SUPPORTING INFORMATION

for

DOTA complexes with divalent zinc, cadmium and mercury: X-ray and solid-state NMR studies, and solution isomerism.

Jakub Obuch[a,b], Ivana Císařová[a], Jiří Brus[b]* and Petr Hermann[a]*

[a]Department of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 2030/8, 128 40 Prague 2, Czech Republic.

[b]Institute of Macromolecular Chemistry, Czech Academy of Science, Heyrovského náměstí 2, 162 00 Prague 6, Czech Republic.

Contents

X-ray diffraction studies

Table S1. Experimental X-ray diffraction data and details of the structure determination.

Formula	$C_{16}H_{26}CdN_4O_8{\cdot}H_2O$	$C_{32}H_{48}Ba_2N_8O_{16}Zn_2{\cdot}11H_2O$	$C_{32}H_{48}Ba_2Cd_2N_8O_{16}{\cdot}24H_2O$	$C_{64}H_{96}Ba_4Hg_4N_{16}O_{32}{\cdot}34H_2O$	$C_{32}H_{48}Ca_2Hg_2N_8O_{16}{\cdot}19H_2O$
Formula weight	532.82	1404.40	1732.64	3565.82	1624.42
Crystal system	monoclinic	monoclinic	triclinic	triclinic	monoclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)
a, b, c [Å]	6.8060(4), 11.3430(5), 25.0311(13)	8.9961(7), 43.831(5), 12.7975(12)	14.6753(8), 15.6300(9), 16.857(1)	17.7595(13), 17.8182(12),	25.0258(18), 18.5447(13), 17.764(2)
α, β, γ [°]	90, 95.702(2), 90	90, 106.327(6), 90	107.257(2), 106.919(2), 108.312(2)	81.131(2), 88.647(2), 64.396(2)	90, 133.221(2), 90
V [Å^3]	1922.85(17)	4842.7(8)	3175.2(3)	5893.3(7)	6007.7(9)
Z	4	4	2	2	4
D(calc) [g cm^{-3}]	1.841	1.926	1.812	2.010	1.796
μ [mm^{-1}]	1.197	14.461	1.987	6.607	5.373
F(000)	1088	2824	1744	3464	3256
Crystal size [mm]	0.13 × 0.13 × 0.21	0.02 × 0.02 × 0.41	0.20 × 0.22 × 0.28	0.12 × 0.17 × 0.32	0.06 × 0.12 × 0.14
Temperature [K]	100	120	120	120	120
Radiation [Å]	Mo-$K\alpha$, 0.71073	Cu-$K\alpha$, 1.54178	Mo-$K\alpha$, 0.71073	Mo-$K\alpha$, 0.71073	Mo-$K\alpha$, 0.71073
θ Min, Max [°]	2.0, 28.3	3.7, 63.8	2.2, 30.0	2.2, 27.5	2.2, 27.5
h; k; l indices	−9:9; −15:15; −33:33	−10:9; −51:44; −14:14	−20:20; −21:21; −23:23	−23: 23 −23:23; −27:27	−32:32; −24:24; −23:23
Total / Unique data, R(int)	55773 / 4759, 0.019	43425 / 7983, 0.176	163298 / 18462, 0.025	269744 / 27005, 0.037	204121 / 6913, 0.050
Observed data	4681	5657	18111	26226	6415
N_{ref}, N_{par}	4759, 277	7983, 645	18462, 847	27005, 1486	6913, 376
R, wR_2, S	0.0188, 0.0518, 1.12	0.0945, 0.2163, 1.06	0.0218, 0.0523, 1.05	0.0205, 0.0536, 1.04	0.0568, 0.1339, 1.15
Min./Max. resid. el. density [e Å^{-3}]	−0.85 / 0.50	−1.42 / 2.56	−1.71 / 2.24	−1.79 / 1.79	−1.55 / 7.83
CCDC number	2477250	2477254	2477253	2477252	2477251

Details on refinements of the diffraction data and further discussion

[Cd(H$_2$dota)]·H$_2$O

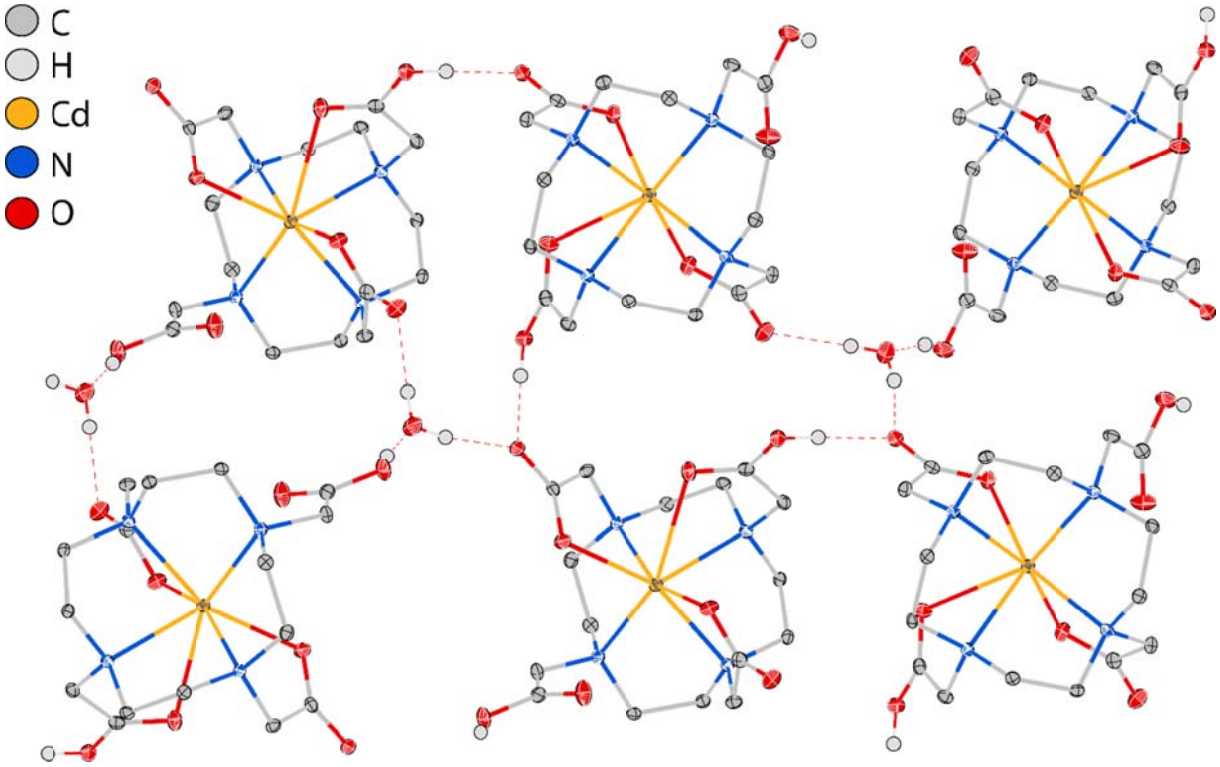

Figure S1. View perpendicular to the crystallographic *bc* plane of packing in the crystal structure of [Cd(H$_2$dota)]·H$_2$O. Carbon-bound hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50 % probability level. Color code: **red: oxygen**, **blue: nitrogen**, **grey: carbon**, **yellow: cadmium**, **light gray: hydrogen**.

Table S2. Selected geometric parameters of the [Cd(H$_2$dota)] molecules found in the solid-state structure of [Cd(H$_2$dota)]·H$_2$O.

Distances, Å		Angles, °	
Cd1–O11	2.2560(10)	O11–Cd1–O31	106.09(4)
Cd1–O22	2.7665(11)	O22–Cd1–O42	127.40(3)
Cd1–O31	2.3169(11)	N1–Cd1–N3	117.97(4)
Cd1–N1	2.3971(12)	N2–Cd1–N4	119.10(4)
Cd1–N2	2.4529(11)	O11–O22–O31	72.59(3)
Cd1–N3	2.3973(11)	O22–O31–O42	108.35(4)
Cd1–N4	2.4544(13)	O42–O11–O22	66.74(3)
Cd1–Q_N	1.239	O11–O22–O31	112.18(4)
Cd1–Q_O	1.339	N1–N2–N3	88.50(4)
Q_NA–Q_O	2.575	N2–N3–N4	91.70(4)
		N3–N4–N1	88.16(4)
		N4–N1–N2	91.64(4)
		N1–Q_N–Q_O–O11	28.22
		N2–Q_N–Q_O–O22	24.50
		N3–Q_N–Q_O–O31	23.83
		N4–Q_N–Q_O–O42	25.96

Q_N is the centroid of the N_4 plane; Q_O is the centroid of the O_4 plane.

Ca[Hg(dota)]·9.5H_2O

Out of the 9.5 water molecules of crystallization, seven are localized, one is disordered over two positions (in roughly 53:47 ratio), with both parts of the disorder hydrogen atoms bonded as donor to carboxylic oxygen atom O12A, whereas only the major part forms hydrogen bond to O5X. Furthermore, one water molecule is disordered over four positions with equal occupancies and one site was the best refined as water molecule with an occupancy of 0.5. The ADPs of the disordered groups of water molecules were fixed to be equal using EADP commands. Structural parameters are listed in **Table S2**.

Crystal packing

The two complex anions in this structure are linked via coordination to the same Ca^{2+} counter-cation (**Figure S1**). Through the interactions between the macrocyclic anions and Ca^{2+} counter-cations, two complex anions and two Ca^{2+} cations form a dimer. These dimers are further linked to form linear strands in the direction of the cell axis *c*. The individual strands are separated by water molecules of crystallization. These Ca^{2+} counter-cations are octacoordinated κ^2-*O,O′*-didentately by the carboxylate group of complex anion "B", monodentately by the oxygen atom of the acetate pendant arm of complex anion "A", didentately by the carboxylate group of complex anion "A" (1−*x*, 1−*y*, 1−*z*) in the κ^2-*O,O′* mode, and by three water molecules. The Ca–O bond lengths are 2.339–2.641 Å. The whole structure is further stabilized by several hydrogen bonds between oxygen atoms from acetate pendant arms water molecules of crystallization.

