Supporting information for:

Encapsulation of atmospheric CO_2 by a self-assembled decanuclear cadmium complex via unfamiliar perchlorato and carbonato bridges

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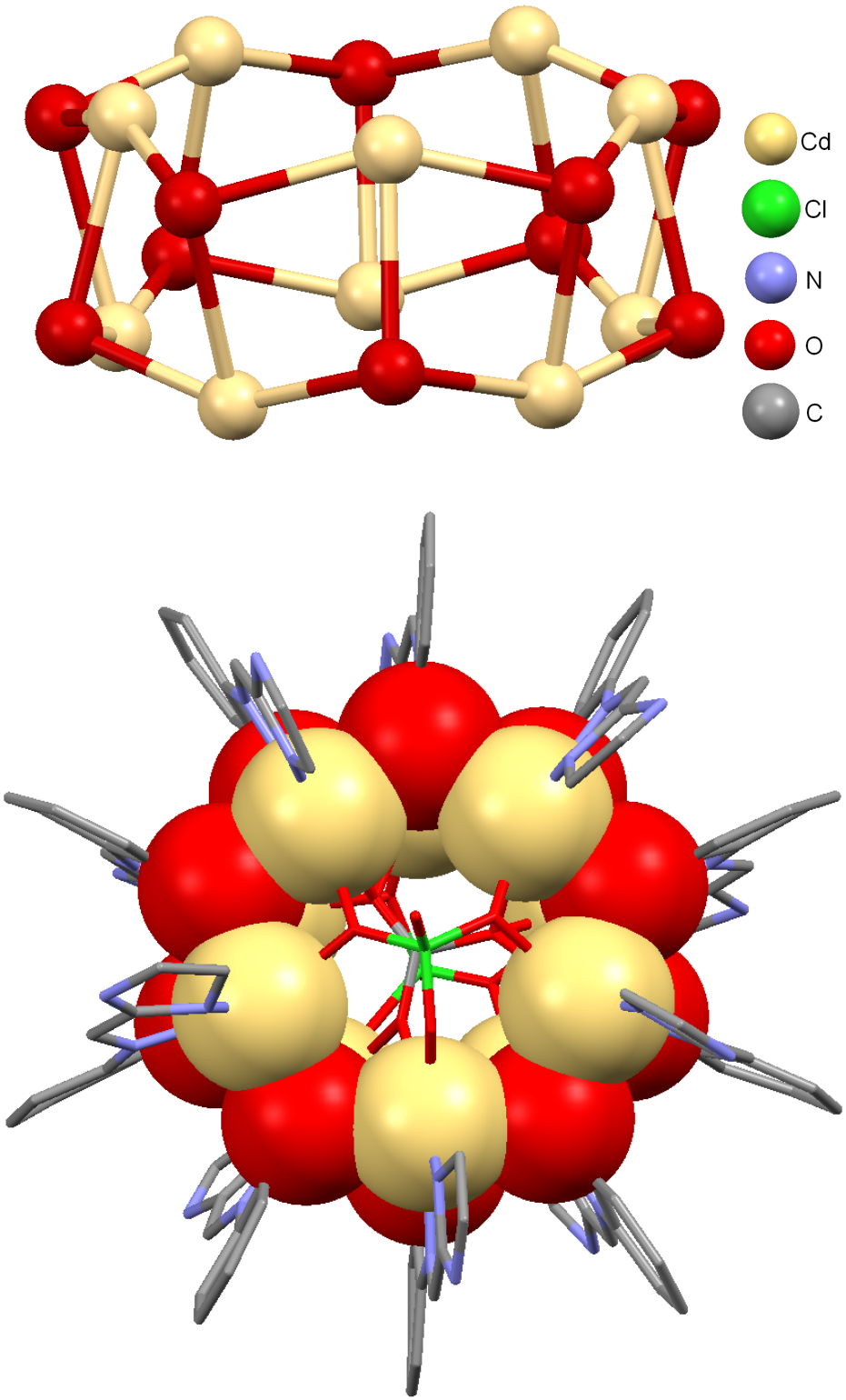


Figure S1. Double crown $Cd_{10}O_{10}$ formed by ten μ_3-phenoxo atoms of the Schiff base and the ten Cd^{II} ions (top) and view of molecular structure like a ten-blade propeller (bottom).

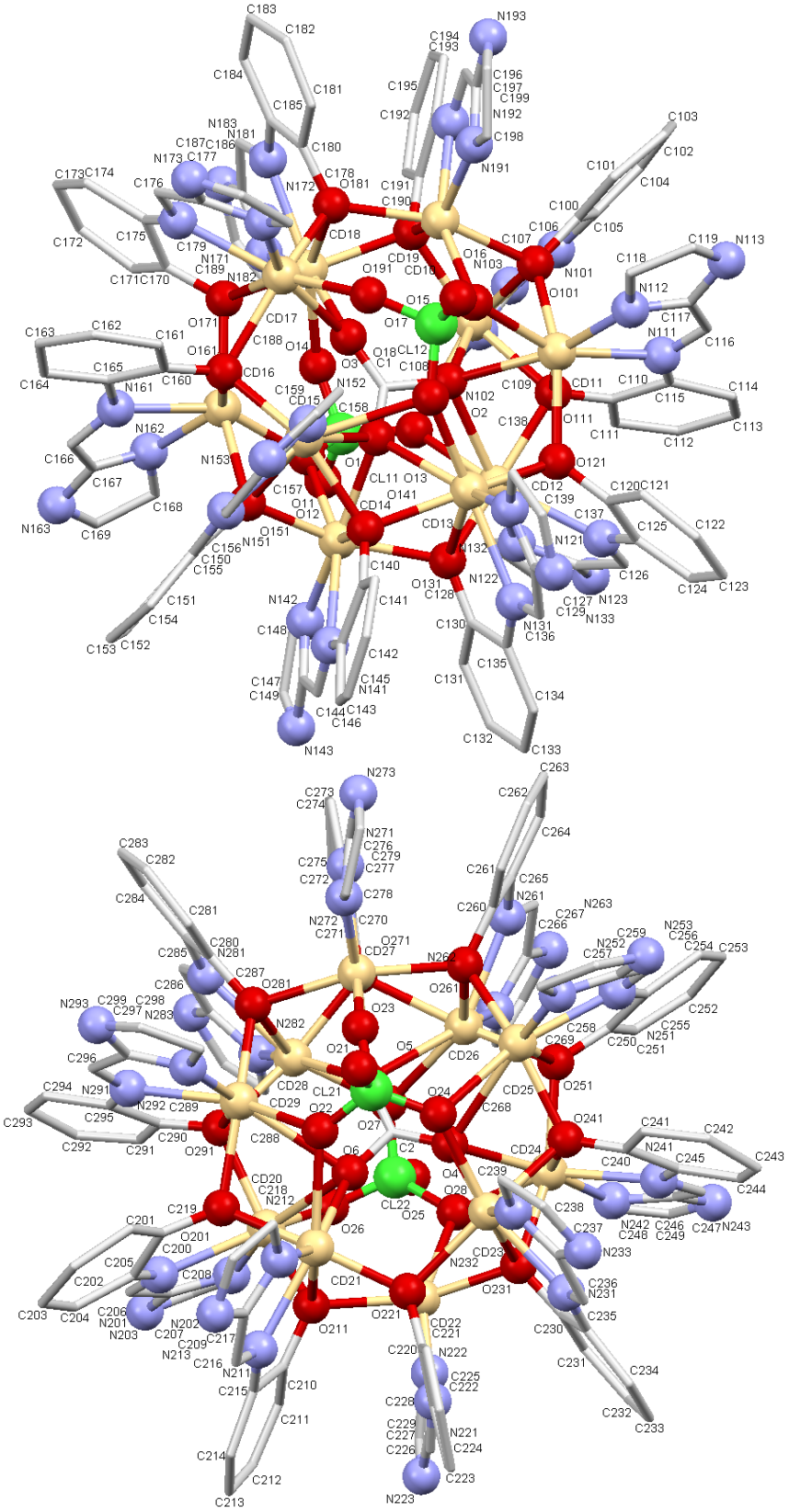


Figure S2. Labeling schemes for the two cations of **1** found in $2[Cd_{10}(L)_4(HL)_6(ClO_4)_2(CO_3)](ClO_4)_4 \cdot 2MeOH \cdot 11H_2O$. Each ligand preserves a labeling scheme (in the third figure) similar to that used in the free ligand (*vide infra*), while the two first figures correspond to those of the metal ligand that are chelating.

Table S1. Main bond distances [Å] for $2[Cd_{10}(L)_4(HL)_6(ClO_4)_2(CO_3)](ClO_4)_4 \cdot 2MeOH \cdot 11H_2O$

Cd(10)-O(191)	2.249(12)	Cd(15)-O(161)	2.232(14)	Cd(20)-O(211)	2.185(14)	Cd(25)-O(241)	2.200(13)
Cd(10)-N(102)	2.253(12)	Cd(15)-O(141)	2.246(14)	Cd(20)-O(291)	2.267(15)	Cd(25)-O(261)	2.279(14)
Cd(10)-O(111)	2.295(12)	Cd(15)-N(152)	2.308(11)	Cd(20)-N(202)	2.268(14)	Cd(25)-N(252)	2.309(14)
Cd(10)-N(101)	2.369(14)	Cd(15)-N(151)	2.347(15)	Cd(20)-N(201)	2.410(14)	Cd(25)-N(251)	2.355(15)
Cd(10)-O(2)	2.47(2)	Cd(15)-O(1)	2.477(19)	Cd(20)-O(6)	2.587(18)	Cd(25)-O(251)	2.601(13)
Cd(10)-O(101)	2.573(12)	Cd(15)-O(151)	2.539(13)	Cd(20)-O(201)	2.593(13)	Cd(25)-O(24)	2.64(2)
Cd(11)-O(101)	2.183(12)	Cd(16)-O(171)	2.235(13)	Cd(21)-O(221)	2.090(15)	Cd(26)-O(251)	2.229(14)
Cd(11)-O(121)	2.246(15)	Cd(16)-N(162)	2.304(16)	Cd(21)-N(212)	2.261(13)	Cd(26)-N(262)	2.302(14)
Cd(11)-N(112)	2.313(14)	Cd(16)-O(151)	2.348(13)	Cd(21)-O(201)	2.302(14)	Cd(26)-O(271)	2.375(14)
Cd(11)-N(111)	2.338(14)	Cd(16)-N(161)	2.367(16)	Cd(21)-N(211)	2.380(16)	Cd(26)-N(261)	2.415(16)
Cd(11)-O(16)	2.402(18)	Cd(16)-O(161)	2.503(14)	Cd(21)-O(22)	2.46(2)	Cd(26)-O(261)	2.513(13)
Cd(11)-O(2)	2.477(19)	Cd(17)-O(17)	2.213(18)	Cd(21)-O(6)	2.480(18)	Cd(27)-O(23)	2.16(2)
Cd(11)-O(111)	2.484(11)	Cd(17)-O(181)	2.214(13)	Cd(21)-O(211)	2.482(13)	Cd(27)-O(261)	2.238(14)
Cd(12)-O(111)	2.244(13)	Cd(17)-N(172)	2.273(14)	Cd(22)-O(231)	2.164(16)	Cd(27)-N(272)	2.283(14)
Cd(12)-O(131)	2.279(17)	Cd(17)-O(161)	2.329(16)	Cd(22)-N(222)	2.260(13)	Cd(27)-O(281)	2.299(13)
Cd(12)-N(122)	2.286(14)	Cd(17)-N(171)	2.380(14)	Cd(22)-O(211)	2.287(14)	Cd(27)-O(5)	2.40(2)
Cd(12)-N(121)	2.423(14)	Cd(17)-O(3)	2.47(2)	Cd(22)-N(221)	2.349(14)	Cd(27)-N(271)	2.431(15)
Cd(12)-O(2)	2.50(2)	Cd(17)-O(171)	2.497(12)	Cd(22)-O(221)	2.496(14)	Cd(27)-O(271)	2.552(13)
Cd(12)-O(121)	2.547(13)	Cd(18)-O(171)	2.231(14)	Cd(23)-N(232)	2.263(13)	Cd(28)-O(271)	2.167(14)
Cd(13)-O(121)	2.270(16)	Cd(18)-O(191)	2.248(13)	Cd(23)-O(24)	2.31(2)	Cd(28)-O(291)	2.214(15)
Cd(13)-O(141)	2.283(16)	Cd(18)-N(182)	2.281(14)	Cd(23)-N(231)	2.327(15)	Cd(28)-N(282)	2.328(13)
Cd(13)-O(18)	2.287(16)	Cd(18)-N(181)	2.384(15)	Cd(23)-O(241)	2.329(13)	Cd(28)-N(281)	2.442(13)
Cd(13)-N(132)	2.336(12)	Cd(18)-O(3)	2.41(2)	Cd(23)-O(221)	2.332(16)	Cd(28)-O(5)	2.45(2)
Cd(13)-N(131)	2.444(13)	Cd(18)-O(181)	2.509(11)	Cd(23)-O(4)	2.460(19)	Cd(28)-O(281)	2.561(12)
Cd(13)-O(1)	2.515(19)	Cd(19)-O(181)	2.231(13)	Cd(23)-O(231)	2.564(14)	Cd(29)-O(201)	2.221(14)
Cd(13)-O(131)	2.576(14)	Cd(19)-N(192)	2.284(14)	Cd(24)-O(231)	2.245(16)	Cd(29)-N(292)	2.241(13)
Cd(14)-O(151)	2.201(14)	Cd(19)-O(101)	2.297(13)	Cd(24)-O(251)	2.247(14)	Cd(29)-O(281)	2.252(13)
Cd(14)-O(131)	2.265(17)	Cd(19)-N(191)	2.305(15)	Cd(24)-N(242)	2.340(11)	Cd(29)-N(291)	2.366(14)
Cd(14)-N(142)	2.305(15)	Cd(19)-O(191)	2.474(11)	Cd(24)-N(241)	2.353(14)	Cd(29)-O(22)	2.40(2)
Cd(14)-O(1)	2.365(18)	Cd(19)-O(16)	2.475(19)	Cd(24)-O(4)	2.475(18)	Cd(29)-O(291)	2.532(12)
Cd(14)-N(141)	2.473(15)			Cd(24)-O(241)	2.489(12)		
Cd(14)-O(141)	2.527(13)						

