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Synthesis and structural characterization of discrete mono-, bi-, tri- and tetranuclear complexes of cadmium(II) with triphenylphosphoniopropionate

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Abstract

Five mono-, bi-, tri- and tetranuclear cadmium(II) complexes have been synthesized from the reaction of a tertiary phosphine betaine, $Ph_3P^+(CH_2)_2CO_2^-$, with various cadmium(II) salts, namely $[Cd\{Ph_3P(CH_2)_2CO_2\}_4(H_2O)_2](ClO_4)_2 \cdot 2H_2O$ (**1**), $[CdCl_2\{Ph_3P(CH_2)_2CO_2\}_2] \cdot 7H_2O$ (**2**), $[CdI_2\{Ph_3P(CH_2)_2CO_2\}]_2$ (**3**), *trans*-$Cd(H_2O)_4[Cl_2Cd(\mu\text{-}Cl)\{Ph_3P(CH_2)_2CO_2\}]_2 \cdot 4H_2O$ (**4**) and $[Cd_2Br_4\{Ph_3P(CH_2)_2CO_2\}_2]_2 \cdot dmf$ (**5**). In complex **1** the cadmium(II) atom is located at an inversion center, and is coordinated in a nearly perfect CdO_6 octahedron with four unidentate betaine ligands defining the equatorial plane and two *trans* aqua ligands occupying the axial positions. Complex **2** exists as discrete mononuclear species which are linked by donor hydrogen bonds from the solvated water molecules to form a layer structure. Complex **3** is a discrete dimer in which the betaine ligands act in both one-atom bridge and bidentate chelate modes. Complex **4** comprises linear trimers which are joined by hydrogen bonds involving the chloro and aqua ligands and solvated water molecules to form a layer structure. Complex **5** is a novel tetranuclear molecule in which two of the four betaine ligands act in a very unusual μ_3 bridging mode.

Keywords: Crystal structures; Cadmium complexes; Phosphoniopropionate complexes

1. Introduction

The coordination chemistry of cadmium(II) in both the non-biological and biological areas has been the subject of intensive research [1]. Generally, the d^{10} electron configuration of cadmium(II) rules out a ligand-field stabilizing effect for its complexes and, as a consequence, one of its most striking features is stereochemical adaptability. A statistical study on the structural aspects of metal ion-carboxylate interactions showed that the maximum deviation of the cadmium(II) atom from the carboxylate plane can reach up to ~ 1.5 Å, but for most transition metal ions such as manganese(II, III), cobalt(II, III), nickel(II), iron(II, III), copper(I, II) and zinc(II), they tend to lie in the carboxylate plane [2]. This means that the cadmium(II) ion is much more accommodating to the arrangement of carboxylate anions around it. In fact, with few other ligand classes does cadmium(II) form so many structurally varied complexes as with carboxylic acids or carboxylic acid-like ligands [1,3].

Cadmium(II) intrinsically tends to form polymeric structures with carboxylic acids. The crystal structures of a number of simple cadmium(II) carboxylates as well as complexes with amino acids and tertiary amine betaines have been determined, most of which showing one-, two- or three-dimensional arrangements of carboxylate groups bridging adjacent Cd(II) atoms [3–11]. On the other hand, cadmium(II) carboxylates containing both monomeric and oligomeric discrete units are relatively rare. Known examples include the unusual monomeric complex $[Cd(PhOCH_2CO_2)_2(H_2O)_2]$ [12] in which the cadmium(II) atom is chelated by two carboxylic acid ligands in the equatorial plane and two *trans* aqua ligands occupying the axial positions; binuclear complexes such as $[Cd_2\{\mu\text{-}F_3CCO_2\text{-}O,O'\}_4(PPh_3)_2]$ [13], $[Cd_2(MeCO_2)\{SC(NH_2)_2\}_4]$ [14] and $[\{Cd_2(BET)_2(H_2O)_2Cl_2(\mu\text{-}Cl)_2]$ ($BET = Me_3N^+CH_2CO_2^-$) [15]; trinuclear species such as $[Cd_3(C_{19}H_{13}N_3O_2)_2(MeCO_2)_2(dmf)_2]$ [16], $[Cd_3(Hedta)_2(H_2O)_6] \cdot 4H_2O$ [17,18] and $[Cd_3(pyBET)_4Cl_6]$ [19] ($pyBET = C_5H_5N^+CH_2CO_2^-$); tetranuclear complexes such as $[Cd_4(C_{21}H_{17}N_3O_2)_2(MeCO_2)_4] \cdot (dmf) \cdot H_2O$ [16] and $[Cd_4(phdta)_2(H_2O)_8] \cdot 8H_2O$ (phdta = *p*-phenylenediamine-*N,N,N′,N′*-tetraace-

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tato) [20]. The trinuclear and tetranuclear complexes except $[Cd_3(pyBET)_4Cl_6]$ all involve multidentate ligands.

In order to synthesize cadmium(II) complexes of carboxylic acid-like ligands containing both monomeric and oligomeric discrete units, we have recently used a triphenylphosphine betaine, $Ph_3P^+(CH_2)_2CO_2^-$. Several cadmium(II) complexes containing a tetrakis(μ-carboxylato-*O,O′*) bridged dimetal core have been synthesized from this ligand and the occurrence of this structural type ascribed to the steric effect of the bulky PPh_3 group [21]. In the present study, we report the synthesis and structural characterization of a series of cadmium(II) complexes containing discrete mono-, bi-, tri- and tetranuclear units, namely $[Cd\{Ph_3P(CH_2)_2CO_2\}_4(H_2O)_2](ClO_4)_2\cdot 2H_2O$ (**1**), $[CdCl_2\{Ph_3P(CH_2)_2CO_2\}_2]\cdot 7H_2O$ (**2**), $[CdI_2\{Ph_3P(CH_2)_2CO_2\}]_2$ (**3**), *trans*-$Cd(H_2O)_4[Cl_2Cd(\mu\text{-}Cl)\{Ph_3P(CH_2)_2CO_2\}]_2\cdot 4H_2O$ (**4**) and $[Cd_2Br_4\{Ph_3P(CH_2)_2CO_2\}_2]_2\cdot$dmf (**5**).

2. Experimental

2.1. Synthesis of the complexes

$Ph_3P^+(CH_2)_2CO_2^-$ was synthesized by a literature method [22]. Cadmium(II) perchlorate was prepared from the reaction of CdO with $HClO_4$ (70%) and recrystallized in ethanol/H_2O. Solvents and other chemicals were used as purchased.

Caution: Metal perchlorates are potentially explosive in reactions with organic ligands. Only small amounts should be prepared and handled with great care.

2.1.1. Synthesis of $[Cd\{Ph_3P(CH_2)_2CO_2\}_4(H_2O)_2](ClO_4)_2\cdot 2H_2O$ (1)

To a mixture of $Ph_3P^+(CH_2)_2CO_2^-$ (336 mg, 1.0 mmol) and $Cd(ClO_4)_2\cdot xH_2O$ (203 mg) was added distilled water (~5 cm^3), and a white precipitate was formed immediately. After the slurry was stirred for about 5 min at ~60°C, CH_3CN was added until the precipitate dissolved completely. A colorless crystalline solid was obtained after the solution was allowed to stand for 2 days. Recrystallization of this product in dmf/H_2O yielded complex **1** (280 mg, 66%).

2.1.2. Synthesis of $[CdCl_2\{Ph_3P(CH_2)_2CO_2\}_2]\cdot 7H_2O$ (2)

To a mixture of $Ph_3P^+(CH_2)_2CO_2^-$ (336 mg, 1.0 mmol) and $CdCl_2\cdot 2H_2O$ (110 mg, 0.5 mmol) was added distilled water (~5 cm^3), and a white precipitate formed immediately. Then dmf was added until the precipitate dissolved completely, and the resulting solution was stirred for about 5 min at ~60°C. After the solution was allowed to stand for 3 days at ambient temperature, colorless prismatic crystals of complex **2** were obtained (370 mg, 78%).

2.1.3. Synthesis of $[CdI_2\{Ph_3P(CH_2)_2CO_2\}]_2$ (3)

Following the procedure for the preparation of complex **2**, the use of $Ph_3P^+(CH_2)_2CO_2^-$ (336 mg, 1.0 mmol) and CdI_2 (180 mg, 0.5 mmol) yielded colorless prismatic crystals of complex **3** (190 mg, 54%).

2.1.4. Synthesis of trans-$Cd(H_2O)_4[Cl_2Cd(\mu\text{-}Cl)\{Ph_3P(CH_2)_2CO_2\}]_2\cdot 4H_2O$ (4)

$Ph_3P^+(CH_2)_2CO_2^-$ (335 mg, 1.0 mmol) and $CdCl_2\cdot 2H_2O$ (445 mg, 2.0 mmol) were dissolved in CH_3CN (~10 cm^3), and the solution was stirred for about 5 min at ~60°C. After the solution was allowed to stand for 2 days at ambient temperature, colorless prismatic crystals of complex **4** were obtained (230 mg, 34%).

2.1.5. Synthesis of $[Cd_2Br_4\{Ph_3P(CH_2)_2CO_2\}_2]_2\cdot$dmf (5)

Following the procedure for the preparation of complex **2**, the use of $Ph_3P^+(CH_2)_2CO_2^-$ (340 mg, 1.0 mmol) and $CdBr_2$ (540 mg, 2.0 mmol) yielded colorless prismatic crystals of complex **5** (240 mg, 38%).

The IR spectra of complexes **1**–**5** were recorded from KBr pellets in the range 400–4000 cm^{-1} but the asymmetric stretching vibration of the carboxylate group (~1650 cm^{-1}) was masked by the absorption band of the Ph_3P group.

2.2. Crystal structure determination of the complexes

Information concerning X-ray data collection and structure refinement is summarized in Table 1. The intensities were collected at 290° K in the ω-scan mode [23] on a Nicolet R3m/V and a Siemens P4/PC four-circle diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å). Unit-cell parameters were calculated from least-squares fitting of the 2θ angles for 20 selected strong reflections. Crystal stability was monitored by recording three check reflections at intervals of 120 data measurements, and no significant variation was detected. An empirical absorption correction based on azimuthal scans was applied during intensity data processing for all five complexes.

