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Structural diversity in lanthanum(III) coordination polymers constructed with the isomeric flexible double betaines 1,4-bis(*n*-picolyloxyl)benzene-*N*,*N*′-diacetate ($n = 2$, 3)

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Abstract

Six coordination polymers: $\{[La(H_2O)_6L^1]_2Cl_6 \cdot 12H_2O\}_\infty$ (**1**), $[La(H_2O)_2L^1(NO_3)_3]_\infty$ (**2**), $\{[La(H_2O)_4(L^1)_2](CF_3SO_3)_3 \cdot H_2O\}_\infty$ (**3**), $\{[La(H_2O)_7(L^2)_{0.5}]Cl_3\}_\infty$ (**4**), $\{[La(H_2O)_2L^2(NO_3)_2]NO_3 \cdot 0.5H_2O\}_\infty$ (**5**) and $\{[La(H_2O)_3(L^2)_2](CF_3SO_3)_3 \cdot 6H_2O\}_\infty$ (**6**) have been synthesized by the reaction between lanthanum(III) salts and the isomeric double betaines 1,4-bis(2-picolyloxyl)benzene-*N*,*N*′-diacetate (L^1) and 1,4-bis(3-picolyloxyl)benzene-*N*,*N*′-diacetate (L^2). Compound **1**, **2** and **3** are all mononuclear: **1** shows a double-layer network constructed by $M-L^1$ coordination bonds together with hydrogen bonds, while **2** and **3** are 3D frameworks. In compound **4**, **5** and **6**, dinuclear units are linked by one, two and four L^2 ligands, respectively, leading to different kinds of polymeric chains; in each compound the chains are further connected through intermolecular hydrogen bonding and $\pi-\pi$ stacking to generate a 2D network.

Keywords: Carboxylate; Coordination network; Double betaine; Lanthanide salt

1. Introduction

During the last two decades, there has been an upsurge of research activity in the use of labile coordination bonds involving d-block metal ions and multidentate ligands for the selective preparation of open coordination frameworks [1]. The lanthanides have been less studied in this context in view of their weak stereochemical preferences which prevent reliable preconceived molecular assembly in solution [2]. Nevertheless, prior knowledge of persistent structural motifs has been shown to offer a viable approach to the design of lanthanide coordination networks [3], and one can induce controllable one-, two- and three-dimensional assemblies with the aid of complementary hydrogen bonding functional groups [4–11].

Ligands of the double betaine type are known to be generators of variable coordination frameworks in organic–inorganic hybrid materials, especially those containing dinuclear units, with considerable control of their topology and composition [12]. In previous studies we have explored the use of various kinds of double betaine ligands for the construction of lanthanide coordination polymers [13]. In the present work, we report the structural diversity in a series of new lanthanum(III) coordination polymers, namely $\{[La(H_2O)_6L^1]_2Cl_6 \cdot 12H_2O\}_\infty$ (**1**), $[La(H_2O)_2L^1(NO_3)_3]_\infty$ (**2**), $\{[La(H_2O)_4(L^1)_2](CF_3SO_3)_3 \cdot H_2O\}_\infty$ (**3**), $\{[La(H_2O)_7(L^2)_{0.5}]Cl_3\}_\infty$ (**4**), $\{[La(H_2O)_2L^2(NO_3)_2]NO_3 \cdot 0.5H_2O\}_\infty$ (**5**) and $\{[La(H_2O)_3(L^2)_2](CF_3SO_3)_3 \cdot 6H_2O\}_\infty$ (**6**) synthesized with the isomeric double betaines 1,4-bis(2-picolyloxyl)benzene-*N*,*N*′-diacetate (L^1) [14] and 1,4-bis(3-picolyloxyl)benzene-*N*,*N*′-diacetate (L^2) (Scheme 1). In these six dicarboxylate complexes, the La(III) ions exhibit three kinds of coordination environments: 8-coordinated in compound **3**, 9-coordinated in **4** and **6**, and 10-coordinated in **1**, **2** and **5**.

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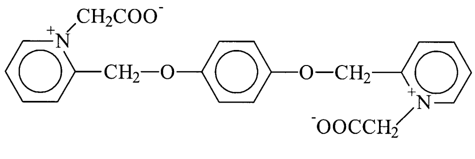
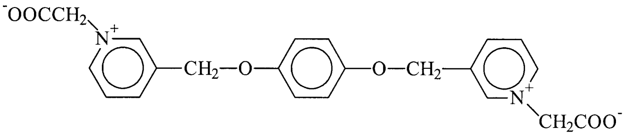


1,4-bis(2-picolyloxyl)benzene-N,N'-diacetate (L[1])



1,4-bis(3-picolyloxyl)benzene-N,N'-diacetate (L[2])

Scheme 1.

2. Experimental

2.1. Materials

The lanthanum salts $LaCl_3 \cdot 7H_2O$, $La(NO_3)_3 \cdot 6H_2O$ and $La(CF_3SO_3)_3$ were obtained commercially (Aldrich) and used without further purification. The double betaine ligand 1,4-bis (2-picolyloxyl)benzene-*N,N'*-diacetate (L^1) was synthesized as described previously [14].

2.2. Synthesis of 1,4-bis(3-picolyloxyl)benzene-N,N'-diacetate (L^2)

This double betaine ligand was synthesized in a similar way to that of 1,4-bis(2-picolyloxyl)benzene-*N,N'*-diacetate (L^1) [14], but using 3-picolychoride hydrochloride instead of 2-picolylchloride hydrochloride to carry out the reaction. Colorless hydrate $L^2 \cdot 6H_2O$ solid was obtained. Yield: 54%. *Anal.* Calc. for $C_{22}H_{20}N_2O_6 \cdot 6H_2O$: C, 51.16; H, 6.24; N, 5.42. Found: C, 51.19; H, 6.71; N, 5.44%. IR (KBr, cm^{-1}): 3399*brs*, 3073*w*, 1639*s*, 1508*m*, 1451*w*, 1373*s*, 1231*s*, 1059*m*, 917*w*, 809*w*, 769*w*, 711*w*. ^1H NMR (300 Hz, D_2O): δ_H 8.83 (2H, s, py-2), 8.68(2H, d, py-4), 8.56(2H, d, py-6), 8.03(2H, dd, py-5), 7.01(4H, s, C_6H_6), 5.32(4H, s, $-CH_2-O$), 5.18(4H, s, CH_2COO^-).

2.3. Synthesis of $\{[La(H_2O)_6L^1]_2Cl_6 \cdot 12H_2O\}_\infty$ (**1**)

An aqueous solution (4 ml) containing $LaCl_3 \cdot 7H_2O$ (0.371 g, 1 mmol) was mixed with an aqueous solution (6 ml) of L^1 (anhydrous, 0.08 g, 0.2 mmol), and the mixture was stirred at 70 °C for about 10 min and then filtered. The filtrate was allowed to stand at room temperature. Several days later, colorless block-like crystals of **1** were obtained. Yield: 43%. *Anal.* Calc. for $C_{22}H_{44}Cl_3LaN_2O_{18}$: C, 30.38; H, 5.10; N, 3.22. Found: C, 29.84; H, 5.27; N, 3.04%. IR (KBr, cm^{-1}): 3385*brs*, 1599*s*, 1514*w*, 1454*w*, 1401*m*, 1320*w*, 1239*m*, 1078*w*, 796*w*, 729*w*.