Table S2. Main angles [°] for $2[Cd_{10}(L)_4(HL)_6(ClO_4)_2(CO_3)](ClO_4)_4 \cdot 2MeOH \cdot 11H_2O$

O(191)-Cd(10)-N(102)	105.8(5)	O(151)-Cd(14)-O(141)	74.7(5)	O(211)-Cd(20)-O(291)	150.2(5)	O(241)-Cd(25)-O(261)	148.3(5)
O(191)-Cd(10)-O(111)	148.2(4)	O(131)-Cd(14)-O(141)	79.8(5)	O(211)-Cd(20)-N(202)	107.0(6)	O(241)-Cd(25)-N(252)	102.4(6)
N(102)-Cd(10)-O(111)	102.8(5)	N(142)-Cd(14)-O(141)	138.3(5)	O(291)-Cd(20)-N(202)	101.3(6)	O(261)-Cd(25)-N(252)	107.5(6)
O(191)-Cd(10)-N(101)	86.8(5)	O(1)-Cd(14)-O(141)	61.6(5)	O(211)-Cd(20)-N(201)	90.6(5)	O(241)-Cd(25)-N(251)	91.4(6)
N(102)-Cd(10)-N(101)	71.6(4)	N(141)-Cd(14)-O(141)	67.1(4)	O(291)-Cd(20)-N(201)	89.6(5)	O(261)-Cd(25)-N(251)	88.5(6)
O(111)-Cd(10)-N(101)	89.2(5)	O(161)-Cd(15)-O(141)	148.9(5)	N(202)-Cd(20)-N(201)	71.8(4)	N(252)-Cd(25)-N(251)	71.6(4)
O(191)-Cd(10)-O(2)	98.2(5)	O(161)-Cd(15)-N(152)	104.4(6)	O(211)-Cd(20)-O(6)	73.0(5)	O(241)-Cd(25)-O(251)	75.6(5)
N(102)-Cd(10)-O(2)	144.8(6)	O(141)-Cd(15)-N(152)	103.7(6)	O(291)-Cd(20)-O(6)	85.1(5)	O(261)-Cd(25)-O(251)	75.4(5)
O(111)-Cd(10)-O(2)	64.2(5)	O(161)-Cd(15)-N(151)	90.1(6)	N(202)-Cd(20)-O(6)	155.4(6)	N(252)-Cd(25)-O(251)	137.8(4)
N(101)-Cd(10)-O(2)	136.2(5)	O(141)-Cd(15)-N(151)	85.1(6)	N(201)-Cd(20)-O(6)	132.4(5)	N(251)-Cd(25)-O(251)	66.4(4)
O(191)-Cd(10)-O(101)	76.8(4)	N(152)-Cd(15)-N(151)	74.1(4)	O(211)-Cd(20)-O(201)	76.2(5)	O(241)-Cd(25)-O(24)	76.6(5)
N(102)-Cd(10)-O(101)	138.1(4)	O(161)-Cd(15)-O(1)	100.2(6)	O(291)-Cd(20)-O(201)	76.7(5)	O(261)-Cd(25)-O(24)	113.2(5)
O(111)-Cd(10)-O(101)	72.7(4)	O(141)-Cd(15)-O(1)	64.0(5)	N(202)-Cd(20)-O(201)	137.9(5)	N(252)-Cd(25)-O(24)	89.6(7)
N(101)-Cd(10)-O(101)	66.7(3)	N(152)-Cd(15)-O(1)	141.5(6)	N(201)-Cd(20)-O(201)	66.2(4)	N(251)-Cd(25)-O(24)	155.2(6)
O(2)-Cd(10)-O(101)	72.1(5)	N(151)-Cd(15)-O(1)	135.2(6)	O(6)-Cd(20)-O(201)	66.6(5)	O(251)-Cd(25)-O(24)	129.0(6)
O(101)-Cd(11)-O(121)	151.1(5)	O(161)-Cd(15)-O(151)	76.0(5)	O(221)-Cd(21)-N(212)	106.3(6)	O(251)-Cd(26)-N(262)	102.0(6)
O(101)-Cd(11)-N(112)	100.5(6)	O(141)-Cd(15)-O(151)	73.7(5)	O(221)-Cd(21)-O(201)	152.5(5)	O(251)-Cd(26)-O(271)	156.3(5)
O(121)-Cd(11)-N(112)	107.2(6)	N(152)-Cd(15)-O(151)	143.0(4)	N(212)-Cd(21)-O(201)	99.9(5)	N(262)-Cd(26)-O(271)	99.6(6)
O(101)-Cd(11)-N(111)	89.3(5)	N(151)-Cd(15)-O(151)	68.9(4)	O(221)-Cd(21)-N(211)	93.8(6)	O(251)-Cd(26)-N(261)	92.1(6)
O(121)-Cd(11)-N(111)	91.1(6)	O(1)-Cd(15)-O(151)	71.7(5)	N(212)-Cd(21)-N(211)	73.0(4)	N(262)-Cd(26)-N(261)	71.1(5)
N(112)-Cd(11)-N(111)	73.0(4)	O(171)-Cd(16)-N(162)	108.8(7)	O(201)-Cd(21)-N(211)	85.9(6)	O(271)-Cd(26)-N(261)	85.9(6)
O(101)-Cd(11)-O(16)	80.0(5)	O(171)-Cd(16)-O(151)	150.5(5)	O(221)-Cd(21)-O(22)	112.8(6)	O(251)-Cd(26)-O(261)	78.1(5)
O(121)-Cd(11)-O(16)	110.2(6)	N(162)-Cd(16)-O(151)	99.9(6)	N(212)-Cd(21)-O(22)	84.9(7)	N(262)-Cd(26)-O(261)	138.7(5)
N(112)-Cd(11)-O(16)	84.6(6)	O(171)-Cd(16)-N(161)	93.9(5)	O(201)-Cd(21)-O(22)	77.4(6)	O(271)-Cd(26)-O(261)	79.4(5)
N(111)-Cd(11)-O(16)	153.0(6)	N(162)-Cd(16)-N(161)	71.6(5)	N(211)-Cd(21)-O(22)	149.5(7)	N(261)-Cd(26)-O(261)	67.7(4)
O(101)-Cd(11)-O(2)	78.9(6)	O(151)-Cd(16)-N(161)	88.8(6)	O(221)-Cd(21)-O(6)	88.8(6)	O(23)-Cd(27)-O(261)	97.0(9)
O(121)-Cd(11)-O(2)	78.6(6)	O(171)-Cd(16)-O(161)	79.2(5)	N(212)-Cd(21)-O(6)	147.5(6)	O(23)-Cd(27)-N(272)	74.6(9)
N(112)-Cd(11)-O(2)	157.3(6)	N(162)-Cd(16)-O(161)	139.0(5)	O(201)-Cd(21)-O(6)	72.9(6)	O(261)-Cd(27)-N(272)	99.4(6)
N(111)-Cd(11)-O(2)	129.5(5)	O(151)-Cd(16)-O(161)	74.7(5)	N(211)-Cd(21)-O(6)	135.8(5)	O(23)-Cd(27)-O(281)	96.2(9)
O(16)-Cd(11)-O(2)	72.9(7)	N(161)-Cd(16)-O(161)	67.8(4)	O(22)-Cd(21)-O(6)	62.7(7)	O(261)-Cd(27)-O(281)	153.4(5)
O(101)-Cd(11)-O(111)	76.3(4)	O(17)-Cd(17)-O(181)	95.8(8)	O(221)-Cd(21)-O(211)	78.0(5)	N(272)-Cd(27)-O(281)	106.4(6)
O(121)-Cd(11)-O(111)	77.1(5)	O(17)-Cd(17)-N(172)	73.7(7)	N(212)-Cd(21)-O(211)	140.1(4)	O(23)-Cd(27)-O(5)	81.6(9)
N(112)-Cd(11)-O(111)	140.8(4)	O(181)-Cd(17)-N(172)	106.9(6)	O(201)-Cd(21)-O(211)	76.5(5)	O(261)-Cd(27)-O(5)	85.4(6)
N(111)-Cd(11)-O(111)	68.0(4)	O(17)-Cd(17)-O(161)	97.5(8)	N(211)-Cd(21)-O(211)	67.2(4)	N(272)-Cd(27)-O(5)	156.1(6)
O(16)-Cd(11)-O(111)	131.6(6)	O(181)-Cd(17)-O(161)	154.0(5)	O(22)-Cd(21)-O(211)	131.0(6)	O(281)-Cd(27)-O(5)	73.8(6)
O(2)-Cd(11)-O(111)	61.5(5)	N(172)-Cd(17)-O(161)	98.3(6)	O(6)-Cd(21)-O(211)	70.3(5)	O(23)-Cd(27)-N(271)	146.6(8)
O(111)-Cd(12)-O(131)	154.3(5)	O(17)-Cd(17)-N(171)	145.1(7)	O(231)-Cd(22)-N(222)	109.4(6)	O(261)-Cd(27)-N(271)	88.2(5)
O(111)-Cd(12)-N(122)	100.4(6)	O(181)-Cd(17)-N(171)	93.7(5)	O(231)-Cd(22)-O(211)	151.5(5)	N(272)-Cd(27)-N(271)	72.0(4)
O(131)-Cd(12)-N(122)	102.9(6)	N(172)-Cd(17)-N(171)	71.3(4)	N(222)-Cd(22)-O(211)	98.4(6)	O(281)-Cd(27)-N(271)	93.3(5)
O(111)-Cd(12)-N(121)	86.0(5)	O(161)-Cd(17)-N(171)	88.1(5)	O(231)-Cd(22)-N(221)	94.4(6)	O(5)-Cd(27)-N(271)	131.8(6)
O(131)-Cd(12)-N(121)	92.0(6)	O(17)-Cd(17)-O(3)	81.6(8)	N(222)-Cd(22)-N(221)	72.9(4)	O(23)-Cd(27)-O(271)	147.1(8)
N(122)-Cd(12)-N(121)	70.0(4)	O(181)-Cd(17)-O(3)	70.7(6)	O(211)-Cd(22)-N(221)	88.1(6)	O(261)-Cd(27)-O(271)	81.1(5)
O(111)-Cd(12)-O(2)	64.4(5)	N(172)-Cd(17)-O(3)	154.9(6)	O(231)-Cd(22)-O(221)	80.2(5)	N(272)-Cd(27)-O(271)	138.2(4)
O(131)-Cd(12)-O(2)	100.3(6)	O(161)-Cd(17)-O(3)	89.3(6)	N(222)-Cd(22)-O(221)	140.7(5)	O(281)-Cd(27)-O(271)	75.3(5)
N(122)-Cd(12)-O(2)	145.6(6)	N(171)-Cd(17)-O(3)	133.2(6)	O(211)-Cd(22)-O(221)	74.4(5)	O(5)-Cd(27)-O(271)	65.6(6)
N(121)-Cd(12)-O(2)	134.1(6)	O(17)-Cd(17)-O(171)	146.5(7)	N(221)-Cd(22)-O(221)	68.4(4)	N(271)-Cd(27)-O(271)	66.2(4)
O(111)-Cd(12)-O(121)	75.9(5)	O(181)-Cd(17)-O(171)	79.0(5)	N(232)-Cd(23)-O(24)	81.1(7)	O(271)-Cd(28)-O(291)	151.8(5)
O(131)-Cd(12)-O(121)	79.9(5)	N(172)-Cd(17)-O(171)	139.6(4)	N(232)-Cd(23)-N(231)	73.7(4)	O(271)-Cd(28)-N(282)	106.0(6)
N(122)-Cd(12)-O(121)	136.1(4)	O(161)-Cd(17)-O(171)	77.6(5)	O(24)-Cd(23)-N(231)	151.9(7)	O(291)-Cd(28)-N(282)	98.9(6)
N(121)-Cd(12)-O(121)	66.1(4)	N(171)-Cd(17)-O(171)	68.4(3)	N(232)-Cd(23)-O(241)	100.6(6)	O(271)-Cd(28)-N(281)	86.4(5)
O(2)-Cd(12)-O(121)	72.8(5)	O(3)-Cd(17)-O(171)	65.4(6)	O(24)-Cd(23)-O(241)	81.2(7)	O(291)-Cd(28)-N(281)	89.9(5)
O(121)-Cd(13)-O(141)	155.8(5)	O(171)-Cd(18)-O(191)	153.8(4)	N(231)-Cd(23)-O(241)	91.2(6)	N(282)-Cd(28)-N(281)	69.8(4)
O(121)-Cd(13)-O(18)	107.4(6)	O(171)-Cd(18)-N(182)	104.7(7)	N(232)-Cd(23)-O(221)	107.1(6)	O(271)-Cd(28)-O(5)	70.9(6)
O(141)-Cd(13)-O(18)	83.6(6)	O(191)-Cd(18)-N(182)	100.4(7)	O(24)-Cd(23)-O(221)	109.5(7)	O(291)-Cd(28)-O(5)	91.3(6)
O(121)-Cd(13)-N(132)	106.7(5)	O(171)-Cd(18)-N(181)	91.3(6)	N(231)-Cd(23)-O(221)	90.0(6)	N(282)-Cd(28)-O(5)	156.6(6)
O(141)-Cd(13)-N(132)	96.1(5)	O(191)-Cd(18)-N(181)	89.9(6)	O(241)-Cd(23)-O(221)	151.5(5)	N(281)-Cd(28)-O(5)	131.5(6)
O(18)-Cd(13)-N(132)	81.2(6)	N(182)-Cd(18)-N(181)	71.1(5)	N(232)-Cd(23)-O(4)	145.0(6)	O(271)-Cd(28)-O(281)	77.3(5)
O(121)-Cd(13)-N(131)	88.5(5)	O(171)-Cd(18)-O(3)	70.6(6)	O(24)-Cd(23)-O(4)	65.4(8)	O(291)-Cd(28)-O(281)	75.8(5)
O(141)-Cd(13)-N(131)	91.3(5)	O(191)-Cd(18)-O(3)	90.1(6)	N(231)-Cd(23)-O(4)	135.2(6)	N(282)-Cd(28)-O(281)	134.3(4)
O(18)-Cd(13)-N(131)	151.2(6)	N(182)-Cd(18)-O(3)	153.1(7)	O(241)-Cd(23)-O(4)	65.6(5)	N(281)-Cd(28)-O(281)	64.9(3)
N(132)-Cd(13)-N(131)	71.2(4)	N(181)-Cd(18)-O(3)	134.1(6)	O(221)-Cd(23)-O(4)	94.1(5)	O(5)-Cd(28)-O(281)	68.5(6)
O(121)-Cd(13)-O(1)	101.0(5)	O(171)-Cd(18)-O(181)	78.4(5)	N(232)-Cd(23)-O(231)	141.9(4)	O(201)-Cd(29)-N(292)	101.1(5)
O(141)-Cd(13)-O(1)	62.9(5)	O(191)-Cd(18)-O(181)	77.8(4)	O(24)-Cd(23)-O(231)	135.0(7)	O(201)-Cd(29)-O(281)	154.5(5)
O(18)-Cd(13)-O(1)	66.8(7)	N(182)-Cd(18)-O(181)	139.2(5)	N(231)-Cd(23)-O(231)	68.2(4)	N(292)-Cd(29)-O(281)	100.5(5)
N(132)-Cd(13)-O(1)	142.6(6)	N(181)-Cd(18)-O(181)	68.2(4)	O(241)-Cd(23)-O(231)	78.2(5)	O(201)-Cd(29)-N(291)	88.1(6)
N(131)-Cd(13)-O(1)	134.8(5)	O(3)-Cd(18)-O(181)	67.1(6)	O(221)-Cd(23)-O(231)	75.8(5)	N(292)-Cd(29)-N(291)	75.2(4)
O(121)-Cd(13)-O(131)	79.5(6)	O(181)-Cd(19)-N(192)	100.8(6)	O(4)-Cd(23)-O(231)	69.7(5)	O(281)-Cd(29)-N(291)	84.4(5)
O(141)-Cd(13)-O(131)	78.4(5)	O(181)-Cd(19)-O(101)	153.4(4)	O(231)-Cd(24)-O(251)	153.4(5)	O(201)-Cd(29)-O(22)	80.2(6)
O(18)-Cd(13)-O(131)	139.3(6)	N(192)-Cd(19)-O(101)	105.5(6)	O(231)-Cd(24)-N(242)	106.3(5)	N(292)-Cd(29)-O(22)	80.7(7)
N(132)-Cd(13)-O(131)	136.5(4)	O(181)-Cd(19)-N(191)	89.2(6)	O(251)-Cd(24)-N(242)	100.1(5)	O(281)-Cd(29)-O(22)	116.8(6)
N(131)-Cd(13)-O(131)	65.9(3)	N(192)-Cd(19)-N(191)	74.0(4)	O(231)-Cd(24)-N(241)	94.5(6)	N(291)-Cd(29)-O(22)	150.6(7)
O(1)-Cd(13)-O(131)	72.6(5)	O(101)-Cd(19)-N(191)	94.1(6)	O(251)-Cd(24)-N(241)	91.5(6)	O(201)-Cd(29)-O(291)	78.8(5)
O(151)-Cd(14)-O(131)	153.3(5)	O(181)-Cd(19)-O(191)	78.8(4)	N(242)-Cd(24)-N(241)	71.2(4)	N(292)-Cd(29)-O(291)	143.0(4)
O(151)-Cd(14)-N(142)	106.4(6)	N(192)-Cd(19)-O(191)	142.1(4)	O(231)-Cd(24)-O(4)	74.8(6)	O(281)-Cd(29)-O(291)	75.8(5)
O(131)-Cd(14)-N(142)	97.8(6)	O(101)-Cd(19)-O(191)	78.0(4)	O(251)-Cd(24)-O(4)	81.6(6)	N(291)-Cd(29)-O(291)	67.7(4)
O(151)-Cd(14)-O(1)	80.0(6)	N(191)-Cd(19)-O(191)	68.1(4)	N(242)-Cd(24)-O(4)	158.4(6)	O(22)-Cd(29)-O(291)	134.5(6)
O(131)-Cd(14)-O(1)	81.1(6)	O(181)-Cd(19)-O(16)	110.5(5)	N(241)-Cd(24)-O(4)	130.3(5)	O(1)-C(1)-O(3)	130(2)
N(142)-Cd(14)-O(1)	159.8(6)	N(192)-Cd(19)-O(16)	84.9(6)	O(231)-Cd(24)-O(241)	81.4(5)	O(1)-C(1)-O(2)	113.9(17)
O(151)-Cd(14)-N(141)	91.8(6)	O(101)-Cd(19)-O(16)	76.3(5)	O(251)-Cd(24)-O(241)	77.1(5)	O(3)-C(1)-O(2)	115.2(18)
O(131)-Cd(14)-N(141)	85.4(6)	N(191)-Cd(19)-O(16)	153.7(6)	N(242)-Cd(24)-O(241)	138.4(4)	O(6)-C(2)-O(5)	110.9(18)
N(142)-Cd(14)-N(141)	71.2(4)	O(191)-Cd(19)-O(16)	131.3(6)	N(241)-Cd(24)-O(241)	67.4(4)	O(6)-C(2)-O(4)	117(2)
O(1)-Cd(14)-N(141)	128.5(5)			O(4)-Cd(24)-O(241)	63.1(5)	O(5)-C(2)-O(4)	130(2)

