Electronic Supplementary Material for CrystEngComm
This journal is (c) The Royal Society of Chemistry 2009

Electronic Supplementary Information

Synthesis of phenyl substituted bisphosphonates and crystal structures and characterization of Cd complexes of (dichloromethylene)bisphosphonic acid phenyl and alkyl ester derivatives

Jonna Jokiniemi*, Jouko. J. Vepsäläinen, Harri Nätkinniemi, Sirpa Peräniemi and Markku Ahlgrén

Table S2. Selected bond lengths (Å) and angles (°) for compounds **7–9**

	7	**8**	**9**
P(1)−O(11)	1.492(2)	1.522(2)	1.535(2)
P(1)−O(12)	1.495(2)	1.518(2)	1.514(2)
P(1)−O(13)	1.588(2)	1.516(2)	1.513(2)
P(2)−O(21)	1.519(2)	1.574(2)	1.505(2)
P(2)−O(22)	1.525(2)	1.590(2)	1.497(2)
P(2)−O(23)	1.516(2)	1.469(2)	1.569(2)
P(3)−O(31)	1.499(2)		
P(3)−O(32)	1.495(2)		
P(3)−O(33)	1.587(2)		
P(4)−O(41)	1.515(2)		
P(4)−O(42)	1.523(2)		
P(4)−O(43)	1.505(2)		
P(1)−C(1)	1.846(3)	1.876(3)	1.856(3)
P(2)−C(1)	1.867(3)	1.831(3)	1.858(3)
P(3)−C(2)	1.849(2)		
P(4)−C(2)	1.868(3)		
O(11)−P(1)−C(1)	108.32(11)	104.99(11)	105.18(10)
O(12)−P(1)−C(1)	106.63(11)	105.08(12)	104.04(10)
O(13)−P(1)−C(1)	105.88(11)	104.34(11)	107.85(11)
O(21)−P(2)−C(1)	106.71(11)	102.81(12)	106.31(10)
O(22)−P(2)−C(1)	106.64(10)	105.03(12)	109.88(11)
O(23)−P(2)−C(1)	105.43(11)	114.25(12)	105.54(11)
O(31)−P(3)−C(2)	109.01(11)		
O(32)−P(3)−C(2)	107.12(11)		
O(33)−P(3)−C(2)	102.17(11)		
O(41)−P(4)−C(2)	105.98(11)		
O(42)−P(4)−C(2)	105.20(11)		
O(43)−P(4)−C(2)	106.01(11)		
P(1)−C(1)−P(2)	113.77(14)	115.62(15)	113.12(13)
P(3)−C(2)−P(4)	114.22(14)		
Cl(1) −C(1)−Cl(2)	108.79(14)	109.27(15)	108.09(13)
Cl(3) −C(2)−Cl(4)	108.72(14)		

Table S3. Selected bond lengths (Å) and angles (°) around the metal atoms in compounds **7**–**9**[a]