The crystal structures of all five complexes were solved by direct methods. For complexes **1**–**4**, all non-hydrogen atoms were refined anisotropically by full-matrix least squares. For complex **5**, all the phenyl groups were treated as rigid groups (with C–C = 1.385 Å and C–C–C = 120°) and refined isotropically. The hydrogen atoms of the ligands were placed in their calculated positions with C–H = 0.96 Å, assigned fixed isotropic thermal parameters, and allowed to ride on their respective parent carbon atoms. These hydrogen atoms were included in the structure factor calculations, but their positions were not varied.

All calculations were carried out on a PC 486 using the SHELXTL-PLUS program package [24]. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [25]. Final atomic coordinates and equivalent isotropic thermal parameters for the five crystal structures, along with their

Table 1
Crystallographic data for compounds **1**–**5** ($L = Ph_3P^+(CH_2)_2CO_2^-$)

Complex	**1**	**2**	**3**	**4**	**5**
Formula	$[CdL_4(H_2O)_2](ClO_4)_2 \cdot 2H_2O$	$[CdCl_2L_2] \cdot 7H_2O$	$[CdI_2L]_2$	*trans*-$Cd(H_2O)_4[Cl_2Cd(\mu\text{-}Cl)L]_2 \cdot 4H_2O$	$[Cd_2Br_4L_2]_2 \cdot dmf$
Molecular weight	1718.7	978.1	1401	1346.6	2471
Crystal system	triclinic	orthorhombic	monoclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$Pca2_1$	$P2_1/n$	$P2_1/n$	$P2_1/c$
Crystal size (mm)	0.18×0.20×0.25	0.36×0.40×0.40	0.20×0.24×0.28	0.40×0.40×0.44	0.36×0.36×0.44
a (Å)	9.246(2)	17.496(8)	10.077(2)	8.997(1))	13.380(5)
b (Å)	13.070(3)	19.727(7)	14.839(3)	13.171(3)	14.593(3)
c (Å)	18.689(4)	13.303(2)	15.641(3)	23.000(7)	15.228(4)
α (°)	77.83(3)	90	90	90	71.79(2)
β (°)	89.68(3)	90	106.66(3)	96.47(2)	80.61(3)
γ (°)	70.24(3)	90	90	90	65.27(3)
U (Å^3)	2072(1)	4591(2)	2241(1)	2710(1)	2564(1)
Z	1	4	2	2	1
D_c (g cm^{-3})	1.377	1.415	2.077	1.650	1.601
$F(000)$	888	1500	1320	1324	1188
μ (cm^{-1})	4.75	7.17	38.51	15.74	40.45
Transmission coefficients	0.945–1.000	0.539–0.586	0.383–0.439	0.676–0.801	0.203–0.254
2θ range (°)	2–48	3–50	2–50	3–52	3–48
No. independent data	6482	4261	3906	5361	8106
No. used data, n ($\lvert F \rvert > 4\sigma(F)$)	4284	2788	2331	4315	4073
No. variables, p	539	523	245	296	248
R [a]	0.062	0.048	0.060	0.064	0.075
R' [b]	0.072	0.047	0.067	0.083	0.087
S [c]	1.36	1.32	1.16	1.64	1.63

[a] $R = \Sigma\Delta / \Sigma \lvert F_o \rvert$.

[b] $R' = [\Sigma w\Delta^2 / \Sigma \lvert F_o \rvert^2]^{1/2}$.

[c] $S = [w\Delta^2/(n-p)]^{1/2}$ where $w = [\sigma^2(F_o) + K\lvert F_o \rvert^2]^{-1}$, $\Delta = \lvert \lvert F_o \rvert - \lvert F_c \rvert \rvert$; 10^5 K = 800, 300, 1200, 20 and 1000 for complexes **1**, **2**, **3**, **4** and **5**, respectively. Extinction parameter $\chi = 0.00000$, 0.00011, 0.00019, 0.00047 and 0.00040 for complexes **1**, **2**, **3**, **4** and **5**, respectively where the 'corrected' calculated structural factor $F_{corr} = F_c(1 + 0.002\chi F_c^2/\sin 2\theta)^{-1/4}$.

estimated standard deviations, are presented in Tables 2–6, and selected bond lengths and angles are listed in Tables 7–11.

3. Results and discussion

3.1. Crystal structure of $[Cd\{Ph_3P(CH_2)_2CO_2\}_4(H_2O)_2](ClO_4)_2 \cdot 2H_2O$ (1)

Complex **1** consists of $[Cd\{Ph_3P(CH_2)_2CO_2\}_4(H_2O)_2]^{2+}$ cations, ClO_4^- anions and H_2O molecules packed in the crystal lattice. In the cation the cadmium(II) atom is located at an inversion center and six-coordinated by two *trans* aqua ligands (Cd–O = 2.308(3) Å) and two pairs of unidentate $Ph_3P^+(CH_2)_2CO_2^-$ ligands (Cd–O = 2.219(5) and 2.231(4) Å) in a nearly perfect octahedral environment (the bond angles about the Cd(II) atom ranging from 88.7–92.3°). The Cd–O(aqua) bond length in complex **1** are similar to those found in cadmium(II) maleate dihydrate (2.317(5) and 2.281(5) Å) [26] in which the cadmium(II) atom is coordinated in an analogous CdO_6 octahedral environment, but significantly longer than those in $[Cd(PA)_2(H_2O)_2]$ (PAH = phenoxyacetic acid) (2.110(5) Å) [12] in which the cadmium(II) atom is in a distorted CdO_6 octahedral environment with a pair of symmetric chelating carboxylato groups. The four carboxylate groups are arranged in such a way that each aqua ligand forms strong intramolecular hydrogen bonds (O···O = 2.682(5) and 2.704(5) Å) with the pendant oxygen atoms of two adjacent betaine ligands (Fig. 1). To our knowledge, this complex provides the first example among cadmium(II) carboxylates in which the Cd(II) atom is coordinated by four unidentate carboxylate groups. A plausible reason for the occurrence of this unusual complex is ascribed to the strong intramolecular hydrogen bonds which play a dominant role in stabilizing the octahedral coordination geometry involving both the aqua and unidentate betaine ligands. On the other hand, the Cd–O(carboxylate) distances and the geometry of the carboxylate groups in complex **1** are comparable to those in the tetrakis-μ-carboxylato-*O,O′*-bridged dicadmium(II) complexes (Table 12) [21], and so the carboxylate groups in **1** may be described as acting in a 'pseudo *syn–syn* bidentate bridging' mode.

3.2. Crystal structure of $[CdCl_2\{Ph_3P(CH_2)_2CO_2\}_2] \cdot 7H_2O$ (2)

Complex **2** consists of a packing of mononuclear species $[CdCl_2\{Ph_3P(CH_2)_2CO_2\}_2]$ and lattice H_2O molecules. The cadmium(II) atom is in a $CdCl_2O_4$ environment, being asym-

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients U_{eq} (Å$^2 \times 10^4$ for Cd, Å$^2 \times 10^3$ for other atoms) for complex **1**

Atom	x	y	z	U_{eq} [a]
Cd(1)	0	0	0	374(4)
O(1W)	2309(4)	−993(3)	−402(2)	37(1)
P(1)	5463(2)	906(1)	2355(1)	30(1)
C(1)	4561(5)	2789(4)	1219(3)	55(1)
C(2)	4300(5)	3912(4)	928(4)	76(1)
C(3)	4493(5)	4582(4)	1352(4)	69(1)
C(4)	4972(5)	4162(4)	2073(4)	67(1)
C(5)	5251(5)	3043(4)	2385(3)	50(1)
C(6)	5027(4)	2358(4)	1949(3)	34(1)
C(7)	3128(5)	1551(4)	3286(3)	56(1)
C(8)	2320(5)	1363(4)	3887(3)	69(1)
C(9)	2762(5)	354(4)	4351(3)	72(1)
C(10)	4010(5)	−520(4)	4219(4)	75(1)
C(11)	4806(5)	−334(4)	3611(3)	62(1)
C(12)	4388(4)	702(4)	3148(3)	37(1)
C(13)	8536(4)	−180(4)	2184(3)	37(1)
C(14)	10076(4)	−636(4)	2418(3)	48(1)
C(15)	10552(5)	−663(4)	3126(3)	50(1)
C(16)	9513(5)	−204(4)	3588(3)	55(1)
C(17)	7960(5)	257(4)	3353(3)	48(1)
C(18)	7459(4)	283(4)	2651(3)	32(1)
C(19)	4974(4)	226(4)	1701(3)	40(1)
C(20)	3254(4)	507(4)	1573(3)	42(1)
C(21)	2754(4)	65(4)	972(3)	40(1)
O(1)	3787(4)	−522(4)	658(3)	77(1)
O(2)	1356(4)	338(3)	841(2)	52(1)
P(2)	1298(2)	4196(1)	−2358(1)	31(1)
C(22)	−1379(5)	5405(4)	−3228(3)	53(1)
C(23)	−2435(5)	5631(4)	−3827(4)	68(1)
C(24)	−2066(5)	4968(4)	−4328(3)	76(1)
C(25)	−724(5)	4092(5)	−4241(3)	81(1)
C(26)	312(5)	3864(4)	−3654(3)	61(1)
C(27)	−21(4)	4542(4)	−3144(3)	35(1)
C(28)	3620(5)	4128(4)	−3313(3)	49(1)
C(29)	5114(5)	3814(4)	−3482(3)	60(1)
C(30)	6259(5)	3125(4)	−2967(4)	64(1)
C(31)	5903(5)	2730(4)	−2277(4)	62(1)
C(32)	4402(4)	3022(4)	−2089(3)	48(1)
C(33)	3231(4)	3721(4)	−2617(3)	35(1)
C(34)	1170(5)	5263(4)	−1222(3)	63(1)
C(35)	1041(5)	6173(4)	−933(4)	84(1)
C(36)	838(5)	7194(4)	−1401(4)	75(1)
C(37)	736(5)	7314(4)	−2123(4)	61(1)
C(38)	843(4)	6414(4)	−2425(3)	45(1)
C(39)	1038(4)	5380(4)	−1974(3)	34(1)
C(40)	970(4)	3091(4)	−1697(3)	40(1)
C(41)	−661(4)	3407(4)	−1449(3)	45(1)
C(42)	−876(4)	2499(4)	−836(3)	33(1)
O(3)	−1992(4)	2805(3)	−474(3)	60(1)
O(4)	78(4)	1541(3)	−762(2)	50(1)
O(2W)	6674(4)	−1906(4)	267(3)	88(1)
Cl(1)	2522(3)	7281(2)	5483(1)	70(1)
O(5)	1924(5)	6802(5)	5918(5)	193(1)
O(6)	3695(5)	7732(5)	5734(4)	102(1)
O(7)	3720(5)	6320(5)	5315(5)	114(1)
O(8)	1895(5)	7900(5)	4860(5)	146(1)
O(5′)	3005(5)	7093(5)	4841(4)	127(1)
O(6′)	1300(5)	6661(5)	5740(4)	74(1)
O(7′)	3288(5)	7166(5)	6077(5)	169(1)
O(8′)	1424(5)	8405(5)	5359(5)	116(1)

[a] U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor.
Atoms O(5)–O(8) and O(5′)–O(8′) belong to a two-fold distorted perchlorate group and each has a site occupancy of 1/2.