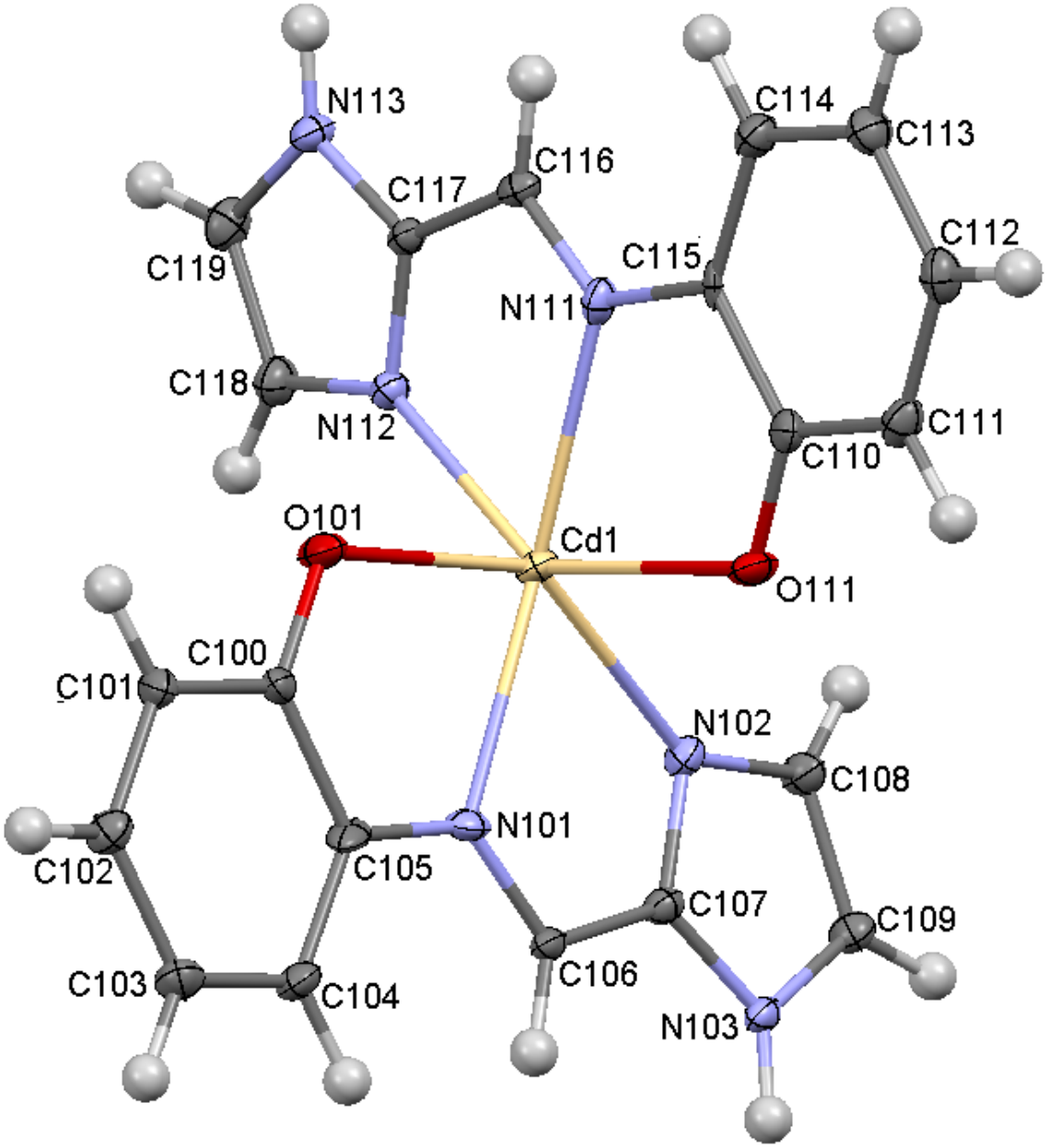


Figure S3. Representation of the molecular structure of $Cd(HL)_2$. Ellipsoids are represented at the 50% probability level.

Table S3. Main bond distances [Å] and angles [º] for $Cd(HL)_2$

Cd(1)-N(101)	2.327(3)	Cd(2)[#1]-N(211)	2.33(3)
Cd(1)-N(112)	2.337(3)	Cd(2)-N(212)	2.35(2)
Cd(1)-O(101)	2.337(3)	Cd(2)-O(211)	2.35(2)
Cd(1)-O(111)	2.337(3)	Cd(2)-O(201)	2.36(2)
Cd(1)-N(111)	2.342(4)	Cd(2)-N(202)	2.36(2)
Cd(1)-N(102)	2.368(4)	Cd(2)-N(201)	2.38(3)
O(101)-C(100)	1.305(5)	O(201)-C(200)	1.297(15)
C(105)-N(101)	1.391(6)	C(205)-N(201)	1.409(15)
N(101)-C(106)	1.284(5)	N(201)-C(206)	1.269(16)
C(107)-N(102)	1.337(5)	C(207)-N(202)	1.331(15)
C(107)-N(103)	1.350(5)	C(207)-N(203)	1.348(15)
N(102)-C(108)	1.378(5)	N(202)-C(208)	1.383(16)
C(109)-N(103)	1.368(5)	C(209)-N(203)	1.362(16)
O(111)-C(110)	1.304(5)	O(211)-C(210)	1.301(15)
C(115)-N(111)	1.402(5)	C(215)-N(211)	1.403(15)
N(111)-C(116)	1.267(5)	N(211)-C(216)	1.271(16)
C(117)-N(112)	1.337(5)	C(217)-N(212)	1.331(15)
C(117)-N(113)	1.339(5)	C(217)-N(213)	1.349(15)
N(112)-C(118)	1.376(5)	N(212)-C(218)	1.377(16)
C(119)-N(113)	1.367(5)	C(219)-N(213)	1.361(16)
N(101)-Cd(1)-N(112)	129.04(12)	N(211)-Cd(2)-N(212)	71.9(7)
N(101)-Cd(1)-O(101)	70.02(12)	N(211)-Cd(2)-O(211)	70.5(7)
N(112)-Cd(1)-O(101)	87.53(12)	N(212)-Cd(2)-O(211)	141.4(9)
N(101)-Cd(1)-O(111)	88.63(11)	N(211)-Cd(2)-O(201)	87.9(12)
N(112)-Cd(1)-O(111)	141.07(11)	N(212)-Cd(2)-O(201)	90.0(12)
O(101)-Cd(1)-O(111)	98.86(12)	O(211)-Cd(2)-O(201)	97.3(12)
N(101)-Cd(1)-N(111)	145.28(13)	N(211)-Cd(2)-N(202)	130.8(12)
N(112)-Cd(1)-N(111)	72.20(12)	N(212)-Cd(2)-N(202)	110.5(12)
O(101)-Cd(1)-N(111)	86.11(11)	O(211)-Cd(2)-N(202)	87.9(13)
O(111)-Cd(1)-N(111)	70.02(11)	O(201)-Cd(2)-N(202)	139.7(9)
N(101)-Cd(1)-N(102)	72.16(12)	N(211)-Cd(2)-N(201)	144.4(12)
N(112)-Cd(1)-N(102)	110.95(13)	N(212)-Cd(2)-N(201)	132.6(13)
O(101)-Cd(1)-N(102)	141.39(11)	O(211)-Cd(2)-N(201)	84.9(12)
O(111)-Cd(1)-N(102)	87.60(12)	O(201)-Cd(2)-N(201)	69.7(6)
N(111)-Cd(1)-N(102)	131.15(12)	N(202)-Cd(2)-N(201)	71.1(7)

[#1]Cd(2) is the label assigned to the metal ion corresponding to the disordered complex molecule with a lower occupation site.