7				**8**		**9**	
Cd(1)−O(1)	2.310(2)	Cd(3)−O(4)	2.338(2)	Cd(1)−O(1)	2.311(2)	Cd(1)−O(1)	2.293(2)
Cd(1)−O(11)	2.278(2)	Cd(3)−O(5)	2.355(2)	Cd(1)−O(2)	2.341(2)	Cd(1)−O(11)	2.278(2)
Cd(1)−O(21)	2.256(2)	Cd(3)−O(22)	2.371(2)	Cd(1)−O(3)	2.338(2)	Cd(1)−O(21)	2.266(2)
Cd(2)−O(2)	2.311(2)	Cd(3)−O(32)	2.280(2)	Cd(1)−O(11)	2.257(2)	Cd(2)−O(1)	2.573(2)
Cd(2)−O(3)	2.402(2)	Cd(3)−O(42)	2.232(2)	Cd(1)−O(12a)	2.261(2)	Cd(2)−O(2)	2.307(2)
Cd(2)−O(12)	2.263(2)	Cd(3)−O(43c)	2.188(2)	Cd(1)−O(13b)	2.279(2)	Cd(2)−O(11c)	2.365(2)
Cd(2)−O(22)	2.258(2)	Cd(4)−O(6)	2.338(2)			Cd(2)−O(12)	2.318(2)
Cd(2)−O(23b)	2.193(2)	Cd(4)−O(31)	2.305(2)			Cd(2)−O(13d)	2.262(2)
Cd(2)−O(42)	2.348(2)	Cd(4)−O(41)	2.189(2)			Cd(2)−O(22)	2.241(2)
O(21)−Cd(1)−O(21a)	180.0(1)	O(43c)−Cd(3)−O(42)	169.14(6)	O(11)−Cd(1)−O(12a)	80.04(7)	O(21)−Cd(1)−O(21e)	180.00(8)
O(11)−Cd(1)−O(11a)	180.0(1)	O(43c)−Cd(3)−O(32)	101.99(6)	O(11)−Cd(1)−O(13b)	111.96(6)	O(11)−Cd(1)−O(11e)	180.00(8)
O(1)−Cd(1)−O(1a)	180.0(1)	O(42)−Cd(3)−O(32)	87.08(6)	O(12a)−Cd(1)−O(13b)	166.41(6)	O(1)−Cd(1)−O(1e)	180.00(8)
O(21)−Cd(1)−O(11)	90.07(6)	O(43c)−Cd(3)−O(4)	92.67(6)	O(11)−Cd(1)−O(1)	99.44(7)	O(21)−Cd(1)−O(11)	90.01(6)
O(21)−Cd(1)−O(11a)	89.93(6)	O(42)−Cd(3)−O(4)	95.06(6)	O(12a)−Cd(1)−O(1)	89.12(7)	O(21)−Cd(1)−O(11e)	89.99(6)
O(21)−Cd(1)−O(1)	93.51(6)	O(32)−Cd(3)−O(4)	78.14(7)	O(13b)−Cd(1)−O(1)	82.73(7)	O(21)−Cd(1)−O(1)	88.04(6)
O(21)−Cd(1)−O(1a)	86.49(6)	O(43c)−Cd(3)−O(5)	80.05(6)	O(11)−Cd(1)−O(3)	84.54(7)	O(21)−Cd(1)−O(1e)	91.96(6)
O(11)−Cd(1)−O(1)	87.82(7)	O(42)−Cd(3)−O(5)	90.43(6)	O(12a)−Cd(1)−O(3)	101.54(7)	O(11)−Cd(1)−O(1)	86.71(6)
O(11)−Cd(1)−O(1a)	92.18(7)	O(32)−Cd(3)−O(5)	118.40(7)	O(13b)−Cd(1)−O(3)	86.43(7)	O(11)−Cd(1)−O(1e)	93.29(6)
O(23b)−Cd(2)−O(22)	165.85(7)	O(4)−Cd(3)−O(5)	162.89(7)	O(1)−Cd(1)−O(3)	169.16(7)	O(22)−Cd(2)−O(13d)	109.37(6)
O(23b)−Cd(2)−O(12)	98.56(6)	O(43c)−Cd(3)−O(22)	94.16(6)	O(11)−Cd(1)−O(2)	165.42(6)	O(22)−Cd(2)−O(2)	162.97(6)
O(22)−Cd(2)−O(12)	86.50(6)	O(42)−Cd(3)−O(22)	78.51(6)	O(12a)−Cd(1)−O(2)	87.36(7)	O(13d)−Cd(2)−O(2)	82.42(6)
O(23b)−Cd(2)−O(2)	86.39(6)	O(32)−Cd(3)−O(22)	159.16(6)	O(13b)−Cd(1)−O(2)	81.46(7)	O(22)−Cd(2)−O(12)	80.71(6)
O(22)−Cd(2)−O(2)	79.75(6)	O(4)−Cd(3)−O(22)	88.13(6)	O(1)−Cd(1)−O(2)	87.59(7)	O(13d)−Cd(2)−O(12)	155.22(6)
O(12)−Cd(2)−O(2)	121.86(7)	O(5)−Cd(3)−O(22)	77.08(6)	O(3)−Cd(1)−O(2)	90.88(7)	O(2)−Cd(2)−O(12)	83.76(6)
O(23b)−Cd(2)−O(42)	103.32(6)	O(41)−Cd(4)−O(41d)	180.00(5)			O(22)−Cd(2)−O(11c)	108.14(6)
O(22)−Cd(2)−O(42)	78.49(6)	O(31)−Cd(4)−O(31d)	180.00(5)			O(13d)−Cd(2)−O(11c)	106.85(6)
O(12)−Cd(2)−O(42)	146.21(7)	O(6)−Cd(4)−O(6d)	180.00(5)			O(2)−Cd(2)−O(11c)	78.80(6)
O(2)−Cd(2)−O(42)	85.25(7)	O(41)−Cd(4)−O(31)	90.33(6)			O(12)−Cd(2)−O(11c)	90.44(6)
O(23b)−Cd(2)−O(3)	95.47(6)	O(41)−Cd(4)−O(31d)	89.67(6)			O(22)−Cd(2)−O(1)	88.64(6)
O(22)−Cd(2)−O(3)	98.59(6)	O(41)−Cd(4)−O(6)	94.96(6)			O(13d)−Cd(2)−O(1)	78.70(6)
O(12)−Cd(2)−O(3)	75.89(7)	O(41)−Cd(4)−O(6d)	85.04(6)			O(2)−Cd(2)−O(1)	81.56(6)
O(2)−Cd(2)−O(3)	161.77(7)	O(31)−Cd(4)−O(6)	90.44(6)			O(12)−Cd(2)−O(1)	79.00(6)
O(42)−Cd(2)−O(3)	76.67(6)	O(31)−Cd(4)−O(6d)	89.56(6)			O(11c)−Cd(2)−O(1)	158.60(6)