2.4. Synthesis of $[La(H_2O)_2L^1(NO_3)_3]_\infty$ (**2**)

Complex **2** was obtained as colorless block-like crystals using L^1(0.08 g, 0.2 mmol) and $La(NO_3)_3 \cdot 6H_2O$ (0.433 g, 1 mmol). Yield: 37%. *Anal.* Calc. for $C_{22}H_{24}LaN_5O_{17}$: C, 34.35; H, 3.14; N, 9.10. Found: C, 34.06; H, 3.20; N, 8.88%. IR (KBr, cm^{-1}): 3536*br*, 3086*w*, 1621*s*, 1508*m*, 1447*s*, 1376*s*, 1306*s*, 1219*m*, 1071*w*, 836*w*, 729*w*.

2.5. Synthesis of $\{[La(H_2O)_4(L^1)_2](CF_3SO_3)_3 \cdot H_2O\}_\infty$ (**3**)

Complex **3** was also prepared as colorless block-like crystals using L^1 (0.08 g, 0.2 mmol) and $La(CF_3SO_3)_3$ (0.586 g, 1 mmol). Yield: 35%. *Anal.* Calc. for $C_{47}H_{50}F_9LaN_4O_{26}S_3$: C, 37.81; H, 3.38; N, 3.75. Found: C, 37.82; H, 3.39; N, 3.73%. IR (KBr, cm^{-1}): 3456*brs*, 3100*w*, 1643*s*, 1512*m*, 1447*w*, 1386*m*, 1275*vs*, 1239*vs*, 1168*m*, 1071*w*, 1028*m*, 829*w*, 725*w*.

2.6. Synthesis of $\{[La(H_2O)_7(L^2)_{0.5}]Cl_3\}_\infty$ (**4**)

Complex **4** was synthesized as colorless block-like crystals using L^2 (0.08 g, 0.2 mmol) and $LaCl_3 \cdot 7H_2O$ (0.371 g, 1 mmol). Yield: 42%. The crystals effloresce upon exposure to air, gradually losing three of the seven aqua ligands. The elemental analysis results of a dried sample fit the formula $[La(H_2O)_4(L^2)_{0.5}]Cl_3$: C, 25.33; H, 3.48; N, 2.69. Found: C, 25.54; H, 3.37; N, 2.74%. IR (KBr, cm^{-1}): 3368*brs*, 3052*w*, 1606*s*, 1508*m*, 1447*w*, 1401*m*, 1313*w*, 1225*m*, 1058*w*, 843*w*, 776*w*.

2.7. Synthesis of $\{[La(H_2O)_2L(NO_3)_2]NO_3 \cdot 0.5H_2O\}_\infty$ (**5**)

Complex **5** was synthesized as colorless block-like crystals using L^2 (0.08 g, 0.2 mmol) and $La(NO_3)_3 \cdot 6H_2O$ (0.433 g, 1 mmol). Yield: 36%. *Anal.* Calc. for $C_{22}H_{25}LaN_5O_{17.5}$: C, 33.93; H, 3.24; N, 9.00. Found: C, 33.55; H, 3.06; N, 8.62%. IR (KBr, cm^{-1}): 3419*brs*, 3079*w*, 1652*s*, 1590*m*, 1506*m*, 1440*s*, 1386*vs*, 1318*m*, 1226*m*, 1071*w*, 823*w*, 722*w*.

2.8. Synthesis of $\{[La(H_2O)_3(L^2)_2](CF_3SO_3)_3 \cdot 6H_2O\}_\infty$ (**6**)

Complex **6** was obtained as colorless block-like crystals using L^2 (0.08 g, 0.2 mmol) and $La(CF_3SO_3)_3$ (0.586 g, 1 mmol). Yield: 46%. *Anal.* Calc. for $C_{47}H_{58}F_9LaN_4O_{30}S_3$ requires: C, 36.07; H, 3.74; N, 3.58. Found: C, 36.31; H, 3.87; N, 3.42%. IR (KBr,

cm^{-1}): 3433*brs*, 3086*w*, 1635*s*, 1510*m*, 1449*w*, 1388*s*, 1279*vs*, 1241*vs*, 1167*s*, 1031*m*, 836*w*, 716*w*.

2.9. X-ray crystallography

Intensity data collection of complex **1**–**6** was performed on a Bruker SMART 1000 CCD diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K. Absorption corrections were performed using the SADABS program [15]. The structures were solved by direct methods and refined by full-matrix least squares based on F^2 using the SHELXTL program package [16]. All the non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were generated geometrically except for those of water molecules, which were located from difference Fourier maps and not refined. The crystallographic data for complex **1**–**6** are summarized in Table 1.

3. Results and discussion

A metal/ligand molar ratio of 5:1 was used in the preparation of complex **1**–**6**, and excess La(III) salt was needed to prevent the deposit of hydrated double betaine ligands [17].

All six compounds exhibit the characteristic ν_{CO} absorption at about 1630–1650 cm^{-1}. The IR spectra of compound **1** and **4** are almost identical, as are those of **2** and **5**, as well as **3** and **6**, since the complexes in each pair were prepared from the same metal salt. In **2** and **5** the vibrational modes of NO_3^- show up as strong peaks at 1440–1647, 1376–1386 and 1306–1386 cm^{-1}. In **3** and **6** the $CF_3SO_3^-$ group absorbs at 1635–1645, 1240–1279, 1166–1168 and 1028–1031 cm^{-1}. Owing to the existence of many aqua ligands and lattice water molecules, a strong broad ν_{OH} absorption band (3300–3650 cm^{-1}) was observed in the IR spectra of all six complexes.

In compound **1**, each asymmetric unit contains two L^1 ligands, two La(III) ions, twelve aqua ligands, six chloride ions and twelve lattice water molecules (Fig. 1). Each La(III) is in a bicapped square-antiprismatic environment, being coordinated by the chelating carboxylate groups from two different L^1 and six aqua ligands (Fig. 2). Though both independent La(III) ions have the same coordination geometry, the bond lengths and angles are significantly different. The three rings of each independent L^1 ligand are not parallel to each

Table 1
Crystallographic data of complex **1**–**6**

Complex	**1**	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{22}H_{44}Cl_3N_2O_{18}La$	$C_{22}H_{24}N_5O_{17}La$	$C_{47}H_{50}N_4O_{26}F_9S_3La$	$C_{22}H_{48}Cl_6N_2O_{20}La_2$	$C_{22}H_{25}N_5O_{17.5}La$	$C_{47}H_{58}F_9N_4O_{30}S_3La$
Formula weight	869.85	769.37	1493.00	1151.14	778.38	1565.06
Crystal size	0.40 × 0.20 × 0.12	0.50 × 0.40 × 0.30	0.40 × 0.20 × 0.20	0.40 × 0.20 × 0.20	0.30 × 0.24 × 0.18	0.42 × 0.22 × 0.18
Crystal system	monoclinic	orthorhombic	monoclinic	triclinic	triclinic	triclinic
Space group	$P2_1/c$ (No. 14)	*Pccn* (No. 56)	$P2_1/n$ (No. 14)	$P\bar{1}$(No. 2)	$P\bar{1}$(No. 2)	$P\bar{1}$(No. 2)
a (Å)	13.248(2)	19.360(2)	11.1352(7)	8.038(1)	9.970(5)	14.254(1)
b (Å)	19.361(3)	8.4115(8)	21.006(2)	11.168(1)	12.705(6)	15.147(1)
c (Å)	28.408(5)	17.401(2)	25.726(2)	13.073(2)	12.922(6)	16.533(1)
α (°)	90	90	90	68.858(3)	66.30(1)	67.519(2)
β (°)	102.764(4)	90	101.756(2)	74.260(2)	82.51(1)	87.125(2)
γ (°)	90	90	90	81.907(2)	78.24(1)	85.456(2)
V (Å^3)	7106(2)	2833.7(5)	5891.2(7)	1052.4(2)	1465(1)	3287.2(4)
Z	8	4	4	1	2	2
D_{calc} (g cm^{-3})	1.626	1.803	1.683	1.816	1.764	1.581
μ(Mo Kα) (mm^{-1})	1.502	1.598	0.947	2.455	1.547	0.857
F(0 0 0)	3536	1536	3016	570	778	1588
Reflections collected	47 786	17 865	27 332	5699	10 139	22 597
Independent reflections (R_{int})	17 063(0.077)	3411(0.059)	13 313(0.102)	3685(0.042)	7037(0.061)	15 611(0.055)
Observed reflections [$I > 2\sigma(I)$]	10 117	2584	5330	3391	3757	7391
Parameters	838	205	812	235	443	862
Goodness-of-fit	0.945	1.034	0.849	1.029	0.880	0.914
R_1 [$I > 2\sigma(I)$] [a]	0.0563	0.0370	0.0618	0.0504	0.0665	0.0731
wR_2 (all data) [b]	0.1506	0.1133	0.1538	0.1301	0.1589	0.1982