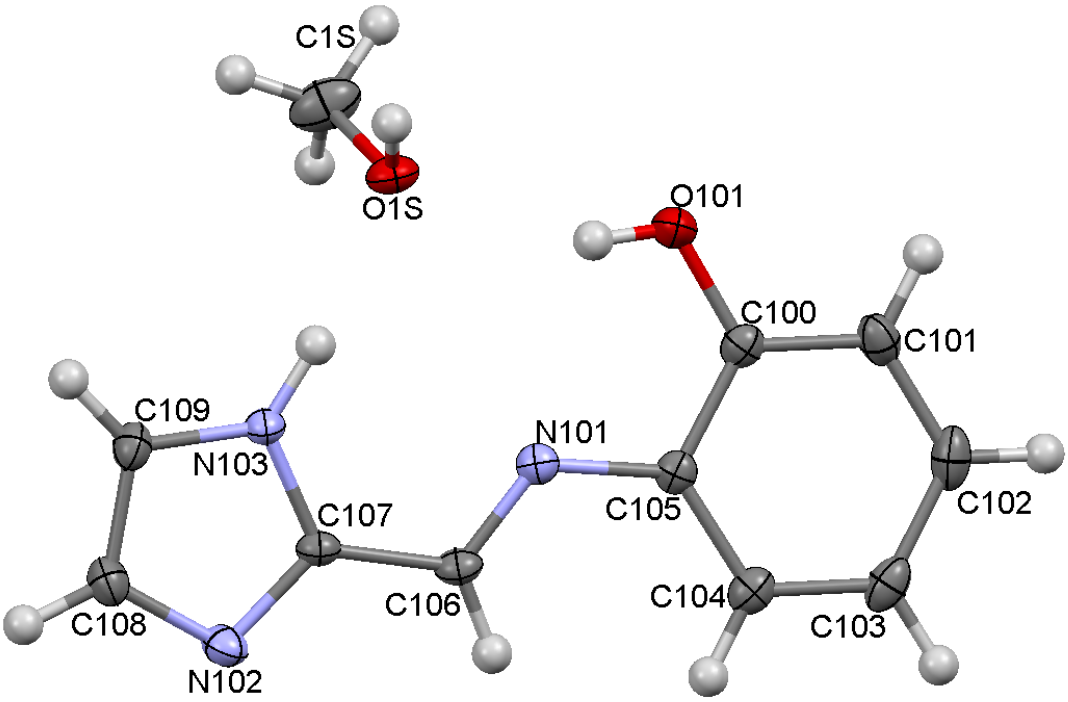


Figure S4. Representation of the molecular structure of H_2L·MeOH. Ellipsoids are represented at the 50% probability level. The numbering scheme was also used for the assignment of the NMR signals

Table S4. Selected bond lengths [Å] and angles [°] for H_2L·MeOH.

O(101)-C(100)	1.365(2)	O(101)-C(100)-C(101)	118.77(17)
C(105)-N(101)	1.405(2)	O(101)-C(100)-C(105)	121.06(17)
C(106)-N(101)	1.273(2)	C(104)-C(105)-N(101)	126.73(17)
C(107)-N(102)	1.334(2)	N(101)-C(105)-C(100)	114.36(16)
C(108)-N(102)	1.368(3)	N(101)-C(106)-C(107)	119.07(17)
C(107)-N(103)	1.354(2)	C(106)-N(101)-C(105)	123.03(16)
N(103)-C(109)	1.354(2)	N(102)-C(107)-N(103)	110.71(17)
		N(102)-C(107)-C(106)	126.19(16)
		N(103)-C(107)-C(106)	123.10(16)
		C(109)-N(103)-C(107)	107.69(15)
		N(103)-C(109)-C(108)	106.33(17)
		C(109)-C(108)-N(102)	109.99(17)
		C(107)-N(102)-C(108)	105.29(15)

Table S5 Diffraction data for $H_2L \cdot MeOH$, $Cd(HL)_2$ and $2[Cd_{10}(L)_4(HL)_6(ClO_4)_2(CO_3)](ClO_4)_4 \cdot 2MeOH \cdot 11H_2O$

Formula	$C_{11}H_{13}N_3O_2$	$C_{20}H_{16}CdN_6O_2$	$C_{204}H_{182}Cd_{20}Cl_8N_{60}O_{71}$
Molecular weight	219.24	484.79	7141.70
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P\,2_1/c$	$P\,2_1/n$	$P\,1$
a (Å)	7.0400(4)	9.0408(5)	16.4976(6)
b (Å)	11.0757(8)	17.4676(9)	17.7965(6)
c (Å)	14.6098(10)	11.6328(5)	24.6568(9)
α (°)	90	90	86.700(2)
β (°)	96.183(3)	90.467(2)	86.475(2)
γ (°)	90	90	65.444(2)
Z	4	4	1
Volume (Å^3)	1132.54(13)	1837.00(16)	6567.9(4)
Density (calculated, Mg/m^3)	1.286	1.753	1.806
Absorption coefficient (mm^{-1})	0.091	1.220	1.750
F(000)	464	968	3490
Crystal size (mm^3)	0.32 x 0.14 x 0.01	0.16 x 0.08 x 0.03	0.24 x 0.24 x 0.02
θ range for data collection (completeness)	2.31 to 26.47° (99.6 %).	2.10 to 26.37° (99.9 %)	1.26 to 26.51°(98.7 %)
Index ranges	$-8 \le h \le 8$, $0 \le k \le 13$, $0 \le l \le 18$	$-11 \le h \le 11$, $0 \le k \le 21$, $0 \le l \le 14$	$-20 \le h \le 20$, $-21 \le k \le 22$, $-30 \le l \le 30$
Reflections collected	16340	28901	98575
Independent reflections	2328 (R_{int} = 0.0537)	3766 (R_{int} = 0.0742)	47940 (R_{int} = 0.0820)
Data / restraints / parameters	2328 / 0 / 159	3766 / 770 / 519	47940 / 7355 / 1736
Goodness-of-fit on F^2	1.050	1.030	1.089
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0447, wR_2 = 0.0837	R_1 = 0.0429, wR_2 = 0.1095	R_1 = 0.0877, wR_2 = 0.2335
R indices (all data)	R_1 = 0.0947, wR_2 = 0.1009	R_1 = 0.0646, wR_2 =0.1233	R_1 = 0.1703, wR_2 = 0.2831
Largest diff. peak and hole (e.Å^{-3})	0.210 and -0.249	1.583 and -0.861	1.344 and -1.338

Experimental details for single crystal X-ray diffraction data.

Diffraction data for $H_2L \cdot MeOH$, $Cd(HL)_2$ and $2[Cd_{10}(L)_4(HL)_6(ClO_4)_2(CO_3)](ClO_4)_4 \cdot 2MeOH \cdot 11H_2O$ were collected at 100(2) K, using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) from a fine focus sealed tube. Some significant crystal parameters and refinement data are summarized in Table S4. Data were processed and corrected for Lorentz and polarisation effects. Multi-scan absorption corrections were performed using the SADABS routine.[1] Structures were solved by standard direct methods using SIR2004,[2] and then were refined by full matrix least squares on F^2 using SHELXL97.[3]

Both $Cd(HL)_2$ and $2[Cd_{10}(L)_4(HL)_6(ClO_4)_2(CO_3)](ClO_4)_4 \cdot 2MeOH \cdot 11H_2O$ presented a very significant disorder. In the case of $Cd(HL)_2$, each complex unit of $Cd(HL)_2$ can be found in the asymmetric unit on two different positions with 0.91:0.09 occupation sites, approximately. The case of the decanuclear complex is much more complicated, since crystals of $2[Cd_{10}(L)_4(HL)_6(ClO_4)_2(CO_3)](ClO_4)_4 \cdot 2MeOH11H_2O$ were twinned, so despite attempts to find a non-merohedral twin law, the structure was finally solved in the P1 space group as a racemic twin. Thus, the Flack parameter[4] refines with a 0.54(4) value (20688 Friedel pairs), indicating a 0.54:0.46 ratio between the non-centrosymmetric and centrosymmetric crystal domains. Furthermore, the unit cell contains two slightly different cations of $[Cd_{10}(L)_4(HL)_6(ClO_4)_2(CO_3)]^{2+}$ that also appear to be disordered on two different sites (0.83:0.17) and (0.72:0.28), respectively. This could result from the twinning, or from a real disorder. In any case, the high density of disordered atoms with so different occupation, but in short proximity (in ranges 0.45-0.57 and 0.63-0.82 Å for the cadmium atoms), only allowed determining the disordered sites of the cadmium atoms, but not for the remaining atoms. With these difficulties, only heavy atoms (Cd and Cl) with high occupation sites could be anisotropically treated. All the other atoms were refined with an isotropic treatment, and very restrained. Hydrogen atoms of organic groups were included at geometrically calculated positions, with thermal parameters derived from the parent atoms. H atoms attached to water molecules or to groups suitable to form hydrogen bonds could not be located on Fourier maps, so their assignment to protonated imidazole residues was associated to logical H bonds. Finally, although many solvated molecules, some of them with partial occupation sites, could be modeled for $2[Cd_{10}(L)_4(HL)_6(ClO_4)_2(CO_3)](ClO_4)_4 \cdot 2MeOH \cdot 2H_2O$, but the additional contribution of the electron density of disordered solvate molecules (methanol or water) was subtracted from the measured structure factors using SQUEEZE.[5] Thus, up to nine voids are present in the unit cell, with volumes of less than 246 $Å^3$, meaning 216 e^- in total.

CCDC 892600-892602 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

[1] a) SADABS– Bruker AXS area detector scaling and absorption correction. Version 2008/1, University of Göttingen, Germany 2008; b) R. H. Blesing, *Acta Cryst.*, 1995, **A51**, 33–38.
[2] M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, R. Spagna, *J. Appl. Cryst.*, 2005, *38*, 381–388.
[3] SHELX97. G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112–122.
[4] H. D. Flack, *Acta Cryst* , 1983, **A39**: 876–881
[5] (*a*)A.L. Spek, *Acta Cryst.*, 1990, **A46**, C34; (*b*) A.L. Spek,PLATON,*A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 1998.

Computational details and coordinates for $[Cd_2(L)(HL)(ClO_4)(MeOH)_2]$

The calculations were carried out at the DFT-B3LYP level with the Gaussian 09 program. The geometries were fully optimized by the gradient technique with the following basis: for Cd, the LANL2DZ basis set; for C, H, N, O and Cl were described by the standard polarized 6-31G* basis set. The nature of the optimized structures was assessed through a frequency calculation and the changes of Gibbs free reaction energies (ΔG values) were obtained by taking into account zero-point energies, thermal motion, and entropy contribution at standard conditions (temperature of 298.15 K, pressure of 1 atm).

