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Synthesis and structural characterization of homochiral coordination polymers with imidazole-based monocarboxylate ligands[†]

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Chiral Na[(S)-L^R] (R = Me, **1a**; ⁱPr, **1b**; CH₂ⁱPr, **1c**, and (S)-^{sec}Bu, **1d**) and Na[(R)-L^R] (R = Me, **1a**') compounds were synthesised following standard procedures. New compounds 1d and 1a' were analytically and spectroscopically characterised. 1a and 1c were structurally identified by single-crystal X-ray diffraction methods as homochiral 2D coordination polymers, $\{Na(H_2O)[(S)-L^{Me}]\}_n$ and $\{Na[(S)-L^{CH_2|Pr}]\}_n$, respectively. Both (S)-2alkyl,2-(1H-imidazol-1-yl)acetate anions displayed unprecedented coordination modes in these coordination polymers: $\mu_{3}\kappa^{2}O\kappa O'$ for **1a** and $\mu_{4}\kappa^{2}O\kappa^{2}O'$ for **1c**. Enantiomeric species **1a'**, {Na(H₂O)[(*R*)- L^{Me}]_n, showed the same X-ray powder diffractogram (XRPD) as **1a**, in agreement with a similar crystal structure. DFT calculations on the $[L^R]^-$ anions confirmed their coordination capabilities as ditopic linkers. In fact, the reaction of Na[L^R] with several metal salts yielded the following coordination polymers: $\{Ag[(S)-L^{Me}]\}_{n}$, 2a, $\{Ag[(R)-L^{Me}]\}_{n}$, 2a', $\{Cu[(S)-L^{R}]_{2}\}_{n}$ (R = Me, 3a; ⁱPr, 3b), $\{Cu[(R)-L^{Me}]\}_{n}$, 3a', $\{Zn[(S)-L^{R}]_{2}\}_{n}$ $(R = Me, 4a; {}^{i}Pr, 4b; (S)-{}^{sec}Bu, 4d)$ and ${Zn}[(R)-L^{Me}]_{2}_{n}$, 4a'. For the known compounds 3a and 4a, this procedure is a new synthetic route that avoided high temperature reaction conditions. New complexes 2, 3a', b, and 4a', b, d were characterised by elemental analysis, infrared and XRPD methods and complex 2a by single-crystal X-ray diffraction. This complex is also a two-dimensional coordination polymer in which the [(S)-L^{Me]⁻ anion acts as a $\mu_4\kappa N, \kappa^2 O, \kappa^2 O'$ bridging ligand. Compounds **1–4a'** are the first examples of} homochiral coordination polymers with imidazole-monocarboxylate ligands based on non-natural amino acids. Preliminary studies on the metal-catalysed preparation of chiral α -aminophosphonates were carried out but, unfortunately, no enantioselectivity was observed.

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Introduction

The interest in chiral imidazole-based monocarboxylate and imidazolium-based dicarboxylate compounds has increased markedly in the past few years.^{1–3} Their ease of preparation makes them useful starting precursors for the synthesis of chiral derivatives, such as ionic liquids,^{4–6} supported ionic liquids^{7,8} and NHC–carbene ligands.^{9–15} Additionally, they behave as suitable linkers in the construction of homochiral coordination polymers^{16–18} and metal–organic frameworks.^{19,20}

Following our interest in chiral imidazolium-based dicarboxylate ligands,^{21–23} we decided to explore the use of imidazole-based monocarboxylate ligands (see Scheme 1) as chiral bridging ligands of metal complexes. Here, we report the synthesis and characterization of several homochiral coordination polymers of sodium, 1, silver, 2, copper, 3, and zinc, 4, with chiral 2alkyl,2-(1*H*-imidazol-1-yl)acetate linkers ([[*S*)-L^R]⁻ for R = Me, ⁱPr, CH₂ⁱPr and (*S*)-^{sec}Bu and [(*R*)-L^{Me}]⁻). 1a, 1c and 2a were structurally identified by single-crystal X-ray diffraction

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[†]Electronic supplementary information (ESI) available: DFT optimised structures and MOs, crystal data, supramolecular packings, comparison of IR spectra and XRPD patterns, and coordinates of optimised compounds. CCDC 1904848 (1a), 1904849 (1c) and 1904850 (2a). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9dt01237k



Scheme 1 Coordination modes of the 2-(1*H*-imidazol-1-yl)acetate moiety.



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methods as two-dimensional coordination polymers {Na(H₂O) [(*S*)-L^{Me}]}_n, **1a**, {Na[(*S*)-L^{CH₂^{iP}r]}_n, **1c**, and {Ag[(*S*)-L^{Me}]}_n, **2a**, respectively. The bonding mode of $[(S)-L^{R}]^{-}$ ligands found in **1a**, $\mu_{3}\kappa^{2}O,\kappa O'$, and **1c**, $\mu_{4}\kappa N,\kappa^{2}O,\kappa^{2}O'$, is novel for ligands based on the 2-(1*H*-imidazol-1-yl)acetate moiety.}

Results and discussion

Coordination capabilities of imidazole-based monocarboxylate ligands

Imidazole-carboxylate ligands based on the 2-(1*H*-imidazol-1yl)acetate moiety (Scheme 1) feature one carboxylate group plus one nitrogen atom of imidazole as potential donor functionalities. Consequently, the bridging μ -coordination is the foreseeable bonding mode of this type of ligand. In fact, a search in the Cambridge Structural Database²⁴ indicates that this is the most common binding mode, in which the ligand is capable of bridging two ($\mu_2 \kappa N, \kappa O$, **I** in Scheme 1), three ($\mu_3 \kappa N, \kappa O, \kappa O'$, **II**, and $\mu_3 \kappa N, \kappa^2 O, \kappa O'$, **III**) or four metals ($\mu_4 \kappa N, \kappa^2 O, \kappa O'$, **IV**). Additionally, other bonding modes are found if the 2-(1*H*-imidazol-3-ium-1-yl)acetate moiety is considered (see Scheme S1 in the ESI[†]).