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

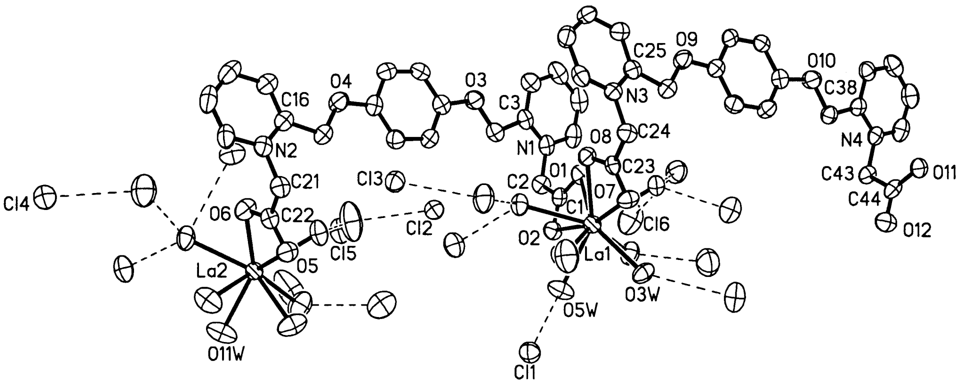


Fig. 1. Asymmetric unit with atom labeling in compound **1**.

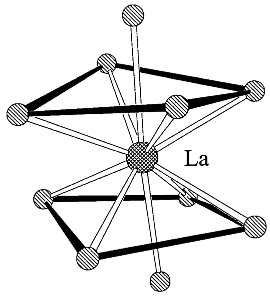


Fig. 2. Coordination geometry of La(III) in compound **1**.

other: the torsion angles are C9–O3–C8–C3 174.4(4)°, C12–O4–C15–C16 178.2(4)°, C31–O9–C30–C25 175.0(4)° and C34–O10–C37–C38 174.5(4)°. The two carboxylate groups of each ligand lie on the same side but extend in opposite directions to bind two La(III) ions at a separation of 11.77 Å. The relevant torsion angels are C(3)–N(1)–C(2)–C(1) −79.8(6)°, O(1)–C(1)–C(2)–N(1) −7.5(7)°, C(16)–N(2)–C(21)–C(22) −85.7(6)°, N(2)–C(21)–C(22)–O(6) −9.5(7)°, C(25)–N(3)–C(24)–C(23) −81.4(6)°, O(8)–C(23)–C(24)–N(3) −10.6(7)°, C(38)–N(4)–C(43)–C(44) −87.5(6)° and N(4)–C(43)–C(44)–O(11) is −4.0(7)°. The La(III) ions are linked by the tetradentate L^1 ligands, generating parallel infinite zigzag chains along the mutually orthogonal [1 1 0] and [$\bar{1}$ 1 0] directions (Fig. 3). These two set of chains are further connected through hydrogen bonds O3W–H···O5a, 169.4°, O3W···O5a 2.842(6) Å; O5W–H···O12b 158.5°, O5W···O12b 2.822(6) Å; and O11W–H···O2c 157.5°, O11W···O2c 2.792(6) (a: $-x+1$, $y-1/2$, $-z+3/2$; b: $-x+1$, $y+1/2$, $-z+3/2$; c: $-x$, $y+1/2$, $-z+3/2$), generating a double-layer network with larger channels (10 × 12 Å), as shown in Fig. 4. The lattice water molecules and chloride ions are accommodated in the channels, forming hydrogen bonds with the chains or with other lattice water molecules. There is no significant π–π interaction in this crystal structure.

In compound **2**, the La(III) ion has a similar bicapped square-antiprismatic coordination geometry as in **1**. The La(III) ion is located at a site of symmetry 2, and the ligand sites are occupied by three chelating nitrate ions, two monodentate carboxylate groups from two L^1

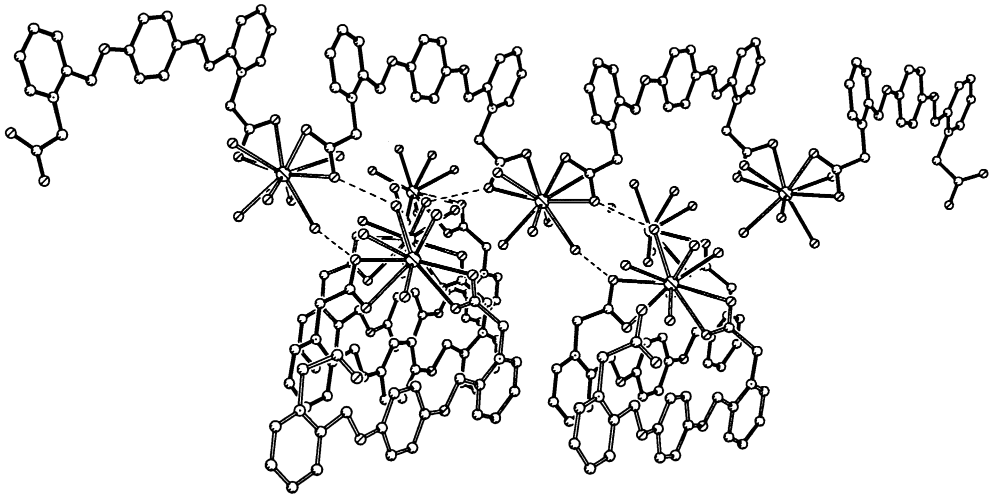


Fig. 3. 2D network in compound **1** formed by two sets of infinite chains along the [1 1 0] and [1 $\bar{1}$ 0] directions that are connected through hydrogen bonding. Lattice water molecules and chloride ions and all the hydrogen atoms are omitted for clarity.

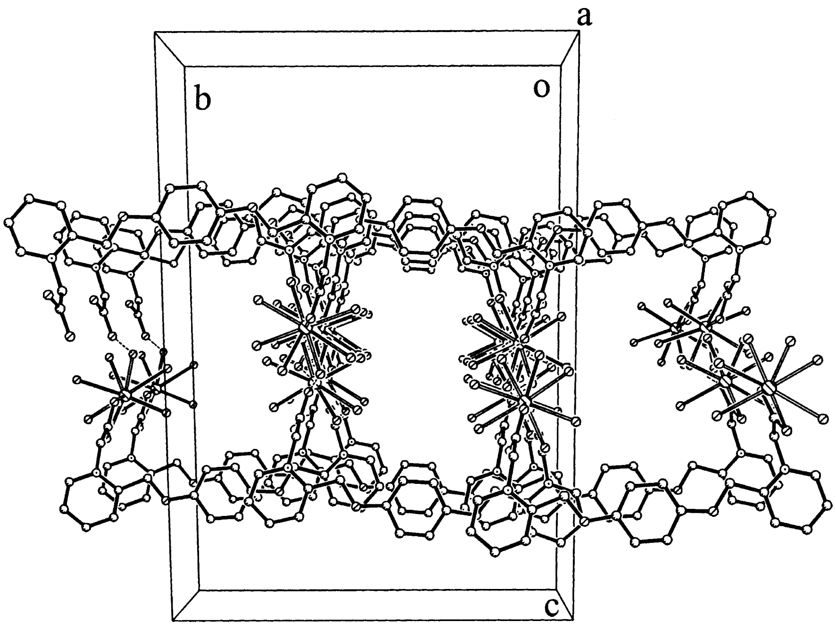


Fig. 4. 2D framework with large channels of compound **1** viewed along the *a* direction.