[a] Symmetry transformations used to generate equivalent atoms for **7**: a 1 − x, −y, z; b x − 1, y, z; c 1 + x, y, z; d −x, −y, 1 − z; for **8**: a 1 − x, y − 0.5, 1 − z; b 1 + x, y, z; for **9**: c x, −y, 0.5 + z; d 0.5 − x, 0.5 + y, 0.5 − z; e 0.5 − x, 0.5 − y, −z.

Table S4. Hydrogen-bond geometry (Å, °) in compound **9**

D − H···A	**D − H**	**H···A**	**D···A**	**D − H···A**	**Symmetry operation**
O1 − H1B···O3	0.99	1.81	2.784(3)	168	[−x + ½, y + ½, −z + ½]
O1 − H1A···O12	0.99	1.87	2.668(2)	136	[−x + ½, y + ½, −z + ½]
O2 − H2A···O3	0.84	1.86	2.696(3)	172	
O2 − H2B···O21	0.85	1.90	2.745(2)	176	[−x + ½, y − ½, −z + ½]
O3 − H3A···O6	0.86	1.94	2.788(3)	174	[−x + ½, −y + ½, z + 1]
O3 − H3B···O4	0.86	1.93	2.772(3)	170	[−x + ½, y − ½, −z + ½]
O4 − H4A···O22	0.85	2.03	2.864(3)	164	
O4 − H4B···O2	0.85	1.93	2.754(3)	162	[−x + ½, −y + ½, z + 1]
O5 − H5A···O4	0.85	1.99	2.815(3)	163	
O5 − H5B···O6	0.85	2.06	2.906(3)	171	
O6 − H6A···O8	0.85	2.02	2.828(3)	159	
O7 − H7···O5	0.84	2.01	2.837(3)	166	
O6 − H6B···O7	0.84	2.28	2.861(3)	126	[−x, −y + 1, −z + 1]

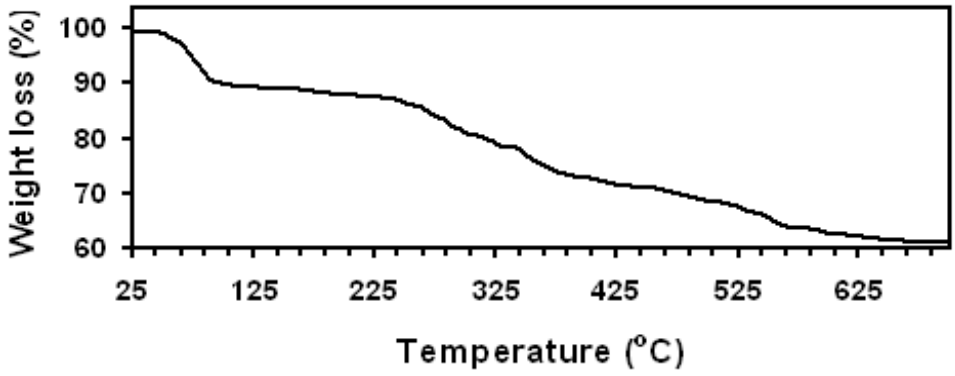

Figure S1: A thermogravimetric curve of $[\{Cd_3(Cl_2CP_2O_6Ph)_2(H_3COH)(H_2O)_5\}(H_2O)_2]_n$ (**7**) performed under synthetic air in a temperature range of 25−700 ºC and at a heating rate of 5 ºC /min.