Table 3
Atomic coordinates ($\times 10^5$ for Cd, $\times 10^4$ for other atoms) and equivalent isotropic displacement coefficients U_{eq} (Å$^2 \times 10^4$ for Cd, Å$^2 \times 10^3$ for other atoms) for complex **2**

Atom	x	y	z	U_{eq} [a]
Cd(1)	39519(5)	23763(3)	7073	529(3)
Cl(1)	4932(2)	2752(2)	8307(3)	79(1)
Cl(2)	3023(2)	1627(2)	7940(3)	84(1)
P(1)	3147(2)	5101(1)	4029(2)	42(1)
C(1)	2794(7)	6070(5)	5481(9)	57(5)
C(2)	2971(8)	6561(6)	6146(10)	73(6)
C(3)	3719(9)	6791(6)	6245(10)	72(5)
C(4)	4289(7)	6510(6)	5667(9)	64(5)
C(5)	4110(6)	5998(6)	4991(8)	52(4)
C(6)	3354(6)	5791(5)	4880(8)	42(4)
C(7)	3680(6)	4658(6)	2207(11)	56(4)
C(8)	4024(7)	4749(8)	1268(10)	69(5)
C(9)	4278(7)	5372(8)	963(10)	74(6)
C(10)	4205(7)	5929(8)	1583(11)	67(5)
C(11)	3860(6)	5839(7)	2528(9)	47(4)
C(12)	3598(6)	5218(5)	2829(8)	40(4)
C(13)	1779(6)	4443(6)	3679(8)	47(4)
C(14)	1018(8)	4433(7)	3353(9)	69(5)
C(15)	666(7)	5030(8)	3116(9)	69(5)
C(16)	1013(7)	5637(7)	3176(9)	66(5)
C(17)	1757(6)	5659(6)	3504(8)	54(5)
C(18)	2136(5)	5069(5)	3768(7)	39(3)
C(19)	3491(7)	4333(5)	4572(9)	57(4)
C(20)	3198(8)	4189(6)	5624(9)	62(5)
C(21)	3524(9)	3540(6)	6088(10)	64(5)
O(1)	3124(5)	3265(4)	6782(6)	77(4)
O(2)	4155(6)	3329(4)	5786(7)	75(4)
P(2)	4460(2)	428(1)	2853(2)	44(1)
C(22)	5812(7)	1156(6)	2655(8)	57(5)
C(23)	6550(8)	1262(8)	2332(11)	80(6)
C(24)	6949(8)	733(9)	1930(13)	91(7)
C(25)	6611(9)	120(8)	1812(10)	89(7)
C(26)	5857(6)	2(6)	2123(11)	68(4)
C(27)	5442(6)	532(6)	2540(8)	51(4)
C(28)	3892(7)	−183(6)	1135(9)	56(4)
C(29)	3509(8)	−201(7)	238(10)	66(5)
C(30)	3145(7)	364(7)	−88(10)	72(5)
C(31)	3142(7)	949(7)	465(9)	67(5)
C(32)	3516(6)	980(5)	1382(8)	53(4)
C(33)	3901(6)	401(5)	1726(7)	43(4)
C(34)	3566(8)	−545(6)	3645(9)	60(5)
C(35)	3399(8)	−1107(7)	4269(10)	77(6)
C(36)	3995(12)	−1444(7)	4718(11)	91(7)
C(37)	4725(10)	−1247(7)	4604(10)	85(7)
C(38)	4899(8)	−697(6)	4003(10)	63(5)
C(39)	4314(7)	−346(5)	3521(8)	48(4)
C(40)	4151(6)	1097(5)	3664(8)	53(4)
C(41)	4585(7)	1073(6)	4658(8)	62(5)
C(42)	4285(8)	1567(5)	5441(8)	47(4)
O(3)	4719(5)	1648(4)	6195(5)	63(3)
O(4)	3654(5)	1830(4)	5358(6)	58(3)
O(1W)	2689(8)	2759(4)	4318(11)	155(7)
O(2W)	5028(7)	2874(6)	4011(10)	157(6)
O(3W)	7935(7)	2673(5)	3258(10)	142(6)
O(4W)	6389(6)	1995(7)	6355(11)	147(6)
O(5W)	3901(10)	2761(6)	2419(11)	219(10)
O(6W)	3787(7)	2921(8)	320(10)	171(7)
O(7W)	6572(8)	2486(6)	4374(11)	179(8)

[a] U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4
Atomic coordinates ($\times 10^5$ for Cd and I, $\times 10^4$ for other atoms) and equivalent isotropic displacement coefficients U_{eq} ($Å^2 \times 10^4$ for Cd and I, $Å^2 \times 10^3$ for other atoms) for complex 3

Atom	x	y	z	U_{eq} [a]
Cd(1)	10158(11)	60060(7)	56761(7)	372(4)
I(1)	−2442(12)	75599(8)	49913(7)	547(4)
I(2)	21829(11)	57912(6)	74512(6)	479(4)
P(1)	2436(4)	3371(2)	2514(2)	27(1)
C(1)	1365(16)	4852(11)	1466(9)	47(6)
C(2)	1350(19)	5463(12)	802(11)	62(7)
C(3)	2334(19)	5466(12)	367(12)	57(8)
C(4)	3376(21)	4850(14)	589(12)	70(9)
C(5)	3462(17)	4219(10)	1251(10)	50(6)
C(6)	2432(14)	4221(9)	1691(8)	32(5)
C(7)	233(16)	2643(11)	1186(10)	51(6)
C(8)	−847(18)	2025(15)	870(12)	73(8)
C(9)	−1037(20)	1381(13)	1450(14)	70(9)
C(10)	−202(19)	1331(12)	2312(12)	60(8)
C(11)	803(17)	1925(11)	2606(10)	52(6)
C(12)	1062(13)	2578(9)	2057(8)	30(5)
C(13)	4229(16)	2099(11)	2242(10)	46(6)
C(14)	5440(17)	1594(10)	2478(11)	50(7)
C(15)	6384(15)	1703(11)	3296(12)	50(7)
C(16)	6162(16)	2343(9)	3917(11)	46(6)
C(17)	4975(13)	2868(9)	3668(9)	35(5)
C(18)	4020(14)	2743(9)	2836(9)	31(5)
C(19)	2023(13)	3897(9)	3446(8)	29(5)
C(20)	2842(16)	4749(10)	3843(9)	40(6)
C(21)	2220(14)	5195(9)	4529(8)	29(5)
O(1)	1096(11)	4946(7)	4608(7)	51(4)
O(2)	2874(11)	5816(8)	4961(7)	59(5)

[a] U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 5
Atomic coordinates ($\times 10^5$ for Cd, $\times 10^4$ for other atoms) and equivalent isotropic displacement coefficients U_{eq} ($Å^2 \times 10^4$ for Cd, $Å^2 \times 10^3$ for other atoms) for complex 4

Atom	x	y	z	U_{eq} [a]
Cd(1)	9316(7)	19864(5)	1635(2)	435(2)
Cd(2)	5000	0	0	414(3)
Cl(1)	1868(4)	3664(2)	470(1)	82(1)
Cl(2)	−1227(3)	2190(3)	−572(1)	75(1)
Cl(3)	2900(3)	1263(2)	−431(1)	53(1)
P(1)	−1490(2)	−700(2)	2451(1)	34(1)
C(1)	650(10)	22(7)	3330(3)	51(3)
C(2)	1142(12)	671(8)	3780(4)	61(3)
C(3)	186(13)	1406(8)	3965(4)	63(4)
C(4)	−1247(14)	1492(9)	3685(5)	72(4)
C(5)	−1743(11)	842(7)	3231(4)	58(3)
C(6)	−774(9)	92(6)	3054(3)	40(2)
C(7)	−4420(9)	−1183(7)	2014(3)	46(3)
C(8)	−5824(10)	−1552(8)	2073(4)	55(3)
C(9)	−6228(10)	−1750(7)	2622(4)	54(3)
C(10)	−5253(12)	−1583(8)	3112(4)	63(4)
C(11)	−3823(10)	−1223(8)	3063(3)	51(3)
C(12)	−3405(8)	−1010(6)	2512(3)	36(2)
C(13)	−93(10)	−2299(6)	1945(3)	44(3)
C(14)	571(12)	−3244(7)	1953(4)	58(3)
C(15)	821(11)	−3792(7)	2474(5)	61(3)
C(16)	426(12)	−3378(8)	2983(4)	59(3)
C(17)	−231(11)	−2417(7)	2986(3)	51(3)
C(18)	−471(8)	−1874(6)	2460(3)	39(2)
C(19)	−1352(9)	−12(6)	1779(3)	39(2)
C(20)	242(10)	302(7)	1702(3)	49(3)
C(21)	347(10)	917(6)	1142(3)	42(2)
O(1)	1609(7)	986(5)	964(3)	58(2)
O(2)	−780(7)	1336(6)	887(3)	64(2)
O(1W)	3607(8)	−463(5)	727(3)	58(2)
O(2W)	6105(7)	1223(5)	608(3)	57(2)
O(3W)	5531(12)	3241(7)	593(4)	94(4)
O(4W)	8009(15)	4421(10)	432(5)	131(6)

[a] U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor.

metrically chelated by two $Ph_3P^+(CH_2)_2CO_2^-$ ligands (Cd–O 2.306(9), 2.567(9), Δ(Cd–O) = 0.263 Å; 2.287(8), 2.576(8), Δ(Cd–O) = 0.289 Å) with O···O bite distances of 2.241 and 2.200 Å, and surrounded by two *cis* chloro ligands (2.487(4) and 2.481(4) Å) with a Cl–Cd–Cl angle of 108.8(1)° (Fig. 2). The dihedral angles between the $CdCl_2$ plane and each of the two carboxylato chelate rings are 70.9 and 74.0°, and that between the chelate rings is 72.2°. The coordination geometry about the cadmium(II) atom is best described as a distorted octahedron with the chelate bond angles O–Cd–O at 53.4(3) and 54.5(3)°. It is noteworthy that the angles between the vectors from the cadmium(II) atom to the midpoints of the O···O line of individual carboxylato groups and to the chloro ligands lie in the range 98.5–124.5°, which are close to the expected tetrahedral bond angle in an idealized environment. This structural feature has been noted in a few eight-coordinated complexes, where the ligand bite distances are less than 2.2 Å [26–28]. However, the structure of complex 2 is different from that of $[Cd(PhOCH_2CO_2)_2(H_2O)_2]$ [12] in which the cadmium(II) atom is symmetrically chelated by a pair of carboxylate ligands (Cd–O = 2.363(4), 2.365(4) Å) in the equatorial plane and the axial positions are occupied by two water molecules. The tightly bound Cd–O bond lengths in 2 are significantly longer than those in $[Cd(PhOCH_2CO_2)_2(H_2O)_2]$, being consistent with the asymmetric chelate mode of the betaine ligand which releases the high strain imposed by the four-membered chelate ring.

