Synthesis and crystal structure of a chiral two-dimensional metal-organic coordination polymer: (*S*-(−)-lactate)(isonicotinato)zinc(II)

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Letter

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The synthesis and X-ray characterization of the first example of an L-lactic acid two-dimensional metal coordination polymer with an additional bridging ligand, (*S*-(−)-lactate)-(isonicotinato)zinc(II), (*S*-μ-2-hydroxypropanoinato)zinc(II), 1 is reported. It crystallizes in the acentric orthorhombic space group $P2_12_12_1$ and displays powder SHG efficiencies *ca.* 1.2 times that of urea.

Since the discovery of the laser by Maiman in 1960, extensive research attention has been paid to the field of nonlinear optics in order to develop opto-electronic technologies, such as high-speed information processing and optical communications.[1] In the early stages, research investigations were mainly focused on pure inorganic materials, but the interest in organic materials for nonlinear optical applications has increased markedly in the last 20 years.[2] They display several advantages over inorganic materials, such as high nonlinearity, ultrafast response times and easy and economical processability. However, few examples can be used as applicable materials due to the mechanical and thermal instability of organic systems. More recently, metal-organic coordination polymers have been extensively studied and are expected to overcome the above-mentioned hurdles and bridge the gap between pure inorganic and organic nonlinear optical materials.[3,4] Furthermore, two typical examples exhibit the potential to overcome this problem[5] these being acentric coordination polymers constructed from asymmetric multidentate anionic ligands such as nicotinate, isonicotinate, 4-pyridylacritate and 3-[2-(4-pyridyl)ethenyl]benzoate which are thermally stable up to 360 °C. Herein, we report the synthesis, structure and second harmonic generation (SHG) property of (*S*-(−)-lactate)(isonicotinato)zinc(II), (S-μ-2-hydroxypropanoinato)zinc(II), **1**, which represents the first example of an L-lactic acid two-dimensional metal coordination polymer with an additional bridging ligand.

The reaction of isonicotinic acid with Zn^{2+} yields a monomeric tetrakis(aqua)bis(isonicotinato)zinc(II) complex, leaving carboxylate uncoordinated in the solution.[6] Recently, Atwood *et al.* and Burrows *et al.* both reported the use of the isonicotinate group for the construction of a cationic coordination polymer in which one of the oxygens of the carboxylate takes part in coordination to the metal.[7] Moreover, one of us also reported the hydrothermal synthesis of a novel condensed bis(isonicotinato)iron(II) complex in which both N and O atoms in the isonicotinate group coordinate to the iron ion.[8] It is noteworthy that use of the precursor of isonicotinic acid, 4-pyridinecarboxaldehyde, is crucial for the successful synthesis of the condensed coordination polymer under hydrothermal conditions. Bearing this in mind, we successfully obtained a novel and chiral two-dimensional zinc coordination polymer, **1**, under hydrothermal conditions in which the precursors of both L-lactic acid and isonicotinic acid, ethyl *S*-(−)-lactate and 4-pyridinecarboxaldehyde, respectively, were used as starting materials. The presence of carboxylate groups in **1** was definitely confirmed by the strong peaks at 1597, 1548 and 1391 cm^{-1} (C=O stretching mode) in the infrared spectrum. Moreover, the peak at 3446 cm^{-1} indicates the existence of a hydroxy group in **1**.

The two-dimensional polymeric structure of **1** was revealed by an X-ray single crystal diffraction study in which the coordination environment around the Zn(II) center in **1** is a slightly distorted octahedron (Fig. 1). The Zn(II) atom is located approximately at the center of the near plane formed by four oxygen atoms from three lactic acid ligands. The remaining apical positions are occupied by N and O atoms from different isonicotinic acid ligands. With the isonicotinate groups omitted for clarity, Fig. 2 shows how the lactate group bridges three zinc atoms in which the carboxylate adopts a μ_3-bridging mode and the hydroxy group connects to one zinc atom in a monodentate fashion to form a five-membered ring (ZnOCCO). At the same time, a μ_2-oxygen atom bridges two

