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Layered, network and chain structures of cadmium(II) malonate: crystal structure and cadmium-113 nuclear magnetic resonance studies

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Three structurally non-identical cadmium(II) malonate compounds have been obtained: polymeric tetraaquabis(malonato)dicadmium(II) **1**, polymeric monoaqua(malonato)cadmium(II) monohydrate **2** and polymeric triaqua(malonato)cadmium(II) monohydrate **3**. The layered-structure compound **1** is the initial product formed at room temperature, and has two cadmium sites in distinct chemical and magnetic environments: six- and eight-co-ordinate cadmium involving oxygen donors including two water molecules, characterized by two ^{113}Cd NMR resonances at δ 18 and −107, respectively. Compound **2**, which has a three-dimensional network structure, is formed irreversibly when **1** is heated at 60 °C or exposed to sunlight: its seven-co-ordinate cadmium site involves one six-membered and two four-membered chelate rings and one water molecule (δ −47). Compound **3** has an unusual chain structure and is formed reversibly when **2** is heated at 100 °C: a different seven-co-ordinated cadmium site involves two four-membered rings and three water molecules (δ −53). The results of the cross polarization magic angle spinning ^{113}Cd NMR study of the six-, seven- and eight-co-ordination sites show that cadmium atoms with higher co-ordination numbers tend to be more shielded.

The high sensitivity of the ^{113}Cd chemical shift to the co-ordination environment (donor atom, co-ordination number and geometry) enables ^{113}Cd NMR spectroscopy to be applied as a probe of the metal-ion binding sites in biological systems, such as metallothionein [1,2] and metalloenzymes.[3–7] When cross polarization magic angle spinning (CP MAS) ^{113}Cd NMR spectroscopy is combined with X-ray crystallography an excellent opportunity is provided to study and correlate metal-ion geometry with ^{113}Cd NMR chemical shift.[8–15] The ultimate goal is to be able to describe the ligand and its geometry about the cadmium atom from observed ^{113}Cd NMR signals in the solid or solution. An interesting example is the ^{113}Cd chemical shift $\delta \approx -100$ observed for the S_2 site of concanavalin A[16,17] and the EF site of parvalbumin.[17–19] Amma and co-workers[9,10,20,21] synthesized and carried out comprehensive studies on many model compounds for such sites, but were unable to observe chemical shifts near δ −100. Recently, cadmium(II) dicarboxylates (*e.g.* oxalate, malonate, succinate) formed in aqueous solution were investigated using ^{113}Cd NMR spectroscopy.[22] The experimental results were interpreted in terms of the formation of just two species $[\mathrm{CdL}]^+$ (L = carboxylate) (δ −22 to −24) and $[\mathrm{CdL_2}]$ (δ −39 to −40). However, no description of the co-ordination geometry around the cadmium atom can be deduced from the solution NMR data.

It is reported that dicarboxylates of divalent cadmium or copper can form polymeric species with unusually high co-ordination numbers.[23,24] Therefore several new polymeric compounds of cadmium have been prepared in aqueous solution with malonate as ligand. Reported herein are detailed accounts of the synthesis, structural chemistry and ^{113}Cd NMR study of three structurally non-identical cadmium(II) malonate complexes. A portion of this work describing compound **1** has previously been communicated.[25] Since the six-, seven- and eight-co-ordinated cadmium sites described in this work are formed with only malonate and water molecules as ligands, they provide good examples for correlating metal-ion geometry with ^{113}Cd chemical shift.

Experimental

Preparations

Polymeric tetraaquabis(malonato)dicadmium(II) $[\{\mathrm{Cd_2(mal)_2(H_2O)_4}\}_n]$ 1. Compound **1** was prepared by dissolving $\mathrm{Cd(ClO_4)_2{\cdot}6H_2O}$ (4.19 g, 0.01 mol) (Alfa) in an aqueous solution (250 cm^3) containing disodium malonate monohydrate (3.32 g, 0.02 mol) (Aldrich) at pH 6 in the absence of external heating. On standing for approximately 1 week the transparent crystals obtained were filtered off, washed with doubly deionized water and dried in an oven at 40 °C (Found: C, 14.55; H, 2.40. Calc for $\mathrm{C_6H_{12}Cd_2O_{12}}$: C, 14.4; H, 2.40%). IR (KBr): 3601m, 3522w, 2947w, 1603s, 1549vs, 1428s, 1377vs, 1266s, 1191m, 1163vw, 971vw, 947w, 829m, 723m, 715s, 665vw, 626m and 599m cm^{-1}.

Polymeric monoaqua(malonato)cadmium(II) monohydrate $[\{\mathrm{Cd(mal)(H_2O){\cdot}H_2O}\}_n]$ 2. Compound **1** can be kept in the dark at room temperature, but it is converted into a new powder phase **I** when oven heated at 60 °C (> 1 h) or exposed to the open air and light for 2 d. Transparent crystals of **2** were obtained after 1 month from a saturated solution of this powder phase dissolved in doubly deionized water. They were filtered off, washed with doubly deionized water and oven dried at 60 °C. Crystals of **2** were also obtained when the same sample solution as that used in the preparation of **1** was externally heated to near boiling for 15 min (Found: C, 14.6; H, 2.45. Calc. for $\mathrm{C_3H_6CdO_6}$: C, 14.4; H, 2.40%). IR (KBr): nearly the same as that of **1** within the limit of resolution.