ligands and two aqua ligands. The La1, N3 and O8 atoms lie on a crystallographic 2 axis, and the ring of ligand L^1 is located at an inversion center. The two pyridine rings of L^1 are necessarily parallel to each other, each making a dihedral angle of 5° with the phenylene ring. The torsion angle C9–O3–C8–C3 is 170.5(3)°. Adjacent La(III) ions are bridged by L^1 at a separation of 13.39 Å, longer than that in **1**, generating an infinite chain along the [1 0 0] direction (Fig. 5). The torsion angle C(3)–N(1)–C(2)–C(1) is 81.6(3)° and O(1)–C(1)–C(2)–N(1) is $-19.3(4)$°. These chains are further connected through hydrogen bonds between adjacent chains (O1W···O8a, 2.793(5) Å; a: x, $-y+3/2$, $z+1/2$), giving an infinite 3D network with large cavities (Fig. 6). Intermolecular π–π interactions exist between the pyridine and phenylene rings of adjacent ligands, with center-to-center distance 3.74 Å and dihedral angle 5° (Fig. 7). In this compound the L^1 ligands bridge La(III) ions in a mode different from that in **1**. In **1**, the two nitrogen atoms of the betaine groups lie on the same side of the ligand with the carboxylate groups outstretching in opposite directions; on the other hand, in **2** the L^1 ligand adopts its fully extended configuration so that the two nitrogen atoms are at maximum separation from each other. Interestingly, ligand L^1 has been found to coordinate Zn(II) ions in a *syn* mode that differs from those in **1** and **2** [14].

Compound **3** exhibits an infinite 3D framework connected by metal-coordination and hydrogen bonds. The asymmetric unit is composed of a La(III) ion, two bridging L^1 ligands, four aqua ligands, three triflate anions and a lattice water molecule (Fig. 8). The La(III)

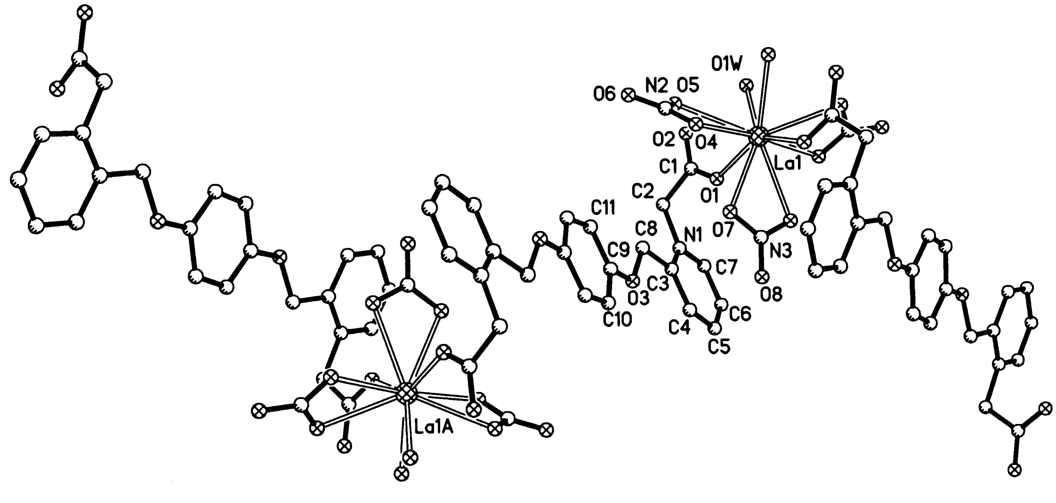


Fig. 5. Zigzag chain along the [1 0 0] direction in compound **2**.

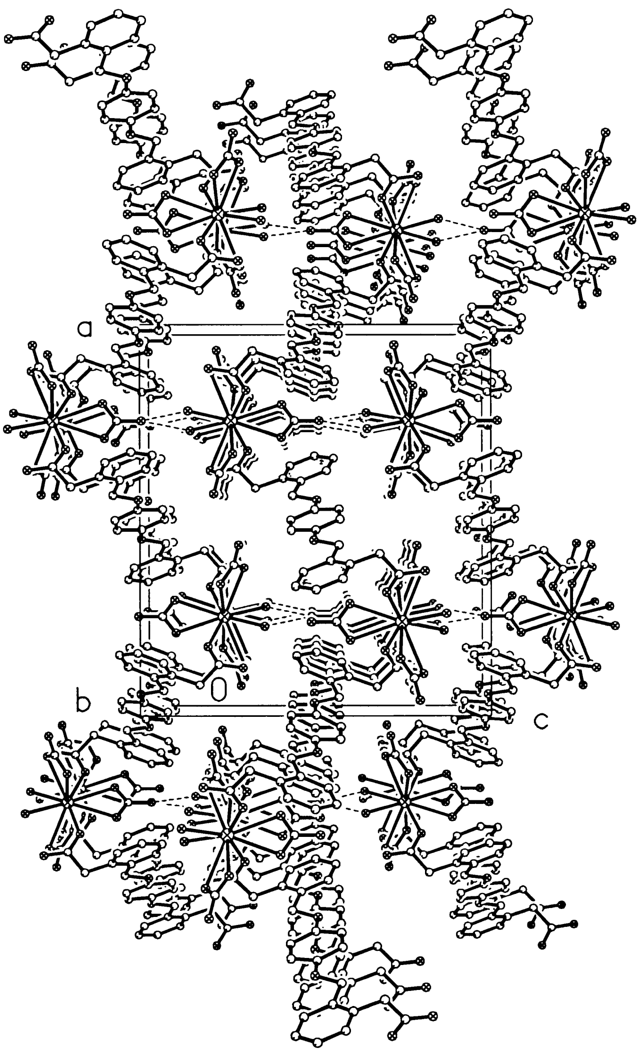


Fig. 6. 3D network connected by hydrogen bonds in compound **2**.

ion is 8-coordinated in a dodecahedral geometry (Fig. 9), being coordinated by four aqua ligands and four monodentate carboxylate groups from different L^1 ligands. The torsion angel C(3)–N(1)–C(2)–C(1) is −79.6(8)°, O(2)–C(1)–C(2)–N(1) is 15.0(9)°, C(16)–N(2)–C(21)–C(22) is 74.9(8)°, N(2)–C(21)–C(22)–O(6) is −10(1)°, C(25)–N(3)–C(24)–C(23) is 77.1(9)°, O(7)–C(23)–C(24)–N(3) is 0.6(1)°, C(38)–N(4)–C(43)–C(44) is −84.5(8)°, and N(4)–C(43)–C(44)–O(12) is 18.6(9)°. The L^1 ligands bridge the metal centers in the *anti* mode, as in the case of **2**, leading to an infinite double-layer framework with large channels (23 × 7 Å) (Fig. 10). The three rings of each independent ligand are not parallel to each other but twisted to facilitate two carboxylate groups to bridge two metal centers. The torsion angles are C9–O3–C8–C3 172.5(6)°, C16–C15–O4–C12 −171.7(6)°, C25–C30–O9–C31 173.3(6)°, and C34–O10–C37–C38 −173.0(7)°. There is no significant π–π interaction between the ligands in the double-layer. These double-layers are further connected through hydrogen bonds: O3W–H···O5a 149°, O3W···O5a 2.765(7) Å; O2W–H···O1b 156°, O2W···O1b 2.716(7) Å (a: $-x-1/2$, $y-1/2$, $-z+1/2$; b: $-x+1$, $-y$, $-z+1$), generating an infinite 3D network. The distance between the closest La(III) ions belonging to different double-layers is about 6.252 Å, longer than the corresponding distance 5.802 Å within a double-layer. The triflate ions occupy the channels of the framework, forming hydrogen bonds with the lattice water molecules and aqua ligands: O2W–H···O21 167°, O2W···O21 2.739(8) Å; O4W–H···O20 156°, O4W···O20 2.929(9) Å; O4W–H···O15a 145°, O2W···O15a 2.902(9) Å; O5W–H···O13b 148°, O5W···O13b 2.887(8) Å; and O5W–H···O21 117°, O5W···O21 2.881(9) Å (a: $x+1/2$, $-y+1/2$, $z+1/2$; b: $x+3/2$, $-y+1/2$, $z+1/2$).