In order to gain further information about the features of the $[(S)-L^R]^-$ anions as potential ligands, DFT calculations²⁵ for these anions were carried out with R = Me, ⁱPr, CH₂ⁱPr and (S)-^{sec}Bu. Fig. 1 depicts the optimised structures of anions and three selected MOs for each species. The HOMO and HOMO–1 orbitals are centred on the O atoms and are clearly identified as the two σ O lone pairs of the carboxylate group. HOMO–5 is centred on the N atom of the imidazole moiety and is essentially the σ N lone pair. The coordination mode I (Scheme 1) is compatible with the use of HOMO and HOMO–5 orbitals in the bonding to metals, while the three MOs are involved in the coordination modes **II–IV**. As



Fig. 1 Optimised structures of $[(S)-L^R]^-$ anions (R = Me, ⁱPr, CH₂ⁱPr and (S)-^{sec}Bu) and selected MOs (from top to bottom: HOMO, HOMO–1 and HOMO-5, respectively).

expected, the structural and MO characteristics of the computed enantiomeric species $[(R)-L^R]^-$ (R = Me, ⁱPr, CH₂ⁱPr and (*S*)-^{sec}Bu) are completely similar (see Fig. S1 in the ESI†).

Synthesis and characterisation of sodium coordination polymers

Compounds $Na[(S)-L^R]$ (R = Me, 1a; ⁱPr, 1b; CH₂ⁱPr, 1c, and (S)-^{sec}Bu, 1d) and Na[(R)-L^R] (R = Me, 1a') were prepared following the procedure described by Bao and co-workers (Scheme 2). **1a** and **1b** are known and well characterised,⁴ while the preparation of **1c** as an intermediate in the preparation of chiral ionic liquids has been described but its spectroscopic characterization was not detailed.⁵ 1d and 1a' are new and they were analytically and spectroscopically characterised. In general, compounds 1 show a broad and intense IR absorption at around 1590 cm⁻¹, due to the antisymmetric COO vibration of the carboxylate group, and a second one at *ca*. 1390 cm^{-1} , which is assigned to the symmetric v(COO). The imidazole group of compounds 1 gives a common NMR pattern with three singlets in ¹H NMR (*ca.* at 6.9, 7.2 and 7.7 ppm for C^4H , C^5H and C^2H , respectively) and three singlets in ¹³C{¹H} NMR (ca. at 120, 128 and 138 ppm for C^4H , C^5H and C^2H , respectively). CH(R)groups of 1 show the conventional NMR resonances, while the carboxylate carbon atom appears as a singlet at around 176 ppm in the ¹³C¹₁H} NMR (for instance, at 175.0 and 178.6 ppm for 1d and 1a', respectively).

To our knowledge, no structural data has been reported for chiral Na[L^R] compounds. There is only an X-ray structure of a related non-chiral example of lithium 2-(1H-imidazol-3-ium-1yl)acetate²⁶ and that of the chiral imidazole-carboxylic compound [HL^{CH₂Ph].²⁷ For this reason, we decided to characterize} 1a and 1c by single-crystal X-ray crystallography. The selected structural parameters of 1a and 1c are collected in Table 1. Fig. 2 shows the asymmetric unit of 1a that consists of the (S)-2-(1H-imidazol-1-yl)propanoate anion, one sodium cation and one water molecule. The structure of 1a shows an unprecedented coordination mode for the $[(S)-L^{Me}]^{-}$ anion in which it acts as a $\mu_3 \kappa^2 O_1 \kappa O'$ ligand and the nitrogen atom of imidazole is not bonded to the sodium ion (Fig. 2, bottom). The distances of the sodium-oxygen interactions fall in the 2.33–2.42 Å range and each sodium cation is surrounded by five oxygen atoms (O1 and O2 from three symmetry related $[(S)-L^{Me}]^{-}$ anions and O3 from two symmetry related water molecules). Cations are bridged by O atoms of water and carboxylate groups, O3 and O1, respectively, and this originates an arrangement of sodium cations with an Na…Na separation of 3.6428(5) Å and an Na…Na…Na angle of 139.90(3)°. The



Scheme 2 Synthesis of compounds NaL^R.

Table 1 Selected structural parameters for complexes 1a and 1c^a

Distances (Å)	1a		1c	
Na-O	Na(1)-O(1) Na(1)-O(1)#2 Na(1)-O(2)#1 Na(1)-O(3) Na(1)-O(3)#2.	$\begin{array}{c} 2.4019(15) \\ 2.4188(15) \\ 2.3308(15) \\ 2.3909(15) \\ 2.3908(11) \end{array}$	Na(1)-O(1) Na(1)-O(1)#2 Na(1)-O(2)#1 Na(1)-O(2)#2	2.2637(18) 2.6096(17) 2.2639(17) 2.3727(16)
Na-N O-C		1.252(2) 1.256(2)	Na(1)-N(1) O(1)-C(4) O(2)-C(4)	$\begin{array}{c} 2.4193(19) \\ 1.243(3) \\ 1.238(3) \end{array}$
Angles (°) O-Na-O	$\begin{array}{c} O(2)\#1-Na(1)-O(3)\#2\\ O(2)\#1-Na(1)-O(1)\\ O(3)\#2-Na(1)-O(1)\\ O(2)\#1-Na(1)-O(3)\\ O(3)\#2-Na(1)-O(3)\\ O(1)-Na(1)-O(3)\\ O(2)\#1-Na(1)-O(1)\#2\\ O(3)\#2-Na(1)-O(1)\#2\\ O(3)-Na(1)-O(1)\#2\\ O(3)-Na(1)-O(1)+2\\ O($	$\begin{array}{c} 97.73(5)\\ 102.20(6)\\ 101.03(5)\\ 111.65(6)\\ 149.54(4)\\ 81.04(5)\\ 108.54(5)\\ 80.96(5)\\ 148.67(4)\\ 82.18(5)\end{array}$	$\begin{array}{c} O(1)-Na(1)-O(2)\#1\\ O(1)-Na(1)-O(2)\#2\\ O(2)\#1-Na(1)-O(2)\#2\\ O(1)-Na(1)-O(1)\#2\\ O(2)\#1-Na(1)-O(1)\#2\\ O(2)\#2-Na(1)-O(1)\#2\\ O(2)\#2-Na(1)-O(1)\#2\\ \end{array}$	$\begin{array}{c} 113.25(6)\\ 90.63(6)\\ 132.72(5)\\ 135.24(6)\\ 84.83(5)\\ 52.27(5)\end{array}$
O-Na-N			O(1)-Na(1)-N(1) O(2)#1-Na(1)-N(1) O(2)#2-Na(1)-N(1) N(1)-Na(1)-O(1)#2	$105.64(7) \\93.54(7) \\119.58(7) \\114.02(7)$
C-O-Na	C(5)-O(1)-Na(1) C(5)-O(1)-Na(1)#3 C(5)-O(2)-Na(1)#4	128.48(12) 130.60(12) 130.03(12)	$\begin{array}{c} C(4) - O(1) - Na(1) \\ C(4) - O(1) - Na(1) \\ C(4) - O(1) - Na(1) \# 3 \\ C(4) - O(2) - Na(1) \# 5 \\ C(4) - O(2) - Na(1) \# 3 \end{array}$	$168.40(16) \\85.35(12) \\145.80(13) \\96.50(12)$
O-C-O	O(1)-C(5)-O(2)	126.10(17)	O(2)-O(2)-O(1)	125.45(16)

