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# Two novel Zn(II) helical chain polymers containing both bridging and terminal carboxylato groups

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#### Abstract

Two novel carboxylato-bridged Zn(II) polymeric complexes  $[Zn(L)(CCl_3COO)]_n$  and  $[Zn(L)(CF_3COO)]_n$ , where [L = 2-N-(2'-pyridylimine)benzoic acid] have been synthesized and structurally characterized. The structures of the two complexes are similar with the  $Zn(L)(Cl_3CCO_2)$  or  $Zn(L)(F_3CCO_2)$  units being repeated to form infinite helical chains. In each structure, the neighbouring Zn atoms are bridged sequentially by syn-anti carboxylate groups of the Schiff base. © 2003 Elsevier Science B.V. All rights reserved.

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The crystal engineering of solid materials is of ever increasing interest to chemists and material scientists alike. It has become apparent that coordination polymers of specific network topology may be prepared by the appropriate selection of metal and multifunctional ligands [1–3]. The different network derived so far include one-dimensional chains, which can be helical, twodimensional sheets with a variety of connectivities and various three-dimensional structures [4]. In this regard studies on metal carboxylato complexes as models for metalloproteins have long been of interest [5–7]. Moreover, because in metalloproteins, carboxylate ligands are provided by side amino acid chains, polydentate chelating ligands containing a carboxylate groups are of biological relevance [8].

As a general trend on the basis of their representative geometries, the syn-syn conformations prefer to form dinuclear complexes while the syn-anti or anti-anti bridges prefer the formation of chain or layer structures [9,10]. Carboxylate groups are known to assume different types of bridging conformations: triatomic syn-syn, syn-anti, anti-anti and monoatomic [10]. Carboxylatobridged zinc complexes are of continuous interest because of their potential relevance as enzyme model [11]. In recent years, there has been a growing interest in enzymes with more than one zinc atom in the active site [12–15]. Another reason for the importance of zinc in enzyme chemistry is that it can adopt various coordination numbers, i.e., 4, 5, or 6 relatively easily [16,17]. Recently Colacio et al. [18] has reported some new carboxylato-bridged copper(II) complexes with tridentate Schiff-base ligands containing one carboxylate group, where the carboxylato group undergoes selfassembly process promoted by metal ions leading to syn-anti polymeric network.

In our efforts to investigate the bonding nature of carboxylato-bridged zinc(II) complexes, we have now synthesized and structurally characterized two helical chain polymeric network  $[Zn(\mu-L)(CCl_3COO)]_n$  (1) and  $[Zn(\mu-L)(CF_3COO)]_n$  (2)  $(L = C_{13}H_{10}N_2O_2)$ . To our knowledge, these complexes are the first examples of carboxylato-bridged zinc(II) polymers, containing both

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bridging and terminal unidentate carboxylate groups derived from zinc-trichloro or trifluoroacetate and Schiff base. The synthesis <sup>2</sup> and structural characterization <sup>3</sup> of these interesting complexes are reported herein. Recently, it has been reported that in a new oxalatobridged complex, the same Schiff-base ligand acts as a tridentate [19], but in the present case it behaves as a tetradentate ligand. It should be mentioned that the helical chain structural motif is of current interest in supramolecular chemistry owing to its involvement in biological systems and enantioselective catalysis [20].

The structures of the complexes 1 and 2 are similar in the sense that they are both polymeric, in which the  $Zn(L)(Cl_3CCO_2)$  or  $Zn(L)(F_3CCO_2)$  ( $L = C_{13}H_9N_2O_2^-$ ) units are repeated to form infinite helical chains. In each structure, the neighbouring Zn atoms are bridged sequentially by syn-anti carboxylate groups of the Schiff base. The immediate environments of the Zn centre and a perspective view of the helical chain of 1 are given in Figs. 1 and 2, respectively; the corresponding views of 2 are given in Figs. 3 and 4, respectively.

In the structure of 1, the Schiff-base anion acts as a tridentate ligand involving its two nitrogen [N(1), N(2)] and one carboxylate oxygen [O(1)] atoms towards a zinc(II) ion, while it utilizes its other carboxylate oxygen [O(2)] atom to form a bridge with another zinc(II) ion. The  $Cl_3CCO_2^-$  anion is bonded to the Zn ion through one of its oxygen [O(3)] atoms only. The metal ion ex-