The Cd–Cl distances in complex 2 are significantly longer than that found in $[Cd\{\mu\text{-}Ph_3P(CH_2)_2CO_2\text{-}O,O'\}_2Cl]_2(ClO_4)_2$ (2.432(8) Å) [21] in which the Cd(II) atom is five-coordinated, and is similar to those in $[Cd_2(BET)_2(H_2O)_2Cl_2(\mu\text{-}Cl)_2]$ (Cd–Cl(terminal) = 2.480(2) Å) [15] and $[Cd_3(pyBET)_4Cl_6]$ (2.497(1) Å) [19].

Another interesting feature of complex 2 is that it is highly hydrated. Consequently the monomeric entities are linked by donor hydrogen bonds from solvated water molecules to the chloro ligands and oxygen atoms of the betaine ligands to form a polymeric chain extending parallel to *c*. Such chains are further joined by hydrogen bonds to form a layer which is perpendicular to *b* and intersects it at *b*/4. Hence the interlayer distance between adjacent layers is *b*/2 = 9.864 Å. Within each layer, eight water molecules and one chloro ligand form a nine-membered ring and two of the water molecules are shared by adjacent rings (Fig. 3). The PPh_3 groups

Table 6
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients U_{eq} ($Å^2 \times 10^3$) for complex **5**

Atom	x	y	z	U_{eq} [a]
Cd(1)	6168(1)	−1326(1)	−157(1)	51(1)
Cd(2)	4719(1)	−1380(1)	2485(1)	73(1)
Br(1)	8225(2)	−1632(2)	−674(2)	76(1)
Br(2)	5883(2)	−3069(1)	52(1)	72(1)
Br(3)	6701(2)	−1878(1)	1741(1)	65(1)
Br(4)	4783(3)	−2839(2)	3983(2)	129(2)
P(1)	2359(4)	−934(4)	−1583(3)	55(2)
C(1)	3360(12)	−99(10)	−3138(10)	105(7)
C(2)	3793	−18	−4044	143(10)
C(3)	3825	−716	−4509	146(10)
C(4)	3424	−1495	−4068	185(13)
C(5)	2991	−1576	−3163	135(9)
C(6)	2959	−878	−2698	73(5)
C(7)	3241(8)	−3074(10)	−977(8)	86(6)
C(8)	3205	−4058	−559	107(7)
C(9)	2199	−4141	−245	101(7)
C(10)	1229	−3241	−350	98(7)
C(11)	1265	−2257	−768	72(5)
C(12)	2271	−2174	−1082	56(4)
C(13)	285(12)	119(10)	−2217(9)	109(8)
C(14)	−745	949	−2343	133(9)
C(15)	−1001	1767	−1947	121(8)
C(16)	−229	1755	−1424	112(8)
C(17)	800	925	−1298	89(6)
C(18)	1057	107	−1694	59(5)
C(19)	3237(13)	−817(13)	−906(10)	55(9)
C(20)	2912(13)	−1071(13)	150(11)	60(10)
C(21)	3683(12)	−989(12)	731(14)	47(9)
O(1)	4304(8)	−507(8)	338(7)	47(5)
O(2)	3605(9)	−1394(9)	1583(8)	66(7)
P(2)	2296(5)	3596(4)	3047(5)	95(3)
C(22)	384(8)	5213(10)	2620(8)	97(9)
C(23)	−524	5832	2065	114(11)
C(24)	−652	532	320	107(10)
C(25)	128	613	1129	156(16)
C(26)	1037	3994	1684	105(10)
C(27)	1165	4294	2429	98(13)
C(22′)	564	5439	2043	31(17)
C(23′)	−463	6006	646	75(28)
C(24′)	−1080	5480	1542	88(32)
C(25′)	−670	4387	1836	120(42)
C(26′)	356	3821	2233	87(30)
C(27′)	974	4347	2337	29(23)
C(28)	3546	4690	1884	138(18)
C(29)	4057	5397	1662	146(20)
C(30)	3962	5972	2273	93(10)
C(31)	3357	5839	3106	116(13)
C(32)	2846	5131	3328	127(14)
C(33)	2940	4557	2717	88(10)
C(28′)	3282	4888	2070	168(47)
C(29′)	4083	5303	1925	98(31)
C(30′)	4858	4949	2594	91(23)
C(31′)	4832	4179	3407	132(31)
C(32′)	4031	3764	3552	108(26)
C(33′)	3256	4119	2884	57(16)
C(34)	901(15)	3163(14)	4507(14)	182(13)
C(35)	631	2857	5447	240(18)
C(36)	1362	2657	6105	156(11)
C(37)	2363	2763	5824	217(16)
C(38)	2633	3069	4884	171(12)
C(39)	1902	3269	4225	101(7)
C(40)	3246(27)	2628(17)	2474(24)	86(18)
C(40′)	2912(40)	2210(17)	3174(28)	142(25)
C(41)	3093(32)	1600(23)	2857(33)	152(26)
C(41′)	3769(35)	1904(20)	2417(27)	113(21)
C(42)	4007(17)	775(14)	2442(15)	94(7)
O(3)	3961(13)	−22(13)	3109(11)	122(5)
O(4)	4363(9)	666(9)	1709(8)	71(3)
Solvated dmf molecule				
C(43)	7601(45)	4332(36)	4266(28)	184(26)
C(44)	8495(32)	3229(28)	3226(29)	140(19)
N(1)	7609(28)	4150(26)	3462(22)	132(14)
C(45)	6757(33)	4897(32)	2800(29)	159(22)
O(5)	7983(93)	3575(56)	4955(32)	575(80)

[a] U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor.
Atoms C(22)–C(27) and C(22′)–C(27′) belong to a two-fold disordered phenyl group. For atoms C(22)–C(27) each has a site occupancy of 0.78, and for atoms C(22′)–C(27′) each has a site occupancy of 0.22.
Atoms C(28)–C(33) and C(28′)–C(33′) belong to a two-fold disordered phenyl group. For atoms C(28)–C(33) each has a site occupancy of 0.69, and for atoms C(28′)–C(33′) each has a site occupancy of 0.31.
Atoms C(40), C(41) and C(40′)–C(41′) belong to a disordered CH_2–CH_2 chain. For atoms C(40) and C(41) each has a site occupancy of 0.51, and for atoms C(40′), C(41′) each has a site occupancy of 0.49.
Atoms C(43)–O(5) represent a disordered dmf molecule and each has a occupancy of 1/2.

protrude on both sides of each layer and are located above the nine-membered rings.

3.3. Crystal Structure of $[CdI_2\{Ph_3P(CH_2)_2CO_2\}]_2$ (3)

Complex **3** comprises a packing of discrete $[CdI_2\{Ph_3P(CH_2)_2CO_2\}]_2$ molecules in the crystal lattice. As depicted in Fig. 4, two cadmium(II) atoms related by an inversion center are linked by the oxygen atoms of two $Ph_3P^+(CH_2)_2CO_2^-$ ligands (Cd(1)–O(1) = 2.31(1) Å, Cd(1)–O(1a) = 2.49(1) Å) to give a Cd_2O_2 unit. Each betaine ligand also acts in a chelate mode toward a cadmium(II) atom (Cd(1)–O(2) = 2.46(1) Å, Cd(1)–O(1) = 2.31(1) Å), whose distorted trigonal-bipyramidal coordination polyhedron is completed by two iodo ligands (Cd–I = 2.701(2) and 2.706(1) Å; I–Cd–I = 121.6(1)°). The non-bonded Cd···Cd separation of 3.885(1) Å in complex **3** is much longer than those (3.278, 3.361 Å) found in the tetrakis-μ-carboxylato-*O,O′*-dicadmium(II) paddle wheel-like complexes of the same betaine ligand [21]. On the other hand, all six atoms Cd(1), Cd(1a), O(1), O(2), O(1a) and O(2a) lie in a plane with a mean atomic deviation of 0.012 Å.

In complex **3** the betaine ligand exhibits both mono-atom bridging and bidentate chelate modes which is relatively rare among metal carboxylates [29–34]. Examples of this coordination mode of carboxylato groups for cadmium(II) complexes as well as the relevant Cd–O bond lengths are listed in Table 13. The values of d_1, d_2 and d_3 do not show any obvious trend. In complex **3**, $[Cd(O_2CMe)_2]\cdot 2H_2O$ [35]

Table 7
Selected bond lengths (Å) and angles (°) for complex **1**

Cd(1)–O(1w)	2.308 (3)	Cd(1)–O(2)	2.219 (5)
Cd(1)–O(4)	2.231 (4)	C(21)–O(1)	1.239 (6)
C(21)–O(2)	1.230 (5)	C(42)–O(3)	1.229 (6)
C(42)–O(4)	1.244 (5)		
O(1w)–Cd(1)–O(2)	87.7(1)	O(1w)–Cd(1)–O(4)	89.1(1)
O(2)–Cd(1)–O(4)	88.5(2)	O(2)–Cd(1)–O(1wa)	92.3(1)
O(4)–Cd(1)–O(1wa)	90.9(1)	O(1w)–Cd(1)–O(2a)	92.3(1)
O(2)–Cd(1)–O(2a)	180.0(1)	O(4)–Cd(1)–O(2a)	91.5(2)
O(1wa)–Cd(1)–O(2a)	87.7(1)	O(1w)–Cd(1)–O(4a)	90.9(1)
O(2)–Cd(1)–O(4a)	91.5(2)	O(4)–Cd(1)–O(4a)	180.0(1)
O(1wa)–Cd(1)–O(4a)	89.1(1)	O(2a)–Cd(1)–O(4a)	88.5(2)
O(1)–C(21)–O(2)	127.0(6)	Cd(1)–O(2)–C(21)	131.4(4)
O(3)–C(42)–O(4)	127.2(5)	Cd(1)–O(4)–C(42)	126.7(3)
Hydrogen bonds			
O(1W)···O(1)	2.704(5)	O(1W)···O(3a)	2.682(5)
O(2W)···O(1)	2.865(5)		
O(1W)···O(1)···O(3a)	94.2(1)	O(2W)···O(1)···O(1W)	89.9(1)

Symmetry code: (a) $-x, -y, -z$.