Polymeric triaqua(malonato)cadmium(II) monohydrate $[\{\mathrm{Cd(mal)(H_2O)_3{\cdot}H_2O}\}_n]$ 3. Heating compound **1** in a sealed NMR tube to 95 °C, then in an oven at 100 °C for 1 h or more, resulted in the formation of a powder phase **II**. Transparent crystals of **3** were obtained after 1 month from a saturated solution of this powder phase dissolved in doubly deionized water. They were filtered off, washed with doubly deionized water and oven dried at 40 °C. No elemental analysis data are given since **3** slowly converts into **2** on standing at room temperature. IR (KBr): nearly the same as that of **1** within the limit of resolution.

Crystallography

Diffraction-quality crystals were obtained directly from the synthetic batches in all cases as described above. For compounds **1** and **3** suitable crystals were prepared by cutting large crystals. All crystals were mounted on glass fibres and diffraction data were collected on an Enraf-Nonius CAD4TSB diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ 0.710 73 Å) at 296 K. In the case of **3** a freshly prepared crystal and rapid data collection were employed. Accurate unit-cell parameters and orientation matrices were determined by using SET 4[26] from the least-squares fits of 25 accurately centred reflections in the 2θ ranges 20.04–30.70° for **1**, 19.16–28.17° for **2**, and 18.16–38.19° for **3**. All data were collected with the ω–2θ scan mode, except for **2** where the ω–θ scan mode was employed, and corrected for Lorentz-polarization effects. The intensities of three standard reflections were monitored for every 7200 (for **1**) or 3600 s (for **2** and **3**) of exposure, and no significant decay was observed in all three cases. Absorption corrections (ψ scans) were applied for all compounds except **1**. Details of the crystal data are summarized in Table 1.

The structures were solved by direct methods (for **1**, SHELXS 86)[27] or by Patterson heavy-atom methods (for **2** and **3**, SHELXS 86).[27] Atoms not located from the initial structure solution were found by successive Fourier-difference maps with iterative cycles of full-matrix least-squares refinement (on F^2) (SHELXL 93)[28] on an IBM RISC/6000 or Silicon Graphics Indigo^{2}XZ Workstation. All non-hydrogen atoms were treated anisotropically. Hydrogen atoms were located from a difference synthesis and refined isotropically for **2** and **3**, but placed at their geometrically calculated positions (d_{C-H} = 0.970 Å for methylene hydrogens) for **1** and refined riding on the corresponding carbon atoms with isotropic thermal parameters $[1.2U(C_{CH_2})]$. In the case of the non-centrosymmetric system **2**, the floating-origin restraint was applied automatically by the use of SHELXL 93[28] and attempts to derive the correct absolute structure were made by evaluating the Flack absolute structure X-parameter of −0.23(10) and applying the TWIN instruction.

Atomic coordinates, thermal parameters, and bond lengths and angles, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/143.

Cadmium-133 NMR spectroscopy

The ^{113}Cd NMR spectra of compounds **1**–**3** were measured with the same single crystals used previously in crystallography, in a finely ground form. The spectra were also measured of the powder phases **I** and **II**. All were obtained using the CP MAS ^{113}Cd NMR techniques on a Bruker AM 300 spectrometer operating at 66.576 MHz. The contact time was 4 ms, the delay time 2 s, and the rotor speed set at 3.5 kHz. The spectra required 150 transients. Chemical shifts are quoted relative to 0.1 mol dm^{-3} $Cd(ClO_4)_2$ aqueous (D_2O) solution as the reference with positive chemical shifts downfield. A variable-temperature NMR experiment was carried out on a single crystal of **1** by gradually heating it in a sealed NMR tube from 25 to 95 °C.

Results and Discussion

Crystal structures

Three malonate compounds of cadmium(II) in polymeric forms with unusually high co-ordination numbers were prepared. The crystal of **1** [polymeric tetraaquabis(malonato)dicadmium], initially obtained at room temperature in an aqueous sample solution, has a layered structure with an intercadmium layer distance of 6.7 Å and this is shown in Fig. 1. Compound **1** has an unusual structure and contains three crystallographically distinct cadmium atoms, but only two are chemically and magnetically distinct. The molecular structure showing the three cadmium atoms is given in Fig. 2. The eight-co-ordinated atom Cd(1) is bonded to two water molecules [O(9) and O(10)], two carboxy-oxygens [O(1) and O(8)] and two four-membered chelated carboxy groups that also bridge to Cd(2) and Cd(3) atoms, which lie on inversion centres. The geometry around Cd(1) may be described as a distorted dodecahedron. As expected for the carboxylate groups that are both chelating and bridging, two oxygens [O(4) and O(6)] are more distant from Cd(1) atom than the other six oxygens. Selected bond lengths and angles of **1** are listed in Table 2. With the carboxylates acting as chelating ligands, two distinct Cd–O distances are found in cadmium(II) maleate (2.255 and 2.843 Å)[23] and cadmium(II) calcium(II) acetate hexahydrate (2.289 and 2.677 Å).[29] Atoms Cd(2) and Cd(3) in **1** have the same chemical and magnetic environments. They have octahedral geometry (see Fig. 2) and are six-co-ordinated forming bonds with two water molecules and two six-membered chelated carboxyl oxygens.