Refinement remarks

To prevent ADPs for N2A becoming non-positive definite during the refinement process, SIMU restraint was used. Positions of all hydrogen atoms of the water molecules were fixed during the final refinement cycle. Large residual electron density maxima localized around Hg^{2+} were caused by minor disorder/twinning; and the resulting A- and B-level checkcif alerts (PLAT971, PLAT975, PLAT094) could not be resolved.

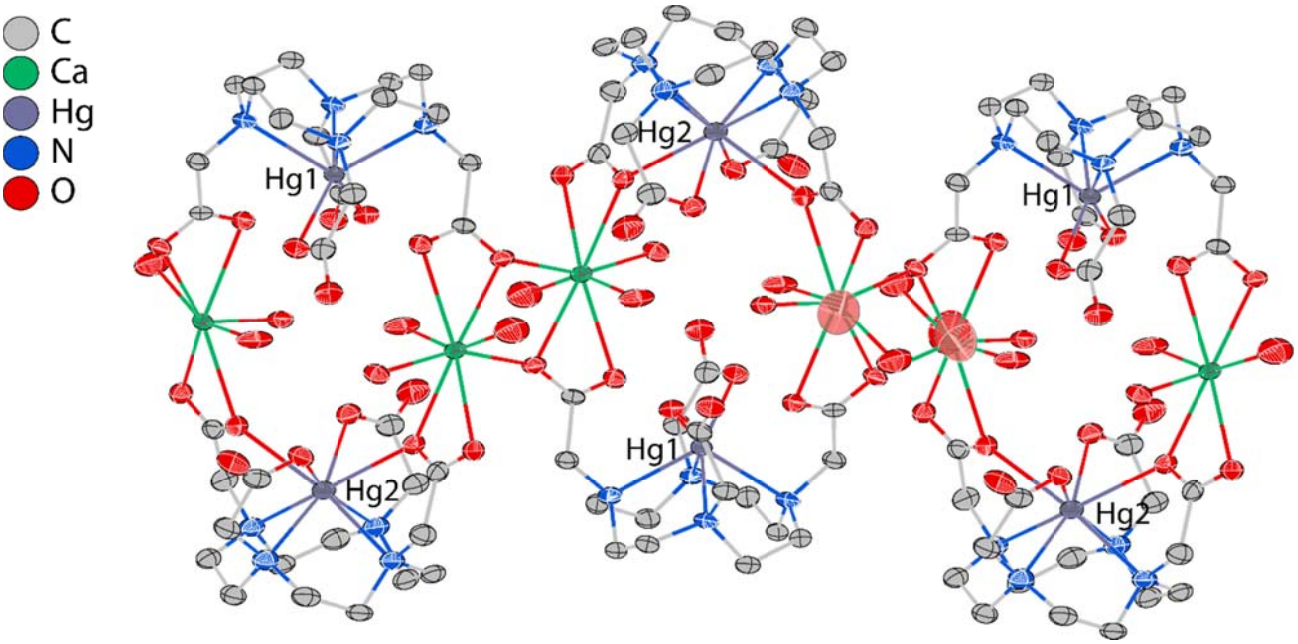

Figure S2. View along the crystallographic axis *a* of packing in the crystal structure of Ca[Hg(dota)]·9.5H_2O. Hydrogen atoms and Ca-non-coordinated water molecules are omitted for clarity. Thermal ellipsoids are drawn at 50 % probability level. Color code: **red: oxygen**, **blue: nitrogen**, **grey: carbon**, **green: calcium**, **purple: mercury**

Table S3. Selected geometric parameters of the $[Hg(dota)]^{2-}$ anions found in the solid-state structure of $Ca[Hg(dota)]\cdot 9.5H_2O$.

Distances, Å			
Hg1–O11A	2.4411(56)	Hg2–O11B	2.5595(52)
Hg1–O21A	2.6646(54)	Hg2–O21B	2.5727(60)
Hg1–N1A	2.4327(65)	Hg2–N2B	2.4655(79)
Hg1–N2A	2.4480(67)	Hg2–N1B	2.4839(66)
$Hg1–Q_NA$	1.24	$Hg2–Q_NB$	1.286
$Hg1–Q_OA$	1.37	$Hg2–Q_OB$	1.359
$Q_NA–Q_OA$	2.610	$Q_NB–Q_OB$	2.645
Angles, °			
O21A–Hg1–O21A^{i}	117.79(22)	O21B–Hg2–O21B^{ii}	116.24(25)
O11A–Hg1–O11A^{i}	112.35(25)	O11B–Hg2–O11B^{ii}	115.85(23)
N1A–Hg1–N1A^{i}	118.63(30)	N1B–Hg2–N1B^{ii}	117.32(31)
N2A–Hg1–N2A^{i}	118.86(29)	N2B–Hg2–N2B^{ii}	117.48(34)
O11A–O21A–O11A^{i}	83.3(2)	O11B–O21B–O11B^{ii}	89.5(3)
O21A–O11A–O21A^{i}	96.7(3)	O21B–O11B–O21B^{ii}	90.5(3)
N2A–N1A–N2A^{i}	90.4(3)	N2B–N1B–N2B^{ii}	89.6(3)
N1A–N2A–N1A^{i}	89.6(3)	N1B–N2B–N1B^{ii}	90.4(3)
$N1A–Q_NA–Q_OA–O11A$	−25.98	$N1B–Q_NB–Q_OB–O11B$	22.11
$N2A–Q_NA–Q_OA–O21A$	−26.03	$N2B–Q_NB–Q_OB–O21B$	23.19

Symmetry codes: i: 1−*x*, *y*, 3/2−*z*, ii: −*x*+1, *y*, 1/2−*z*.

Q_N is the centroid of the N_4 plane; Q_O is the centroid of the O_4 plane.

Ba[Hg(dota)]·8.5H_2O

Out of the 34 water molecules in the asymmetric unit, 25 are localized, 6 are disordered over two positions, 1 is disordered over three positions and 2 are disordered over four positions. In most cases, the disordered water molecules were refined with oxygen atoms disordered over two (or more) close positions with one or two common hydrogen atoms, with ADPs made equal using the EADP command. Structural parameters are listed in **Table S3**.

Disorder of the pendant arms in anion "B"

The first pendant arm in the anion "B" is disordered in two positions in a 66:33 ratio with one common oxygen atom O12B which is not involved in coordination with the central metal ion. The Hg-coordinated oxygen atom is disordered in two bonding positions (with Hg–O bond lengths of 2.333 Å and 2.570 Å). The second pendant arm is disordered in two positions in a 70:30 ratio with no shared atoms. More importantly, one oxygen atom of the pendant arm is disordered coordinated/non-coordinated to the Hg(II) ion (the major part O21B is coordinated, the minor part O24B is non-coordinated). The Hg–O distances of coordinated and non-coordinated oxygen atom are 2.476 Å and 2.977 Å, respectively. The fourth pendant arm is disordered in two positions in a 60:40 ratio with one common oxygen atom, O41B. This oxygen atom is coordinated to the Hg(II) ion in a longer distance than the other donor atoms (Hg–O distance 2.751 Å). The disordered atoms were refined over two positions with equal ADPs.

Crystal packing

Complex anions A, B and C, D are linked via coordination to the same $Ba1^{2+}$, $Ba2^{2+}$ and $Ba3^{2+}$, $Ba4^{2+}$counter-cations, respectively, thus forming $Ba_2[Hg(dota)]_2$ dimers which are linked to other such dimers to form 1D polymeric strands in the direction of cell axis *b* (**Figure S2**) The strands formed by the anions A, B and C, D are distributed alternatively through the crystal packing, parallelly oriented, separated by water molecules of crystallization. The Ba^{2+} counter-cations are coordinated by (*i*) ten oxygen atoms originating from four acetate pendant arms (two of which are coordinated in a κ^2-*O,O′* fashion) of three different complex anions and by four water molecules; (*ii*) ten oxygen atoms originating from five acetate pendant arms (two of which are bound in a κ^2-*O,O′* mode) of three different complex anions and three water molecules; (*iii*) ten oxygen donor atoms originating from four acetate pendant arms (two of which are coordinated in the κ^2-*O,O′* mode) of three different complex anions and four water molecules; and (*iv*) nine oxygen donor atoms originating from four acetate pendant arms (two of which are coordinated in the κ^2-*O,O′* fashion) of three different complex anions and three water molecules. The Ba–O bond lengths are in a range 2.695–3.199 Å.

Refinement remarks

ADPs of several disordered water molecules were restricted to be approximately isotropic using ISOR command. Positions of all hydrogen atoms of the water molecules were fixed during the final refinement cycle. Some low-angle reflections were affected by the beamstop, due to the large unit cell, resulting in B-level checkcif alert PLAT910.