Composed of the same ligand L^1 and metal ion La(III) but different anions, compounds **1**, **2** and **3** show different crystal structures. The nitrate ion readily coordinates to the La(III) center, so that it constitutes a part of the framework, while the weaker chloride and triflate ligands only occupy the channels or cavities

Table 2
Conformational parameters of the flexible double betaine ligands L^1 and L^2 (°)

Compound	Ligand	τ	δ_{py_1}	δ_{py_2}	$\delta_{(\mathrm{CO}_2)_1}$	$\delta_{(\mathrm{CO}_2)_2}$
1	L^1	(A) 11.6	10.6	10.8	96.9	90.3
		(B) 12.2	8.0	14.2	94.3	90.6
2	L^1	180	5.0		75.8	
3	L^1	(A) −176.1	6.0	13.5	75.2	74.8
		(B) 175.8	9.9	9.4	81.2	80.7
4	L^2	180	3.3		106.0	
5	L^2	−29.2	6.3	2.6	84.3	100.9
6	L^2	(A) −16.3	11.9	13.3	89.9	101.1
		(B) 31.6	3.2	31.0	105.3	104.2

The labels (A) and (B) indicate independent double betaine ligands. τ is the torsion angle CH_2–O···O–CH_2. δ_{py_1} is the dihedral angle between the central phenylene ring and a N1 or N3 pyridyl ring. δ_{py_2} is the dihedral angle between the central phenylene ring and a N2 or N4 pyridyl ring. $\delta_{(\mathrm{CO}_2)_1}$ is the dihedral angle between a pyridyl ring and its adjacent O1 or O7 carboxymethyl group. $\delta_{(\mathrm{CO}_2)_2}$ is the dihedral angle between the second pyridyl ring and its adjacent O6 or O12 carboxymethyl group.

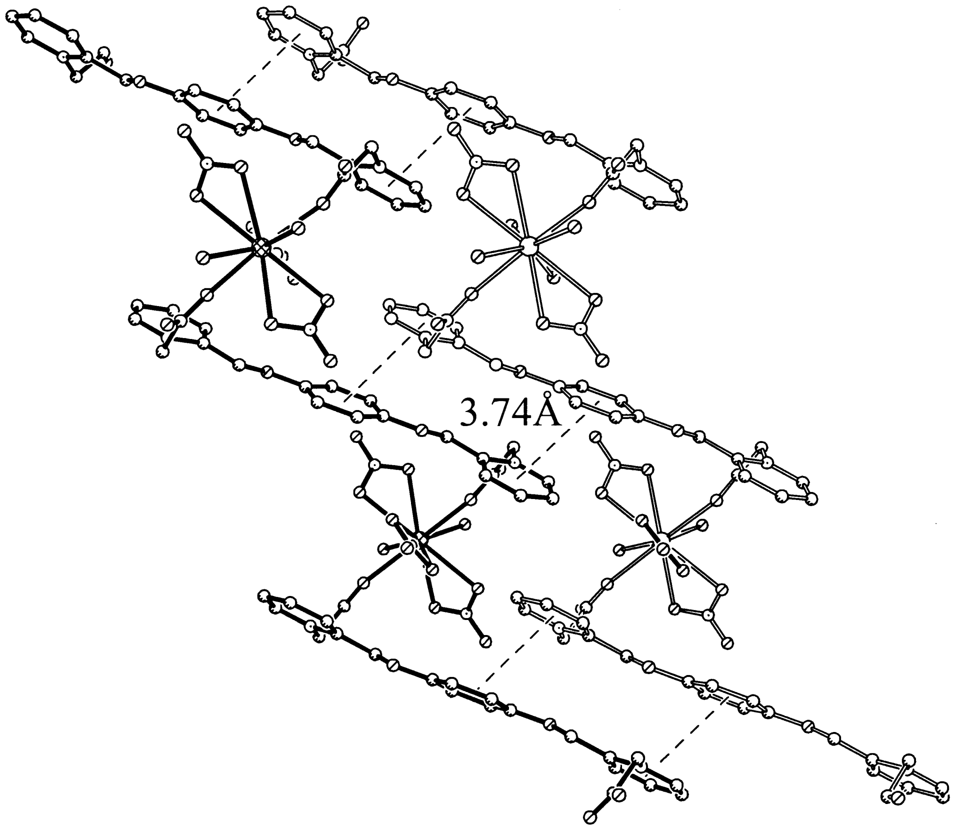


Fig. 7. π–π interactions between the chains in compound **2**.

formed by the framework. This finding complements our previous study which showed that, with the same anion and ligand L^1, different divalent transition metal cations Co(II), Mn(II), Cu(II), Zn(II) and Cd(II) give rise to different crystal structures [14].

Compound **4** adopts a 2D framework constructed with centrosymmetric dinuclear units. Each La (III) ion is located inside a tricapped trigonal-prism (Fig. 11), being coordinated by seven aqua ligands and bridged by two carboxylate groups acting in the *syn–anti* mode (Fig. 12). The torsion angles are O(1)–C(1)–C(2)–N(1)

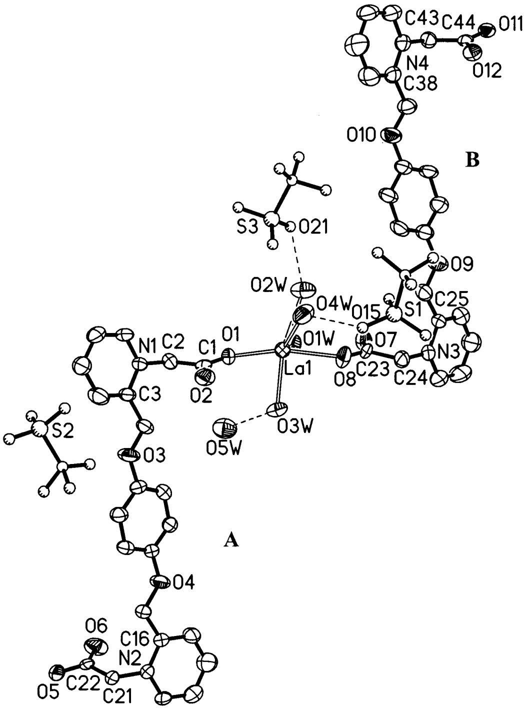


Fig. 8. The asymmetric unit with atom labeling in compound **3**.