Table 8
Selected bond lengths (Å) and angles (°) for complex **2**

Cd(1)–Cl(1)	2.487 (4)	Cd(1)–Cl(2)	2.481 (4)
Cd(1)–O(1)	2.306 (9)	Cd(1)–O(2)	2.567 (9)
Cd(1)–O(3)	2.287 (8)	Cd(1)–O(4)	2.576 (8)
C(21)–O(1)	1.28 (2)	C(21)–O(2)	1.25 (2)
C(42)–O(3)	1.27 (1)	C(42)–O(4)	1.22 (2)
Cl(1)–Cd(1)–Cl(2)	108.8(1)	Cl(1)–Cd(1)–O(1)	108.5(2)
Cl(2)–Cd(1)–O(1)	96.8(2)	Cl(1)–Cd(1)–O(2)	97.3(2)
Cl(2)–Cd(1)–O(2)	146.8(2)	O(1)–Cd(1)–O(2)	54.5(3)
Cl(1)–Cd(1)–O(3)	96.9(2)	Cl(2)–Cd(1)–O(3)	104.4(2)
O(1)–Cd(1)–O(3)	139.5(3)	O(2)–Cd(1)–O(3)	92.1(3)
Cl(1)–Cd(1)–O(4)	148.1(2)	Cl(2)–Cd(1)–O(4)	91.7(2)
O(1)–Cd(1)–O(4)	92.5(3)	O(2)–Cd(1)–O(4)	75.2(3)
O(3)–Cd(1)–O(4)	53.4(3)	C(20)–C(21)–O(1)	116(1)
C(20)–C(21)–O(2)	119(1)	O(1)–C(21)–O(2)	125(1)
Cd(1)–O(1)–C(21)	95.8(8)	Cd(1)–O(2)–C(21)	84.7(7)
O(3)–C(42)–O(4)	124(1)	Cd(1)–O(3)–C(42)	97.6(7)
Cd(1)–O(4)–C(42)	85.1(6)		
Hydrogen bond			
Cl(1)···O(6wa)	3.361(7)	Cl(2)···O(1wb)	3.145(7)
O(2)···O(2w)	2.95(1)	O(4)···O(1w)	2.85(1)
O(1w)···O(6wb)	2.92(1)	O(5w)···O(6w)	2.82(1)
O(2w)···O(5w)	2.90(1)	O(2w)···O(7w)	2.85(1)
O(7w)···O(3w)	2.83(1)	O(7w)···O(4w)	2.83(1)
O(1w)···O(4)–Cd(1)	106.3(4)	O(2w)···O(2)–Cd(1)	112.5(4)
Cl(1)–Cd(1)···O(6wa)	98.3(2)	Cl(2)–Cd(1)···O(1wb)	96.2(2)
O(2w)···O(5w)···O(6w)	140(1)	O(5w)···O(2w)···O(2)	105(1)
O(7w)···O(2w)···O(2)	116(1)	O(5w)···O(2w)···O(7w)	138(1)
O(2w)···O(7w)···O(3w)	132(1)	O(2w)···O(7w)···O(4w)	98(1)
O(3w)···O(7w)···O(4w)	129(1)		

Symmetry codes: (a) $x, y, 1+z$; (b) $1/2-x, y, 1/2+z$.

and $[Cd\{Me_3N(CH_2)_2CO_2\}(NCS)_2]$ [11] d_3 is greater than d_2, but the reverse relation holds for all other complexes presented in Table 13, although theoretical and experimental studies have indicated that the *syn* lone pairs of the carboxylato group are more basic than the *anti* lone pairs [2,39]. These results suggest that the Cd–O bond lengths d_1, d_2 and

Table 9
Selected bond lengths (Å) and angles (°) for complex 3

Cd(1)–I(1)	2.701 (2)	Cd(1)–I(2)	2.706(1)
Cd(1)–O(1)	2.31 (1)	Cd(1)–O(2)	2.46 (1)
Cd(1)–O(1a)	2.49 (1)	C(21)–O(1)	1.23 (2)
C(21)–O(2)	1.22 (2)		
I(1)–Cd(1)–I(2)	121.6(1)	I(1)–Cd(1)–O(1)	113.8(2)
I(2)–Cd(1)–O(1)	124.5(2)	I(1)–Cd(1)–O(2)	104.5(3)
I(2)–Cd(1)–O(2)	106.8(2)	O(1)–Cd(1)–O(2)	53.4(4)
I(1)–Cd(1)–O(1a)	97.7(2)	I(2)–Cd(1)–O(1a)	102.4(2)
O(1)–Cd(1)–O(1a)	71.9(5)	O(2)–Cd(1)–O(1a)	125.3(4)
C(20)–C(21)–O(1)	121(1)	C(20)–C(21)–O(2)	117(1)
O(1)–C(21)–O(2)	123(2)	Cd(1)–O(1)–C(21)	95.3(8)
Cd(1)–O(1)–Cd(1a)	108(1)	C(21)–O(1)–Cd(1a)	157(1)
Cd(1)–O(2)–C(21)	89(1)		

Symmetry code: (a) $-x, 1-y, 1-z$.

Table 10
Selected bond lengths (Å) and angles (°) for complex 4

Cd(1)–Cl(1)	2.440 (3)	Cd(1)–Cl(2)	2.442 (3)
Cd(1)–Cl(3)	2.541 (2)	Cd(1)–O(1)	2.290 (6)
Cd(1)–O(2)	2.541 (7)	Cd(2)–Cl(3)	2.626 (2)
Cd(2)–O(1W)	2.283 (7)	Cd(2)–O(2W)	2.285 (6)
C(21)–O(1)	1.25 (1)	C(21)–O(2)	1.24 (1)
Cl(1)–Cd(1)–Cl(2)	108.8(1)	Cl(1)–Cd(1)–Cl(3)	104.8(1)
Cl(2)–Cd(1)–Cl(3)	102.5(1)	Cl(1)–Cd(1)–O(1)	103.7(2)
Cl(2)–Cd(1)–O(1)	137.6(2)	Cl(3)–Cd(1)–O(1)	94.5(2)
Cl(1)–Cd(1)–O(2)	109.3(2)	Cl(2)–Cd(1)–O(2)	89.8(2)
Cl(3)–Cd(1)–O(2)	137.4(2)	O(1)–Cd(1)–O(2)	53.5(2)
Cl(3)–Cd(2)–O(1W)	90.8(2)	Cl(3)–Cd(2)–O(2W)	91.7(2)
O(1W)–Cd(2)–O(2W)	88.7(2)	Cl(3)–Cd(2)–Cl(3a)	180.0(1)
O(1W)–Cd(2)–Cl(3a)	89.2(2)	O(2W)–Cd(2)–Cl(3a)	88.3(2)
Cl(3)–Cd(2)–O(1Wa)	89.2(2)	O(1W)–Cd(2)–O(1Wa)	180.0(1)
O(2W)–Cd(2)–O(1Wa)	91.3(2)	Cl(3a)–Cd(2)–O(1Wa)	90.8(2)
Cl(3)–Cd(2)–O(2Wa)	88.3(2)	O(1W)–Cd(2)–O(2Wa)	91.3(2)
O(2W)–Cd(2)–O(2Wa)	180.0(1)	Cl(3a)–Cd(2)–O(2Wa)	91.7(2)
O(1Wa)–Cd(2)–O(2Wa)	88.7(2)	Cd(1)–Cl(3)–Cd(2)	123.4(1)
O(1)–C(21)–O(2)	122.4(7)	Cd(1)–O(1)–C(21)	97.8(5)
Cd(1)–O(2)–C(21)	86.3(5)		
Hydrogen bond			
O(3W)···Cl(1)	3.32(1)	O(4Wd)···Cl(1)	3.28(1)
O(1Wc)···Cl(2)	3.12(1)	O(1W)···O(1)	2.72(1)
O(2Wb)···O(2)	2.81(1)	O(2W)···O(3W)	2.71(1)
O(3W)···O(4W)	2.78(1)	O(4wb)···Cl(1)	3.60(1)
O(3W)···Cl(1)–Cd(1)	100.4(2)	O(4Wd)···Cl(1)–Cd(1)	123.3(2)
O(1Wc)···Cl(2)–Cd(1)	111.4(2)	O(2Wb)···O(2)–Cd(1)	122.1(2)
O(3W)···O(2W)–Cd(2)	128.0(2)	O(4W)···O(3W)···O(2W)	113.3

Symmetry codes: (a) $1-x, -y, -z$; (b) $-1+x, y, z$.

d_3 are mainly influenced by geometrical factors rather than the electronic properties of the lone pairs of the carboxylato group.