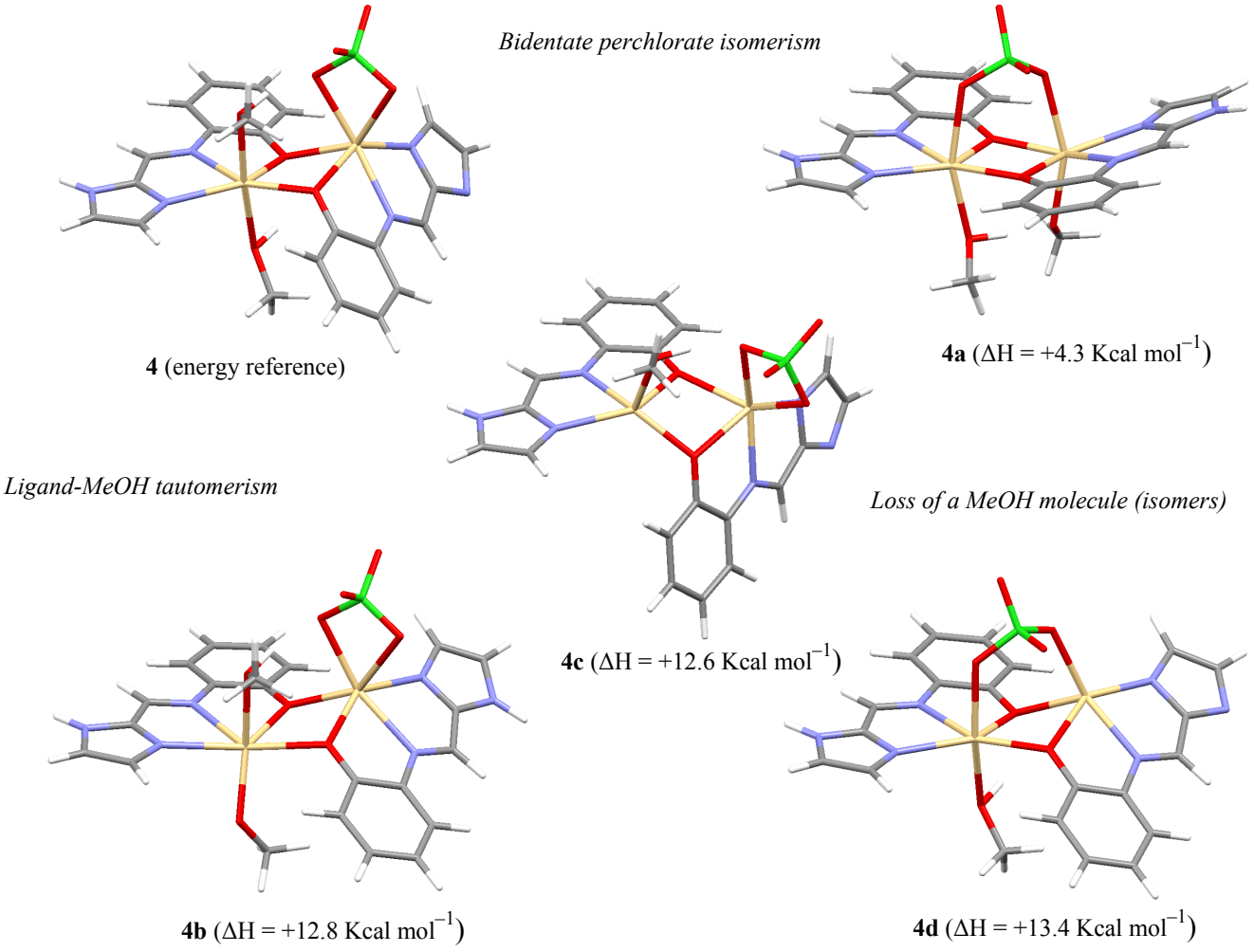


Figure S5. Representative calculated structures

Energy values (in Kcal mol^{-1}) and Cartesian coordinates of the calculated structures

Structure of the compound 4

E = −2338.561159

O	1.324284	1.031489	-2.322448
C	1.017572	2.235129	-3.042654
H	0.571979	0.409120	-2.365754
H	0.889512	2.016555	-4.109196
H	1.873141	2.901443	-2.918397
H	0.122039	2.724342	-2.648586
C	6.272271	1.064930	0.133085
C	5.038870	1.640910	0.313303
N	4.053143	0.747658	-0.021540
C	4.666728	-0.376388	-0.405037
N	6.017877	-0.210494	-0.323022
Cd	1.675687	0.418390	-0.022739
C	3.999823	-1.585118	-0.856095
N	2.711252	-1.591497	-0.856336
C	1.850620	-2.594778	-1.261655
C	0.456069	-2.238267	-1.264460
C	-0.471281	-3.225092	-1.677661
C	-0.046046	-4.487341	-2.054495
C	1.321196	-4.832745	-2.042511
C	2.254057	-3.891449	-1.651681
O	0.065899	-1.025110	-0.922981
Cd	-1.754393	-0.210398	0.286792
O	-0.128619	1.511109	0.610770
C	-0.503696	2.728360	0.188819
C	-1.724523	2.903890	-0.539895
C	-2.098477	4.188053	-0.967144
C	-1.294279	5.295999	-0.706190
C	-0.100611	5.130129	0.002868
C	0.284248	3.864517	0.444305
N	-2.454314	1.734738	-0.752922
C	-3.505795	1.568916	-1.502453
C	-4.112056	0.277956	-1.601864
N	-3.614389	-0.809222	-0.920138
C	-4.447109	-1.818029	-1.262864
C	-5.415757	-1.308679	-2.142294
N	-5.201245	0.006563	-2.352688
O	-2.686308	-0.280062	2.569703
Cl	-1.690169	-1.237556	3.190739
O	-2.340632	-2.484201	3.616645
O	-0.932804	-0.588084	4.281134
O	-0.703631	-1.540951	2.023059
H	-3.035852	4.319569	-1.501450
H	-1.603148	6.281625	-1.042501
H	0.527882	5.989998	0.221162
H	1.199224	3.733219	1.019167
H	3.308671	-4.154688	-1.630624
H	1.636155	-5.830150	-2.333060
H	-0.781275	-5.225570	-2.364064
H	-1.524014	-2.958651	-1.697103
H	-3.962170	2.374470	-2.084125
H	-6.237192	-1.837395	-2.611341
H	-4.325551	-2.820392	-0.870684
H	4.808014	2.638424	0.657803
H	6.711715	-0.909462	-0.549645
H	7.274029	1.436304	0.282456
H	4.619670	-2.421802	-1.191457
O	1.797430	-0.339247	2.201693
H	0.957730	-0.841458	2.324691
C	1.884795	0.646415	3.246531
H	1.083628	1.385994	3.156190
H	1.827682	0.162726	4.225497
H	2.857932	1.132958	3.140084

Structure of the compound 4a

E = −2338.5515307

C	-5.662175	-2.649008	0.189423
C	-4.322827	-2.805764	-0.063940
N	-3.704326	-1.581246	-0.085486
C	-4.650027	-0.667584	0.155054
N	-5.852612	-1.288726	0.323924
Cd	-1.564710	-0.524550	-0.305204
O	-1.210137	-0.439254	-2.581536
C	-1.168187	-1.620321	-3.368948
C	-4.429194	0.764094	0.237376
N	-3.222918	1.188530	0.066128
C	-2.738744	2.476323	0.119209
C	-1.313491	2.604013	-0.094234
C	-0.770281	3.918265	-0.030463
C	-1.569775	5.016503	0.216072
C	-2.961374	4.879915	0.417347
C	-3.528255	3.622085	0.369168
O	-0.571882	1.570147	-0.344371
Cd	1.534256	0.629134	-0.500351
O	1.081208	0.599478	-2.641410
C	1.136601	1.762122	-3.422647
O	0.474694	-1.464511	-0.361120
C	1.211127	-2.530301	-0.221140
C	2.640318	-2.429161	-0.059081
C	3.424776	-3.594434	0.077092
C	2.845531	-4.849619	0.059598
C	1.448247	-4.959206	-0.092261
C	0.653614	-3.835797	-0.229687
N	3.138362	-1.141548	-0.053289
C	4.338694	-0.748903	0.199987
C	4.601055	0.678164	0.165198
N	3.697866	1.623389	-0.107703
C	4.347911	2.827208	-0.018153
C	5.665184	2.625484	0.311727
N	5.809014	1.258320	0.422519
O	1.108870	0.661094	1.901231
Cl	0.211710	-0.237270	2.740800
O	-0.025484	0.416087	4.040050
O	0.839310	-1.568268	2.887060

O	-1.135156	-0.390389	2.031249
H	4.503007	-3.502889	0.184217
H	3.458373	-5.740350	0.158644
H	0.987033	-5.944005	-0.103248
H	-0.423427	-3.925952	-0.343673
H	-4.598244	3.509022	0.527032
H	-3.575342	5.754194	0.610782
H	-1.119723	6.005660	0.257269
H	0.299523	4.028309	-0.183775
H	-0.253939	0.032239	-2.651880
H	5.164694	-1.417740	0.461104
H	6.485093	3.307508	0.473918
H	3.835075	3.761866	-0.192028
H	-3.772471	-3.721014	-0.226105
H	-6.727893	-0.827927	0.528877
H	-6.469883	-3.357498	0.285758
H	-5.286971	1.407951	0.452965
H	0.535751	2.594967	-3.011217
H	0.759587	1.571372	-4.442876
H	2.171578	2.131444	-3.534909
H	-0.908093	-1.381549	-4.408872
H	-2.161873	-2.083600	-3.364119
H	-0.436971	-2.346013	-2.986513
H	6.656355	0.767023	0.669625

Structure of the compound 4b

E = −2338.5394264

O	2.370703	2.100116	-1.740488
C	1.632381	2.376612	-2.884428
H	2.023812	3.280793	-3.391458
H	0.557224	2.580975	-2.697259
H	1.662359	1.565918	-3.643400
C	6.497618	0.771527	0.803905
C	5.300076	1.450018	0.837132
N	4.286892	0.640355	0.406720
C	4.843010	-0.527588	0.096680
N	6.190778	-0.484764	0.333849
Cd	1.852730	0.651200	-0.321509
C	4.140513	-1.677488	-0.438368
N	2.887684	-1.565393	-0.707732
C	2.055307	-2.554626	-1.218283
C	0.662849	-2.210301	-1.271486
C	-0.229157	-3.180392	-1.788053
C	0.222784	-4.416658	-2.223284
C	1.588516	-4.744996	-2.171014
C	2.487925	-3.816001	-1.673040
O	0.246583	-1.030775	-0.859659
Cd	-1.570674	-0.281957	0.161617
O	-0.292427	1.597150	0.309305
C	-0.831129	2.716166	-0.102487
C	-2.159757	2.761963	-0.667923
C	-2.724350	3.993825	-1.075319
C	-2.013034	5.169219	-0.954334
C	-0.703075	5.132369	-0.424527
C	-0.126705	3.947579	-0.012549
N	-2.788262	1.541972	-0.775722
C	-3.940457	1.253095	-1.282936
C	-4.340394	-0.141187	-1.268528
N	-3.594097	-1.144522	-0.797406
C	-4.332430	-2.291239	-0.944590
C	-5.543593	-1.994818	-1.518588
N	-5.531448	-0.629565	-1.718869
O	-2.768888	-0.145766	2.329415
Cl	-1.880461	-1.104579	3.103359
O	-2.634384	-2.296234	3.523012
O	-1.218274	-0.419718	4.229660
O	-0.803835	-1.519394	2.061517
H	-3.731615	4.011751	-1.484674
H	-2.451010	6.112493	-1.266204
H	-0.135574	6.056108	-0.342876
H	0.887294	3.922486	0.371264
H	3.546880	-4.060692	-1.647070
H	1.936287	-5.711360	-2.523386
H	-0.489266	-5.137776	-2.617534
H	-1.283546	-2.922860	-1.846735
H	-4.622662	1.988037	-1.718694
H	-6.386131	-2.610652	-1.791560
H	-3.954525	-3.252021	-0.626838
H	5.117425	2.471327	1.138614
H	6.846982	-1.234438	0.167542
H	7.504436	1.061090	1.062368
H	4.715963	-2.597917	-0.587501
O	1.639160	-0.030899	1.971527
H	0.855905	-0.604912	2.103147
C	1.630317	0.977148	2.990773
H	0.810526	1.687333	2.839140
H	1.538979	0.520355	3.981360
H	2.587083	1.500631	2.922224
H	-6.280927	-0.080303	-2.115430

Structure of the compound 4c

E = −2222.8240201

C	-6.195925	-0.988029	-0.618922
C	-4.988127	-1.555048	-0.299063
N	-4.020618	-0.582551	-0.236205
C	-4.621292	0.579964	-0.516155
N	-5.945502	0.362227	-0.752002
Cd	-1.716755	-0.234705	0.235598
C	-3.952794	1.865806	-0.570511
N	-2.682236	1.880615	-0.331152
C	-1.805076	2.942051	-0.342218
C	-0.428058	2.597356	-0.073288
C	0.528949	3.645066	-0.127142
C	0.143201	4.943792	-0.396139
C	-1.210300	5.277755	-0.632820
C	-2.166339	4.284019	-0.609797
O	-0.087793	1.367801	0.204401
Cd	1.747601	-0.054510	0.237393
O	-0.070370	-1.493529	-0.369079

C	0.102931	-2.179848	-1.514472
C	1.247388	-1.931761	-2.335571
C	1.425834	-2.672971	-3.513481
C	0.498389	-3.635856	-3.905263
C	-0.625766	-3.874974	-3.109650
C	-0.815911	-3.157002	-1.929178
N	2.116045	-0.949832	-1.859058
C	3.130635	-0.411355	-2.470211
C	3.898446	0.604556	-1.816816
N	3.587162	1.046395	-0.551104
C	4.528061	1.983892	-0.290647
C	5.371605	2.078721	-1.407343
N	4.972121	1.212710	-2.362831
O	2.726161	-1.630978	1.891857
Cl	1.938838	-1.196517	3.107056
O	2.817625	-0.664494	4.157068
O	1.060548	-2.280945	3.597587
O	1.033140	-0.048920	2.560154
H	2.307599	-2.497291	-4.123986
H	0.656507	-4.201136	-4.819267
H	-1.350994	-4.630175	-3.402329
H	-1.676625	-3.356365	-1.293444
H	-3.207764	4.532552	-0.798725
H	-1.491174	6.306418	-0.835807
H	0.897578	5.725692	-0.426804
H	1.571173	3.392181	0.041249
H	3.436499	-0.686194	-3.483057
H	6.230417	2.725375	-1.543825
H	4.559586	2.518677	0.650681
H	-4.760416	-2.595218	-0.117782
H	-6.625140	1.071298	-0.990473
H	-7.178367	-1.409929	-0.761872
H	-4.541870	2.751658	-0.820490
O	-1.662807	-0.530403	2.506921
H	-0.714775	-0.369174	2.740948
C	-2.140439	-1.679925	3.226818
H	-1.534125	-2.563409	3.008781
H	-2.117264	-1.480236	4.302672
H	-3.175020	-1.844097	2.916373