Compound **1** is relatively stable in the dark at room temperature or below. When either heated or left exposed to sunlight in the open air it is converted irreversibly into the powder phase **I** and then into the second compound polymeric monoaqua(malonato)cadmium(II) monohydrate **2**. A crystal of **2** was obtained from a saturated aqueous solution of powder phase **I**. The X-ray diffraction analysis shows that the unit-cell parameters are the same as for cadmium(II) malonate dihydrate reported earlier by Post and Trotter,[30] but no structural

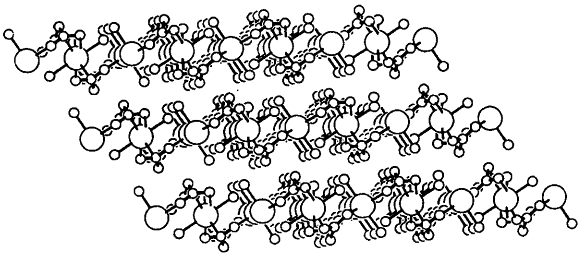

Fig. 1 Layer crystal structure of compound **1**

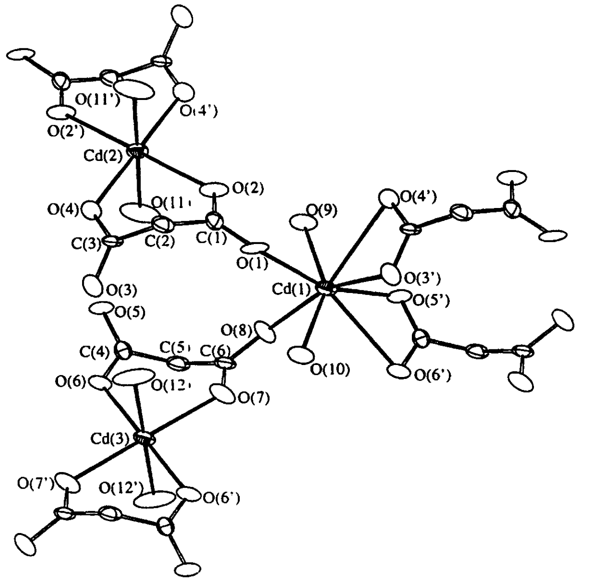

Fig. 2 Molecular structure of compound **1** showing six- and eight-co-ordinated Cd atoms

Table 1 Crystallographic parameters for compounds **1**–**3**

	$[\{Cd_2(mal)_2(H_2O)_4\}_n]$ **1**	$[\{Cd(mal)(H_2O)\cdot H_2O\}_n]$ **2**	$[\{Cd(mal)(H_2O)_3\cdot H_2O\}_n]$ **3**
Empirical formula	$C_6H_{12}Cd_2O_{12}$	$C_3H_6CdO_6$	$C_3H_{10}CdO_8$
M	500.96	250.48	286.51
Crystal type	Triclinic	Trigonal	Monoclinic
Space group	$P\bar{1}$	$R\bar{3}$	*Pc*
a/Å	7.276(2)	17.063(4)	5.7245(8)
b/Å	8.180(2)	17.063(4)	5.6729(10)
c/Å	12.483(2)	12.392(3)	13.4761(9)
α/°	76.14(2)		
β/°	73.13(2)		90.714(14)
γ/°	63.65(2)		
U/(Å^3)	631.8(3)	3124.5(13)	437.60(10)
Z	2	18	2
D_c/g cm^{-3}	2.633	2.396	2.174
μ/mm^{-1}	3.427	3.119	2.505
F(000)	480	2160	280
$2\theta_{max}$/°	48.96	60.04	49.96
hkl Ranges	−8 to 8, −9 to 9, 0–14	0–20, 0–20, 0–17	−6 to 6, 0–6, 0–16
No. unique reflections	1975	1126	802
No. observed reflections [$I > 2\sigma(I)$]	1953	1003	794
No. parameters	185	115	142
*R*1	0.0321	0.0286	0.0198
*wR*2	0.0854	0.0690	0.0486
Goodness of fit	1.105	1.149	1.179
Maximum, minimum electron density/e Å^{-3}	+1.21, −1.167	+0.846, −0.475	+0.329, −0.525
k_1	0.0569	0.0370	0.0324
k_2	2.1534	6.7204	0.0000

$R1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$, where $w = 1/[\sigma^2(F_o^2) + (k_1P)^2 + k_2P]$, $P = (F_o^2 + 2F_c^2)/3$.