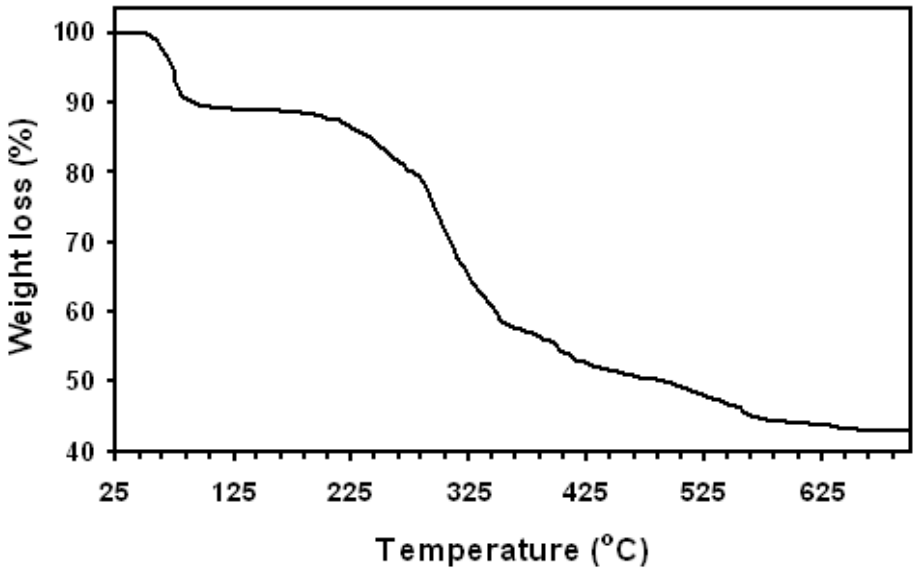

Figure S2: A thermogravimetric curve of $[\{Cd(Cl_2CP_2O_6Ph_2)(H_2O)_3\}(H_2O)]_n$ (**8**) performed under synthetic air in a temperature range of 25−700 ºC and at a heating rate of 5 ºC /min.

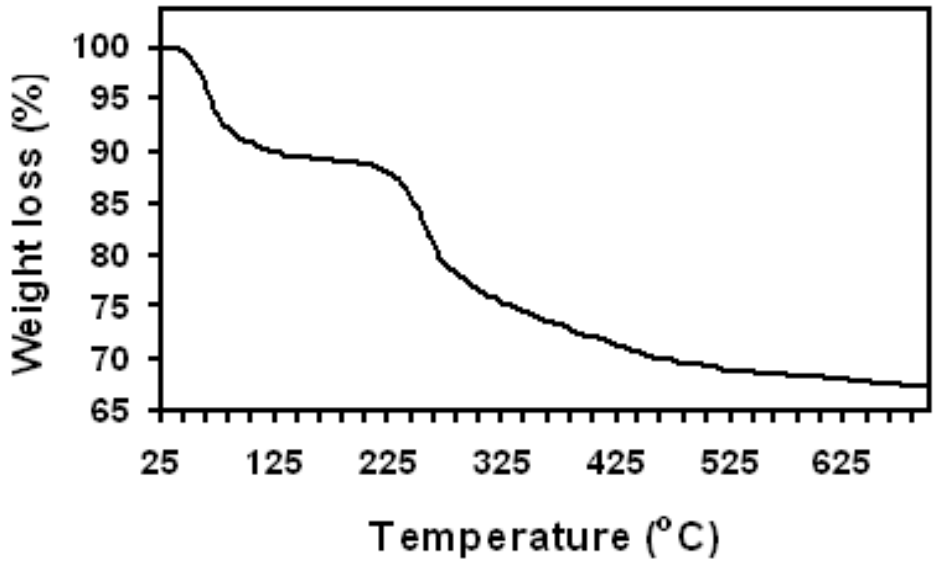

Figure S3: A thermogravimetric curve of $[\{Cd_{1.5}(Cl_2CP_2O_6Et)(H_2O)_2\}(C_3H_6O)_{0.5}\text{-}(H_2O)_{4.5}]_n$ (**9**) performed under synthetic air in a temperature range of 25−700 ºC and at a heating rate of 5 ºC /min.