^{*a*} Symmetry transformations used to generate equivalent atoms: for 1a: #1 - x + 1, y - 1/2, -z + 3/2; #2 - x + 2, y - 1/2, -z + 3/2; #3 - x + 2, y + 1/2, -z + 3/2; and #4 - x + 1, y + 1/2, -z + 3/2. For 1c: #1 x, y - 1, z; #2 - x + 1, y - 1/2, -z; #3 - x + 1, y + 1/2, -z; #4 - x, y - 1/2, -z; #5 x, y + 1, z; and #6 - x, y + 1/2, -z.



Fig. 2 Asymmetric unit of **1a** (top) and the unprecedented $\mu_{3}\kappa^{2}O,\kappa O'$ coordination mode of the [(S)-L^{Me}]⁻ anion in {Na(H₂O)[(S)-L^{Me}]}_n, **1a**, with selected bond distances in Å (bottom).



Fig. 3 Perspective view of the molecular packing of $\{Na(H_2O)[(S)-L^{Me}]\}_n$, 1a, viewed along the crystallographic *b*-axis.

coordination of the second O atom of carboxylate, O2, to a symmetry related arrangement of sodium cations causes the 2D distribution of the polymer (Fig. 3). The absence of metal-coordination through the N atom of imidazole is unique (see the coordination modes above) and the N lone pair is saturated by a hydrogen bond with the water O–H bond (O3– $H\cdots$ N2 length of 2.819(2) Å). Actually, the 3D supramolecular

architecture is constructed by this interaction between the water O3–H bond of one 2D lamellar sheet and the N(2) atom of the imidazole group of a neighbour 2D polymer (Fig. 3 and Fig. S2 in the ESI[†]).

The crystal structure of 1c is different from that of 1a. Its asymmetric unit shows the (*S*)-2-(1*H*-imidazol-1-yl)-4-methylpentanoate anion and one sodium cation without the presence of water molecules (Fig. 4, up). In contrast to 1a, the N1 atom



Fig. 4 Asymmetric unit of **1c** (top) and the novel $\mu_{4\kappa}N_{,\kappa}^{2}O_{,\kappa}^{2}O'$ coordination mode of the $[(S)-L^{CH_{2}^{(Pr)}}]^{-}$ anion in {Na[(S)-L^{CH_{2}^{(Pr)}]}}_n, **1c**, with selected bond distances in Å (bottom).

of imidazole is coordinated to the sodium ion (2.419(2) Å) and the overall coordination mode of the $[(S)-L^{CH_2iPT}]^-$ anion is novel, $\mu_4 \kappa N_i \kappa^2 O_i \kappa^2 O'$ (Fig. 4, bottom). Besides the N coordination, each sodium ion is surrounded by four oxygen atoms (O1 and O2 from two symmetry related $[(S)-L^{CH_2iPT}]^-$ anions). This produces a zigzag disposition of Na ions (with an Na…Na separation of 3.4140(9) Å and an Na…Na…Na angle of 120.47 (4)°) and, accordingly, a 2D coordination polymer along the crystallographic *bc* plane (Fig. 5). Non-covalent interactions between the CH₂ⁱPr groups of the homochiral 2D coordination polymers afford the crystal packing of **1c** (Fig. S3, ESI†).

As one might expect, complex **1a**' showed identical spectroscopic properties (IR, ¹H and ¹³C{¹H} NMR) of its known enantiomer **1a**. The only difference comes from the polarimetry measurements. The observed $[\alpha]_D$ value of **1a** in water is +27.1, which is similar to the values determined for related (*S*)-compounds ($[\alpha]_D$ range of +20–27 for **1a–d**), while $[\alpha]_D$ for **1a**' is approximately the same as **1a** but with the opposite sign ($[\alpha]_D = -27.5$ in water). **1a**' showed identical experimental powder diffractograms to the simulated one of {Na(H₂O)[(*S*)-L^{Me}]}_n, **1a**, from single-crystal X-ray studies (Fig. S4a, ESI†). Rietveld refinement from the XRPD of **1a**' was performed using the as-



Fig. 5 Perspective view of the 2D coordination polymer of $Ag[(S)-L^{Me}]_n$, 2a, viewed along the crystallographic *b*-axis.

generated **1a**' structure (see Experimental) and its final Rietveld plot is given in Fig. S5.[†] The observed differences between the diffraction and simulation patterns are caused by preferential orientation. From these results, we deduced that the overall 3D structure of **1a**' can be identified as the $\{Na(H_2O)[(R)-L^{Me}]\}_n$ coordination polymer and no further comments are required.