Table 2 Selected bond distances (Å) and angles (°) with standard deviations in parentheses for compound **1**

Cd(1)–O(3)	2.307(4)	Cd(1)–O(8)	2.310(4)
Cd(1)–O(5)	2.314(4)	Cd(1)–O(1)	2.324(4)
Cd(1)–O(9)	2.374(4)	Cd(1)–O(10)	2.375(4)
Cd(1)–O(4)	2.775(5)	Cd(1)–O(6)	2.775(5)
Cd(2)–O(4)	2.226(4)	Cd(2)–O(11)	2.277(5)
Cd(2)–O(2)	2.296(4)	Cd(3)–O(6)	2.219(4)
Cd(3)–O(12)	2.274(5)	Cd(3)–O(7)	2.304(4)
C(1)–O(1)	1.233(7)	C(1)–O(2)	1.279(7)
C(1)–C(2)	1.508(7)	C(2)–C(3)	1.511(7)
C(3)–O(3)	1.248(6)	C(3)–O(4)	1.265(7)
C(4)–O(5)	1.243(7)	C(4)–O(6)	1.252(7)
C(4)–C(5)	1.533(7)	C(5)–C(6)	1.526(7)
C(6)–O(7)	1.244(7)	C(6)–O(8)	1.262(7)
O(3)–Cd(1)–O(5)	86.3(2)	O(3)–Cd(1)–O(4)	49.8(2)
O(5)–Cd(1)–O(6)	49.9(2)	O(8)–Cd(1)–O(1)	91.34(14)
O(9)–Cd(1)–O(10)	151.5(2)	O(4)–Cd(2)–O(2)	84.99(14)
O(11)–Cd(2)–O(2)	89.1(2)	O(6)–Cd(3)–O(7)	84.96(14)
O(12)–Cd(3)–O(7)	89.6(2)	O(1)–C(1)–O(2)	122.7(5)
O(1)–C(1)–C(2)	118.2(5)	C(1)–C(2)–C(3)	114.1(4)
O(3)–C(3)–O(4)	120.6(4)	O(3)–C(3)–C(2)	118.9(5)
C(1)–O(1)–Cd(1)	134.7(3)	C(1)–O(2)–Cd(2)	125.6(3)
C(3)–O(4)–Cd(2)	124.1(3)	C(4)–O(6)–Cd(3)	124.3(3)
C(6)–O(7)–Cd(3)	125.6(3)	C(6)–O(8)–Cd(1)	133.7(4)

information on the latter was provided by them. By obtaining the molecular structure of **2**, another example is added to the correlation between metal-ion geometry and ^{113}Cd NMR chemical shift. The crystal structure may be described as a three-dimensional network (Fig. 3). Twelve-membered star-shaped rings formed by alternating Cd and O atoms create a channel made up of methylene groups of malonate, with a C-based diameter of 4.94 Å. Since this channel is hydrophobic the interstitial water [O(6)] is not found in it, but is instead hydrogen bonded to carboxyl oxygens of malonate close to the Cd. The crystal structure is quite similar to that of cadmium(II) malonate monohydrate reported by Post and Trotter[30] but the latter has no interstitial water. The Cd atom in **2** is seven-co-ordinated, has a polyhedron that is similar to a pentagonal bipyramid, and forms bonds with one water molecule [O(5)], one six-membered [O(1$^{\text{I}}$), O(3$^{\text{I}}$)] and two four-membered chelated carboxy-groups [O(1$^{\text{II}}$), O(2$^{\text{II}}$), O(3), O(4)] as shown in Fig. 4. Selected bond lengths and angles are listed in Table 3.

The third compound polymeric triaqua(malonato)cadmium(II) monohydrate **3** is obtained by heating crystal **2** at 100 °C which first yielded powder phase **II**. The crystal of **3** was obtained from the saturated aqueous solution of **II**. Compound **3** is thermally unstable at room temperature, and slowly and reversibly converts back into **2**: after 3 months of standing at room temperature, it had been mostly converted into **2**. The unusual chain structure is shown in Fig. 5. Selected bond lengths and angles are listed in Table 4. The Cd atom in **3** is also seven-co-ordinated, but forms bonds with only four carboxyl oxygens of malonate ions and three water molecules [O(5)–O(7)], Fig. 6. The co-ordination geometry around Cd may be described as a distorted pentagonal bipyramid. Atoms Cd, O(1)–O(4), O(7) all lie close to a plane: maximum deviation of atoms 0.071 Å. The axial O–Cd–O angle is O(5)–Cd–O(6) 176.1(2). Each carboxylate group of malonate is co-ordinated to two different Cd atoms forming four-membered chelate rings, and thus the chain structure (Fig. 5). Unlike in **1** and **2**, two carboxyl oxygens which form four-membered chelate rings in **3** are nearly equidistant from the cadmium atom. There is also an interstitial water molecule [O(8)] packing between the chains. This mode of binding is rather unusual for malonate ligand and is quite different from that in other reported malonatometal complexes which usually have at least one six-membered ring together with four-membered rings.[30]