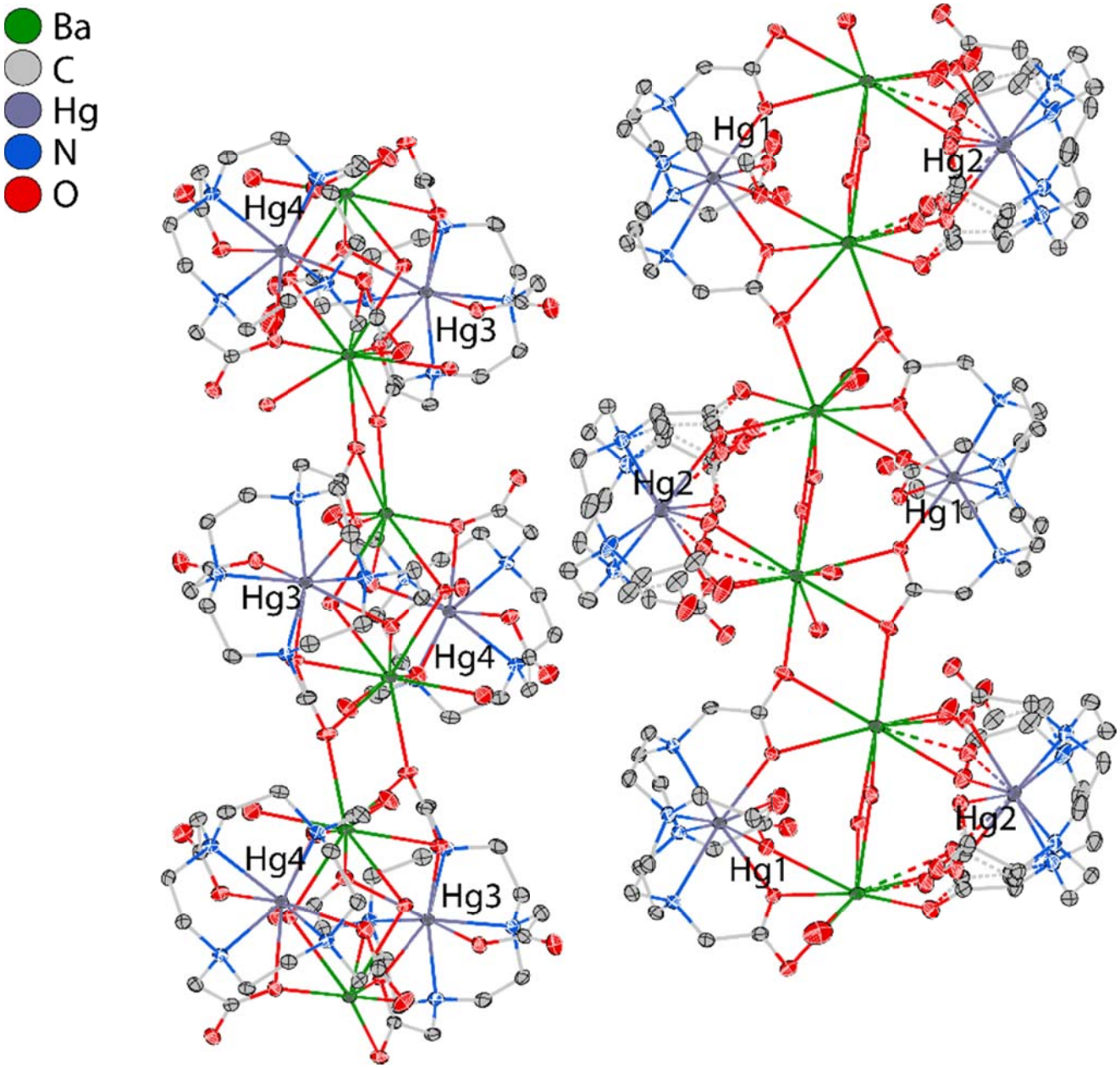

Figure S3. View halfway between the crystallographic axes *a* and *c* of packing in the crystal structure of Ba[Hg(dota)]·8.5H_2O. Hydrogen atoms and Ba-non-coordinated water molecules are omitted for clarity. Thermal ellipsoids are drawn at 50 % probability level. Color code: **red: oxygen**, **blue: nitrogen**, **grey: carbon**, **green: barium**, **purple: mercury**.

Table S4. Selected geometric parameters found in the crystal structure of Ba[Hg(dota)]·8.5H_2O.

Distances, Å			
Hg1–O11A	2.6420(23)	Hg2–O11B	2.5672(54)
Hg1–O21A	2.4870(22)	Hg2–O13B	2.3277(114)
Hg1–O31A	2.6491(24)	Hg2–O21B	2.4749(36)
Hg1–O41A	2.4368(21)	Hg2–O31B	2.4569(21)
		Hg2–O41B	2.7512(24)
Hg1–N1A	2.4387(25)	Hg2–N1B	2.4183(30)
Hg1–N2A	2.4733(25)	Hg2–N2B	2.4594(30)
Hg1–N3A	2.4449(26)	Hg2–N3B	2.4132(26)
Hg1–N4A	2.4654(25)	Hg2–N4B	2.4466(30)
Hg1–Q_NA	1.237	Hg2–Q_NB	1.206

Hg1–Q_OA	1.425	Hg2–Q_OB	1.420
Q_NA–Q_OA	2.661	Q_NB–Q_OB	2.622
Hg3–O11C	2.6527(23)	Hg4–O11D	2.5304(22)
Hg3–O21C	2.4613(20)	Hg4–O21D	2.5662(22)
Hg3–O31C	2.5984(23)	Hg4–O31D	2.6236(21)
Hg3–O41C	2.5291(21)	Hg4–O41D	2.4751(23)
Hg3–N1C	2.4663(26)	Hg4–N1D	2.4613(25)
Hg3–N2C	2.4520(25)	Hg4–N2D	2.4656(25)
Hg3–N3C	2.4207(26)	Hg4–N3D	2.487(24)
Hg3–N4C	2.4697(25)	Hg4–N4D	2.4583(25)
Hg3–Q_NC	1.235	Hg4–Q_ND	1.238
Hg3–Q_OC	1.423	Hg4–Q_OD	1.377
Q_NC–Q_OC	2.656	Q_ND–Q_OD	2.615
	Angles, °		
O11A–Hg1–O31A	116.21(7)	O11B–Hg2–O31B	111.32(13)
O21A–Hg1–O41A	107.71(7)	O21B–Hg2–O41B	114.19(10)
O11A–O21A–O31A	96.6(1)	O11B–O21B–O31B	88.2(2)
O21A–O31A–O41A	83.76(9)	O21B–O31B–O41B	95.3(1)
O31A–O41A–O11A	97.3(1)	O31B–O41B–O11B	85.2(1)
O41A–O11A–O21A	82.25(9)	O41B–O11B–O21B	91.2(2)
N1A–Hg1–N3A	119.56(9)	N1B–Hg2–N3B	120.36(9)
N2A–Hg1–N4A	119.51(8)	N2B–Hg2–N4B	120.86(9)
N1A–N2A–N3A	89.4(1)	N1B–N2B–N3B	89.1(1)
N2A–N3A–N4A	91.1(1)	N2B–N3B–N4B	90.9(1)
N3A–N4A–N1A	89.3(1)	N3B–N4B–N1B	88.9(1)
N4A–N1A–N2A	90.2(1)	N4B–N1B–N2B	91.1(1)
N1A–Q_NA–Q_OA–O11A	−22.83	N1B–Q_NB–Q_OB–O11B	−26.33
N2A–Q_NA–Q_OA–O21A	−20.70	N2B–Q_NB–Q_OB–O21B	−24.34
N3A–Q_NA–Q_OA–O31A	−22.51	N3B–Q_NB–Q_OB–O31B	−27.86
N4A–Q_NA–Q_OA–O41A	−21.11	N4B–Q_NB–Q_OB–O41B	−26.39
O11C–Hg3–O31C	115.43(7)	O11D–Hg4–O31D	115.18(7)
O21C–Hg3–O41C	109.34(7)	O21D–Hg4–O41D	113.98(7)
O11C–O21C–O31C	93.69(9)	O11D–O21D–O31D	90.31(9)
O21C–O31C–O41C	84.52(9)	O21D–O31D–O41D	89.02(9)
O31C–O41C–O11C	96.2(1)	O31D–O41D–O11D	93.01(9)
O41C–O11C–O21C	85.54(9)	O41D–O11D–O21D	87.66(9)
N1C–Hg3–N3C	119.53(9)	N1D–Hg4–N3D	119.35(8)
N2C–Hg3–N4C	119.47(8)	N2D–Hg4–N4D	119.26(8)
N1C–N2C–N3C	89.9(1)	N1D–N2D–N3D	89.4(1)
N2C–N3C–N4C	90.2(1)	N2D–N3D–N4D	90.4(1)
N3C–N4C–N1C	89.3(1)	N3D–N4D–N1D	89.7(1)
N4C–N1C–N2C	90.5(1)	N4D–N1D–N2D	90.6(1)
N1C–Q_NC–Q_OC–O11C	−24.08	N1D–Q_ND–Q_OD–O11D	−24.13
N2C–Q_NC–Q_OC–O21C	−21.96	N2D–Q_ND–Q_OD–O21D	−24.51
N3C–Q_NC–Q_OC–O31C	−22.56	N3D–Q_ND–Q_OD–O31D	−25.3
N4C–Q_NC–Q_OC–O41C	−21.49	N4D–Q_ND–Q_OD–O41D	−23.72

Q_N is the centroid of the N_4 plane; Q_O is the centroid of the O_4 plane.

Ba[Cd(dota)]·12H$_2$O

Out of the 24 water molecules in the asymmetric unit, 15 are localized, 8 are disordered over two positions and 1 is disordered over three positions. In most cases, the disordered water molecules were refined with oxygen atoms disordered over two (or more) close positions with one or two common hydrogen atoms, with ADPs made equal using the EADP command. Structural parameters are listed in **Table S4**.

In the complex anion "A", the two oxygen atoms (O11A, O12A) of the first pendant arm serve as acceptors of two hydrogen bonds. The second pendant arm coordinates two Ba^{2+} counter-cations, one ion is coordinated in the κ^2-*O,O′* mode (**Figure S3**). The third pendant arm coordinates one Ba^{2+} counter-cation monodentately by the Cd-coordinated oxygen atom O31A. The fourth pendant arm coordinates two different Ba^{2+} counter-cations, one of them κ^3-tridentately, with O31A as the third donor atom. In the complex anion "B", the first pendant arm coordinates one Ba^{2+} cation in κ^3-*O,O′,O″* mode, with O41B as the third donor atom. The second pendant arm coordinates one Ba^{2+} cation in κ^2-*O,O′* mode. The Cd-non-coordinated oxygen atom of the third pendant arm (O32B, O33B) is disordered over two positions in an 80:20 ratio. The disordered oxygen atoms were kept at the same distance from the carbonyl using SADI command and their ADPs were kept equal. This pendant arm does not coordinate any Ba^{2+} cation but rather acts as an acceptor of several hydrogen bonds. The fourth pendant arm coordinates one Ba^{2+} cation monodentately by the Cd-coordinated oxygen atom O41B.