Synthesis and characterisation of silver coordination polymers

The interaction of $Na[(S)-L^{Me}]$, 1a, with silver nitrate affords, after the appropriate work up, crystals of complex $\{Ag[(S)\}$ L^{Me}]_n, 2a. They were stable upon exposure to air, but slow decomposition was observed after exposure to light. Complex 2a is insoluble in common organic solvents and only sparingly soluble in water. A broad IR band centred at around 1640 cm⁻¹, due to the antisymmetric COO vibrations, is indicative of the presence of the coordinated carboxylate group in this complex, while the absorption at 1394 cm⁻¹ was attributed to the symmetric COO vibration. A 1:1 ratio of silver cation and (S)-2-(1H-imidazol-1-yl)propanoate ligand was deduced from the microanalysis, but the polymeric nature of complex 2a was only evidenced after a single-crystal X-ray study. Fig. 6a displays the asymmetric unit that consists of the (S)-2-(1H-imidazol-1-yl)propanoate anion and the silver ion. Selected structural parameters of 2a are collected in Table 2. Each cation is surrounded by three oxygen atoms (O1 and O2 from three symmetry related $[(S)-L^{Me}]^-$ anions) and one nitrogen atom of imidazole (N2) with bond distances in the 2.24-2.51 Å range. Similar distances were found in the related complexes: silver 2-(1*H*-imidazol-1-yl)acetate²⁸ and (2-(1*H*-imidazol-3-ium-1-yl) acetato)silver nitrate.²⁹ The coordination mode of the [(S)- L^{Me} anion is $\mu_4 \kappa N, \kappa^2 O, \kappa O'$ (type **IV** in Scheme 1), in which four silver cations are bridged by the ligand (see the selected bond distances in Fig. 6b). This bonding mode produces a 2D coordination polymer extended along the crystallographic bc plane (Fig. 7). The 3D crystal distribution was produced by the



Fig. 6 Asymmetric unit of $\{Ag[(S)-L^{Me}]\}_n$, **2a** (top) and the $\mu_{4\kappa}N,\kappa^2O,\kappa O'$ coordination mode of the $[(S)-L^{Me}]^-$ anion in **2a** with selected bond distances in Å (bottom).

Table 2 Selected structural parameters for complex 2a^a

Distances (Å)		
Ag-O	Ag(1)-O(1)	2.25(2)
0	Ag(1) - O(2) # 2	2.43(2)
	Ag(1)-O(1)#3	2.51(2)
Ag–N	Ag(1) - N(2) # 1	2.25(2)
O-C	O(1) - C(5)	1.21(3)
	O(2) - C(5)	1.31(4)
Angles (°)		
O-Ag-O	O(1)-Ag(1)-O(2)#2	106.6(9)
	O(1)-Ag(1)-O(1)#3	117.6(6)
	O(2)#2-Ag(1)-O(1)#3	102.1(9)
N-Ag-O	N(2)#1-Ag(1)-O(1)	138.3(9)
	N(2)#1-Ag(1)-O(2)#2	86.7(8)
	N(2)#1-Ag(1)-O(1)#3	96.9(7)
C–O–Ag	C(5)-O(1)-Ag(1)	125(2)
	C(5)-O(1)-Ag(1)#2	113(2)
	C(5)-O(2)-Ag(1)#3	143(2)
0-C-0	O(1)-C(5)-O(2)	123(3)

^{*a*} Symmetry transformations used to generate equivalent atoms: #1 x, y, z - 1; #2 -x + 1, y - 1/2, -z; #3 -x + 1, y + 1/2, -z; and #4 x, y, z + 1.



Fig. 7 Perspective view of the 2D coordination polymer of **2a** viewed along the crystallographic *b*-axis.

packing of the 2D lamellar sheets due to non-classical interlaminar interaction between the methyl group of the $[(S)-L^{Me}]^$ ligand and the silver ion, $-CH_3\cdots Ag^+$ (Fig. S6, ESI†). This situation is similar to that found in the crystal structure of the related chiral coordination polymer, silver (2-(4*H*-1,2,4-triazol-4-yl)propanoato) monohydrate.³⁰ The intramolecular contact $-C6\cdots Ag^+$ of *ca.* 3.55 Å in **2a** is slightly longer than the upper part of the observed 3.13–3.42 Å range.²⁴

As occurred with 1a', complex 2a' was identified as the coordination polymer $\{Ag[(R)-L^{Me}]\}_n$ on the basis of its XRPD. 2a' showed an identical experimental powder diffractogram to the simulated one of $\{Ag[(S)-L^{Me}]\}_n$, 2a, from single-crystal X-ray studies (Fig. S7, ESI†). Therefore, the crystal packing of 2a' is similar to that of its enantiomer 2a, as previously discussed.

Synthesis and characterisation of first-row transition metal coordination polymers

The treatment of solutions of different metal salts with Na[L^R], **1**, results in the formation of complexes {Cu[(*S*)-L^R]₂}_{*n*} (R = Me, **3a**; ⁱPr, **3b**), {Cu[(*R*)-L^{Me}]₂}_{*n*}, **3a**', {Zn[(*S*)-L^R]₂}_{*n*} (R = Me, **4a**; ⁱPr, **4b**; (*S*)-^{sec}Bu, **4d**) and {Zn[(*R*)-L^{Me}]₂}_{*n*}, **4a**' after the appropriate work up. All products, which were isolated as crystalline solids, are air stable and not soluble in common solvents. Compounds **3a** and **4a** were previously prepared by Tian and co-workers by solvothermal reactions and were identified as metal–organic frameworks by X-ray single-crystal diffraction.²⁰ The preparation of these compounds does not require high temperature conditions, and **3a** and **4a** were synthesised by us at room temperature. Besides this advantage, this method afforded better yields (*ca.* 35%) than those reported previously (*ca.* 22%). The drawback is that this procedure usually afforded **3a** and **4a** as solid amorphous materials. The IR spectra of these compounds perfectly match with those reported by Tian and co-workers (Fig. S8, ESI†).²⁰ Occasionally, the zinc derivative **4a** was obtained as a microcrystalline solid and the experimental XRPD coincides with the simulated one from single-crystal X-ray diffraction (Fig. S9, ESI†).²⁰

Additionally, **4a**' was also studied by XRPD. Its formulation as the coordination polymer $\{\text{Zn}[(R)-L^{Me}]_2\}_n$ was proposed on the basis of its identical experimental powder diffractogram with respect to the simulated one of **4a**, from the single-crystal X-ray determination of Tian and co-workers (Fig. S10, ESI[†]).