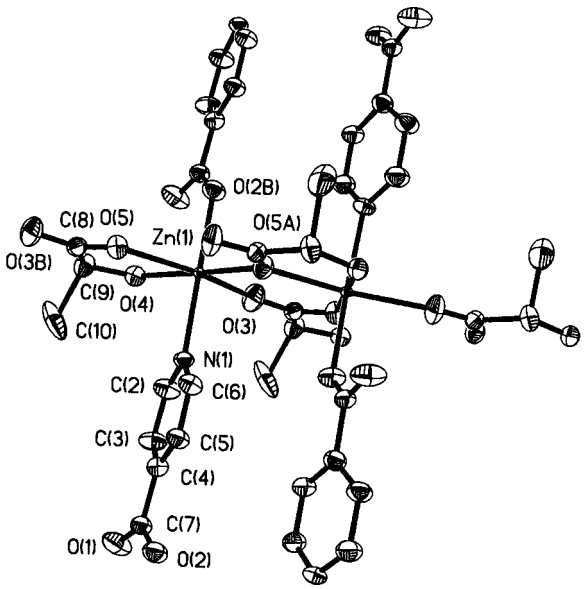

Fig. 1 An ORTEP drawing showing the coordination environment of the Zn(II) center in **1** (30% probability ellipses). Selected bond distances (Å) and angles (°): Zn(1)–O(2B) 2.251, Zn(1)–O(3) 2.290, Zn(1)–O(4) 2.362, Zn(1)–O(5) 2.341, Zn(1)–O(5A) 2.256, Zn(1)–N(1) 2.300; O(2B)–Zn(1)–N(1) 177.4, O(5A)–Zn(1)–O(3) 93.5, N(1)–Zn(1)–O(3) 88.8, N(1)–Zn(1)–O(5A) 91.7, N(1)–Zn(1)–O(4) 89.4, O(4)–Zn(1)–O(3) 87.3.

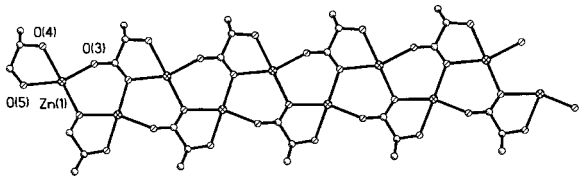

Fig. 2 An infinite chain diagram running along the *b* axis, omitting the isonicotinate groups for clarity.

zinc atoms to give a six-membered ring (ZnOCOZnO) combined with a bridging carboxylate. Running along the *b* axis, the three-center bridging mode can form an infinite chain. Similarly, the isonicotinate group uses the oxygen and nitrogen atoms to connect the infinite chains to form a very narrow two-dimensional pillar-type structure (just two rows), as shown in Fig. 3. The bond distances and angles in **1**, as seen in Fig. 1, are unexceptional.

It is noteworthy that the coordination polymers bis(isonicotinato)zinc(II) and bis(nicotinato)zinc(II) display SHG properties.[5] Their SHG intensity is slightly weaker than that of urea. In addition, it is very interesting to note that Kurtz *et al.* reported powder second generation efficiencies of sacchraride materials (about 0.45 times that of urea), including bis(L-lactate)zinc(II).[9] Compound **1** crystallizes in the acentric orthorhombic space group $P2_12_12_1$ (also a chiral space group), which belongs to the crystal class 222 where optical activity can occur as a specific physical effect.[10] Preliminary experimental results show that **1** displays powder SHG efficiencies *ca.* 1.2 times that of urea. The SHG effect may be ascribed to the orderly arrangement of lactate groups along the *c* axis (Fig. 3). Furthermore, thermal stability up to 200 °C (TGA measurement) and insolubility in common solvents make **1** a good candidate for SHG materials.