Structure of the compound 4d

E = −2222.8228099

O	1.035419	0.873529	-2.528336
C	0.403743	1.910995	-3.292864
H	0.430196	0.108457	-2.441966
H	0.237231	1.576055	-4.323445
H	1.091632	2.758585	-3.303438
H	-0.543045	2.227686	-2.844339
C	5.895394	1.873533	0.096720
C	4.590290	2.293417	0.175852
N	3.749652	1.252725	-0.123707
C	4.522002	0.193266	-0.382987
N	5.833103	0.543969	-0.259804
Cd	1.461171	0.636888	-0.165456
C	4.035960	-1.130004	-0.733898
N	2.761035	-1.303440	-0.779297
C	2.058342	-2.460751	-1.070433
C	0.628665	-2.319339	-1.099819
C	-0.140508	-3.474681	-1.369041
C	0.466915	-4.698569	-1.598989
C	1.868781	-4.830719	-1.572381
C	2.649646	-3.720126	-1.309449
O	0.057724	-1.140078	-0.908307
Cd	-1.702932	-0.502262	0.416169
O	-0.489766	1.492059	0.295882
C	-1.172017	2.579518	-0.077967
C	-2.561422	2.475554	-0.414752
C	-3.270166	3.623279	-0.801330
C	-2.644364	4.866065	-0.866050
C	-1.289500	4.973400	-0.535569
C	-0.566891	3.846575	-0.146943
N	-3.091563	1.189074	-0.316317
C	-4.296392	0.779147	-0.582936
C	-4.627302	-0.603443	-0.402196
N	-3.703289	-1.512963	0.061761
C	-4.384174	-2.683357	0.100411
C	-5.691507	-2.441548	-0.342258
N	-5.839343	-1.135463	-0.656074
O	-0.612621	-1.170286	2.321756
Cl	0.508978	-0.423051	3.057971
O	1.043219	-1.309509	4.098402
O	-0.007389	0.850292	3.585267
O	1.617841	-0.151088	2.038501
H	-4.324908	3.539363	-1.050152
H	-3.209765	5.743888	-1.165153
H	-0.794735	5.940683	-0.573745
H	0.481689	3.931537	0.131498
H	3.731371	-3.821187	-1.274549
H	2.331394	-5.796709	-1.748987
H	-0.150226	-5.569896	-1.801885
H	-1.222200	-3.374135	-1.394213
H	-5.091724	1.435715	-0.945134
H	-6.506855	-3.148653	-0.437895
H	-3.923809	-3.603325	0.438633
H	4.213538	3.272463	0.432941
H	6.622621	-0.073887	-0.387676
H	6.831112	2.384854	0.259860
H	4.772851	-1.911661	-0.940054

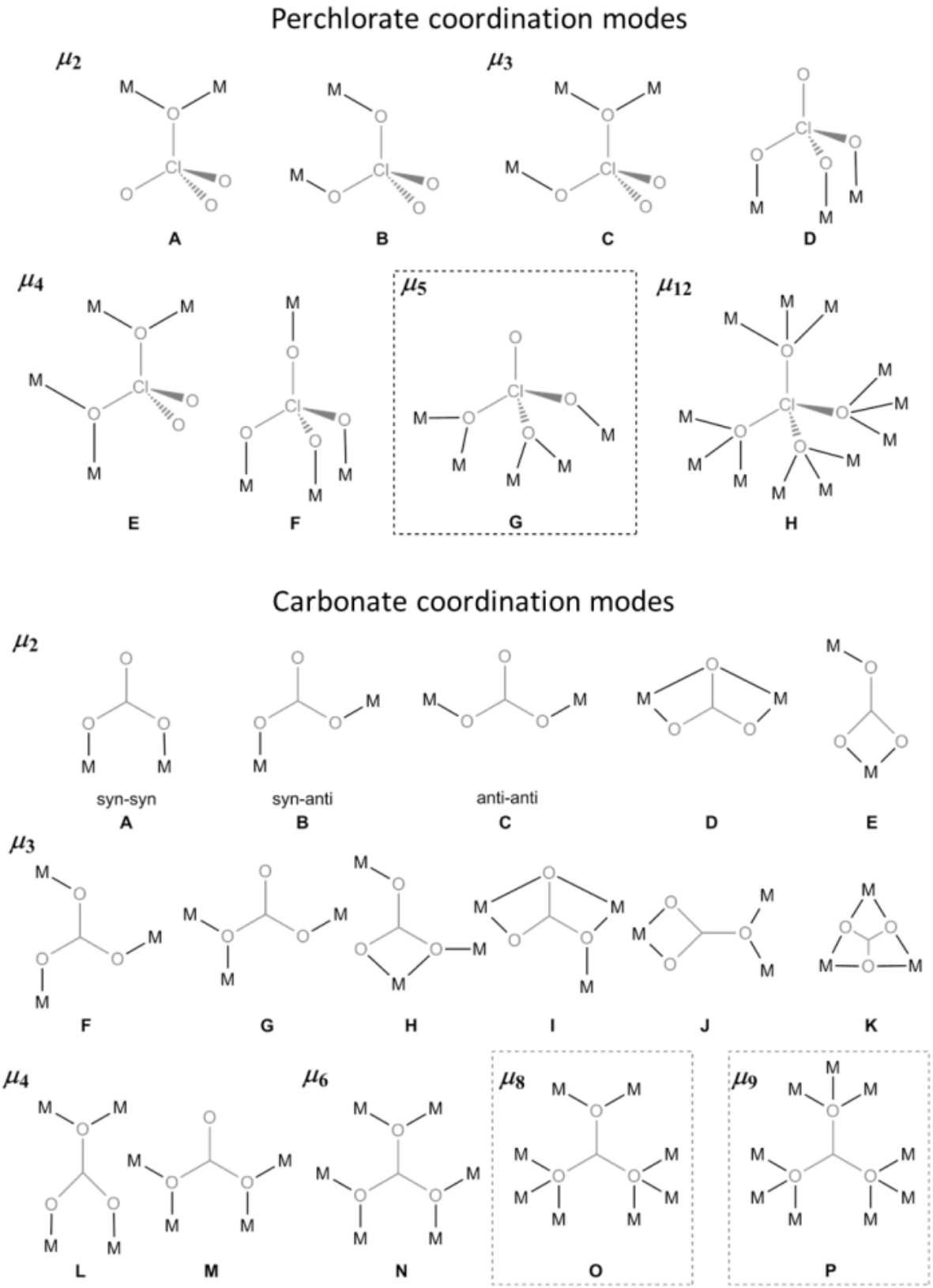
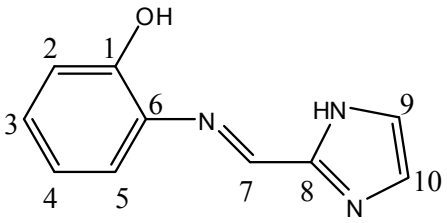


Figure S6 Structurally characterised coordination modes of perchlorate and carbonate bridges, highlighting the unprecedented modes reported here**.**

Experimental Section



Labelling scheme of H_2L for NMR studies

(*E*)-2-((1H-imidazol-2-yl)methyleneamino)phenol (H_2L): A solution of imidazole-2-carboxaldehyde (185 mg, 1.9 mmol) and 2-aminophenol (213 mg, 1.9 mmol) in methanol (60 mL) was heated under reflux for 8 h. The end of the reaction was observed by TLC. After cooling to room temperature, the resulting yellow solution was concentrated in vacuum to give a yellow crystalline product, which was washed with diethyl ether, filtered off and dried in vacuum. Yield = 343 mg (96%); ^{1}H NMR (500 MHz, dmso-d_6): δ 12.95 (s, 1H; N*H*), 8.98 (s, 1H; O*H*), 8.64 (s, 1H; H-7), 7.46 (d, 1H, *J* = 8.0 and 1.4 Hz; H-5), 7.31 (br, 2H, H-9 and H-10), 7.11 (t, 1H, *J* = 8.1, and 1.5 Hz; H-3), 6.89 (d, 1H, *J* = 8.1 and 1.2 Hz; H-2), 6.82 (t, 1H, *J* = 8.0 and 1.3 Hz; H-4); ^{13}C NMR (125 MHz, dmso-d_6): δ 152.4 (C-1), 146.6 (C-7), 145.7 (C-8), 134.9 (C-6), 130.8 (C-10), 128.6 (C-3), 119.9 (C-9), 119.6 (C-4), 117.6 (C-5) and 115.7 (C-2); FTIR (KBr, cm^{-1}): ν(O–H) 3373(s), ν(N–H) 3144(m), 3117(m), ν(C=N_{imine}) 1624(s); MS (FAB$^+$-MS, MNBA): *m*/*z* (%): 188.1 (100) [H_2L + H]$^+$; elemental analysis calcd (%) for $C_{10}H_9N_3O$: C 64.2, H 4.8, N 22.4; found: C 64.3, H 4.9; N 22.4.

$Cd(HL)_2 \cdot H_2O$ was obtained by stirring overnight a methanol solution (60 mL) containing H_2L (134 mg, 0.7 mmol) and $Cd(OAc)_2 \cdot 2H_2O$ (94 mg, 0.35 mmol), at room temperature. This gave a yellow powder, which was filtered off and dried in vacuum. Alternatively, this reaction could be performed under reflux for 5 h when imidazole-2-carboxaldehye (80 mg, 0.8 mmol) and $Cd(ClO_4)_2 \cdot 6H_2O$ (168 mg, 0.4 mmol) were firstly mixed in methanol (50 mL) and then 2-aminophenol (87 mg, 0.8 mmol) was added to the resulting solution. Single crystals of $Cd(HL)_2 \cdot$were obtained from the mother liquor solution (methanol). Yield: 66%; ^{1}H NMR (250 MHz, dmso-d_6): δ 13.14 (br, 2H; N*H*), 8.62 (s, 2H; H-7), 7.43 (d, 2H, *J* = 7.6 Hz; H-5), 7.43 (br, 2H; H-9), 7.19 (br, 2H; H-10), 7.09 (t, 2H, *J* = 7.6 Hz; H-3), 6.82 (d, 2H, *J* = 7.6 Hz; H-2), 6.70 (t, 2H, *J* = 7.6 Hz; H-4); FTIR (KBr, cm^{-1}): ν(O–H_w) 3438 (m), ν(N–H) 3061(w), ν(C=N_{imine}) 1588(m); MS (FAB$^+$, MNBA): *m*/*z* (%): 485.1 (4) [$Cd(HL)_2$+H]$^+$, 298.0 (4) [CdL+H]$^+$; elemental analysis calcd (%) for $C_{20}H_{18}CdN_6O_3$: C 47.8, H 3.6, N 16.7; found: C 47.5, H 3.4; N 16.8.

$Cd_2(L)(HL)(OH)$ was obtained by stirring a methanol solution (60 mL) containing H_2L (187 mg, 1 mmol), $Cd(ClO_4)_2 \cdot 6H_2O$ (209 mg, 0.5 mmol) and $Cd(OAc)_2 \cdot 2H_2O$ (266 mg, 1 mmol), at room temperature over a 24 h period. This gave a yellow powder, which was filtered off and dried in vacuum. Yield: 96 mg (63%); FTIR (KBr, cm^{-1}): ν(O–H) 3433 (m), ν(N–H) 3040(w), ν(C=N_{imine}) 1603(m); MS (FAB$^+$, MNBA): *m*/*z* (%): 614.9 (16) [M+H]$^+$; elemental analysis calcd (%) for $C_{10}H_8CdN_3O_{1.5}$: C 39.2, H 2.6, N 13.7; found: C 39.5, H 2.4; N 13.4.

$2[Cd_{10}(L)_4(HL)_6(ClO_4)_2(CO_3)](ClO_4)_4 \cdot 2MeOH \cdot 11H_2O$. Single crystals of title compound were obtained in small amount by extended exposure of the methanol mother liquor of $Cd_2(L)(HL)(OH)$ to the atmosphere. The title compound was also obtained (after 24 h at ambient temperature) from $Cd_2(L)(HL)(OH)$ (1 equiv.) by passing a stream of carbon dioxide through a methanolic suspension after adding cadmium perchlorate (2 eqiv.). ^{1}H NMR (250 MHz, dmso-d_6): δ 8.70 (s, H-7), 7.18 (d, H-5), 7.10 (t, H-3), 6.90 (s, H-9 or H-10), 6.76 (s, H-9 or H-10), 6.59 (d, H-2), 6.31 (t, H-4); FTIR (KBr, cm^{-1}): ν(O–H) 3435 (sh), ν(O-H_{MeOH}) 3220, ν(C=N_{imine}) 1608(m), ν(CO_3^{2-}) 1463(s), ν(CO_3^{2-}) 1440(s), ν(ClO_4^-) 1144(s), 1113(vs), 618(m); elemental analysis calcd (%) for $C_{204}H_{182}Cd_{20}Cl_8N_{60}O_{71}$: C 34.3, H 2.5, N 11.8; found: C 34.0, H 2.7; N 11.5.