Crystal data for 1, empirical formula C15H9Cl3N2O4Zn, FW 452.96, monoclinic,  $P2_1/n$ , a = 11.6198(12), b = 9.088(2), c =17.0098(8) Å,  $\beta = 109.372(6)^{\circ}$ , V = 1694.6(3) Å<sup>3</sup>, Z = 4, D(calculated) = 1.775 mg/m<sup>3</sup>,  $\lambda$ (Mo-K $\alpha$ ) = 0.71073 Å,  $\mu$ (Mo-K $\alpha$ ) = 1.945 mm<sup>-1</sup>, T = 293(2) K, Nonius CAD4 diffractometer, crystal size  $0.40 \times 0.35 \times 0.30$  mm, 3243 reflections collected, 3082 unique  $(R_{\rm int} = 0.0137), R_1 = 0.0295$  [data with  $I > 2\sigma(I)$ ],  $wR_2 = 0.0808$  (all data). Crystal data for 2,  $C_{15}H_9F_3N_2O_4Zn$ ,  $M_r = 403.61$ , monoclinic, space group  $P2_1/c$ , a = 10.727(8), b = 16.382(9), c = 9.122(7) Å,  $V = 1535(2) \text{ \AA}^{3},$  $\beta = 106.80(6)^{\circ}$ , Z = 4,D(calculated) =1.747 mg/m<sup>3</sup>,  $\lambda$ (Cu-K $\alpha$ ) = 1.54178 Å,  $\mu$ (Cu-K $\alpha$ ) = 2.789 mm<sup>-1</sup>, T = 293(2) K, Picker 4 circle Stoe diffractometer, crystal size  $0.10 \times 0.07 \times 0.05 \text{ mm}, \ 1740$  reflections collected, 1578 unique  $(R_{\text{int}} = 0.0278, R_1 = 0.0667 \text{ [data with } I > 2\sigma(I)\text{]}, wR_2 = 0.1707 \text{ (all } I = 0.0278)$ data). Programs: structure solution (SHELX-S) [22] and refinement (SHELXL-96) [23] for both compounds.

Fig. 1. A general view of the structure of 1 showing the immediate environments of the Zn atom and atom labeling. Atom numbers marked with #1 and #2 are generated by symmetry (1/2 - x, -1/2 + y, 1/2 - z) and (1/2 - x, 1/2 + y, 1/2 - z), respectively. Selected distances (Å) and angles (°): Zn(1)–N(1) 2.161(2), Zn(1)–N(2) 2.163(2), Zn(1)–O(1) 2.018(2), Zn(1)–O(2)#1 1.985(2), Zn(1)–O(3) 1.993(2), O(2)#1–Zn(1)–O(3) 108.71(8), O(2)#1–Zn(1)–O(1), 93.37(8), O(3)–Zn(1)–O(1) 108.78(8), O(2)#1–Zn(1)–N(1) 160.39(9), O(3)–Zn(1)–N(1) 90.63(8), O(1)–Zn(1)–N(1) 83.05(8), O(2)#1–Zn(1)–N(2) 92.84(9), O(3)–Zn(1)–N(2) 116.12(9), O(1)–Zn(1)–N(2) 129.69(9), N(1)–Zn(1)–N(2) 75.17(9), C(1)–O(1)–Zn(1) 130.0(2), C(1)–O(2)–Zn(1)#2 124.6(2), C(14)–O(3)–Zn(1) 119.4(2).





Fig. 2. A view of the structure of **1** showing the formation of the helical chain along the *b*-axis.

<sup>&</sup>lt;sup>2</sup> The Schiff-base ligand (HL) [L = 2-N-(2'-pyridylimine)benzoicacid] was prepared by refluxing pyridine 2-carboxaldehyde (1 mmol)with anthranilic acid (1 mmol) in 20 ml methanol for half an hour. Theresultant brownish-red liquid was used as ligand without further $purification. The <math>[Zn(\mu-L)(CCl_3COO)]_n$  (1) and  $[Zn(\mu-L)(CF_3COO)]_n$ (2) were prepared by drop-wise addition of the ligand solution (1 mmol) to a solution of zinc-trichloroacetate (0.5 g, 1 mmol) or trifluoroacetate (0.48 g, 1 mmol) in methanol. The resulting brownishred solutions for both 1 and 2 were kept at room temperature for two days. This yielded light-brownish rectangular crystals for both complexes, which were isolated by filtration and air-dried. Yield: 46% for 1 and 50% for 2. Anal. Complex 1: Found: C, 39.5; H 1.9; N 6.0; Zn, 14.5. Calcd. for  $C_{15}H_9Cl_3N_2O_4Zn$ : C, 39.7; H, 2.0; N, 6.2; Zn, 14.4. Complex 2: Found. C, 44.4; H, 2.0; N 6.8; Zn, 16.3. Calc. for  $C_{15}H_9F_3N_2O_4Zn$ : C, 44.6; H, 2.2; N, 6.9; Zn, 16.2.



Fig. 3. A general view of the structure of **2** showing the immediate environments of the Zn atom and atom labeling. Atom numbers marked with #1 and #2 are generated by symmetry (x, 1/2 - y, 1/2 + z) and (x, 1/2 - y, 1/2 - z) respectively. Selected distances (Å) and angles (°): Zn–N(1) 2.124(5), Zn–N(8) 2.165(5), Zn–O(16) 2.015(4), Zn–O(17)#1 1.962(5), Zn–O(1F) 1.986(5), O(17)#1–Zn–O(1F) 112.4(2), O(17)#1–Zn–O(16), 99.5(2), O(1F)–Zn–O(16) 96.3(2), O(17)#1–Zn–N(1) 114.7(2), O(1F)–Zn–N(1) 88.8(2), O(16)–Zn–N(1) 140.4(2), O(17)#1–Zn–N(8) 92.8(2), O(1F)–Zn–N(8) 154.5(2), O(16)–Zn–N(8) 82.7(2), N(1)–Zn–N(8) 76.6(2), C(2F)–O(1F)–Zn 122.8(4), C(15)–O(16)–Zn 132.1(4), C(15)–O(17)–Zn#2 128.5(4).