Crystal packing

The complex anions "A" and "B" are linked by coordination to two Ba^{2+} cations to form a $Ba_2[Cd(dota)]_2$ dimer. This dimer is further linked to other such dimers to form a 1D polymeric strand in the direction between the cell axes *a* and *b*. Two Ba^{2+} cations are bridged via two water molecules. In addition, each Ba^{2+} cation is coordinated by six oxygen donor atoms from carboxylic acid groups originating from three different complex anions and two or one other non-bridging water molecules, respectively. Thus, the Ba^{2+} cations are coordinated by ten or nine oxygen donor atoms, respectively. The Ba–O bond lengths range from 2.683 to 3.057 Å.

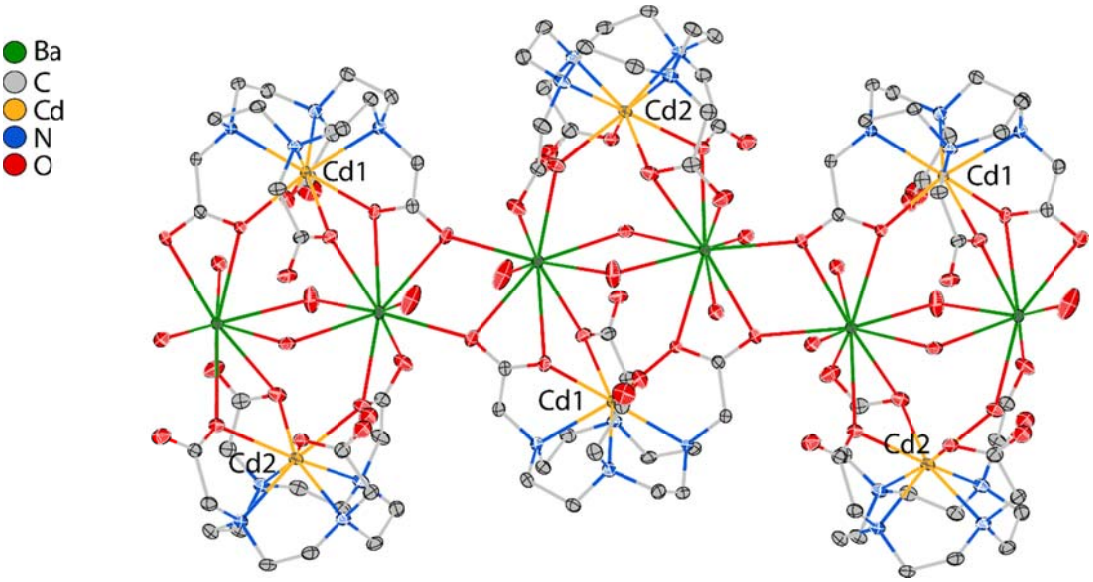

Figure S4. View perpendicular to a plane halfway between the crystallographic axes *a* and *b* of packing in the crystal structure of Ba[Cd(dota)]·12H$_2$O. Hydrogen atoms and Ba-non-coordinated water molecules are omitted for clarity. Thermal ellipsoids are drawn at 50 % probability level. Color code: **red: oxygen**, **blue: nitrogen**, **grey: carbon**, **green: barium**, **yellow: cadmium**.

Table S5. Selected geometric parameters found in the crystal structure of Ba[Cd(dota)]·12H_2O.

Distances, Å			
Cd1–O11A	2.5186(13)	Cd2–O11B	2.3836(13)
Cd1–O21A	2.3682(12)	Cd2–O21B	2.4300(13)
Cd1–O31A	2.5079(13)	Cd2–O31B	2.4572(12)
Cd1–O41A	2.3771(12)	Cd2–O41B	2.4947(13)
Cd1–N1A	2.4434(14)	Cd2–N1B	2.4668(14)
Cd1–N2A	2.4433(14)	Cd2–N2B	2.4603(15)
Cd1–N3A	2.4687(14)	Cd2–N3B	2.4546(14)
Cd1–N4A	2.4834(14)	Cd2–N4B	2.4180(14)
Cd1–Q_NA	1.294	Cd2–Q_NB	1.285
Cd1–Q_OA	1.324	Cd2–Q_OB	1.311
Q_NA–Q_OA	2.618	Q_NB–Q_OB	2.596
Angles, °			
O31A–Cd1–O11A	117.38(4)	O11B–Cd2–O31B	115.03(4)
O41A–Cd1–O21A	111.05(4)	O41B–Cd2–O21B	115.10(4)
O11A–O21A–O31A	95.11(6)	O11B–O21B–O31B	87.97(6)
O21A–O31A–O41A	85.89(6)	O21B–O31B–O41B	90.08(5)
O31A–O41A–O11A	95.52(6)	O31B–O41B–O11B	90.02(6)
O41A–O11A–O21A	83.44(6)	O41B–O11B–O21B	91.92(6)
N1A–Cd1–N3A	116.63(5)	N1B–Cd2–N3B	116.65(5)
N2A–Cd1–N4A	116.42(5)	N2B–Cd2–N4B	116.79(5)
N1A–N2A–N3A	89.91(6)	N2B–N3B–N4B	89.57(6)
N2A–N3A–N4A	90.39(6)	N3B–N4B–N1B	90.25(6)
N3A–N4A–N1A	89.88(6)	N4B–N1B–N2B	89.50(6)
N4A–N1A–N2A	89.83(6)	N1B–N2B–N3B	90.67(7)
N1A–Q_NA–Q_OA–O11A	23.75	N1B–Q_NB–Q_OB–O11B	23.86
N2A–Q_NA–Q_OA–O21A	23.74	N2B–Q_NB–Q_OB–O21B	25.07
N3A–Q_NA–Q_OA–O31A	23.96	N3B–Q_NB–Q_OB–O31B	25.14
N4A–Q_NA–Q_OA–O41A	22.66	N4B–Q_NB–Q_OB–O41B	26.03

Q_N is the centroid of the N_4 plane; Q_O is the centroid of the O_4 plane.

Ba[Zn(dota)]·5.5H_2O

Out of the eleven water molecules in the asymmetric unit, ten are localised and one is disordered over two close positions in a 64:36 ratio, refined with common ADPs. Structural parameters are listed in **Table S5**.

Crystal packing

Complex anions "A" and "B" are linked by coordination to two Ba^{2+} cations to form a $Ba_2[Zn(dota)]_2$ dimer (**Figure S4**). This dimer is further linked to other such dimers to form 1D polymeric strand in the direction of cell axis *b*. The Ba^{2+} counter-cations are coordinated by nine oxygen atoms, originating from five carboxylate functional groups (two of which are coordinated by both oxygen atoms) of three different complex anions and two water molecules. The Ba–O bond lengths range from 2.666 Å to 3.193 Å.

Refinement remarks

The relatively large estimates for distances and bond lengths errors for this structure are a consequence of a low data quality, which is a result of the very small size of the crystals. The crystals grew in a form of very thin needles, as seen from their cell parameter (*b* is roughly four times larger than the other two parameters). This also resulted in difficulties during the refinement process whereby the ADPs of several atoms became (nearly) non-positive definite. Consequently, their thermal parameters had to be restrained to be similar to those of their neighbouring atoms using the SIMU restraint (using smaller than the default value). Alternatively, some atoms were restrained to be approximately isotropic using ISOR command. Furthermore, ADPs of two water molecules were restrained to be approximately isotropic using the ISOR command as their refinement as disordered did not yield a better solution. Positions of all hydrogen atoms of the water molecules were fixed during the final refinement cycle. The B-level checkcif alert PLAT342 was caused by low quality of the data due to the small size of the crystals and PLAT971 was caused by minor disorder/twinning and these electron density maxima close to heavy Ba^{2+} were not resolved.

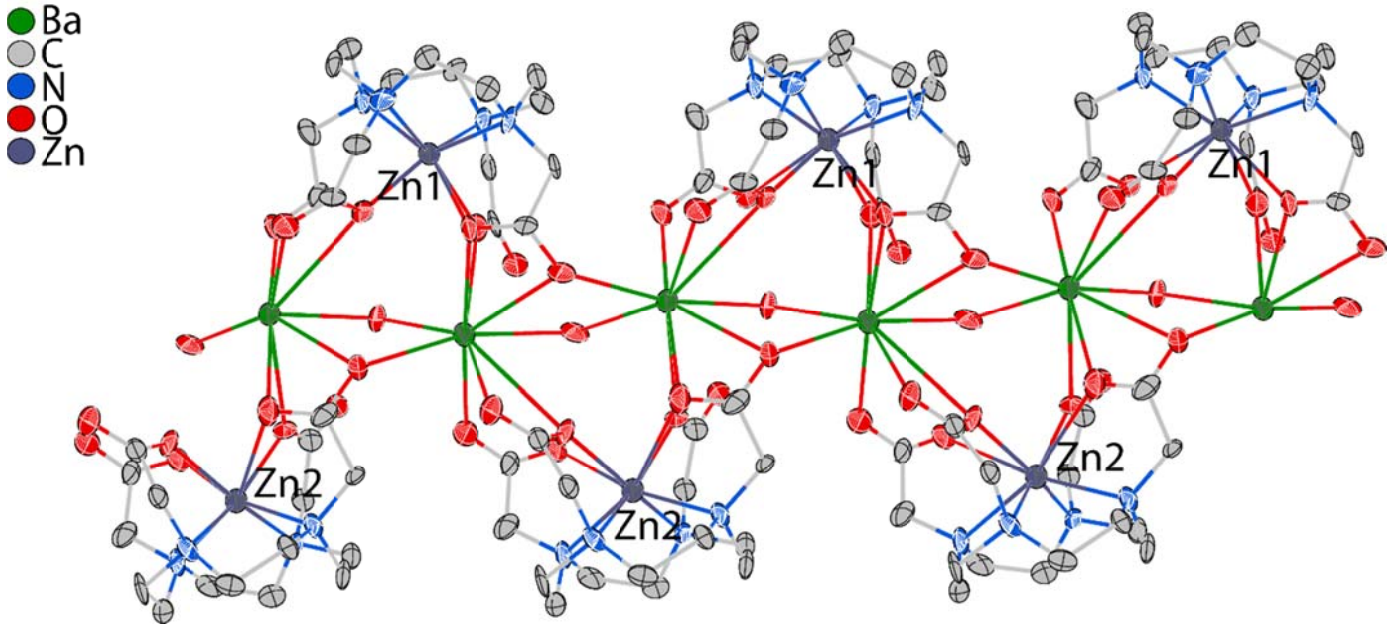

Figure S5. View along the crystallographic axis *c* of packing in the crystal structure of Ba[Zn(dota)]·5.5H_2O. Hydrogen atoms and Ba-non-coordinated water molecules are omitted for clarity. Thermal ellipsoids are drawn at 50 % probability level. Color code: **red: oxygen**, **blue: nitrogen**, **grey: carbon**, **green: barium**, **violet: zinc**.