3.4. *Crystal structure of trans-$Cd(H_2O)_4[Cl_2Cd(\mu\text{-}Cl)\{Ph_3P(CH_2)_2CO_2\}]_2 \cdot 2H_2O$ (4)*

Complex 4 consists of discrete centrosymmetric *trans*-$Cd(H_2O)_4[Cl_2Cd(\mu\text{-}Cl)\{Ph_3P(CH_2)_2CO_2\}]_2$ and water molecules packed in the crystal lattice. In the chloro-bridged trinuclear molecule the cadmium(II) atoms are in two kinds of crystallographically and chemically distinct environments (Fig. 5). The central Cd(2) atom at an inversion center is coordinated in an elongated octahedral environment by four aqua ligands lying in the equatorial plane (Cd–O = 2.283(7) and 2.285(6) Å) and two chloro ligands occupying the axial positions (Cd–Cl = 2.626(2) Å), whereas the terminal Cd(1) atom is five-coordinated, which is relatively rare in cadmium(II) complexes [40]. The coordination geometry about Cd(1) is best described as distorted trigonal bipyr-

Table 11
Selected bond lengths (Å) and angles (°) for complex 5

Cd(1)–Br(1)	2.624 (3)	Cd(1)–Br(2)	2.643 (3)
Cd(1)–Br(3)	2.871 (3)	Cd(1)–O(1)	2.381 (9)
Cd(1)–O(1a)	2.41 (1)	Cd(1)–O(4a)	2.36 (1)
Cd(2)–Br(3)	2.602 (2)	Cd(2)–Br(4)	2.572 (3)
Cd(2)–O(2)	2.20 (2)	Cd(2)–O(3)	2.25 (2)
C(42)–O(3)	1.30 (3)	C(42)–O(4)	1.17 (3)
Br(1)–Cd(1)–Br(2)	108.9(1)	Br(1)–Cd(1)–Br(3)	90.1(1)
Br(2)–Cd(1)–Br(3)	93.4(1)	Br(1)–Cd(1)–O(1)	160.6(3)
Br(2)–Cd(1)–O(1)	90.4(3)	Br(3)–Cd(1)–O(1)	86.4(3)
Br(1)–Cd(1)–O(1a)	91.6(3)	Br(2)–Cd(1)–O(1a)	158.7(3)
Br(3)–Cd(1)–O(1a)	92.0(3)	O(1)–Cd(1)–O(1a)	69.4(5)
Br(1)–Cd(1)–O(4a)	91.5(3)	Br(2)–Cd(1)–O(4a)	92.2(4)
Br(3)–Cd(1)–O(4a)	173.3(3)	O(1)–Cd(1)–O(4a)	90.0(4)
O(1a)–Cd(1)–O(4a)	81.5(4)	Br(3)–Cd(2)–Br(4)	107.3(1)
Br(3)–Cd(2)–O(2)	109.9(3)	Br(4)–Cd(2)–O(2)	106.1(3)
Br(3)–Cd(2)–O(3)	121.1(5)	Br(4)–Cd(2)–O(3)	97.4(4)
O(2)–Cd(2)–O(3)	113.0(5)	Cd(1)–Br(3)–Cd(2)	98.9(1)
O(1)–C(21)–O(2)	126(2)	Cd(1)–O(1)–C(21)	125(1)
Cd(1)–O(1)–Cd(1a)	110.6(5)	O(3)–C(42)–O(4)	120(2)
Cd(2)–O(3)–C(42)	105(1)	C(42)–O(4)–Cd(1a)	140(1)

Symmetry code: (a) $-x, -y, -z$.

amidal and involves a bidentate betaine ligand (Cd–O = 2.290(6) and 2.541(7); Δ(Cd–O) = 0.251 Å), two terminal chloro ligands (Cd–Cl = 2.440(3) and 2.442(3) Å; Cl(1)–Cd(1)–Cl(2) = 108.8(1)°) and a bridging chloro ligand (Cd(1)–Cl(3) = 2.541(2) Å). The angles between the vectors from Cd(1) to the midpoint of the O···O line of the carboxylato group and to the chloro ligands lie in the range 102.5–118.4°, which are within ±9° of the expected angle in an idealized tetrahedral environment. Neighboring cadmium(II) atoms are linked by a single chloro-bridge to form a linear trinuclear complex (Cd(1)–Cl(3)–Cd(2) = 123.4(1)°).

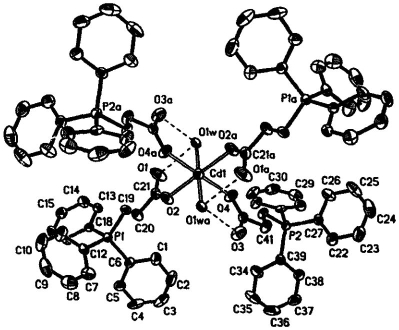


Fig. 1. Molecular structure and atom numbering of the $[Cd\{Ph_3P(CH_2)_2CO_2\}_4(H_2O)_2]^{2+}$ dication in 1. Hydrogen atoms are omitted for clarity, and hydrogen bonds are indicated by broken lines. The thermal ellipsoids are drawn at the 35% possibility level.

The Cd···Cd distance of 4.549(1) Å is much longer than those in the cation $[CdX\{\mu\text{-}Ph_3P(CH_2)_2CO_2\text{-}O,O'\}_2]_2^{2+}$ (X = Cl, NO_3) [21] and in complex 3, as well as in the double chloro-bridged complex $[Cd(Et_3NCH_2CO_2)(\mu\text{-}Cl)_2]_n$ (2.375(1) Å) [15]. This may be ascribed to the fact that the single chloro-bridge poses a lesser geometrical demand than the μ-carboxylate-*O,O′* linkage and double chloro-bridge. The Cd–O(carboxylato) bond lengths and Δ (Cd–O) values compare well with those in complex 2. On the other hand, in complex 4 the Cd–Cl(bridge) bond is significantly longer than the Cd–Cl(terminal) bond but similar to those found in $[Cd(Et_3NCH_2CO)(\mu\text{-}Cl)_2]_n$ (2.529(1)–2.727(1) Å) [15], although the later contains a double chloro-bridge.

As depicted in the stereoview of the crystal structure of complex 4 (Fig. 6), the linear trinuclear species are linked by donor hydrogen bonds from the aqua ligands to the chloro ligands and the oxygen atoms of the betaine ligands to form a composite chain extending parallel to (1 0 0). The solvated water molecules O(3W) and O(4W) and chloro ligand Cl(1) constitute a neighboring chain composed of an alternate arrangement of four- and six-membered hydrogen-bonded rings (O(4wb)···Cl(1) = 3.60(1) Å signified a very weak hydrogen bond). These two types of chains are cross-linked by additional hydrogen bonds to form layers matching the (0 0 2) family of planes, with the Ph_3P groups of the betaine ligands protruding on both sides of each layer.

3.5. Crystal structure of $[Cd_2Br_4\{Ph_3P(CH_2)CO_2\}_2]_2 \cdot dmf$ (5)

Complex 5 comprises discrete tetranuclear $[Cd_4Br_8\{Ph_3P(CH_2)CO_2\}_4]$ and solvated dimethylformamide (dmf) molecules packed together in the crystal lattice.

Table 12
Cd–O(carboxylate) distances and the geometry of carboxylate groups for complex **1** and several tetrakis-*O,O′*-carboxylato dicadmium(II) complexes

Complex		Cd–O (Å)	C–O (Å)	O–C–O (°)
$[Cd\{Ph_3P(CH)_2CO_2\}_2(NO_3)]_2(NO_3)_2$	*a*	2.254(7), 2.240(7)	1.24(1), 1.25(1)	128(1)
		2.223(7), 2.235(8)	1.24(1), 1.26(1)	127(1)
$[Cd\{Ph_3P(CH)_2CO_2\}_2(NO_3)]_2(ClO_4)_2$	*b*	2.240(7), 2.220(8)	1.22(1), 1.25(2)	130(1)
		2.231(9), 2.24(1)	1.25(1), 1.25(2)	127(1)
$[Cd\{Ph_3P(CH)_2CO_2\}_2Cl]_2(ClO_4)_2$	*c*	2.251(6), 2.236(7)	1.26(1), 1.26(1)	127.6(8)
$[Cd\{Ph_3P(CH_2)_2CO_2\}_4(H_2O)_2](ClO_4)_2 \cdot 2H_2O$	**1**	2.219(5), 2.231(4)	1.239(6), 1.230(5)	127.0(6)
			1.244(5), 1.229(6)	127.2(5)

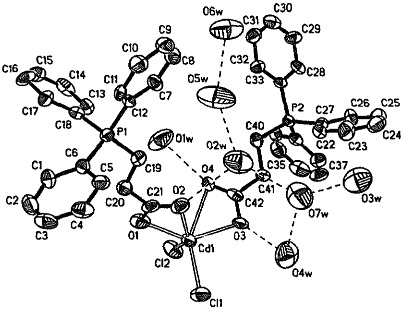


Fig. 2. Molecular structure and atom numbering of $[CdCl_2\{Ph_3P(CH_2)_2CO_2\}_2] \cdot 7H_2O$ (**2**). Hydrogen atoms are omitted for clarity, and hydrogen bonds are indicated by broken lines. The thermal ellipsoids are drawn at the 35% possibility level.

$[Cd_4Br_8\{Ph_3P(CH_2)CO_2\}_4]$ is a centrosymmetric molecule in which a 12-membered ring is constructed from the linkage of four Cd(II) atoms by a pair of bromo ligands and a pair of betaine ligands acting in the *syn–skew* bidentate bridging mode which is similar to that in $[Cd(CH_3CO_2)_2] \cdot 2H_2O$ [35]. Further coordination of the Cd(II) atoms is provided by two betaine ligands lying above and below the ring in a μ_3 tridentate bridging mode, and the remaining ligand sites are occupied by terminal bromo ligands. Details of the molecular structure are shown in Fig. 7 and a clearer view of the coordination geometry of the core in Fig. 8, where all atoms of the betaine ligands except those of the carboxylato groups are omitted for clarity.

The two independent Cd(II) atoms are in chemically distinct environments. The octahedral coordination about Cd(1) involves a pair of terminal bromo ligands (Cd–Br = 2.624(3) and 2.643(3) Å), two oxygen atoms of the tridentate bridging betaine ligands (Cd–O = 2.36(1) and 2.41(1) Å), a bridging bromo ligand (Cd–Br = 2.871(3) Å) and an oxygen atom of the bidentate bridging betaine ligand (Cd–O = 2.36(1) Å). The tetrahedral coordination about Cd(2) consists of a terminal bromo ligand (Cd–Br = 2.572(3) Å), a bridging bromo ligand (Cd–Br = 2.602(2) Å), an oxygen atom of the bidentate betaine ligand (Cd–O = 2.25(2) Å) and an oxygen atom of the tridentate betaine ligand (Cd–O = 2.20(2) Å).