Experimental

(*S*-(−)-Lactate)(isonicotinato)zinc(II) **1** was synthesized by a hydro(solvo)thermal reaction. In a typical procedure a heavy-walled Pyrex tube containing a mixture of $Zn(ClO_4)_2 \cdot 6\ H_2O$, (0.37 g, 1 mmol), ethyl *S*-lactate (1 ml), 4-pyridinecarboxaldehyde (0.11 g, 1 mmol) and H_2O (0.08 ml) was frozen, sealed under vacuum and placed inside an oven at 105 °C. The pale-yellow prismatic crystals were harvested after 24 h of heating. Yield: 0.1 g (43%). Calcd for $C_9H_{10}NO_5Zn$: C, 38.95; H, 3.63; N, 5.05; found: C, 38.89; H, 3.60; N, 5.17%. IR (KBr, cm^{-1}): 3446(m), 3081(w), 2969(w), 2640(w), 2360(m), 1716(w), 1597(s), 1548(s), 1420(sh,w), 1391(s), 1307(m), 1230(m), 1122(m), 1109(w), 1047(m), 1020(m), 870(w), 832(m), 779(m), 692(s), 546(m).

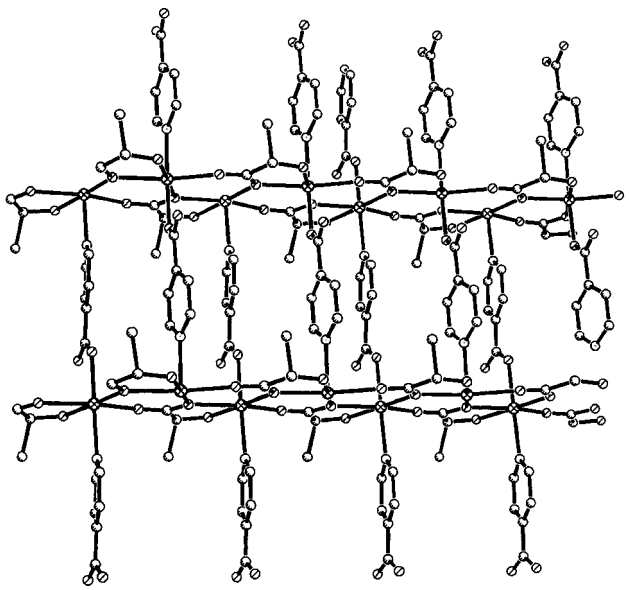

Fig. 3 A two-dimensional pillar representation along the *b* axis.

SHG property measurement

The second order nonlinear optical intensity was estimated by measuring a powder sample of 80–150 μm diameter in the form of a pellet (Kurtz powder test), relative to that of urea.[11] A pulsed Q-switched Nd : YAG laser at a wavelength of 1064 nm was used to generate the SHG signal from the sample. The backward scattered SHG light was collected using a spherical concave mirror and passed through a filter that transmits only 532 nm radiation. It is estimated that the SHG efficiency of **1** is slightly stronger than that of urea by about 1.2 times.

Crystal data for 1

$C_9H_{10}NO_5Zn$, $M = 277.55$, orthorhombic, space group $P2_12_12_1$; $a = 6.3480(1)$, $b = 9.5489(1)$, $c = 18.2304(3)$ Å, $U = 1105.06(3)$ Å^3, $Z = 4$, μ(Mo-Kα) = 22.3 cm^{-1}. The intensity data were collected at 293(2) K on a Siemens SMART CCD diffractometer with a detector distance of 4 cm and frame exposure time of 30 s. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELXTL[12] software, with 2524 unique absorption-corrected (empirical, $T_{min} = 0.3229$, $T_{max} = 0.7171$) reflections. All non-hydrogen atoms were anisotropically refined. The refinement converged at $R = 0.0413$ and $wR = 0.1547$ for a total of 146 parameters and 2463 observed reflections with $I > 2.0\sigma(I)$. CCDC reference number 440/145. See http://www.rsc.org/suppdata/nj/1999/1051/for crystallographic files in .cif format.

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