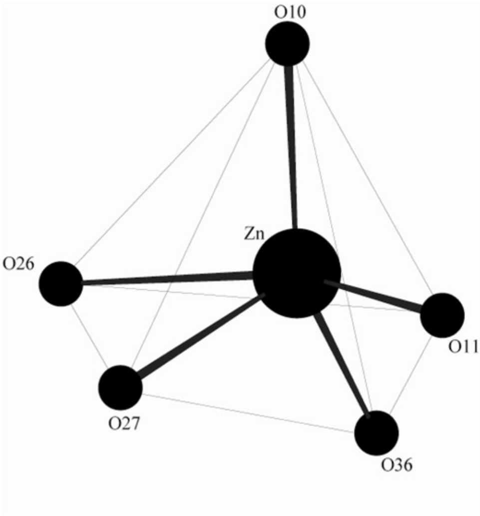

Figure 6. Distorted square pyramidal structure of Zn in **5A**. Interatomic distances between the basal atoms: O(26)–O(27): 2.19 Å, O(27)–O(36): 2.91 Å, O(36)–O(11): 3.03 Å and O(11)–O(26): 3.06 Å. O(10) occupies the apical position.

Manifestation of these long-distance dipolar interactions implies a mesomeric electron density delocalization within the methoxy group, aromatic spacer, and carboxylate (see section 3.2). Regarding the bidentate metal-ligation, the C(26)–O(27) bond was deliberately chosen to make comparison with the methoxy group, guided by *unequal* involvement of O(26) and O(27) in coordination of Zn. In fact, the O(27)–Zn bond length is substantially shorter than O(26)–Zn. The differences between the three $O_{carboxylato}$–Zn bond lengths (Δd), with the corresponding bond stretching percentages in brackets, are Δd [O(26)–Zn–O(27)–Zn]: 0.112 Å (5.3%); Δd [O(27)–Zn–O(36)–Zn]: 0.123 Å (6.2%).

5. Summary and future prospects

By exhibiting a strong dissymmetry, Zn complex **5A** constitutes the most intriguing structure reported in this article. This dissymmetry was interpreted on the basis of a mixed (monodentate and bidentate) metal-ligation and a pyramidal coordination at zinc. Although versatile coordination modes are available with the carboxylate-divalent cation systems, there are very few examples of mixed ligation. In this context, the crystal structure of Co(II) complex of 2-benzoylbenzoic acid (further ligated with one phenanthroline and one water molecule) is of interest [20], exhibiting distorted octahedral coordination at Co and a mixed ligation mode at the two carboxylate sites [$O_{carboxylato}$–Co bond lengths: 2.044 Å (monodentate), 2.137 and 2.224 Å (bidentate)]. Of relevant interest, the crystal structure of a Zn(II) complex of 4-nitro benzoic acid (further ligated with two DMSO and one water molecule) shows a five-coordinate metal of distorted square pyramidal geometry, with a dissymmetric bis-monodentate coordination pattern at the two carboxylate sites ($O_{carboxylato}$–Zn bond lengths: 2.011 Å and 2.045 Å) [21].

We are currently studying the crystal growth of **5A** at various pHs, which might lead to a competitive chelation through the phenoxo site. In fact, such an alternative coordination mode was previously encountered in the "unusual" Mg complex **3B** (figure 1), revealing the ambident behavior of ligand **3**. In other respects, a change in the synthetic protocol (more specifically the utilization of solid-phase chemistry [21]) might, in turn, lead to a variety of polynuclear zinc clusters.

Supplementary material

CCDC 755073, CCDC 755074, and CCDC 755075 contain the supplementary crystallographic data for **3C**, **3D**, and **5A**. These data can be obtained, free of charge, *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK: Fax: (+44) 1223-336-033, or E-mail: deposit@ccdc.cam.ac.uk

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