Preliminary studies in the preparation of chiral α-aminophosphonates

As previously studied by us with related complexes,²² silver and zinc coordination polymers **2a** and **4** were tested as catalysts in the Kabachnik–Fields reaction for the synthesis of chiral α -aminophosphonates.^{31–36} The catalytic efficiency in this reaction was evaluated using the typical one-pot threecomponent procedure and selecting 4-methoxybenzaldehyde, 4-methoxyaniline and diethyl phosphonate as the model reaction (Scheme 3).

Table 3 reports selected results from the reactions carried out in a reactor with a 1:1:1:0.1 ratio of aldehyde: aniline: phosphonate: catalyst for 24 h. Although the observed conversions are high, the selectivity toward the α -aminophosphonate species is good only for Zn derivatives, **4**, at 60 °C. Silver complex **2a** gave a lower selectivity (55%, entry 1) and poorer results were observed at room temperature (entry 5). The best conversion and selectivity were obtained with **4a** in methanol at 60 °C. However, unfortunately, no enantioselectivity was observed in these reactions (<5% ee). Because of these results, no further investigation was carried out. As we described before for related zinc imidazolium-dicarboxylate complexes,²² the low solubility and the ligand dissociation from the coordination sphere of the zinc ion is the reason for the



Scheme 3 Model reaction for the synthesis of chiral $\alpha\text{-aminophosphonates.}$

Entry	Catalyst	Solvent	T (°C)	<i>t</i> (h)	Conversion ^b	Selectivity ^b	%ee ^c
1	2a	MeOH	60	24	92	55	<5
2	4a	H_2O	60	24	80	70	_
3	4a	MeOH	60	24	94	77	<5
4	4b	MeOH	60	24	79	65	<5
5	4b	MeOH	25	24	79	26	<5

Table 3 Synthesis of α-aminophosphonates using silver(I) 2a and zinc(II) 4 coordination polymers as catalysts^d

^{*a*} Reaction conditions: Catalyst 0.05 mmol, 4-methoxybenzaldehyde 0.5 mmol, 4-methoxyaniline 0.5 mmol, diethyl phosphonate 0.5 mmol, solvent 2.0 mL. ^{*b*} Determined by ¹H NMR analysis. ^{*c*} Determined by HPLC.

observed poor enantioselectivities in the Kabachnik-Fields reaction.

Conclusions

Chiral Na[L^R] species are widely used as intermediates in the synthesis of chiral derivatives, carbene ligands and ionic liquids. However, the exact solid-state nature of this species was unknown. Compounds $Na[(S)-L^R]$ (R = Me, 1a, and $CH_2^i Pr$, 1c) have been structurally identified by single-crystal X-ray diffraction methods as two-dimensional homochiral coordination polymers $\{Na(H_2O)[(S)-L^{Me}]\}_n$ and $\{Na[(S)-L^{CH_2Pr}]\}_n$ respectively. In both compounds, novel coordination modes for (S)-2alkyl,2-(1H-imidazol-1-yl)acetate anions, $\mu_3 \kappa^2 O \kappa O'$ for 1a and $\mu_4 \kappa^2 O \kappa^2 O'$ for 1c, have been found. In particular, 1a is a rare example in which the $[(S)-L^{Me}]^{-}$ anion is bonded to sodium ions only through oxygen atoms without the participation of the N atom of imidazole. This situation contrasts with all the reported compounds, where these types of ligands always behave as ditopic linkers. Their coordination capabilities as ligands have been analysed here by DFT calculations on the $[L^{R}]^{-}$ anions. Additionally, several coordination polymers of silver, 2, copper, 3, and zinc, 4, have been prepared by the reaction of $Na[L^R]$ with several metal salts. For known {Cu[(S)- $L^{Me}]_{2}_{n}$, 3a, and $\{Zn[(S)-L^{Me}]_{2}_{n}\}$, 4a, this procedure is a new synthetic route that avoided solvothermal reaction conditions. Enantiomeric species $\{Na(H_2O)[(R)-L^{Me}]\}_n$, 1a', $\{Ag[(R)-L^{Me}]\}_n$ 2a', $\{\operatorname{Cu}[(R)-\operatorname{L}^{\operatorname{Me}}]\}_n$, 3a', and $\{\operatorname{Zn}[(R)-\operatorname{L}^{\operatorname{Me}}]_2\}_n$, 4a', are the first examples of homochiral coordination polymers with imidazole-monocarboxylate ligands based on non-natural amino acids. They showed crystal structures, according to the X-ray powder diffractograms, similar to those of complexes 1-4 with ligands obtained from natural amino acids. Finally, as we previously observed for related zinc complexes,²² the catalytic performance of complexes 2a and 4 in the synthesis of chiral α -aminophosphonates is very poor, with ee values lower than 5%.