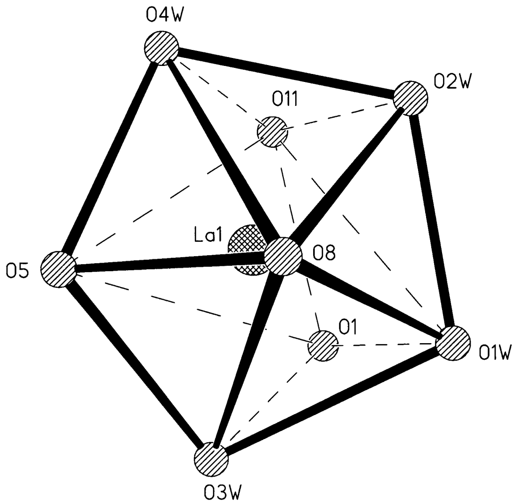


Fig. 9. Coordination geometry of La(III) in compound **3**.

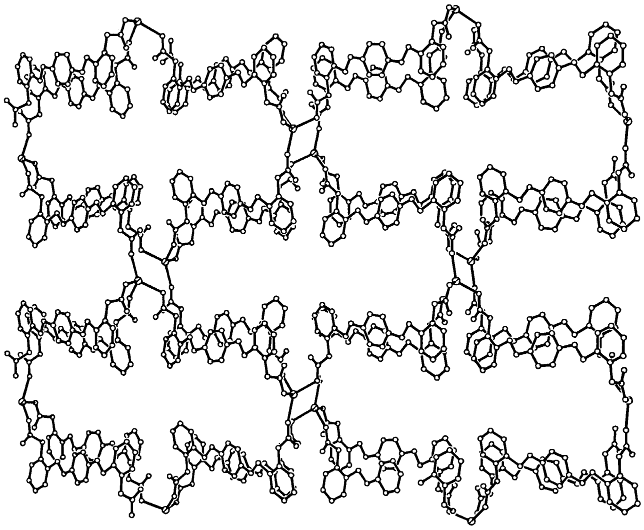


Fig. 10. Double-layer framework with large channels (23 × 7 Å) in compound **3**, viewed along the *a* direction. Hydrogen atoms, triflate ions and water molecules are omitted for clarity.

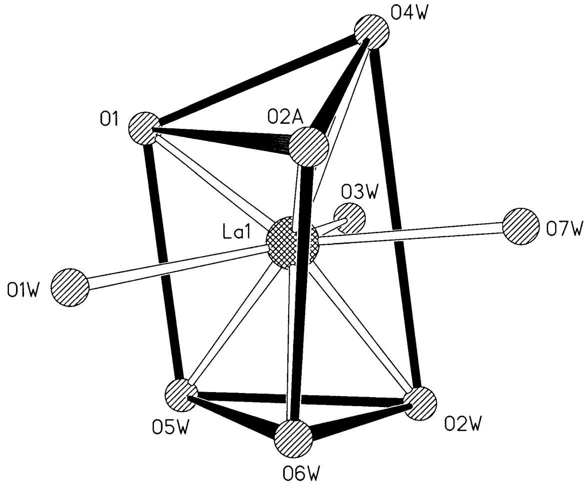


Fig. 11. Coordination geometry of La(III) in compound **4**.

−2.5(8)° and C(3)–N(1)–C(2)–C(1) −103.7(6)°. The chloride ions form weak hydrogen bonds with the aqua ligands: O1W–H···Cl1 155°, O1W···Cl1 3.063(4) Å; O6W–H···Cl2 149°, O1W···Cl2 3.078(4) Å; O7W–H···Cl3 166°, O1W···Cl3 3.066(5) Å. As each L^2 lies at a $\bar{1}$ site, it acts as a tetradentate ligand to link two dinuclear units, leading to an infinite zigzag chain along the [1 1 1] direction. These chains are further connected by the hydrogen bond O4W–H···O4Wa 179°, O4W···O4Wa 2.913(9) Å (a: $-x+1$, $-y+1$, $-z+1$) to generate an infinite 2D network (Fig. 13). In this complex, ligand L^2 bridges the metal in the *anti* configuration with its two pyridine rings parallel to each other and twisted by 3.2° to the phenylene ring. The torsion angle C9–O3–C8–C4 is 176.9(5)°. There is weak π–π interaction between the pyridine and phenylene rings of adjacent chains at a center-to-center distance of about 4.15 Å and a dihedral angle of 3.2°.

Compound **5** also shows a 2D double-chain structure constructed with dinuclear units. The asymmetric unit contains a La(III) ion, two chelating nitrate ions, a L^2 ligand, two aqua ligands, a disordered nitrate group and a lattice water molecule of half-site occupancy. The torsion angles are O(1)–C(1)–C(2)–N(1) −17.1(4)°, C(3)–N(1)–C(2)–C(1) 88.2(3)°, C(17)–N(2)–C(21)–C(22) −82.6(4)° and N(2)–C(21)–C(22)–O(5) 14.2(5)°. The La(III) ion adopts 10-coordinated icosahedral geometry, being surrounded by two oxygen atoms from two bridging L^2 ligands, two oxygen atoms from a chelating L^2 ligand, four oxygen atoms provided by two chelating nitrates, and two aqua ligands (Fig. 14). The two carboxylate groups of ligand L^2 coordinate to three La(III) ions: one bridges two La(III) ions in a skewed fashion, giving a centrosymmetric dinuclear unit at a separation of about 5.92 Å between them, and the other chelates to a neighboring La(III) ion. The dinuclear units are thus connected by the L^2 ligands, generating an infinite double chain along the [1 1 1] direction (Fig. 15) with large cavities (3.6 × 13.5 Å). These double chains are further connected by the hydrogen bond O1W–H···O6a 179°, O1W···O6a 2.976(9) Å (a: $x-1$, y, $z-1$) to generate a 2D double-chain framework (Fig. 16). The distance between adjacent La(III) ions of different double chains is 6.8 Å, about 0.9 Å longer than that in each dinuclear unit. Weak intermolecular π–π interactions are found, both between adjacent L^2 ligands of the same and different double-chains, at center-to-center distances of 3.61 and 3.60 Å, respectively. The disordered nitrate and lattice

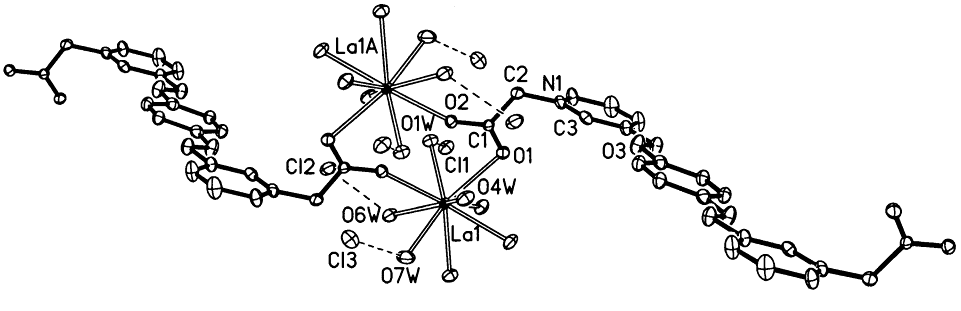


Fig. 12. The dinuclear unit linked by two L^2 ligands in compound **4**.