In the cage-like tetranuclear core of complex **5** (Fig. 8), the Cd(1) and Cd(2a) atoms are bridged by a pair of betaine ligands to form an eight-membered ring exhibiting a 'chair' conformation (note the torsion angles O(3a)–Cd(2a)–O(2a)···O(1a) = −93.3, Cd(2a)–O(2a)···O(1a)–Cd(1) = 73.0, O(2a)···O(1a)–Cd(1)–O(4a) = −49.2, O(1a)–

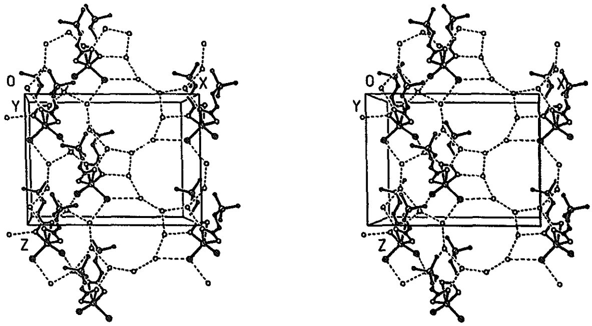


Fig. 3. Stereoview of the crystal structure of complex **2**. Ph_3P groups are represented simply as a C_3P fragment, hydrogen atoms are omitted for clarity, and hydrogen bonds are indicated by broken lines. The origin of the unit cell lies at the left upper corner with *a* pointing from left to right, *b* toward the reader, and *c* downward.

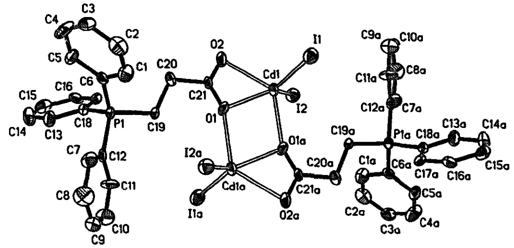
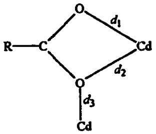


Fig. 4. Molecular structure and atom numbering of $[CdI_2\{Ph_3P(CH_2)_2CO_2\}]_2$ (3). Hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at the 35% possibility level.

Table 13
Cd–O bond lengths (Å) in carboxylate exhibiting the combined monoatomic bridging and bidentate chelating mode



	Complex	d_1	d_2	d_3	Ref.
a	$[CdI_2\{Ph_3P(CH_2)_2CO_2\}]_2$	2.47(1)	2.31(1)	2.49(1)	this work
b	$[Cd(O_2CMe)_2]\cdot 2H_2O$	2.294(4)	2.259(3)	2.297(4)	[35]
c	$[Cd_4Sn_4(\mu_4\text{-}O)_2(O_2CMe)_{10}(OCH_2Bu^t)_{10}]$	2.31(2)	2.35(2)	2.26(2)	[36]
d	$[\{Cd(HOC_6H_4CO_2)_2\cdot 2H_2O\}_2]$	2.314	2.535	2.271	[37]
e	$[Cd\{Me_3N(CH_2)_2CO_2\}(NCS)_2]$	2.432(3)	2.346(3)	2.486(2)	[11]
f	$[\{Cd(Hsal)_2\cdot 2H_2O)_2]$ [a]	2.325(7)	2.530(4)	2.291(4)	[38]
g	$[Cd_4(phdta)_2(H_2O)_8]$	2.391(5)	2.463(5)	2.380(8)	[20]

[a] Hsal = salicylic acid.

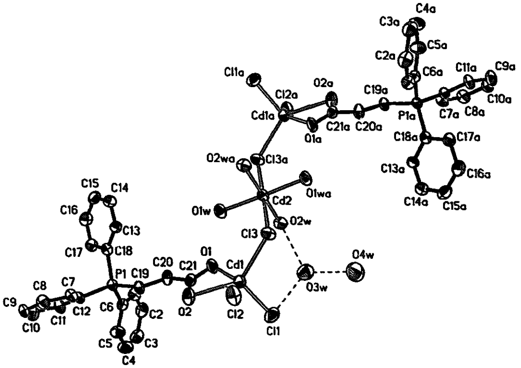


Fig. 5. Molecular structure and atom numbering of *trans*-$Cd(H_2O)_4[Cl_2Cd(\mu\text{-}Cl)\{Ph_3P(CH_2)_2CO_2\}]_2\cdot 4H_2O$ (4). Hydrogen atoms are omitted for clarity, and hydrogen bonds are indicated by broken lines. The thermal ellipsoids are drawn at the 35% possibility level.

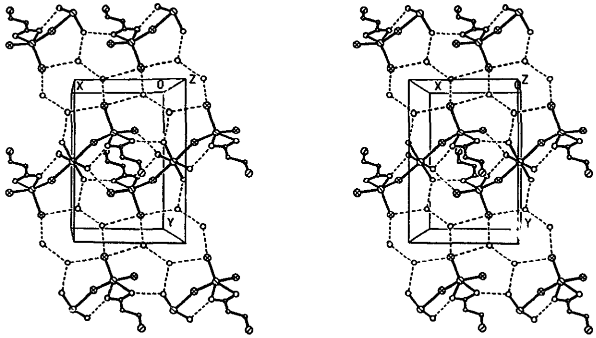


Fig. 6. Stereoview of the crystal structure of complex **4**. Phenyl groups and hydrogen atoms are omitted for clarity, and hydrogen bonds are indicated by broken lines. The origin of the unit cell lies at the right upper corner with *a* pointing from right to left, *b* downward, and *c* toward the reader.

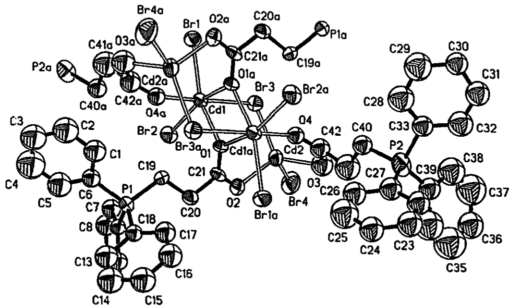


Fig. 7. Molecular structure and atom numbering of $[Cd_2Br_4\{Ph_3P(CH_2)_2CO_2\}_2]_2$ in **5**. Phenyl groups generated by symmetry operation and hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at the 35% possibility level.

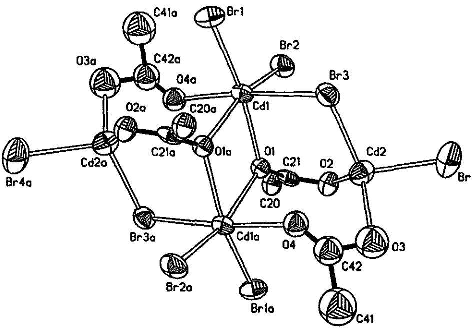


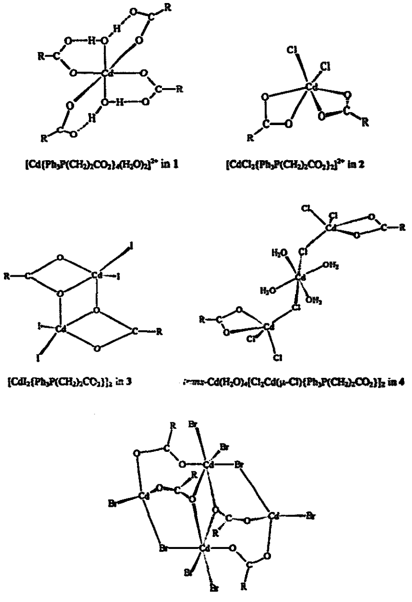
Fig. 8. ORTEP drawing of the cage-like tetranuclear core structure of **5**. The thermal ellipsoids are drawn at the 35% possibility level.

Cd(1)–O(4a)···O(3a) = 70.5, Cd(1)–O(4a)···O(3a)–Cd(2a) = −81.1, O(4a)···O(3a)–Cd(2a)–O(2a) = 76.0°). The non-bonded Cd(1)···Cd(2a) separation of 4.275(1) Å is much longer than those in the cations $[CdX\{\mu\text{-}Ph_3P(CH_2)_2CO_2\text{-}O,O\}_2]_2^{2+}$ (X = Cl, NO_3). The Cd(1) and Cd(2) atoms are bridged by a betaine ligand as well as a bromo ligand to form a six-membered ring in an 'envelop' conformation (the torsion angles Br(3)–Cd(1)–O(1)···O(2) = −48.5, Cd(1)–O(1)···O(2)–Cd(2) = 66.2, O(1)···O(2)–Cd(2)–Br(3) = −45.4, O(2)–Cd(2)–Br(3)–Cd(1) = 23.0, Cd(2)–Br(3)–Cd(1)–O(1) = 10.7°) with an non-bonding distance of 4.164(1) Å. This distance is significantly shorter than that of Cd(1)···Cd(2a) and may be ascribed to the higher constraint imposed by the bromo-bridge. The Cd(1) and Cd(1a) atoms are bridged by a pair of single-oxygen bridges to form a planar four-membered ring with a non-bonding separation of 3.938(1) Å which is somewhat longer than that in complex **3** (3.885(1) Å).

The Cd–Br bond lengths are normal [41]. Of the two independent betaine ligands, one functions in an unusual *syn–skew* mode [42], which is intermediate between the *syn–syn* and *syn–anti* coordination modes commonly found in metal carboxylates [1,6,31]. The torsion angles Cd(2)–O(3)–C(42)–O(4) = 2.2° and O(3)–C(42)–O(4)–Cd(1a) = 122.2° indicate that the atoms Cd(1), O(3), C(42) and O(4) lie in a plane with Cd(1a) being out of this plane by 1.30 Å. The Cd(2)–O(3) bond length of 2.25(2) Å is similar to those (2.220–2.254 Å) found in the cations $[CdX\{\mu\text{-}Ph_3P(CH_2)_2CO_2\text{-}O,O'\}_2]_2^{2+}$ (X = Cl, NO_3) [21], but significantly shorter than the Cd(1a)–O(4) bond of 2.36(1) Å, which can be attributed to the fact that the *syn* lone pair is more basic than the *anti* lone pair. The other independent betaine ligand acts in a μ_3 tridentate bridging mode with one oxygen atom bound to a Cd(II) atom, and the other bridging a pair of Cd(II) atoms. This is an unusual bridging mode for a carboxylate ligand, and hitherto only a few examples have been reported [43–45]. To our knowledge, complex **5** provides the first example of this mode among cadmium carboxylates, although a μ_4 'coat hanger' mode is found in the complex $[Cd_4Sn_4(\mu_4\text{-}O)_2(O_2CMe)_{10}(OCH_2Bu^t)_{10}]$ [36]. In the present μ_3 bridging mode, the planes Cd(2)–O(2)–C(21) and Cd(1)–O(1)–Cd(1a) are mutually perpendicular with a dihedral angle of 92.0°, so that the hybridization of the bridging oxygen atom is best described as sp^3 and this may account for the longer Cd–O(bridging) bond length (2.381(9) and 2.41(1) Å) as compared to the Cd–O(terminal) bond length (2.20(2) Å).