Experimental

General considerations

All preparations and other operations were carried out under aerobic conditions. Solvents were purified appropriately prior to use, using standard procedures. Chemicals were obtained from commercial sources and used as supplied. Infrared spectra were recorded on a PerkinElmer FT-IR Spectrum Two spectrophotometer, using the ATR technique. NMR spectra were recorded on Bruker AMX-300 or Avance III spectrometers at the Centro de Investigaciones, Tecnología e Innovación (CITIUS) of the University of Sevilla. ¹H and ¹³C{¹H} NMR shifts were referenced to the residual signals of deuterated solvents, while ³¹P{¹H} shifts were referenced to external 85% phosphoric acid. All data are reported in ppm downfield from Si(CH₃)₄. Elemental analyses (C, H, N) and X-ray Powder Diffraction (XRPD) studies were conducted at CITIUS of the University of Sevilla on an Elemental LECO CHNS 93 analyser and on a Bruker D8 advance A25 diffractometer, respectively. Polarimetry was carried out using a JASCO P-2000 Digital Polarimeter and the measurements were carried out at room temperature (concentration of *ca*. 10 mg mL⁻¹). HPLC chromatography was performed on an Agilent 1260 Infinity instrument with a Chiralpak IA column at a flow rate of 0.5 mL min^{-1} with heptane/isopropanol = 9/1 (v/v) and using a UV detector at 254 nm. High-resolution mass spectra were recorded using a Q-Exactive Hybrid Quadrupole-Orbitrap Mass Spectrometer from Thermo Scientific at CITIUS of the University of Sevilla. The synthesised transition-metal coordination polymers 2 and 4 are insoluble in common solvents and cannot be purified by recrystallization. For this reason, some of the microanalytical data are out of the required standard accuracy. Figures of 3D coordination polymers were obtained with the ToposPro program.37

Syntheses

Compounds $Na[(S)-L^R]$ (R = Me, 1a; ⁱPr, 1b; CH_2^i Pr, 1c, and (S)-^{sec}Bu, 1d) and $Na[(R)-L^R]$ (R = Me, 1a') were prepared according to the procedure reported by Bao and coworkers (see the ESI† for the data of compounds 1a-c).⁴

Sodium (*R*)-2-(1*H*-imidazol-1-yl)propanoate, 1a'. Yield 71%. IR (cm⁻¹): 3300 (w, br), 3090 (w), 1584 (s), 1513 (m), 1491 (w), 1477 (w), 1449 (m), 1416 (m), 1396 (s) 1374 (s), 1260 (s), 1235 (m), 1114 (m), 1081 (m), 1082 (m), 1032 (m), 920 (m), 888 (w), 867 (w), 810 (s), 753 (s), 678 (s), 660 (s), 539 (w). ¹H NMR (CD₃OD, 300 MHz): δ 1.69 (d, ³*J*_{HH} = 7.2 Hz, 3 H, *CH*₃), 4.74 (q, ³*J*_{HH} = 7.2 Hz, 1H, *CHCH*₃), 6.94 (s, 1H, C⁴*H*), 7.18 (s, 1H, C⁵*H*), 7.72 (s, 1H, C²*H*). ¹³C{¹H} NMR (CD₃OD, 75.47 MHz): δ 20.9 (s, *CH*₃), 60.6 (s, *CHCH*₃), 120.9 (s, *C*⁵H). 129.1 (s, *C*⁴H), 138.6 (s,

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 C^{2} H), 178.6 (s, COO). $[\alpha]_{D}^{21} = -27.5$ (H₂O). ESI-MS: found *m/z* 163.0478 for $[1a' + H]^{+}$, calculated for C₆H₈N₂NaO₂, 163.0483. Elemental Anal. Calc. for C₆H₇N₂NaO₂: C, 40.01; H, 5.04; N, 15.55. Found: C, 39.72; H, 5.26; N, 15.04%.

Sodium (2*S***,3***S***)-2-(1***H***-imidazol-1-yl)-3-methylpentanoate, 1d. Yield 82%. IR (cm⁻¹): 3322 (m br), 2965 (m), 2937 (w), 2876 (w), 1595 (vs), 1500 (m), 1460 (m), 1378 (s), 1313 (w), 1285 (w), 1224 (m), 1153 (w), 1114 (w), 1078 (m), 1035 (w), 917 (w), 821 (w), 735 (m), 665(m), 635 (m). ¹H NMR (CD₃OD, 300 MHz): δ 0.86 (t, ³***J***_{HH} = 7.2 Hz, 3 H, CH₃), 0.96 (m, 2H, CH₂CH₃), 1.04 (d,** *J***_{HH} = 6.7 Hz, 3H, CHC***H***₃), 2.19 (m, 1H, CH₃C***H***CH₂CH₃), 4.29 (d,** *J***_{HH} = 9.7 Hz, 1H, C***H***), 6.97 (s, 1H, C⁴***H***), 7.29 (s, 1H, C⁵***H***) 7.81 (s, 1H, C²***H***). ¹³C{¹H} NMR (CD₃OD, 75.47 MHz): δ 9.89 (s, CH₃), 14.99 (s, CH₃), 24.6 (s, CH₂CH₃), 37.80 (s, CH), 69.24 (s, CH), 119.4 (s, C⁵H), 126.2 (s, C⁴H), 136.8 (s, C²H) 175.0 (s, COO). [\alpha]_D^{21} = +20.5 (H₂O). ESI-MS: found** *m***/***z* **205.0945 for [1d + H]⁺, calculated for C₉H₁₄N₂NaO₂, 205.0953.**

Silver (*S*)-2-(1*H*-imidazol-1-yl)propanoate, {Ag[(*S*)-L^{Me}]}_n, 2a. Over an aqueous solution of Na[(*S*)-L^{Me}] (1a, 0.162 g, 1 mmol), an aqueous solution of silver(1) nitrate (0.1708 g, 1 mmol) was added in a light-protected reactor. The resulting mixture (15 mL) was stirred for 1 hour. Then, 5 mL of DMF was added and the mixture was left in a dark box to avoid photolysis decomposition. Slow evaporation of this solution resulted in the formation of uncoloured crystals of compound 2a (80.9 mg, 32% yield). IR (cm⁻¹): 3122 (w), 3015 (w), 2976 (w) 1595 (vs), 1506 (m), 1488 (m), 1467 (w), 1413 (w), 1378 (s), 1345 (s), 1335 (s), 1288 (w) 1278 (w), 1256 (vs), 1221 (m), 1113 (s), 1085 (s) 1070 (s), 1028 (m), 974 (m), 928 (m), 878 (m), 839 (s) 765 (m), 753 (s), 731 (m), 667 (s), 652 (s), 643 (m). Elemental Anal. Calc. for C₆H₇N₂AgO₂: C, 29.18; H, 2.86; N, 11.34. Found: C, 28.55; H, 2.67; N, 11.60%.