Table S6. Selected geometric parameters found in the crystal structure of Ba[Zn(dota)]·5.5H_2O.

Distances, Å			
Zn1–O11A	2.1240(116)	Zn2–O11B	2.1386(112)
Zn1–O31A	2.0814(117)	Zn2–O31B	2.0482(101)
Zn1–N1A	2.1963(145)	Zn2–N1B	2.1963(115)
Zn1–N2A	2.2871(127)	Zn2–N2B	2.3579(124)
Zn1–N3A	2.2369(129)	Zn2–N3B	2.2447(153)
Zn1–N4A	2.3348(130)	Zn2–N4B	2.2910(128)
Zn1–Q_NA	1.00	Zn2–Q_NB	1.02
Zn1–Q_{O2}A	1.51	Zn2–Q_{O2}B	1.51
Angles, °			
O11A–Zn1–O31A	88.49(42)	O11B–Zn2–O31B	87.68(42)
N1A–Zn1–N2A	80.15(51)	O11B–Zn2–N2B	126.41(48)
N2A–Zn1–N3A	78.57(48)	N2B–Zn2–N3B	78.26(49)
N2A–Zn1–O31A	126.05(50)	N3B–Zn2–N4B	78.07(49)
O31A–Zn1–N4A	91.85(45)	N4B–Zn2–O11B	91.36(45)
N4A–Zn1–N1A	77.62(48)	O11B–Zn2–N1B	77.41(44)
N1A–Q_NA–Q_OA–O11A	27.04	N1B–Q_NB–Q_OB–O11B	−30.01
N2A–Q_NA–Q_OA–O21A	28.30	N2B–Q_NB–Q_OB–O21B	−23.09
N3A–Q_NA–Q_OA–O31A	26.94	N3B–Q_NB–Q_OB–O31B	−29.35
N4A–Q_NA–Q_OA–O41A	24.33	N4B–Q_NB–Q_OB–O41B	−27.92

Q_N is the centroid of N_4 plane; Q_{2O} is a centroid of two coordinated O atoms.

Solid-state NMR spectroscopy

Table S7. Fitting results of ^{13}C ss-NMR spectrum of Ba[Zn(dota)]·5.5H_2O.

Carboxyl region								
#	Shift (ppm)	Height	Width	L/G	Area	A number of nuclei	Deviation[1]	Assignment
1	180.22	30743	29.3	0.8	550481	1	−0.57	Carboxyl **C**O
2	177.95	71772	18.3	0.8	804464	2	−0.30	Carboxyl **C**O
3	177.60	53015	14.9	0.8	481537	1	−0.38	Carboxyl **C**O
4	177.34	25276	16.9	0.8	261303	1	0.25	Carboxyl **C**O
5	176.94	30278	16.1	0.8	297071	1	0.15	Carboxyl **C**O
6	176.31	15052	21.3	0.8	195964	1	0.44	Carboxyl **C**O
7	175.84	11578	29.8	0.8	210835	1	0.40	Carboxyl **C**O
CH_2 region								
#	Shift (ppm)	Height	Width	L/G	Area	A number of nuclei	Deviation[1]	Assignment
1	58.89	13059	71.5	0.8	1141177	2	−0.31	Pendant CH_2
2	58.49	10414	35.9	0.8	457434	1	0.07	Pendant CH_2
3	58.24	13170	27.4	0.8	440909	1	0.11	Pendant CH_2
4	58.02	14789	29.4	0.8	531447	1	−0.08	Pendant CH_2
5	57.71	12304	38.3	0.8	575779	1	−0.16	Pendant CH_2
6	57.50	23192	25.5	0.8	724050	2	0.54	Pendant CH_2
7	53.92	11924	63.8	0.8	930596	2	0.12	Ring CH_2
8	53.24	7818	70.5	0.8	673831	1	−0.36	Ring CH_2
9	52.96	5429	28.1	0.8	186302	1	0.62	Ring CH_2
10	52.70	14033	71.0	0.8	1217480	2	−0.46	Ring CH_2
11	51.90	8080	57.3	0.8	566022	1	−0.15	Ring CH_2
12	51.25	13952	71.7	0.8	1222493	2	−0.47	Ring CH_2
13	50.32	8054	39.8	0.8	391908	1	0.21	Ring CH_2
14	49.73	8252	37.0	0.8	373567	1	0.24	Ring CH_2
15	49.25	16781	52.4	0.8	1074970	2	−0.17	Ring CH_2
16	48.93	12646	32.6	0.8	504423	1	−0.02	Ring CH_2
17	48.70	17456	39.9	0.8	851219	2	0.28	Ring CH_2
Sum / RMSD						32	0.29	

[1]Deviation is given as a difference between the calculated number of nuclei and the assigned integer number of nuclei. Negative deviation means that the area corresponds to a greater number of nuclei than assigned, and *vice versa*.

Table S8. Fitting results of ^{13}C ss-NMR spectrum of $Ba[Cd(dota)]\cdot 12H_2O$.

Carboxyl region								
#	Shift (ppm)	Height	Width	L/G	Area	A number of nuclei	Deviation[1]	Assignment
1	180.24	28601	27.8	0.8	485254	2	0.26	Carboxyl **C**O
2	179.56	18910	30.1	0.8	347623	2	−0.38	Carboxyl **C**O
3	178.48	31129	29.2	0.8	554777	2	0.58	Carboxyl **C**O
4	176.40	18608	29.1	0.8	330532	2	−0.46	Carboxyl **C**O
CH_2 region								
#	Shift (ppm)	Height	Width	L/G	Area	A number of nuclei	Deviation[1]	Assignment
1	58.89	12754	63.0	0.8	490725	2	0.89	Pendant CH_2
2	58.27	18591	55.4	0.8	629348	4	−0.30	Pendant CH_2
3	56.95	8997	63.0	0.8	346315	2	0.04	Pendant CH_2
4	53.40	20475	58.0	0.8	726361	4	0.27	Ring CH_2
5	53.03	6548	32.4	0.8	129613	1	−0.24	Ring CH_2
6	52.30	9442	89.8	0.8	518433	3	0.05	Ring CH_2
7	47.59	22920	68.4	0.8	958707	6	−0.36	Ring CH_2
8	46.91	9606	51.6	0.8	303133	2	−0.22	Ring CH_2
Sum/RMSD						32	0.25	

[1]Deviation is given as a difference between the calculated number of nuclei and the assigned integer number of nuclei. Negative deviation means that the area corresponds to a greater number of nuclei than assigned, and *vice versa*.

Table S9. Fitting results of ^{13}C ss-NMR spectrum of Ba[Hg(dota)]·8.5H_2O.

Carboxyl region								
#	Shift (ppm)	Height	Width	L/G	Area	A number of nuclei	Deviation[1]	Assignment
1	181.69	16443	35.8	0.8	359446	1	0.00	Carboxyl **C**O
2	179.63	34886	28.6	0.8	609633	2	−0.30	Carboxyl **C**O
3	179.40	21518	32.8	0.8	431078	1	0.20	Carboxyl **C**O
4	178.95	55745	30.1	0.8	1024131	3	−0.15	Carboxyl **C**O
5	178.33	42565	28.5	0.8	740623	2	0.06	Carboxyl **C**O
6	177.89	16655	22.8	0.8	232181	1	−0.35	Carboxyl **C**O
7	177.64	22130	34.8	0.8	471283	1	0.31	Carboxyl **C**O
8	176.74	16093	72.4	0.8	712469	2	−0.02	Carboxyl **C**O
9	176.36	35645	38.7	0.8	843174	2	0.35	Carboxyl **C**O
10	176.01	19080	27.6	0.8	322078	1	−0.10	Carboxyl **C**O
CH_2 region								
#	Shift (ppm)	Height	Width	L/G	Area	A number of nuclei	Deviation[1]	Assignment
1	57.95	43114	69.0	0.8	1817167	5	0.39	Pendant **C**H_2
2	57.52	27452	46.5	0.8	779422	2	0.31	Pendant **C**H_2
3	57.19	23423	41.0	0.8	586856	2	−0.26	Pendant **C**H_2
4	56.88	27114	73.2	0.8	1213042	4	−0.40	Pendant **C**H_2
5	56.52	15366	36.3	0.8	340886	1	0.01	Pendant **C**H_2
6	56.08	9640	62.1	0.8	365724	1	0.08	Pendant **C**H_2
7	55.46	12899	42.2	0.8	332888	1	−0.01	Pendant **C**H_2
8	53.89	9625	42.2	0.8	248080	1	−0.26	Ring **C**H_2
9	52.49	49972	108.0	0.8	3298628	10	−0.22	Ring **C**H_2
10	51.80	13471	45.9	0.8	377547	1	0.12	Ring **C**H_2
11	51.41	18283	57.2	0.8	638765	2	−0.11	Ring **C**H_2
12	50.77	14898	67.3	0.8	613123	2	−0.18	Ring **C**H_2
13	49.88	9632	54.9	0.8	323137	1	−0.04	Ring **C**H_2
14	48.89	24328	86.9	0.8	1292426	4	−0.17	Ring **C**H_2
15	48.47	16524	39.2	0.8	395666	1	0.17	Ring **C**H_2
16	48.12	58406	65.3	0.8	2329437	7	−0.10	Ring **C**H_2
17	47.42	13245	113.4	0.8	917775	2	0.72	Ring **C**H_2
18	45.07	6950	76.7	0.8	325769	1	−0.03	Ring **C**H_2
Sum/RMSD						64	0.17	

[1]Deviation is given as a difference between the calculated number of nuclei and the assigned integer number of nuclei. Negative deviation means that the area corresponds to a greater number of nuclei than assigned, and *vice versa*.