$Cd_2(L)(HL)(ClO_4)(MeOH)_2$ was obtained by stirring a methanol solution (60 mL) containing H_2L (100 mg, 0.5 mmol) and $Cd(ClO_4)_2 \cdot 6H_2O$ (223 mg, 0.5 mmol), at room temperature over a 4 h period. Concentration under reduced pressure of the yellow solution yielded an oily product, which was dried in vacuum and dissolved in diethyl ether (20 mL) and stirred during 30 min. This gave a brown powder, which was filtered off and dried in vacuum. Yield: 357 mg (60%); ^{1}H NMR (250 MHz, dmso-d_6): δ 8.67 (s, 2H; H-7), 7.43 (d, 2H, J = 8.0 and 1.4 Hz; H-5), 7.35 (br, 4H; H-9 and H-10), 7.13 (t, 2H, J = 8.2, and 1.5 Hz; H-3), 6.91 (d, 2H, J = 8.1 and 1.3 Hz; H-2), 6.83 (t, 2H, J = 8.0 and 1.3 Hz; H-4), 4.12 (s, 2H, HO_{MeOH}) and 3.16 (s, 6H, H_3C_{MeOH}); FTIR (KBr, cm^{-1}): ν(O-H_{MeOH}) 3250 (m), ν(N–$H_{imidazole}$) 3057(w), ν(C=N_{imine}) 1619(m), ν(Cl-O) 1145(s), 1121(vs), 1087(vs), 636(m), 625(m); MS (MALDI-TOF, DCTB): m/z (%): 696.8 (100) $[Cd_2(L)(HL)(ClO_4)+H]^+$; elemental analysis calcd (%) for $C_{20}H_{15}Cd_2ClN_6O_6 \cdot 2MeOH$: C, 34.8; H, 3.1; N, 11.1; found: C 35.1, H 3.4; N 11.1.

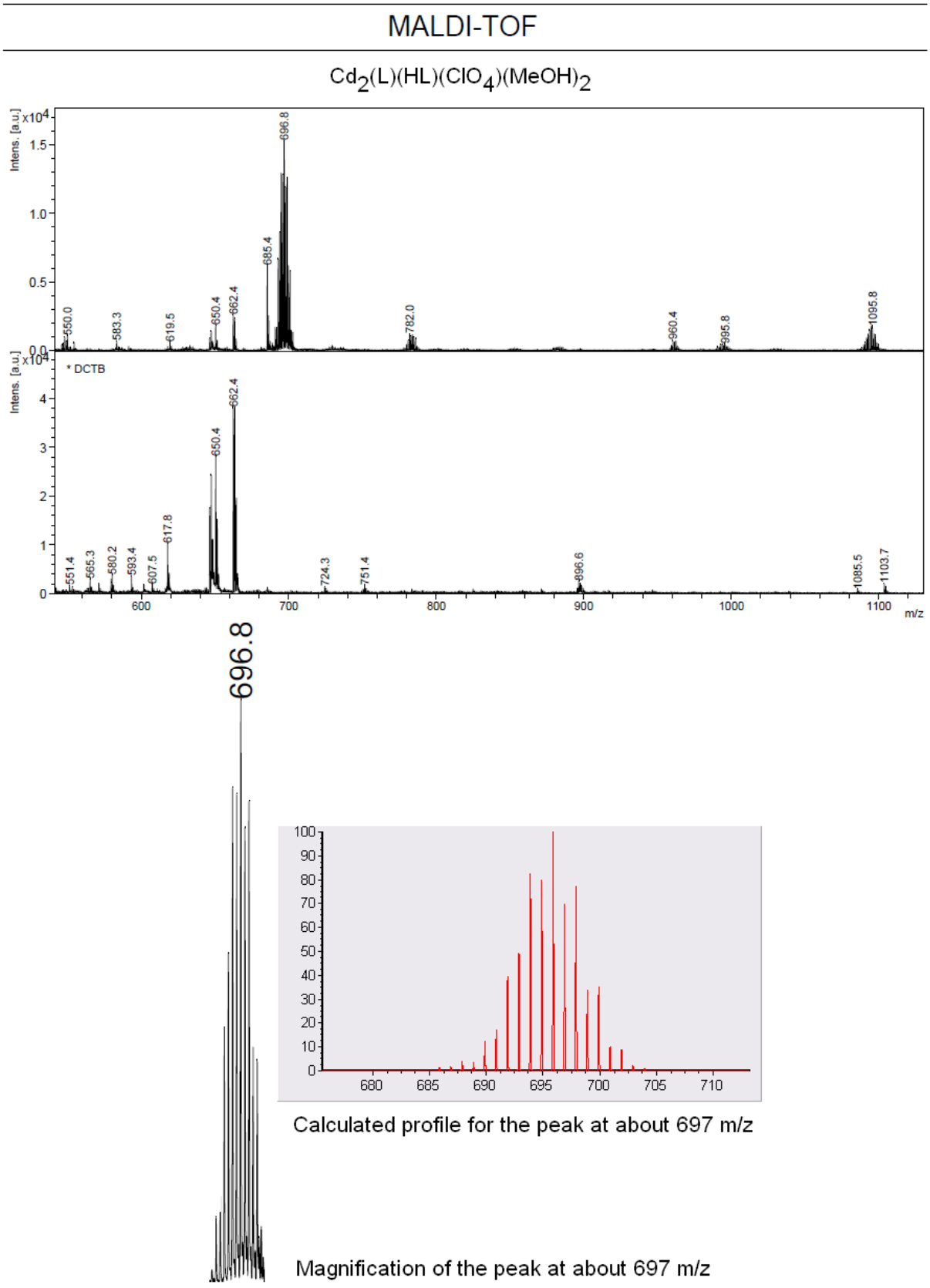
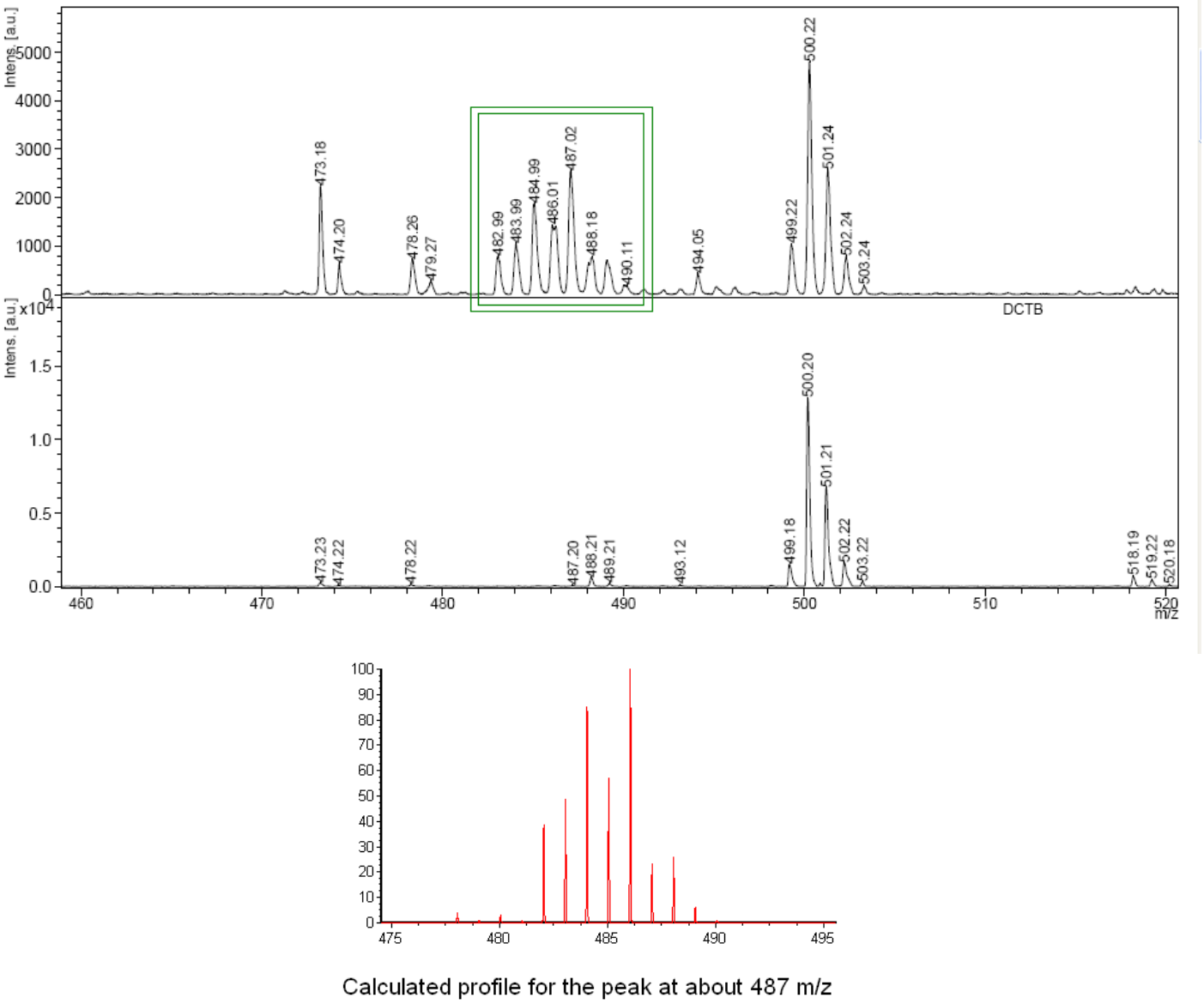


Figure S7. Mass spectra of the compounds of this work. $Cd_2(L)(HL)(ClO_4)(MeOH)_2$