CP MAS ^{113}Cd NMR spectroscopy

The ultimate goal was to use the crystal structures of these compounds together with their CP MAS ^{113}Cd NMR results in the correlation of metal-ion geometry with chemical shift data. The CP MAS ^{113}Cd NMR spectroscopic studies were carried out on finely ground crystals of **1**–**3** and of powder phases **I** and **II**. The spectra are shown in Fig. 7. Compound **1**, which has two cadmium atoms in distinctly different chemical and magnetic environments, gave a spectrum showing two characteristic

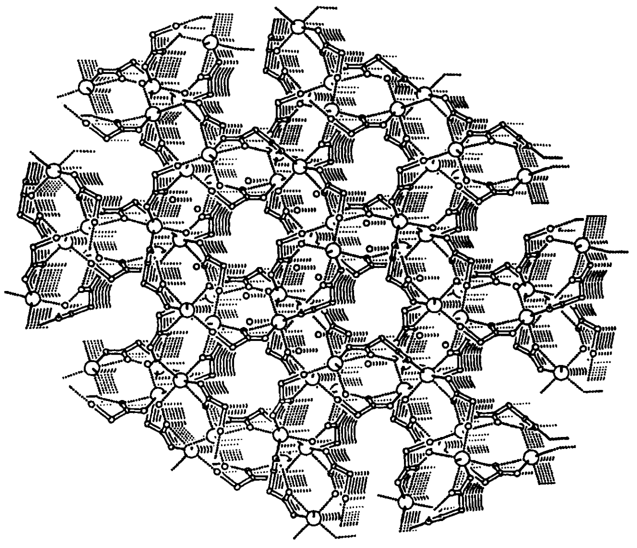

Fig. 3 Network crystal structure of compound **2**

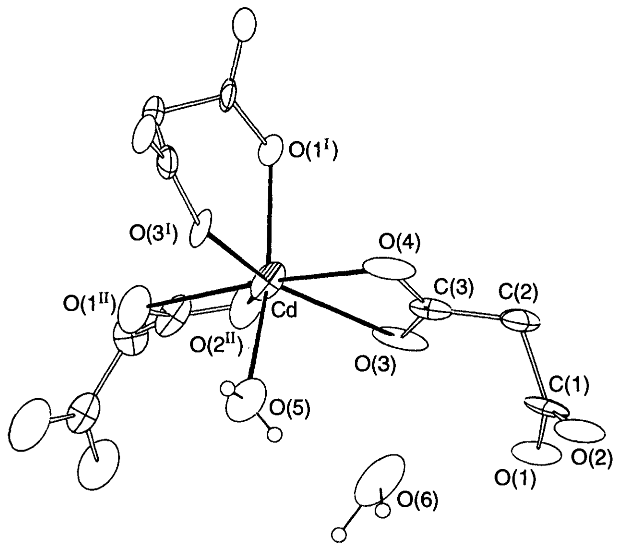

Fig. 4 An ORTEP drawing of compound **2** showing seven-co-ordinated Cd

Table 3 Selected bond distances (Å) and angles (°) with standard deviations in parentheses for compound **2**

Cd–O(1$^{\rm I}$)	2.286(3)	Cd–O5	2.286(4)
Cd–O(3$^{\rm I}$)	2.294(3)	Cd–O(2$^{\rm II}$)	2.295(3)
Cd–O(4)	2.326(4)	Cd–O(3)	2.527(3)
Cd–O(1$^{\rm II}$)	2.545(3)	O(1)–C(1)	1.260(5)
O2–C(1)	1.239(5)	O(3)–C(3)	1.246(5)
O4–C(3)	1.264(5)	C(1)–C(2)	1.511(6)
C2–C(3)	1.521(6)		
O(1$^{\rm I}$)–Cd–O(5)	165.39(12)	O(1$^{\rm I}$)–Cd–O(3$^{\rm I}$)	81.81(11)
O(5)–Cd–O(3$^{\rm I}$)	83.61(13)	O(1$^{\rm I}$)–Cd–O(2$^{\rm II}$)	83.80(12)
O(5)–Cd–O(2$^{\rm II}$)	106.80(13)	O(3$^{\rm I}$)–Cd–O(2$^{\rm II}$)	138.49(12)
O(1$^{\rm I}$)–Cd–O(4)	92.11(13)	O(5)–Cd–O(4)	89.10(15)
O(3$^{\rm I}$)–Cd–O(4)	91.25(13)	O(2$^{\rm II}$)–Cd–O(4)	128.08(12)
O(1$^{\rm I}$)–Cd–O(3)	105.85(12)	O(5)–Cd–O(3)	86.51(13)
O(3$^{\rm I}$)–Cd–O(3)	143.42(12)	O(2$^{\rm II}$)–Cd–O(3)	78.05(11)
O(4)–Cd–O(3)	53.38(11)	O(1$^{\rm I}$)–Cd–O(1$^{\rm II}$)	93.8(2)
O(5)–Cd–O(1$^{\rm II}$)	85.12(14)	O(3$^{\rm I}$)–Cd–O(1$^{\rm II}$)	89.26(12)
O(2$^{\rm II}$)–Cd–O(1$^{\rm II}$)	53.11(11)	O(4)–Cd–O(1$^{\rm II}$)	174.11(12)
O(3)–Cd–O(1$^{\rm II}$)	124.89(10)	C(1$^{\rm I}$)–O(1$^{\rm I}$)–Cd	86.7(3)
Cd$^{\rm I}$–O(1$^{\rm I}$)–Cd	143.02(15)	C(3)–O(3)–Cd	88.2(3)
O(3)–C(3)–O(4)	121.2(4)	O(3)–C(3)–C(2)	120.9(4)
O(4)–C(3)–C(2)	117.9(4)		