Fig. 4. A view of the structure of 2 showing the formation of the helical chain along the *c*-axis.

hibits a  $ZnN_2O_3$  coordination mode, showing a highly distorted trigonal bipyramidal geometry. The basal positions are occupied by the N(2) and O(1) atoms of the Schiff base and the O(3) atom of the  $Cl_3CCO_2^-$  group

and the axial sites are occupied by the N(1) atom of the Schiff base and O(2)#1 atom from a symmetry-related Schiff base. The two Zn–N distances 2.161(1) and 2.163(2) Å are identical. The two Zn–O distances involving the bridging carboxylate group 2.018(2), 1.985(2) Å are also similar and comparable with the Zn–O distance involving the trichloroacetate group 1.993(2) Å. It is to be noted that the C–O distance involving the O(4) atom not bonded to the metal 1.211(4) Å is considerably shorter than those involving the O(1), O(2) and O(3) atoms bonded to zinc 1.250(4)–1.264(3) Å. The intrachain Zn  $\cdots$ Zn separation is 5.080 Å. The orientation of the carboxylate groups leads to an infinite helical chain structure generated by the 2-fold screw axis parallel to the crystallographic *b*-axis.

The structure of **2** is similar to that of **1** in many respects. The Schiff-base anion is again tridentate towards a zinc(II) ion, and simultaneously it also forms a bridge with a neighbouring zinc(II) centre related by a *c*-glide plane. The Schiff-base ligand thus utilizes both of its carboxylato-oxygen atoms, while the  $F_3CCO_2^-$  anion is monodentate. The Zn atom in this structure also exhibits ZnN<sub>2</sub>O<sub>3</sub> coordination environments, but here the geometry may be best described in terms of a distorted square pyramid. The pyramid base is formed by the N(1), N(8), O(16) and O(1f) atoms, while the apical position is occupied by the bridging O(17)#1 atom. The N(1), N(8), O(16) and O(1f) atoms show deviations of -0.114(8), 0.118(8), -0.105(8) and 0.101(8) A, respectively, from the mean plane of these atoms, showing a tetrahedral distortion from planarity. The Zn atom is displaced from this plane by 0.546(5) A towards the apical O(17)#1 atom. The carboxylate bridges are forced to orient in a mutually basal-apical positions. The intrachain  $Zn \cdots Zn$  distance of 5.169 Å is only marginally longer than that in 1. The Zn–N and Zn–O distances [2.124(5), 2.165(5) and 1.962(5)-2.015(4) A, respectively], and the dimensions of the Schiff-base ligand are similar to the corresponding values in 1. Interestingly, the infinite helical chain in 2 propagates along the crystallographic *c*-axis.

In the IR spectrum, complex **1** shows bands at 1695 and 1400 cm<sup>-1</sup> and complex **2** at 1705 and 1395 cm<sup>-1</sup> assigned as  $v_{as}(COO^-)$  and  $v_{sym}(COO^-)$ , respectively. The differences ( $\Delta v$ ) 295 cm<sup>-1</sup> for **1** and 310 cm<sup>-1</sup> for **2** are consistent with the bridging coordination modes of the carboxylate group [21]. The complexes also show two bands  $v_{as}(COO^-)$  and  $v_{sym}(COO^-)$  at 1636 and 1448 cm<sup>-1</sup> for **1** and at 1638 and 1445 cm<sup>-1</sup> for **2**, respectively, suggesting a monodentate coordination mode of the carboxylate group [21]. These findings are confirmed by the X-ray structure analyses, which clearly reveal that the carboxylate groups belonging to the Schiff base and trihaloacetate groups, respectively, are indeed bridging and monodentate in nature. The bands at 1586, 1473 and 1430 cm<sup>-1</sup> for **1** and at 1593, 1491 and 1428  $cm^{-1}$  for **2** may be assigned for the pyridine skeleton.

The complex **1** is stable up to 130 °C and complex **2** is stable up to 137 °C. The mass loss in the TGA curve corresponds to the release of one coordinated trichloroacetate or trifluoroacetate group per  $[Zn(\mu-L)$  $(CCl_3COO)]$  or  $[Zn(\mu-L)(CF_3COO)]$  unit between 131 and 210 °C for **1** and 137 and 219 °C for **2**, followed by the loss of one molecule of the Schiff-base ligand between 211 and 580 °C for **1** and 219 and 592 °C for **2**.

### Supplementary material

Full crystallographic details including atomic coordinates and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 204461 (1) and 204462 (2). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www:www: http://www.ccdc.cam.ac.uk).

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