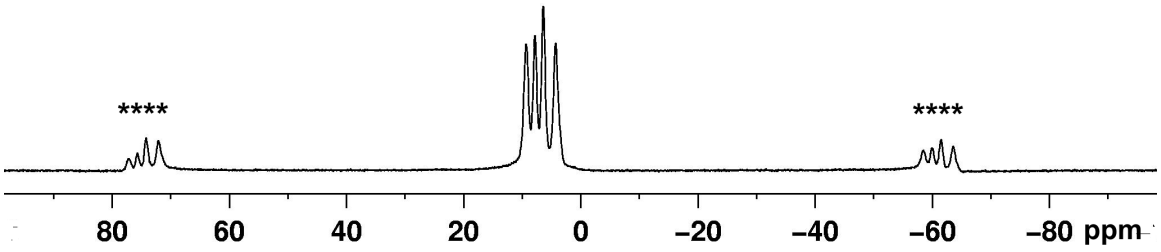

Fig S4: 31P-CP/MAS NMR spectrum of compound **7,** asterisks denote spinning sidebands.

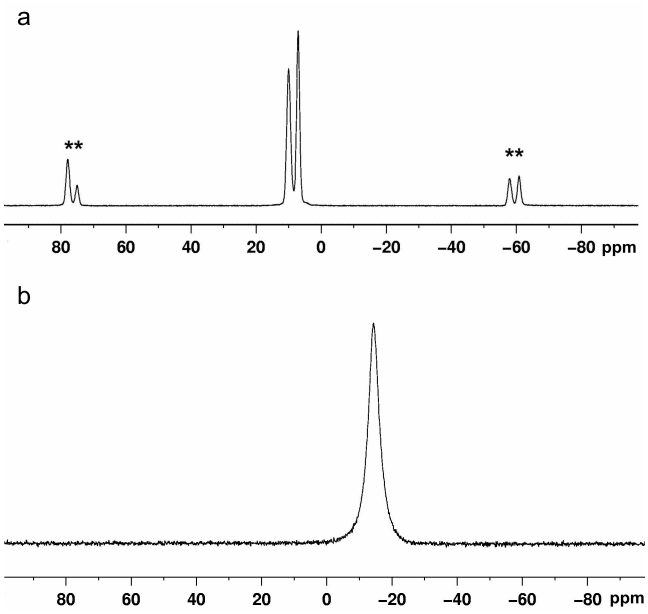

Fig. S5: (a) ^{31}P-CP/MAS NMR spectrum (top) and (b) ^{113}Cd- CP/MAS NMR spectrum (bottom) of compound **8**, asterisks denote spinning sidebands.

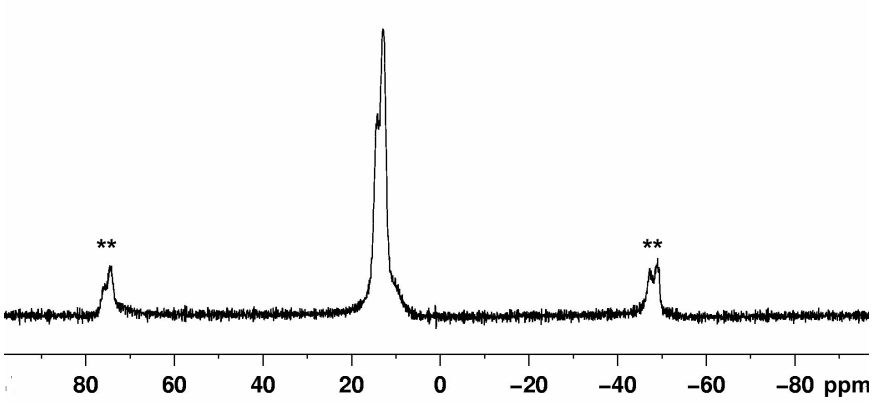

Fig S6: 31P-CP/MAS NMR spectrum of compound **9,** asterisks denote spinning sidebands.