Table S10. Fitting results of ^{15}N ss-NMR spectrum of Ba[Zn(dota)]·5.5H_2O.

#	Shift (ppm)	Height	Width	L/G	Area	A number of nuclei	Deviation[1]
1	35.34	78566	26.5	0.8	4444673	1	–0.11
2	34.17	259002	16.3	0.8	8978510	1	0.81
3	34.01	197829	11.5	0.8	5060043	1	0.02
4	33.41	101524	13.8	0.8	2975892	1	–0.40
5	32.75	66148	28.1	0.8	3967347	1	–0.20
6	32.21	157745	28.1	0.8	9461205	2	–0.10
7	31.22	92037	25.0	0.8	4896821	1	0.38
Sum / RMSD						8	0.36

[1]Deviation is given as a difference between the calculated number of nuclei and the assigned integer number of nuclei. Negative deviation means that the area corresponds to a greater number of nuclei than assigned, and *vice versa*.

Table S11. Fitting results of ^{15}N ss-NMR spectrum of Ba[Cd(dota)]·12H_2O.

#	Shift (ppm)	Height	Width	L/G	Area	A number of nuclei	Deviation[1]
1	33.07	4260542908	57.6	0.8	405751726090	6	0.33
2	30.68	1768133129	36.6	0.8	107142259980	2	−0.33
Sum / RMSD						8	0.16

[1]Deviation is given as a difference between the calculated number of nuclei and the assigned integer number of nuclei. Negative deviation means that the area corresponds to a greater number of nuclei than assigned, and *vice versa*.

Table S12. Fitting results of ^{15}N ss-NMR spectrum of Ba[Hg(dota)]·8.5H_2O.

#	Shift (ppm)	Height	Width	L/G	Area	A number of nuclei	Deviation[1]
1	41.49	42881203295	38.09	0.8	1351086752414	3	0.02
2	40.56	26656323755	62.8	0.8	1384812017697	3	0.10
3	38.87	43206141996	49.51	0.8	1769431631678	4	−0.05
4	38.29	16368381805	36.31	0.8	515169672999	1	0.15
5	37.09	32708531021	43.9	0.8	1187647658864	3	−0.35
6	36.50	24957165279	46.04	0.8	950529526431	2	0.12
Sum / RMSD						16	0.10

[1]Deviation is given as a difference between the calculated number of nuclei and the assigned integer number of nuclei. Negative deviation means that the area corresponds to a greater number of nuclei than assigned, and *vice versa*.

Solution NMR spectroscopy

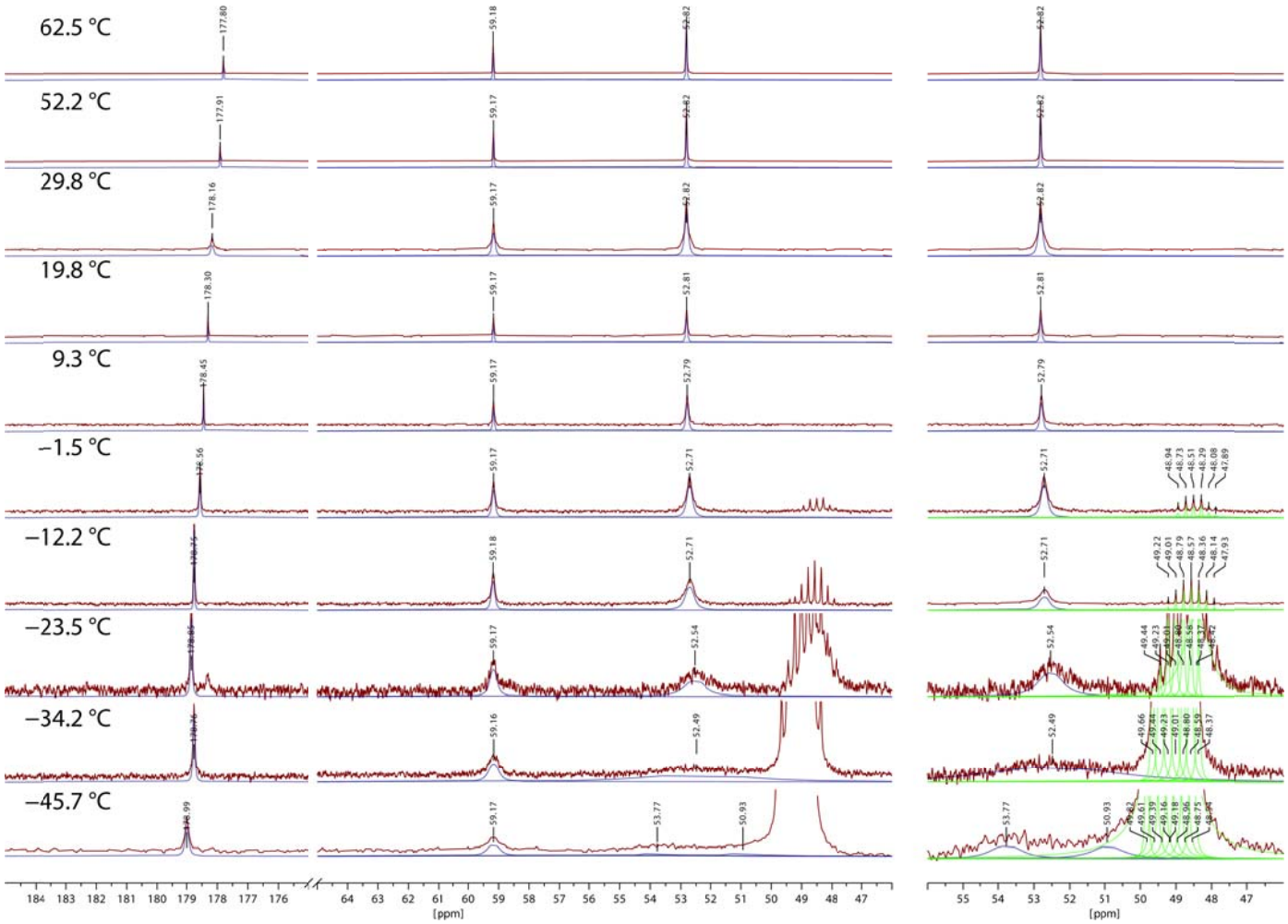

Figure S6. Solution $^{13}C\{^{1}H\}$ NMR spectra of Ba[Zn(dota)] measured at different temperatures. For the measurements at temperatures below water freezing point, CD_3OD was added to the solution. Left panel: all peaks, only peaks of the complex are labeled; right panel: zoom of the ring CH_2 region. Blue lines represent the compound peaks, green lines represent the CD_3OD resonances.

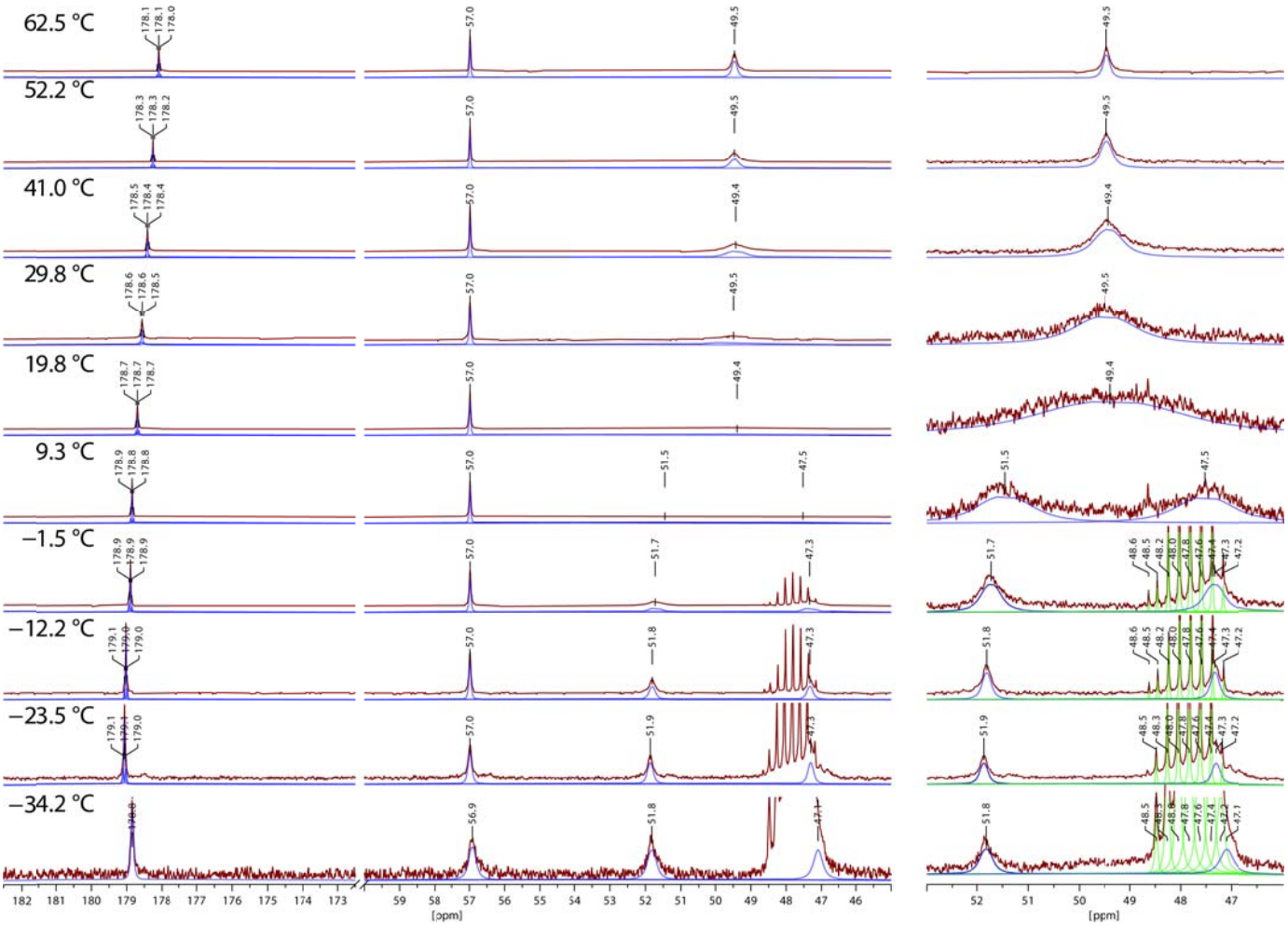

Figure S7. Solution $^{13}C\{^{1}H\}$ NMR spectra of Ba[Cd(dota)] measured at different temperatures. For the measurements at temperatures below water freezing point, CD_3OD was added to the solution. Left panel: all peaks, only peaks of the complex are labeled; right panel: zoom of the ring CH_2 region. Blue lines represent the compound peaks, green lines represent the CD_3OD resonances.