4. Conclusions

Five new cadmium(II) complexes containing discrete mono-, bi-, tri- and tetranuclear units have been synthesized from the reaction of the tertiary phosphine betaine ligand $Ph_3P^+(CH_2)_2CO_2^-$ with various cadmium(II) salts (Fig. 9).



$[Cd\{Ph_3P(CH_2)_2CO_2\}_4(H_2O)_2]^{2+}$ in 1

$[CdCl_2\{Ph_3P(CH_2)_2CO_2\}_2]^{2+}$ in 2

$[CdI_2\{Ph_3P(CH_2)_2CO_2\}]_2$ in 3

trans-$Cd(H_2O)_4[Cl_2Cd(\mu\text{-}Cl)\{Ph_3P(CH_2)_2CO_2\}]_2$ in 4

$[Cd_2Br_4\{Ph_3P(CH_2)_2CO_2\}_2]_2$ in 5

Fig. 9. Line diagrams showing the structures of the discrete Cd(II) species in **1–5**. The $Ph_3P(CH_2)_2$ fragment is represented by R for clarity.

In these complexes the coordination number and geometry about the cadmium(II) atom as well as the coordination modes of the betaine ligand exhibit a rich variety: the coordination number of cadmium(II) ranges from four to six, and the coordination geometry is tetrahedral in complex **5**, distorted trigonal bipyramidal in complexes **3** and **4**, octahedral in complexes **1**, **3** and **5**, and distorted octahedral in complex **2**; the betaine ligand $Ph_3P^+(CH_2)_2CO_2^-$ acts in the unidentate mode in complex **1**, the asymmetric bidentate chelate mode in complexes **2** and **4**, the bidentate '*syn–skew*' mode in complex **5**, a combined monodentate bridging and bidentate chelate mode in complex **3**, and a very unusual μ_3 bridging mode in complex **5** which provides the first such example among cadmium(II) carboxylates. The deviation of the Cd(II) atom from the plane of its bound carboxylate group lies below 0.2 Å in all five compounds except the six-coordinate Cd(1) in complex **5** (Table 14).

In complex **1**, strong intramolecular hydrogen bonding between the aqua ligands and the pendant oxygen atoms of the betaine ligands, which prevent the latter from further coordination to other cadmium(II) atoms, plays a dominant role in stabilizing both the octahedral coordination geometry and the unidentate coordination mode of the betaine ligand,

Table 14
The deviation (Å) of Cd^{2+} from the plane of its bound carboxylate groups in complexes **1**–**5**

		Cd(1)	Cd(2)	Cd(1a)
1	C(21)O(1)O(2)	0.063		
	C(42)O(3)O(4)	−0.165		
2	C(21)O(1)O(2)	−0.057		
	C(42)O(3)O(4)	−0.062		
3	C(21)O(1)O(2)	0.021		−0.052
4	C(21)O(1)O(2)	−0.005		
5	C(21)O(1)O(2)	1.975	0.191	−1.964
	C(42)O(3)O(4)		0.032	−1.301

thus accounting for the occurrence of this unusual structure. On the other hand, hydrogen bonding involving the solvated water molecules, chloro ligands, and oxygen atoms of the betaine ligand in complexes **2** and **4** are responsible for generating the layer-type crystal structures of these complexes.

Compared to simple carboxylic acids and amino acids, the tertiary phosphine betaine ligand $Ph_3P^+(CH_2)_2CO_2^-$ readily forms cadmium(II) complexes containing discrete units. A plausible reason is that the bulky and charged triphenylphosphonio group makes it energetically unfavorable for two discrete units to be positioned in close proximity for subsequent condensation.

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References

[1] R.H. Prince, in G. Wilkinson, R.D. Gillard and J.A. McCleverty (eds.), *Comprehensive Coordination Chemistry*, Vol. 5, Pergamon, Oxford, 1987, Ch. 56, p. 968.
[2] C.J. Carrell, H.L. Carrell, J. Erlebacher and J.P. Glusker, *J. Am. Chem. Soc.*, *110* (1988) 8651.
[3] G.B. Deacon and R.J. Phillips, *Coord. Chem. Rev.*, *33* (1980) 227.
[4] G. Webber, *Acta Crystallogr., Sect. B*, *36* (1980) 1947.
[5] N.C. Charles, E.A.H. Griffith, P.F. Rodesiler and E.L. Amma, *Inorg. Chem.*, *22* (1983) 2717.
[6] D. Dakternieks, *Coord. Chem. Rev.*, *63* (1985) 1.
[7] L.M. Post and J. Trotter, *J. Chem. Soc., Dalton Trans.*, (1974) 285.
[8] J.P. Deloume and H. Loiseleur, *Acta Crystallogr., Sect. B*, *30* (1974) 607.
[9] Y. Yukawa, Y. Inomata, T. Takeuchi, M. Shimoi and A. Ouchi, *Bull. Chem. Soc. Jpn.*, *55* (1982) 3135.
[10] Y. Yukawa, Y. Inomata and T. Takeuchi, *Bull. Chem. Soc. Jpn.*, *56* (1983) 2125.
[11] M.-Y. Chow, X.-M. Chen and T.C.W. Mak, *J. Chem. Soc., Dalton Trans.*, (1993) 3413.
[12] T.C.W. Mak, W.-H. Yip, E.J. O'Reilly, G. Smith and C.H.L. Kennard, *Inorg. Chim. Acta*, *100* (1985) 267.
[13] T. Allman, R.C. Goel, N.K. Jha and A.L. Beauchamp, *Inorg. Chem.*, *23* (1984) 914.
[14] T. Thanmaniwong, V.M. Akimnov, V.G. Andrieanov, Yu.T. Struchkov and A.K. Molodkin, *Zh. Neorg. Khim.*, *29* (1984) 1033 (*Chem. Abstr.*, *100* (1984) 219406).
[15] X.-M. Chen and T.C.W. Mak, *J. Cryst. Spectrosc. Res.*, *21* (1991) 27.
[16] D.C. Liles, M. McPartlin, P.A. Tasker, H.C. Lip and L.F. Lindoy, *J. Chem. Soc., Chem. Commun.*, (1976) 459.
[17] Z. Zhang, M. Shao and X. Jin, *Acta Chim. Sin.*, *39* (1981) 829.
[18] X. Solans, M. Font-Bardia, M. Aguilo, M. Arostegui and J. Oliva, *Acta Crystallogr. Sect. C*, *43* (1987) 648.
[19] T.C.W. Mak and X.-M. Chen, *Aust. J. Chem.*, *44*, (1991), 639.
[20] N. Nakasuka, S. Azuma and M. Tanaka, *Acta Crystallogr., Sect. C*, *42* (1986) 1736.
[21] S.-L. Li and T.C.W. Mak, *J. Chem. Soc., Dalton Trans.*, (1995) 1519.
[22] D.B. Denney and L.C. Smith, *J. Org. Chem.*, *27* (1962) 3404.
[23] R.A. Sparks, in R.F. Ahmed (ed.), *Crystallographic Computing Techniques*, Munksgaard, Copenhagen, 1971, p. 452.
[24] G.M. Sheldrick, in D. Sayre (ed.), *Computational Crystallography*, Oxford University Press, New York, 1982, pp. 506–514.
[25] *International Tables for X-ray Crystallography*, Vol. 4, Kynoch Press, Birmingham, UK, 1974, pp. 55, 99, 149 (present distributer: Kluwer, Dordrecht).
[26] M. Post and J. Trotter, *J. Chem. Soc., Dalton Trans.*, (1974) 674.
[27] J.G. Bergman, Jr. and F.A. Cotton, *Inorg. Chem.*, *5* (1966) 1208.
[28] A. Zalkin, J.D. Forrester and D.H. Templeton, *J. Chem. Phys.*, *39* (1963) 2881.
[29] C. Oldham, in G. Wilkinson, R.D. Gillard and J.A. McCleverty (eds.), *Comprehensive Coordination Chemistry*, Vol. 3, Pergamon, Oxford, 1987, Ch. 15.
[30] A. Bonamartini Corradi, *Coord. Chem. Rev.*, *117* (1992) 46.
[31] R.C. Mehrotra and R. Bohra, *Metal Carboxylates*, Academic Press, New York, 1983.
[32] C. Oldham, *Prog. Inorg. Chem.*, *10* (1968) 223.
[33] U. Castellato and P.A. Vigato, *Coord. Chem. Rev.*, *26* (1978) 85.
[34] C.D. Garner and B. Hughes, *Adv. Inorg. Chem. Radiochem.*, *17* (1975) 1.
[35] W. Harrison and J. Trotter, *J. Chem. Soc., Dalton Trans.*, (1972) 956.
[36] C. Chandler, G.D. Fallon and B.O. West, *J. Chem. Soc., Chem. Commun.*, (1990) 1063.
[37] M.A. Kennedy and P.D. Ellis, *Inorg. Chem.*, *29* (1990) 541.
[38] K. Venkatasubramnian, A.C. Villa, A.G. Manfredott and C. Guastini, *Cryst. Struct. Commun.*, *1* (1972) 427.
[39] M.R. Peterson and I.G. Csizmadia, *J. Am. Chem. Soc.*, *101* (1979) 1076.
[40] H. Sigel and R.B. Martin, *Chem. Soc. Rev.*, *23* (1994) 83.
[41] A.G. Open, L. Brammer, F.H. Allen, O. Kennard, D.G. Waston and R. Taylor, *J. Chem. Soc., Dalton Trans.*, (1989) S69.
[42] X.-M. Chen and T.C.W. Mak, *Inorg. Chim. Acta*, *189* (1991) 3.
[43] A.R. Schake, J.B. Vincent, Q.-Y. Li, Peter D.W. Boyd, K. Folting, J.C. Huffman, D.N. Hendrickson and G. Christou, *Inorg. Chem.*, *28* (1989) 1915.
[44] A.R.E. Baikie, A.J. Howes, M.B. Hursthouse, A.B. Quick and P. Thornton, *J. Chem. Soc., Chem. Commun.*, (1986) 1587.
[45] N.V. Gerbeleu, A.S. Batsanov, G.A. Timko, Yu.T. Struchkov, K.M. Indrichan and G.A. Popovich, *Dokl, Akad. Nauk. SSSR*, *294* (1987) 256.