Symmetry relations: I $y, y - x, -z$; II $\frac{2}{3} + x - y, \frac{1}{3} + x, \frac{1}{3} + z$.

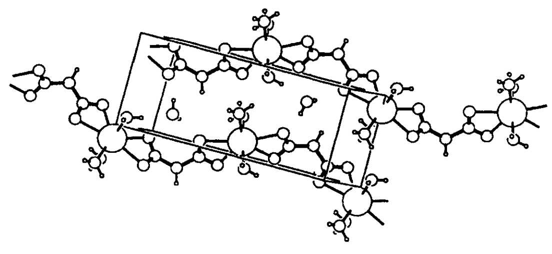

Fig. 5 Crystal structure of compound **3**

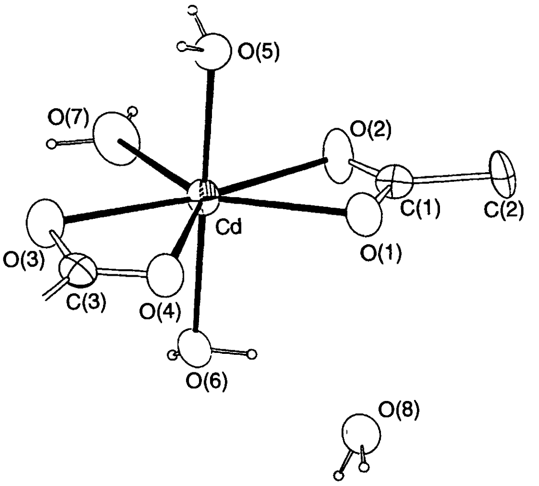

Fig. 6 Unusual seven-co-ordinated Cd atom in compound **3** showing three co-ordinated water molecules

Table 4 Selected bond distances and angles (°) with standard deviations in parentheses for compound **3**

Cd–O(7)	2.277(6)	Cd–O(6)	2.310(5)
Cd–O(5)	2.315(6)	Cd–O(1)	2.319(5)
Cd–O(4)	2.425(4)	Cd–O(3)	2.432(5)
Cd–O(2)	2.487(5)	C(1)–O(2)	1.248(9)
C(1)–O(1)	1.262(10)	C(1)–C(2)	1.524(11)
C(3)–O(4)	1.257(9)	C(3)–O(3)	1.262(9)
C(3)–C(2)	1.539(12)		
O(5)–Cd–O(6)	176.1(2)	O(7)–Cd–O(1)	135.3(3)
O(7)–Cd–O(4)	135.5(2)	O(6)–Cd–O(4)	83.9(2)
O(1)–Cd–O(4)	89.0(2)	O(7)–Cd–O(3)	81.8(2)
O(1)–Cd–O(3)	142.9(2)	O(4)–Cd–O(3)	54.0(2)
O(7)–Cd–O(2)	81.7(2)	O(1)–Cd–O(2)	53.7(2)
O(4)–Cd–O(2)	142.3(2)	O(3)–Cd–O(2)	163.4(2)
O(2)–C(1)–O(1)	121.1(6)	O(2)–C(1)–C(2)	122.6(7)
O(1)–C(1)–C(2)	116.3(7)	O(4)–C(3)–O(3)	120.9(6)
C(1)–O(1)–Cd	96.5(4)	C(1)–O(2)–Cd	88.7(4)
C(3)–O(3)–Cd	92.2(4)	C(3)–O(4)–Cd	92.4(4)

resonances at δ 18 and −107 [Fig. 7(*a*)]. The spectra of the crystal **2** and powder phase **I** are identical, showing that they are the same: a single resonance at δ −47 [Fig. 7(*b*) and 7(*c*)] corresponds to a single type of cadmium atom. The spectrum of the powder phase **II** gave a single resonance at δ −53 [Fig. 7(*d*)], but that of the finely ground crystal **3** gave two resonances at δ −53 and −47 [Fig. 7(*e*)]. The powder phase **II**, which had been kept at room temperature for longer than 1 month, also showed resonances at δ −47 and −53. Compound **3** is formed at high temperature (≈100 °C) and on standing at room temperature it is slowly converted back into **2**. The grinding of crystal **3** into a fine powder for NMR study also seems to aid its conversion into **2**.