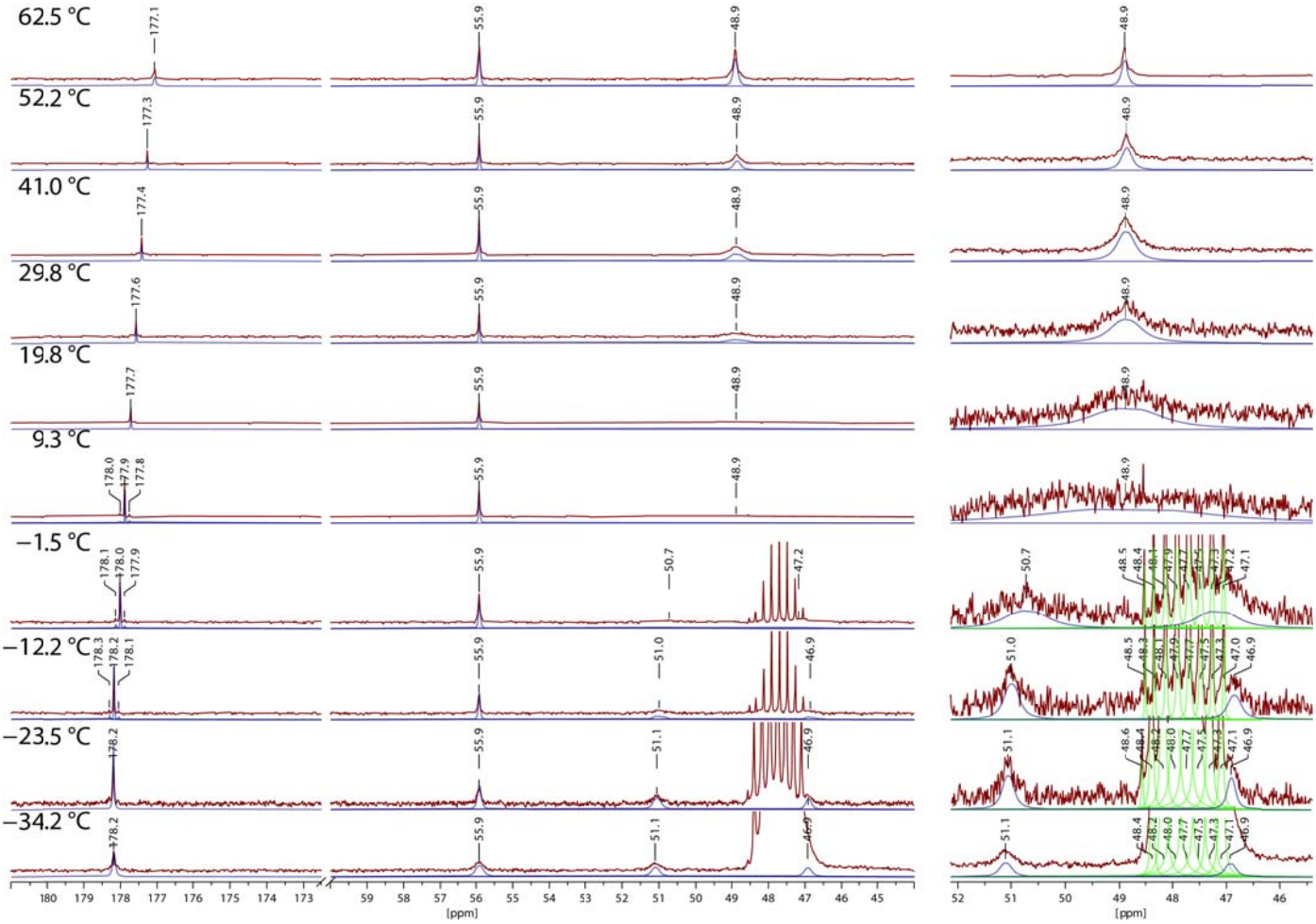

Figure S8. Solution $^{13}C\{^{1}H\}$ NMR spectra of Ba[Hg(dota)] measured at different temperatures. For the measurements at temperatures below water freezing point, CD_3OD was added to the solution. Left panel: all peaks, only peaks of the complex are labeled; right panel: zoom of the ring CH_2 region. Blue lines represent the compound peaks, green lines represent the CD_3OD resonances.

Table S13. Parameters of the exchanging CH_2 ring protons in $[Zn(dota)]^{2-}$ at the studied temperatures. The constants k_1 and k_2 represent the rate constants of interconversion calculated for each individual exchanging peak.

T (K)	δ_1 (ppm)	δ_2 (ppm)	w_1 (Hz)	w_2 (Hz)	k_1 (s^{-1})	k_2 (s^{-1})
227.4	53.77	50.93	107.14	107.14*	205.68	207.59
239.0	52.49		444.8		972.26	
249.7	52.54		85.08		1615.65	
261.0	52.71		35.63		3881.97	
271.7	52.71		22.00		7544.46	
282.4	52.79		10.07		15893.91	
292.9	52.81		6.54		28531.16	
303.0	52.82		14.39		54052.70	
325.4	52.82		3.58		114379.40	
335.6	52.82		3.42		113367.20	

*Parameters that were fixed during the line fitting procedure.

Table S14. Parameters of the exchanging CH_2 ring protons in $[Cd(dota)]^{2-}$ at the studied temperatures. The constants k_1 and k_2 represent the rate constants of interconversion calculated for each individual exchanging peak.

T (K)	δ_1 (ppm)	δ_2 (ppm)	w_1 (Hz)	w_2 (Hz)	k_1 (s^{-1})	k_2 (s^{-1})
239.0	51.82	47.10	30.84	31*	48.61	48.96
249.7	51.86	47.30	18.77	18.8*	35.08	35.14
261.0	51.81	47.33	21.30	20.8*	42.70	41.59
271.7	51.72	47.34	47.49	47.50*	100.68	100.70
282.4	51.45	47.52	132.97	137.83	291.25	302.05
293.8	49.39		347.42		1026.55	
303.0	49.49		147.39		2473.39	
314.2	49.43		70.71		5229.49	
325.4	49.47		30.44		12418.90	
335.6	49.46		18.20		21514.50	

*Parameters that were fixed during the line fitting procedure.

Table S15. Parameters of the exchanging CH_2 ring protons in $[Hg(dota)]^{2-}$ at the studied temperatures. The constants k_1 and k_2 represent the rate constants of interconversion calculated for each individual exchanging peak.

T (K)	δ_1 (ppm)	δ_2 (ppm)	w_1 (Hz)	w_2 (Hz)	k_1 (s^{-1})	k_2 (s^{-1})
239.0	51.10	46.93	26.79	24.2*	54.16	46.02
249.7	51.06	46.91	25.96	26*	68.33	68.46
261.0	51.00	46.86	34.54	30.3	102.60	89.28
271.7	50.72	47.21	95.09	95*	292.20	291.92
282.4	48.88		366.69		756.83	
293.8	48.88		155.84		1799.95	
303.0	48.88		71.44		3987.51	
314.2	48.88		41.53		7081.31	
325.4	48.86		23.81		12792.89	
335.6	48.91|		14.28		40299.48	

*Parameters that were fixed during the line fitting procedure.