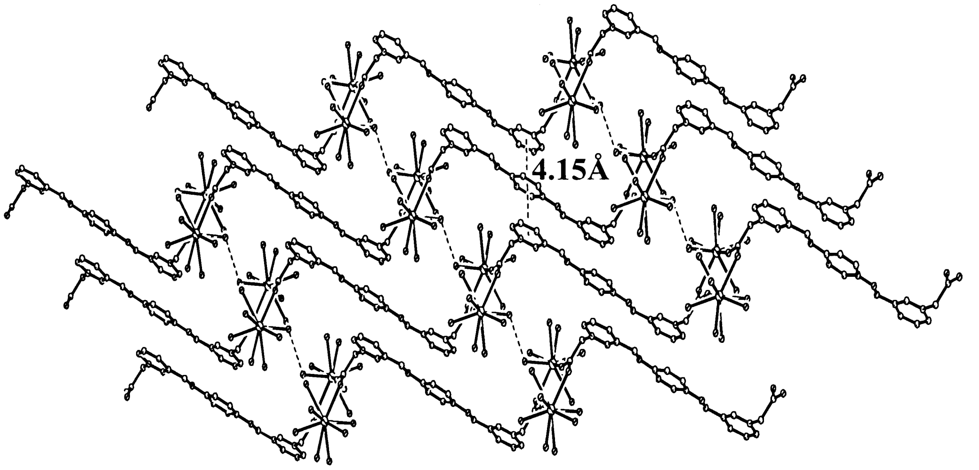


Fig. 13. 2D network in compound **4**, which is formed by linking the hydrogen-bonded zigzag chains.

water molecule occupy the space between the double-chains. In this compound, L^2 bridges the La(III) centers in the *anti* mode as found in **4**, but the three rings are not parallel to each other; the torsion angles are C9–O3–C8–C4 −169.7(9)° and C12–O4–C15–C16 −177.0 (7)°.

Compound **6** also exhibits a 2D network with dinuclear units. The asymmetric unit comprises a La(III) ion, two L^2 ligands, three aqua ligands, three triflate ions and six lattice water molecules. In this compound, the three rings of each L^2 ligand are not parallel, the two nitrogen atoms lie on the same side, as distinct from the case in **4** and **5**, and the carboxylate groups adopt different coordination modes. In L^2 molecule **A** the two carboxylate groups stretch out in opposite directions to link two La(III), whereas in molecule **B** one carboxylate group acts in the chelating mode while the other serves as a *syn–anti* bridge to consolidate a centrosymmetric dinuclear unit (Fig. 17). The relevant torsion angles are C(3)–N(1)–C(2)–C(1) −85.4(8)°, O(2)–C(1)–C(2)–N(1) −9(1)°, C(17)–N(2)–C(21)–C(22) −84.7(8)°, N(2)–C(21)–C(22)–O(6) 21(1)°, C(25)–N(3)–C(24)–C(23) 75.2(8)°, O(8)–C(23)–C(24)–N(3) −2(1)°, C(39)–N(4)–C(43)–C(44) −105.3(8)°, and N(4)–C(43)–C(44)–O(12) 6(1)°. Each La(III) lies within a distorted tricapped trigonal-prism as in **4**, with six oxygen atoms from five L^2 ligand (two from a pair of carboxylate groups in the centrosymmetric dinuclear unit, two from monodentate carboxylate groups, and two from a chelating carboxylate group) plus three aqua ligands. The La(III) ions in the dinuclear unit are separated by about 4.97 Å, and each pair of adjacent dinuclear units are bridged by four L^2 ligands, generating an infinite knotty quadruple chain along the [0 0 1] direction containing large 42-membered rings (Fig. 17). These chains are further linked by intermolecular hydrogen bonds, O1W–H···O5W 130.8°, O1W···O5W 2.810(7) Å; O5W–H···O2a, 179.3°, O5W···O2a 2.759(8) Å (a: $-x, -y+1, -z$), giving an infinite 2D network (Fig. 18). The triflate ions and other lattice water molecules occupy the cavities and channels within the framework. There is no π–π interaction between the adjacent L^2 ligands.

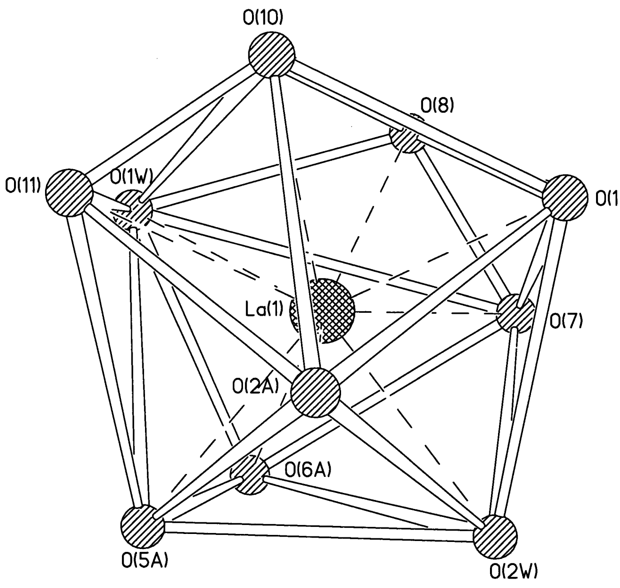


Fig. 14. Coordination geometry of La(III) in compound **5**.

In summary, we have shown that the flexible double betaine ligands L^1 and L^2 are versatile ligands for the generation of novel coordination networks in lanthanum(III) complexes. They can act in the bidentate (in compound **2** and **3**), tridentate (in **6**) and tetradentate (in **1**, **4** and **5**) modes to bridge La(III) centers, forming a 2- or 3D network with the aid of complementary hydrogen bonding involving co-existing aqua ligands and/or lattice water molecules. The conformations of L^1 and L^2 can be conveniently described in terms of the angular parameters listed in Table 2. In all six complexes, the three rings of each double betaine ligand are roughly co-

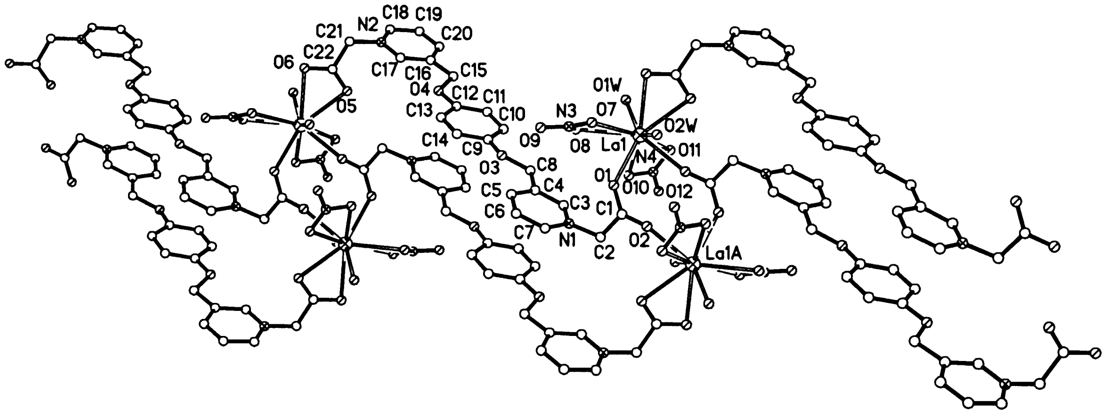


Fig. 15. Zigzag double chain in compound **5**, which is formed by two L^2 ligands bridging adjacent dinuclear units.

planar, with dihedral angles δ_{py} lying in the range 2.6–31.0°, and the relationship between the pair of $O{-}CH_2$ bonds can be either *syn* (torsion angle $|\tau| \approx 0°$) or *anti* ($|\tau| \approx 180°$). The plane of the carboxymethyl group is nearly perpendicular to its parent pyridyl ring, with a dihedral angle δ_{CO_2} that falls in the range 74.8–106.0°.