The processes involving the irreversible formation of compound **2** from **1** and the temperature-dependent interconversion between **2** and **3** can be observed in a series of spectra obtained from variable-temperature NMR experiments (25–

95 °C) with **1** as the starting material. The spectra are given in two series: over the ranges 25–70 (Fig. 8) and 80–95 °C (Fig. 9). The spectrum of the sample measured at 25 °C displayed two resonances at δ 18 and −107 (characteristic of **1**). No change was seen until 60 °C at which the intensities of the two resonances began to decrease and a new peak began to appear at δ −47 (characteristic of **2**). After 55 min at this temperature the peaks at δ 18 and −107 disappeared completely, and were replaced by one at δ −47 (see Fig. 8). The temperature of the sample was lowered back to 25 °C, but no change in the spectrum was seen, which displayed predominantly the peak at δ −47. The spectra taken in the range 60–70 °C still displayed δ −47 as the major peak, but an additional small peak began to be seen at δ −53. At higher temperatures of 80–95 °C the latter peak became progressively stronger and that at δ −47 weaker (see Fig. 9). The same sample, which was heated at 100 °C for several hours, gave a single resonance at δ −53. The spectrum of powder phase **II**, made by heating **2** at 100 °C, gave a single resonance at δ −53. However, when the previously heated sample (100 °C, δ −53 only) was kept at room temperature, then the peak at δ −47 began to reappear, grow more intense and became the major peak after 3 months. These spectral data are in good agreement with the chemical shifts measured for the individual crystals (**1**–**3**) and powder phases (**I** and **II**). The results of the ^{113}Cd NMR study can be summarized as follows: **1** is converted readily into **2** on heating at around 60 °C, but this is an irreversible process; **3** is formed only at a high temperature by heating **2** at 100 °C for several hours, but this is a reversible process and **3** is slowly converted back into **2** which seems to be more stable at room temperature. Just by heating, the starting compound **2** having one co-ordinated water molecule was converted into **3** with three co-ordinated water molecules. There seem to be two possibilities that account for the increased water co-ordination in **3**. One is that water is drawn from an outside source, but this is less likely as **2** was heated in an isolated NMR tube free of external water. A second possibility is that **2** has undergone a disproportionation reaction resulting in the formation of **3** and one other compound with very little or no

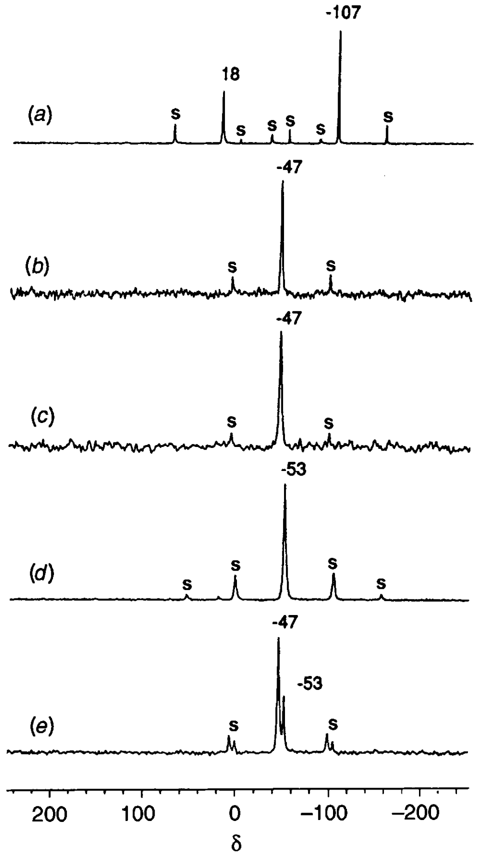

Fig. 7 The ^{113}Cd NMR spectra of finely ground crystals and powder phases: (*a*) **1**, (*b*) **I**, (*c*) **2**, (*d*) **II** and (*e*) **3**. Peaks labelled as 's' are spinning sidebands

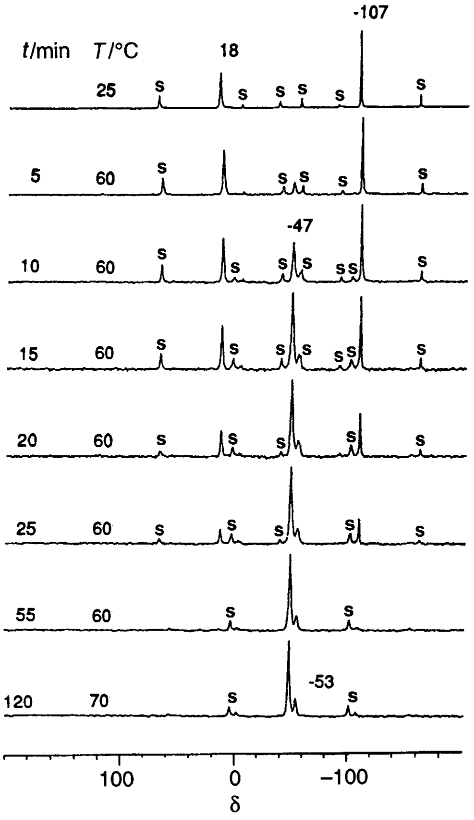

Fig. 8 Series of ^{113}Cd NMR spectra from variable-temperature experiments (25–70 °C). Peaks labelled as 's' are spinning sidebands