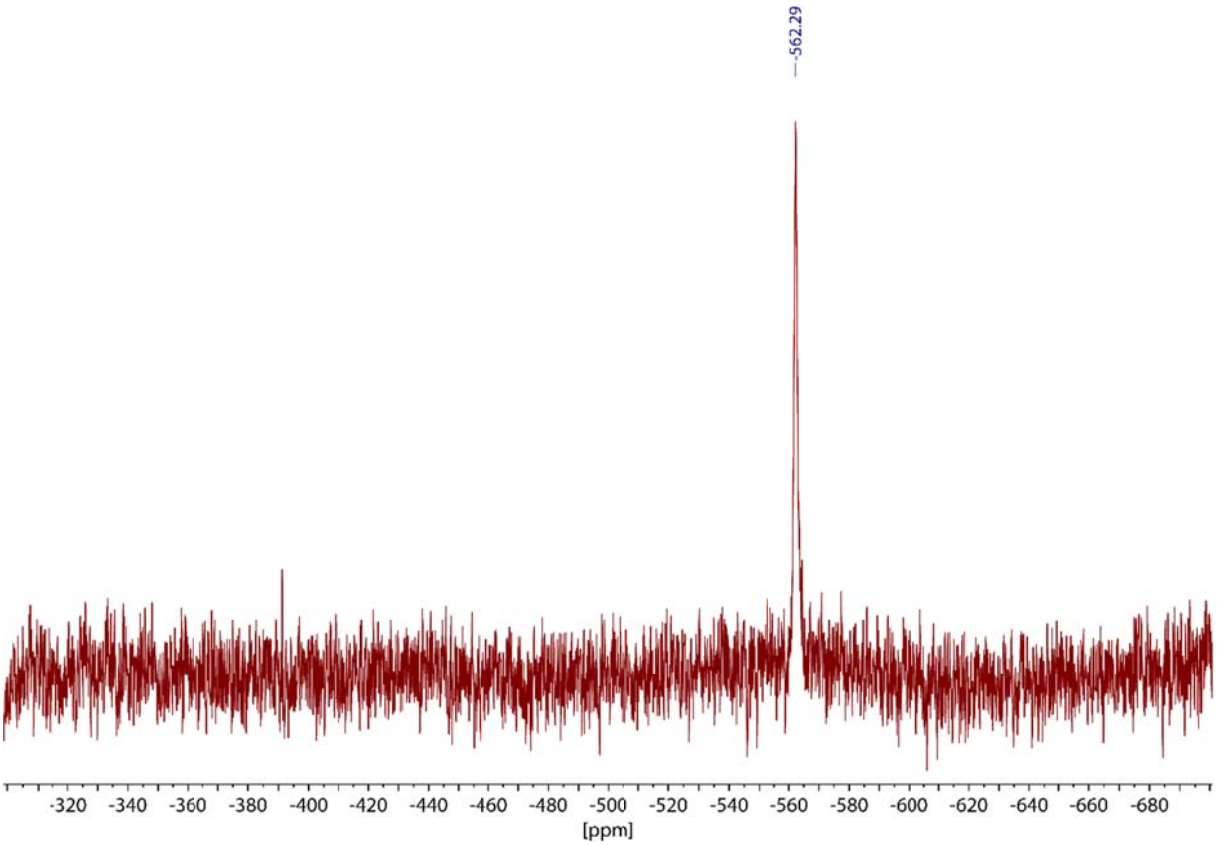

Figure S9. Solution ^{113}Cd NMR spectrum of $[Cd(dota)]^{2-}$ (133.1 MHz, D_2O, LiOH, pD 12, *c* ~0.1 M). Parameters: o1p = −500 ppm, p1 = 12 μs, d1 = 20 s, ns = 1024 were used for the acquisition.

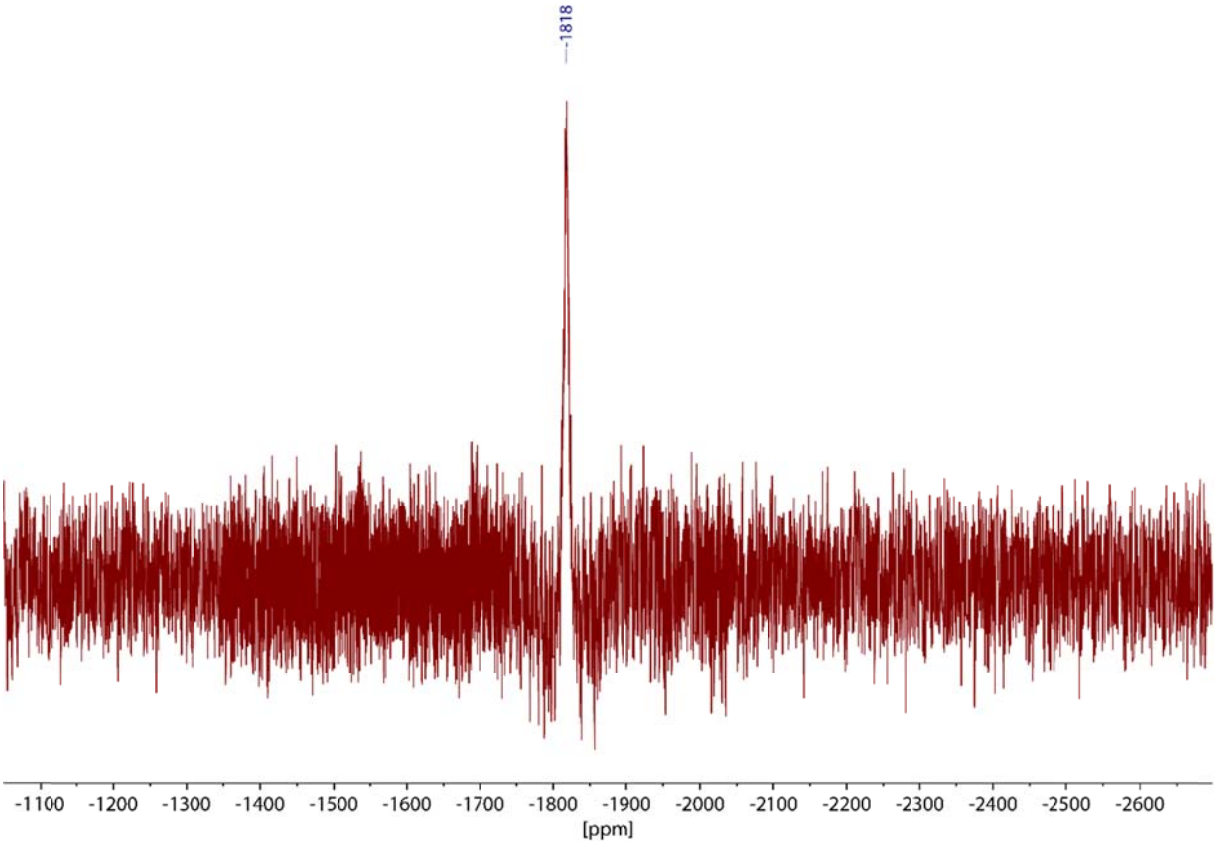

Figure S10. Solution ^{199}Hg NMR spectrum of $[Hg(dota)]^{2-}$ (71.5 MHz, D_2O, LiOH, pD 12, *c* ~0.2 m). The spectrum consists of three sub-spectra with o1p = −1400, −1700 and −2350 ppm.
Parameters: p1 = 8 μs, d1 = 1.5 s, ns = 2048 were used for the acquisition of each sub-spectrum.

Solid-state NMR crystallography

Table S16. Calculated ^{13}C NMR shieldings and the respective experimental chemical shifts. The assignment was done by ordering the shieldings in increasing order and shifts in decreasing order. RMSD = 0.62 ppm shows a very good match between the calculated chemical shieldings and experimental chemical shifts.
Calibration equation, $\sigma = -1.0345 \cdot \delta + 173.42$, was obtained by a linear regression.

Nucleus	GIPAW-PBE (ppm)	Experimental shift (ppm)
C32A	−12.9433	180.22
C32B	−12.0255	177.95
C12B	−10.1619	177.95
C12A	−9.9985	177.60
C22B	−9.9712	177.34
C42A	−9.6443	176.94
C42B	−9.5223	176.31
C22A	−7.6773	175.84
C31B	112.6800	58.88
C11A	112.8659	58.88
C41A	113.9784	58.49
C11B	114.1456	58.24
C41B	114.3272	58.02
C21A	114.5695	57.70
C31A	114.7245	57.50
C21B	114.9099	55.06
C4B	117.2232	53.92
C6B	118.0506	53.92
C1A	118.0907	53.19
C5A	118.1864	53.19
C8B	118.2200	52.72
C3A	118.5134	52.72
C7A	119.8475	51.92
C2A	120.3287	51.25
C1B	120.5150	51.25
C2B	120.5586	50.31
C5B	120.9000	49.74
C7B	122.1583	49.25
C4A	122.3868	49.25
C3B	122.7938	48.94
C8A	123.0038	48.70
C6A	123.4929	48.70

Table S17. Overview of the intermolecular interactions of the carboxyl groups in the structure of Ba[Zn(dota)]·5.5H_2O. The carboxyl groups are denoted only by carbonyl atoms and are given in order of decreasing calculated ^{13}C shielding (increasing calculated chemical shift).

Carbonyl	Coordination bonds to Zn^{2+}	Coordination bonds to Ba^{2+}	Coordination bonds to metal ions	A number of hydrogen bonds	A number of interactions	GIPAW-PBE (ppm)
C22A	0	3	3	0	3	−7.6773
C42B	0	3	3	0	3	−9.5223
C42A	0	1	1	1	2	−9.6443
C22B	0	1	1	2	3	−9.9712
C12A	1	1	2	1	3	−9.9985
C12B	1	1	2	2	4	−10.1619
C32A	1	2	3	1	4	−12.0255
C32B	1	2	3	1	4	−12.9433

Table S18. Overview of the intermolecular interactions of the carboxyl groups in the structure of Ba[Cd(dota)]·12H_2O. The carboxyl groups are denoted only by carbonyl atoms and are given in order of an increasing number of coordination bonds to the metal ions and hydrogen bonds.

Carbonyl	Coordination bonds to Cd^{2+}	Coordination bonds to Ba^{2+}	Coordination bonds to metal ions	A number of hydrogen bonds	A number of interactions
C32B	1	0	1	3	4
C12A	1	0	1	4	5
C42B	1	1	2	2	4
C32A	1	1	2	3	5
C22B	1	2	3	1	4
C12B	1	2	3	1	4
C22A	1	3	4	0	4
C42A	1	3	4	1	5

Table S19. Overview of the intermolecular interactions of the carboxyl groups in the structure of Ba[Hg(dota)]·8.5H_2O. The carboxyl groups are denoted only by carbonyl atoms and are given in order of an increasing number of coordination bonds to the metal ions and hydrogen bonds

Carbonyl	Coordination bonds to Hg^{2+}	Coordination bonds to Ba^{2+}	Coordination bonds to metal ions	A number of hydrogen bonds	A number of interactions
C12A	1	0	1	2	3
C22D	1	0	1	3	4
C32C	1	0	1	4	5
C32B	1	1	2	1	3
C32A	1	1	2	2	4
C12C	1	1	2	2	4
C32D	1	1	2	2	4
C42B	1	1	2	3	5
C12B	1	2	3	1	4
C12D	1	2	3	1	4
C42D	1	2	3	1	4
C22B	1	2	3	2	5
C22A	1	3	4	0	4
C42A	1	3	4	0	4
C22C	1	3	4	0	4
C42C	1	3	4	1	5