In the series of complexes **1**, **2** and **3** derived from L^1, the crystal structures are constructed with mononuclear units. In contrast, **4**, **5** and **6** are all 2D networks based on centrosymmetric dinuclear units. Such dinuclear building blocks are linked by the L^2 ligand to give a zigzag chain structure, and the chains are then further connected by hydrogen bonds, leading to a 2D framework. Notably, in compound **4** adjacent dinuclear units are linked by one L^2 ligand to form a zigzag chain (Fig. 12), in **5** the dinuclear units are linked by two L^2 ligands

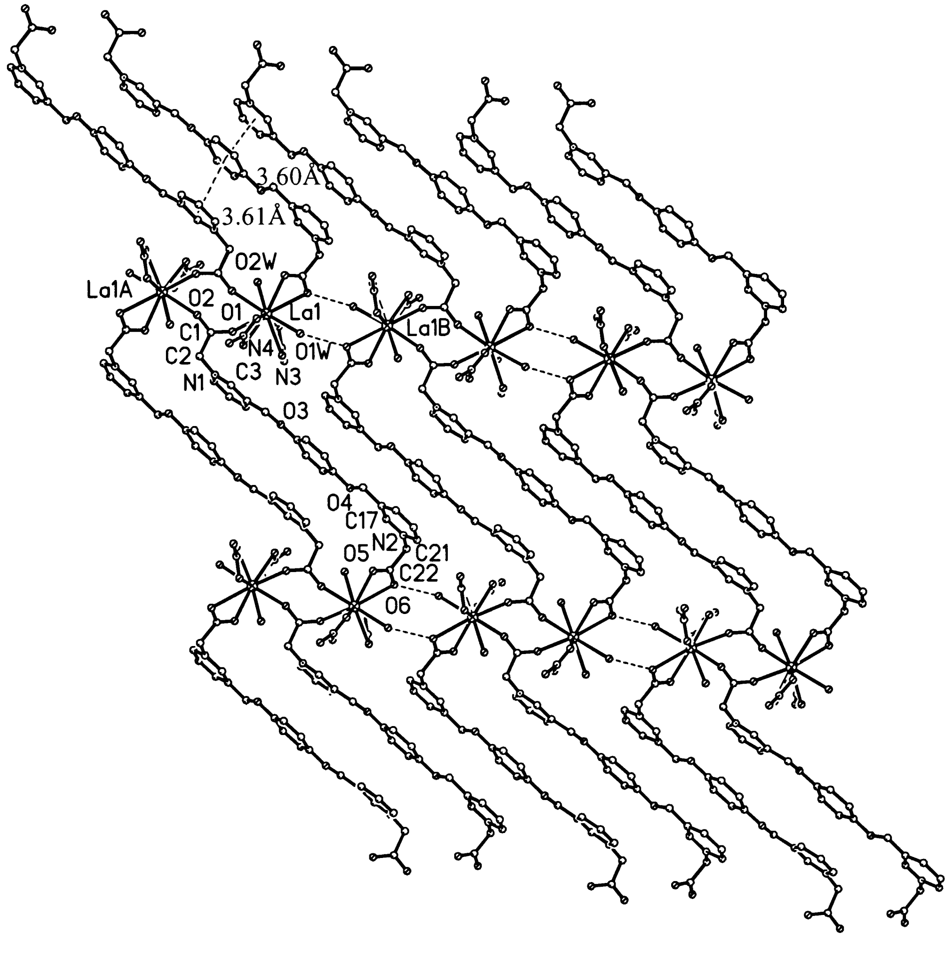


Fig. 16. Layer structure of compound **5** composed of double chains cross-linked by hydrogen bonds and π–π interactions.

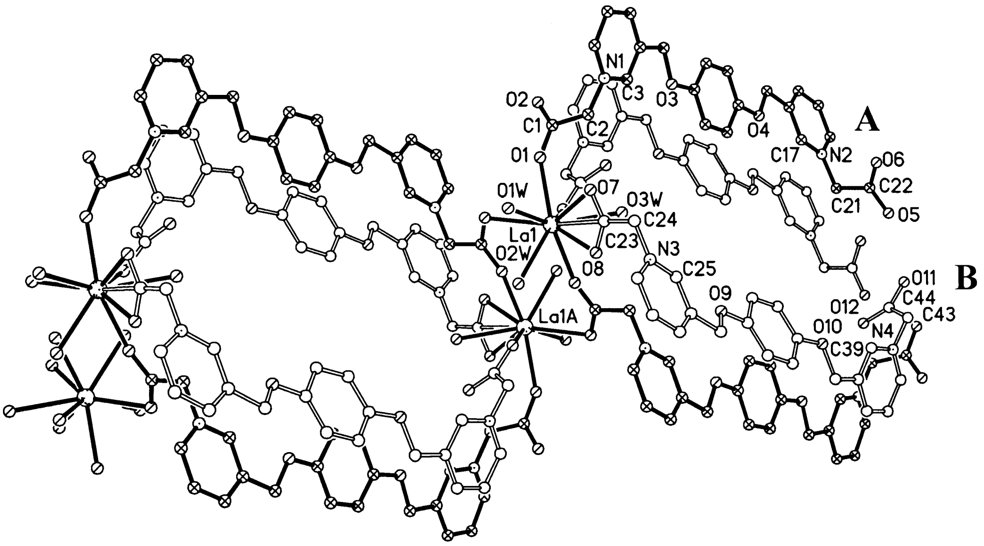


Fig. 17. The dinuclear unit in compound **6**, in which each La(III) center is bound to five L^2 ligands. The two independent L^2 ligands that generate the knotty quadruple chain are labeled **A** and **B**. Hydrogen atoms, lattice water molecules and triflate ions are omitted for clarity.

to give a double chain (Fig. 15), and in **6** the dinuclear units are linked by four L^2 ligands, yielding a more complex quadruple chain (Fig. 18). This structural trend implies that when the volume of the ancillary anion increases, more L^2 ligands are involved in linking the dinuclear units. The difference between the L^1 and L^2 lies only in the positioning of the betaine group, which proved to be the dominant factor in controlling the composition and structure of the lanthanide(III) complexes.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 207466–207471 for compounds **1**–**6**. Copies of this information may be obtained free of charge 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).

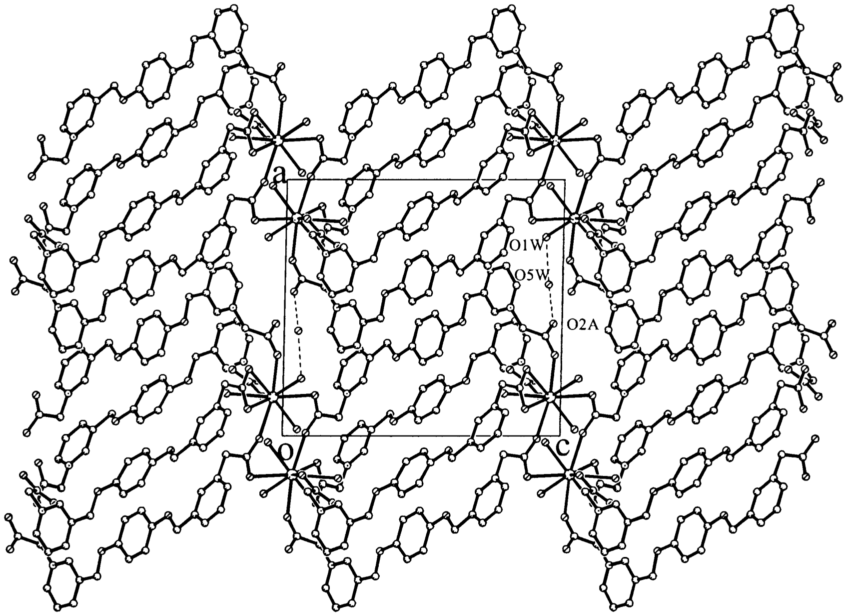


Fig. 18. Hydrogen-bonded 2D network in compound **6**. Hydrogen atoms, lattice water molecules and triflate ions are omitted for clarity.

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