MALDI-TOF



Calculated profile for the peak at about 487 m/z

Figure S7cont. Mass spectra of the compounds of this work. $Cd(HL)_2 \cdot H_2O$

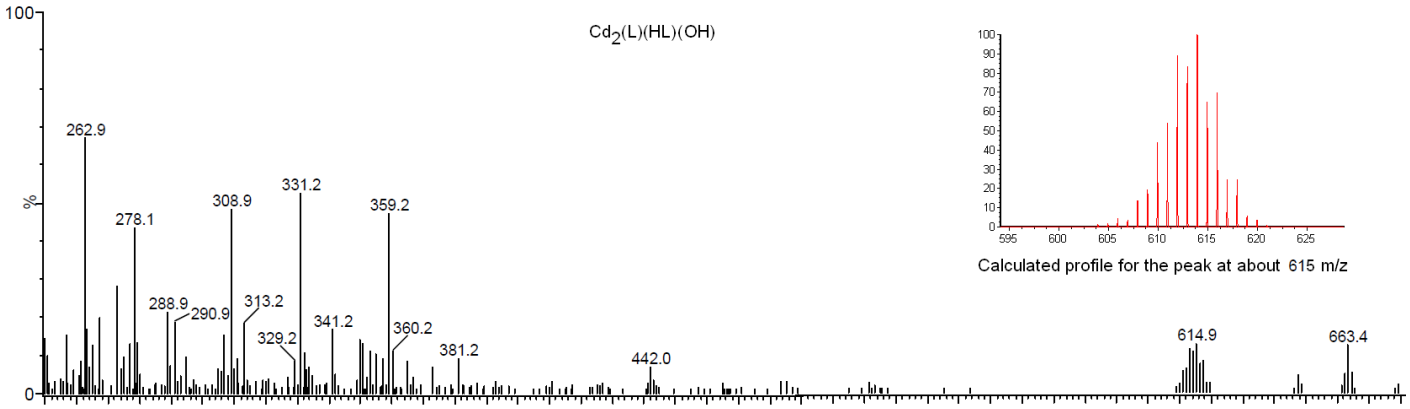


Figure S7cont. Mass spectra of the compounds of this work. $Cd_2(L)(HL)(OH)$

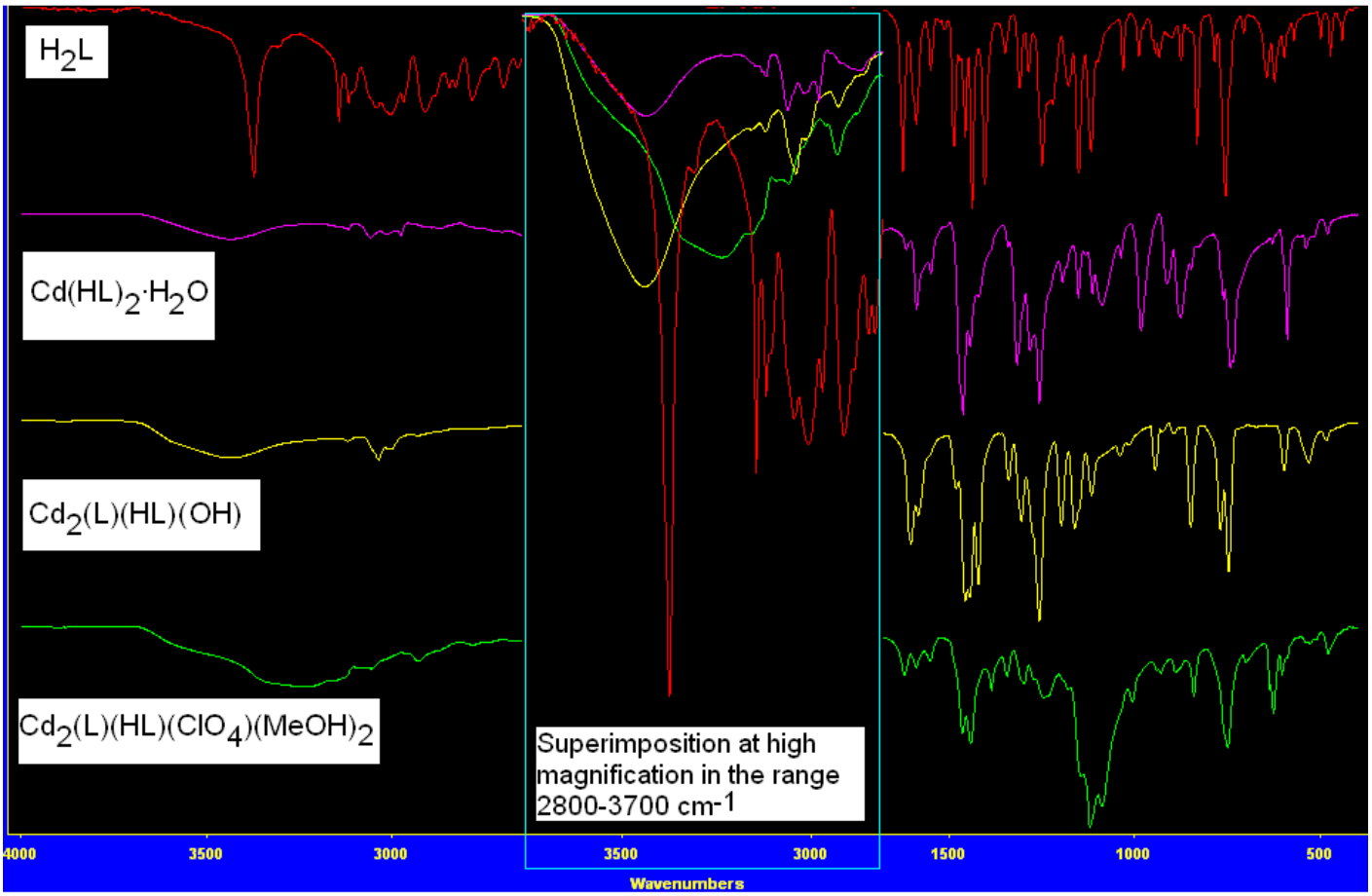


Figure S8. Superimposition of the IR spectra of the compounds of this work

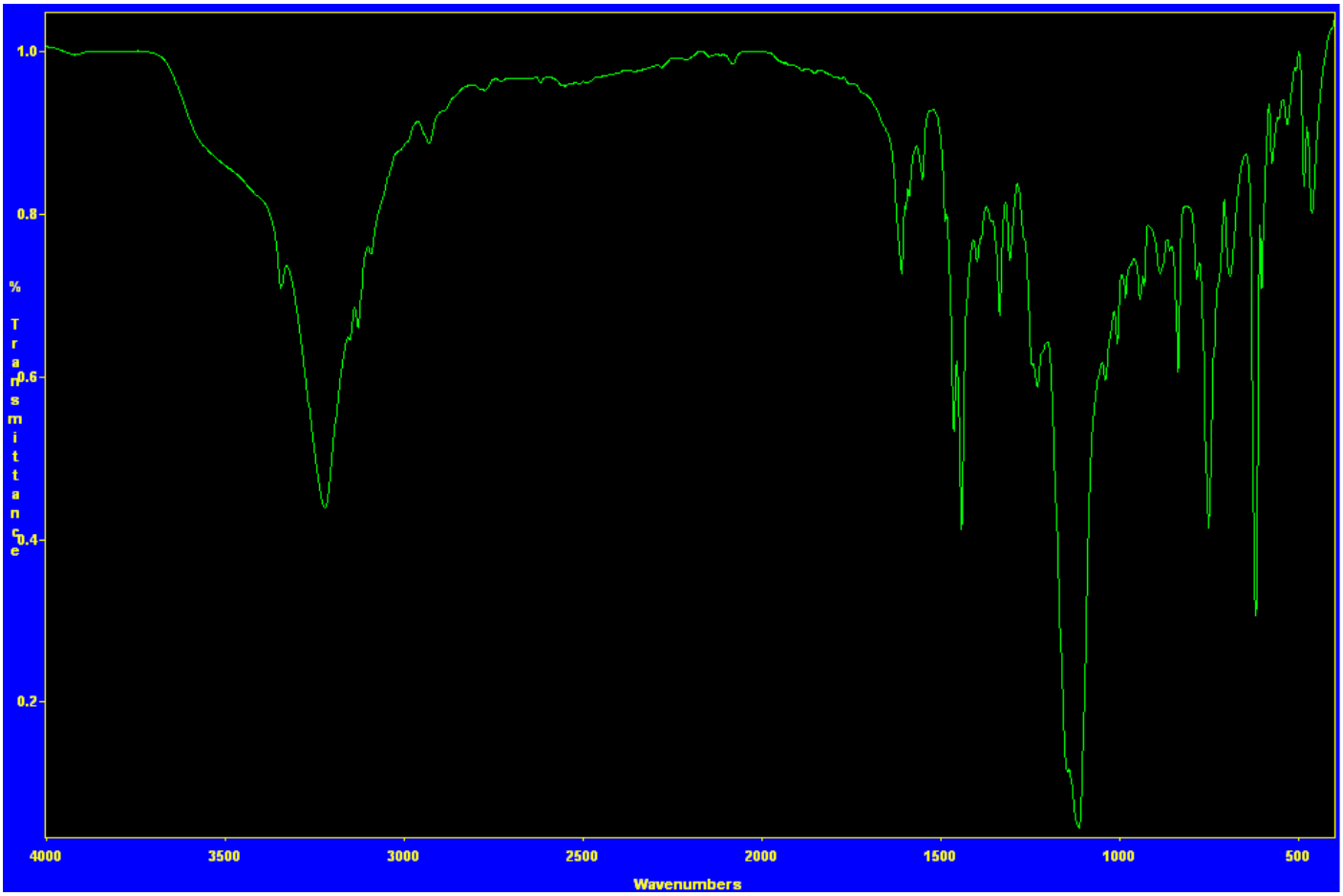


Figure S8 cont. IR spectrum of **1**

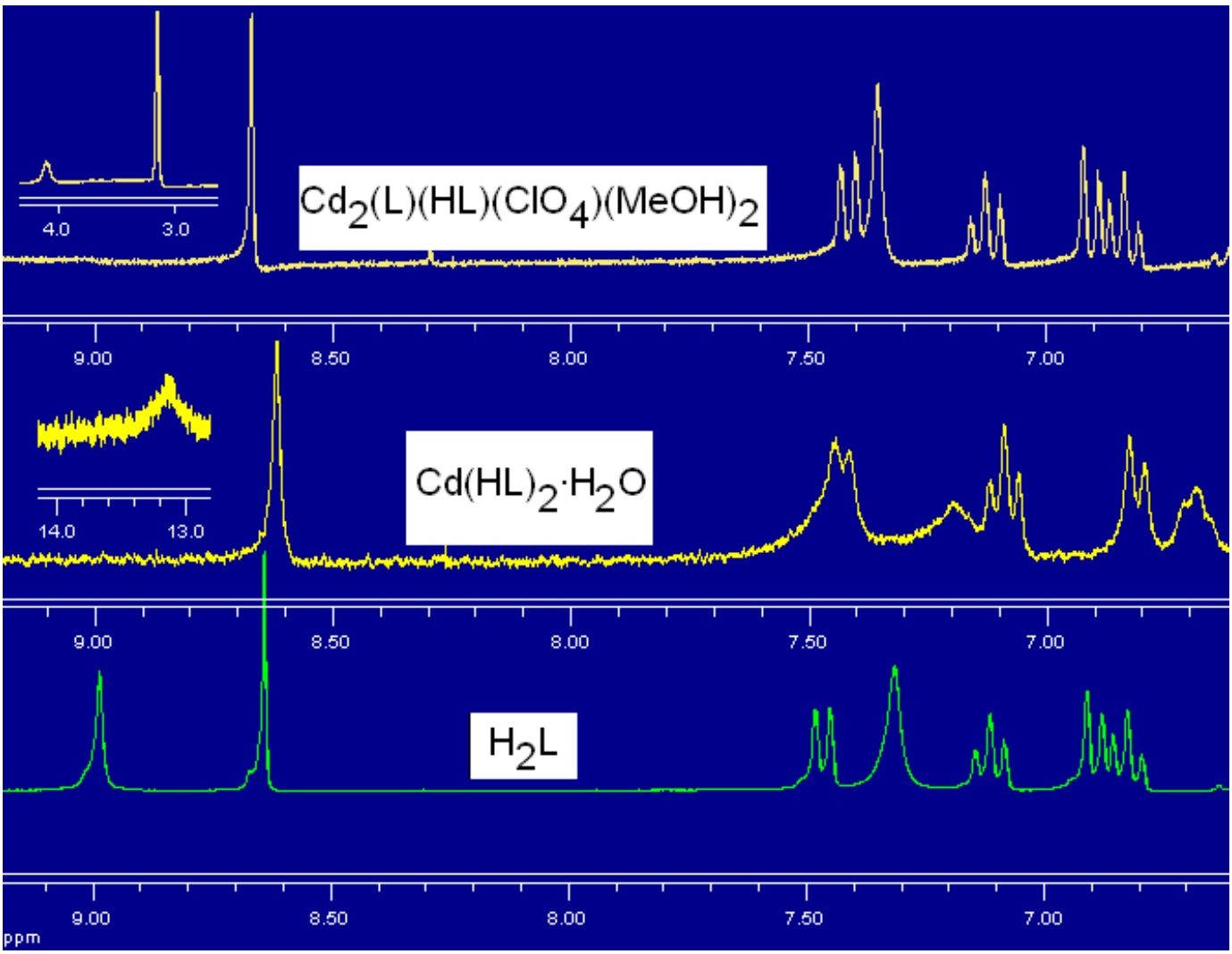


Figure S9. Superimposition of the ^{1}H NMR spectra of the compounds of this work

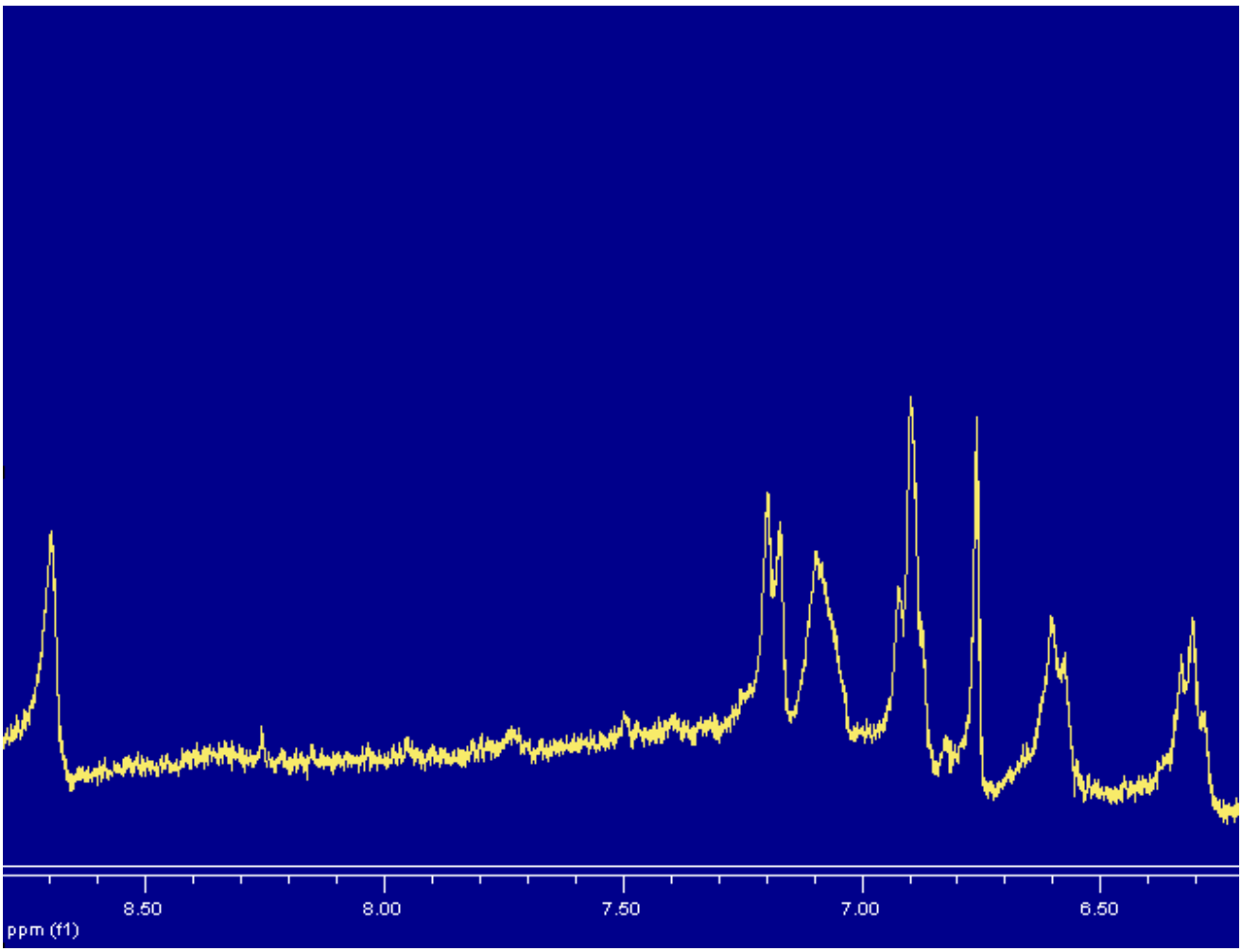


Figure S9 cont. ^{1}H NMR spectum of **1**