Silver (*R*)-2-(1*H*-imidazol-1-yl)propanoate, $\{Ag[(R)-L^{Me}]\}_n$, 2a'. Following a similar procedure, but starting from Na[(*R*)-L^{Me}] (1a', 0.162 g, 1 mmol) and silver(1) nitrate (0.1708 g, 1 mmol), 2a' was obtained as an uncoloured crystalline solid (95 mg, 38% yield). IR (cm⁻¹): 3122 (w), 3015 (w), 2976 (w) 1595 (vs), 1506 (m), 1488 (m), 1467 (w), 1413 (w), 1378 (s), 1345 (s), 1335 (s), 1288 (w) 1278 (w), 1256 (vs), 1221 (m), 1113 (s), 1085 (s) 1070 (s), 1028 (m), 974 (m), 928 (m), 878 (m), 839 (s) 765 (m) 753 (s), 731 (m), 667 (s), 652 (s), 643 (m).

Copper (*S*)-2-(1*H*-imidazol-1-yl)propanoate, { $Cu[(S)-L^{Me}]_2$ }_n, 3a.²⁰ Over an aqueous solution of Na[(*S*)-L^{Me}] (0.500 g, 3.085 mmol), an aqueous solution of copper(II) nitrate trihydrated (0.370 g, 1.54 mmol) was added. The resulting mixture was stirred for 1 h. The solution was slowly evaporated and a blue precipitate was formed. Crystallization from a 1:3 mixture of H₂O/DMF afforded the compound 3a (0.182 g, 34% yield). IR (cm⁻¹): 3129 (w), 2993 (w), 2929 (w) 1595 (vs), 1520 (m), 1456 (m), 1385 (s), 1356 (vs), 1278 (s), 1235 (s), 1110 (s), 1074 (m) 1035 (m), 978 (m), 950 (w), 882 (w), 825 (w), 739 (m), 692 (s), 653 (s).

Copper (*R*)-2-(1*H*-imidazol-1-yl)propanoate, $\{Cu[(R)-L^{Me}]_2\}_n$, 3a'. Following a similar procedure, but starting from Na[(*R*)- L^{Me}] (324 mg, 2 mmol) and copper(II) chloride (170 mg, 1 mmol), 3a' was obtained as a blue crystalline solid (0.182 g,

46% yield). IR (cm⁻¹): 3147 (m), 2964 (w), 2876 (w), 1629 (s), 1514 (m), 1466 (m), 1384 (vs), 1327 (m) 1290 (m), 1224 (m), 1109 (m), 1086 (m) 1028 (w), 981 (w), 954 (w), 918 (w), 837 (w), 755 (m), 665 (w), 536 (w). Elemental Anal. Calc. for $C_{12}H_{14}CuN_4O_4\cdot 3H_2O$: C, 36.41; H, 5.09; N, 14.15. Found: C, 36.48; H, 4.54; N, 14.61%.

Copper (*S*)-2-(1*H*-imidazol-1-yl)-3-methylbutanoate, {Cu[(*S*)- L^{iPr}]_{2}*n*}, **3b**. Following a similar procedure, but starting from Na[(*S*)- L^{iPr}] (**1b**, 0.500 g, 2.63 mmol) and copper(*n*) nitrate trihydrated (0.320 g, 1.32 mmol), **3b** was obtained as a dark blue solid (0.163 g, 28% yield). IR (cm⁻¹): 3147 (m), 2964 (w), 2876 (w), 1629 (s), 1514 (m), 1466 (m), 1384 (vs), 1327 (m) 1290 (m), 1224 (m), 1109 (m), 1086 (m) 1028 (w), 981 (w), 954 (w), 918 (w), 837 (w), 755 (m), 665 (w), 536 (w). Elemental Anal. Calc. for C₁₆H₂₂CuN₄O₄·H₂O: C, 46.20; H, 5.82; N, 13.47. Found: C, 45.41; H, 5.45; N, 12.97%.

Zinc (*S*)-2-(1*H*-imidazol-1-yl)propanoate, $\{Zn[(S)-L^{Me}]_2\}_n$, 4a.²⁰ Over an aqueous solution of Na[(*S*)-L^{Me}] (1a, 0.500 g, 3.085 mmol), an aqueous solution of zinc(II) chloride (0.210 g, 1.54 mmol) was added. The resulting mixture was stirred for 1 h. A small amount of 4a was formed, as a yellow solid, and was isolated by filtration. Slow evaporation of the resulting solution afforded yellow crystals of 4a (0.200 g, 38% yield). IR (cm⁻¹): 3147 (w), 3129 (w), 3004 (w), 2976 (w), 1638 (vs), 1514 (w), 1463 (w), 1417 (w), 1388 (s), 1360 (s), 1302 (s), 1267 (s), 1231 (s), 1110 (s), 1099 (s) 1078 (m), 1031 (w), 985 (m), 956 (m), 856 (m), 841 (m), 785(m), 743 (m), 729 (m), 657 (vs), 524 (m). Elemental Anal. Calc. for: $C_{12}H_{14}N_4O_4Zn$: C, 41.94, H, 4.11, N, 16.30. Found: C, 41.51; H, 4.14; N, 15.64%.

Zinc (*R*)-2-(1*H*-imidazol-1-yl)propanoate, $\{\text{Zn}[(R)-L^{Me}]_2\}_n$, 4a'. Over a solution of Na[(*R*)-L^{Me}] (1a', 0.200 g, 1.23 mmol) in methanol (5 ml), a solution of zinc(II) acetate dihydrated (0.130 g, 0.615 mmol) in methanol (5 ml) was added. The resulting solution was stirred at 60 °C for 24 h. Solid 4a' was precipitated from the reaction and was separated by filtration. From the mother liquor, a second crop of yellow crystals of 4a' was obtained, which were isolated by filtration (243.5 mg, 40% yield). IR (cm⁻¹): 3147 (w), 3129 (w), 3004 (w), 2976 (w), 1638 (vs), 1514 (w), 1463 (w), 1417 (w), 1388 (s), 1360 (s), 1302 (s), 1267 (s), 1231 (s), 1110(s), 1099 (s) 1078 (m), 1031 (w), 985 (m), 956 (m), 856 (m), 841 (m), 785(m), 743 (m), 729 (m), 657 (vs), 524 (m). Elemental Anal. Calc. for: C₁₂H₁₄N₄O₄Zn·H₂O: C, 39.85; H, 4.46; N, 15.49. Found: C, 39.67; H, 4.32; N, 15.18%.

Zinc (S)-2-(1*H*-imidazol-1-yl)-3-methylbutanoate, {Zn[(S)- L^{iPr}]₂}_n, 4b. Following the same procedure as 4a, but starting from Na[(S)- L^{iPr}] (500 mg, 2.63 mmol) and zinc(II) chloride (0.180 g, 1.31 mmol), 4b was obtained as a yellow solid (0.114 g, 23% yield). IR (cm⁻¹): 3136 (w), 2967 (m), 1635 (vs), 1518 (m), 1469 (w), 1384 (s), 1238 (m), 1091 (m), 954 (w), 844 (w), 754 (m), 731 (w), 659 (m). Elemental Anal. Calc. for: C₁₆H₂₂N₄O₄Zn-2H₂O: C, 44.10; H, 6.01; N, 12.86. Found: C, 44.64; H, 5.60; N, 12.82%.

Zinc (2S,3S)-2-(1H-imidazol-1-yl)-3-methylpentanoate, {Zn $[(S)-L^{secBu}]_2$ }, 4d. Over an aqueous solution of Na $[(S)-L^{secBu}]$ (1d, 0.204 g, 1 mmol), an aqueous solution of zinc(II) chloride (68.1 mg, 0.5 mmol) was added. The resulting mixture was

stirred for 1 h at room temperature. Compound **4d** was formed as a yellow solid and was isolated by filtration, washed with ethanol and dried in air (68.8 mg, 32% yield). IR (cm⁻¹): 3460 (w, br), 3136 (w), 2969 (w), 2937 (w), 1634 (vs), 1519 (m), 1380 (s), 1267 (s), 1236 (m), 1110 (s), 1085 (s), 952 (m), 848 (w), 744 (vs), 665 (s). Elemental Anal. Calc. for: $C_{18}H_{26}N_4O_4Zn$: C, 50.54; H, 6.13; N, 13.10. Found: C, 50.98; H, 6.06; N, 12.58%.

X-ray crystallography

A summary of the crystallographic data and structure refinement results for compounds 1a, 1c and 2a is given in Table S1 (ESI).† Crystals of suitable size for X-ray diffraction analysis were coated with dry perfluoropolyether and mounted on glass fibers and fixed in a cold nitrogen stream (T = 213 K) on the goniometer head. Data collection was performed on a Bruker-Nonius X8Apex-II CCD diffractometer, using monochromatic radiation λ (Mo K α) = 0.71073 Å, by means of ω and φ scans with a width of 0.50 degrees. The data were reduced (SAINT³⁸) and corrected for absorption effects by the multi-scan method (SADABS).³⁹ The structures were solved by direct methods (SIR-2002⁴⁰) and refined against all F^2 data by full-matrix leastsquares techniques (SHELXL-2016/6⁴¹) minimizing w[F_0^2 – $F_{\rm c}^{2}$ ². All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included from calculated positions and refined riding on their respective carbon atoms with isotropic displacement parameters. The corresponding crystallographic data were deposited with the Cambridge Crystallographic Data Centre as supplementary publications, CCDC 1904848 (1a), 1904849 (1c) and 1904850 (2a).†

X-ray powder diffraction

X-ray powder diffraction (XRPD) patterns were collected on a Bruker D8 advance A25 diffractometer. The crystal structure refinements were performed by means of the Rietveld method⁴² using the FULLPROF software.⁴³ A Thompson-Cox-Hastings pseudo-Voigt function convoluted with an axial divergence asymmetry function was chosen to generate the peak shapes. The following parameters were refined: background points, zero point, scale factor, pseudo-Voigt parameters of the peak shape, atomic positions and cell parameters. The simulated Crystallographic Information File of $Na[(R)-L^{Me}]$, 1a', was obtained by using the Materials Studio software (BIOVIA DS) and this CIF was used as the starting model (Fig. S4b, ESI[†]). Rietveld adjustment was carried out and the data are shown in Table S2 (ESI),† while selected results of the structure refinement of the XRPD sample 1a' are summarized in Table S3.†

Computational details

The electronic structure and geometries of $[(S)-L^R]^-$ and $[(R)-L^R]^-$ anions were computed using density functional theory at the B3LYP level.^{44,45} The 6-311+G** basis set was used for all atoms. Optimised geometries were characterised as energy minima by a nonexistence of imaginary frequencies (NImag = 0) in the diagonalisation of the analytically computed Hessian (vibrational frequencies calculations). The DFT calculations were performed using the Gaussian 09 suite of programmes.⁴⁶ Coordinates of optimised compounds are collected in Table S4 (ESI).[†]

Catalytic assays

Synthesis of diethyl ((4-methoxyphenyl)((4-methoxyphenyl) amino)methyl)phosphonate. A 50 mL reactor (vial equipped with a Young valve and containing a stirrer flea) was charged with 4-methoxybenzaldehyde (0.5 mmol), 4-methoxyaniline (0.5 mmol), diethyl phosphonate (0.5 mmol), complexes 2a or 4 (0.05 mmol) and the reaction solvent (2 mL), in the aforementioned order. The reactor was sealed and the mixture was stirred at 60 °C in a thermostated bath for 24 h. Upon completion, the resulting mixture was evaporated to dryness affording a residue that was extracted with dichloromethane and then filtered. A 1 mL aliquot of the resulting solution was evaporated to dryness and the residue was analysed by ${}^{31}P{}^{1}H{}$ NMR. A second 1 mL aliquot was diluted with 10 mL of isopropanol and the resulting solution was analysed by chiral HPLC.

Conflicts of interest

There are no conflicts to declare.

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