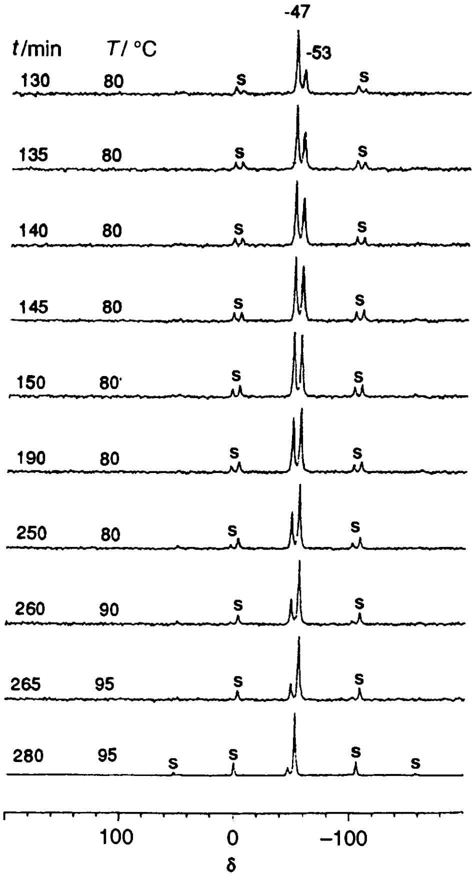

Fig. 9 Series of ^{113}Cd NMR spectra from variable-temperature experiments (80–95 °C). Peaks labelled as 's' are spinning sidebands

Table 5 Summary of CP MAS ^{113}Cd NMR results for cadmium(II) malonate compounds

Compound	Co-ordination number	Source of O	Geometry	δ[a]
Ground crystal **1**				
Cd(2), Cd(3)	6	$2H_2O, 2CO_2,^b 2CO_2$	Octahedral	18
Cd(1)	8	$2H_2O, 2CO_2, 2CO_2^b$	Dodecahedral	−107
Ground crystal **2**	7	$H_2O, 2CO_2,^b 2CO_2$	Pentagonal bipyrimidal	−47
Powder phase **I**				−47
Ground crystal **3**	7	$3H_2O, 2CO_2^c$	Pentagonal bipyrimidal	−53, −47
Powder phase **II**				−53

[a] Chemical shift relative to 0.1 mol dm^{-3} $Cd(ClO_4)_2$ aqueous (D_2O) solution. [b] Bridging carboxyl. [c] Bidentate carboxyl.

water, but no other cadmium signal was observed even at different chemical shift. We have no clear explanation of the formation of this unusual compound **3** or of the increase in water co-ordination in **3** just by heating the starting compound **2**.

Metal-ion geometry and ^{113}Cd NMR chemical shift correlation

The six-, seven- and eight-co-ordination geometries of cadmium atoms obtained from the crystal structures of compounds **1**–**3** together with their ^{113}Cd NMR chemical shift data are summarized in Table 5. With the goal of describing the ligands and their co-ordination geometry about Cd, many cadmium–oxo compounds have been synthesized, their crystal structures determined and CP MAS ^{113}Cd NMR spectra measured.[8,32] A general pattern emerged in which compounds with six-co-ordinated Cd gave chemical shifts in the range δ 140 to −70, seven-co-ordinated δ 0 to −70, and eight-co-ordinated δ 0 to −115.[33,34] Based on these findings the six- and eight-co-ordinated cadmium atoms of **1** were assigned chemical shifts of δ 18 and −107 respectively. Similarly the seven-co-ordinated cadmium atoms of **2** and **3** are assigned chemical shifts of δ −47 and −53.

Several examples of cadmium compounds with cadmium atoms co-ordinated only to carboxy oxygens and water molecules have been reported. Six-co-ordinated cadmiums include cadmium maleate dihydrate (δ −3),[32] cadmium maleate dihydrate (*Cc* form, δ −5),[8] cadmium formate dihydrate (δ 11, 6),[32] and diaquabis(*p*-nitrobenzoato)cadmium(II) (δ 24),[35] and seven-co-ordinated cadmiums bis(acetato)diaquacadmium(II) (δ −58),[9] diaquasuccinatocadmium(II) hemihydrate (δ −52),[10] and bis[diaquabis(*o*-hydroxybenzoato)cadmium(II)] (δ −31).[10] Very few examples of eight-co-ordinated cadmiums have been reported: cadmium(II) calcium(II) acetate hexahydrate (δ −29)[32] and cadmium(II) maleate dihydrate (δ −22).[32] All chemical shifts are given relative to 0.1 mol dm^{-3} $Cd(ClO_4)_2$ aqueous (D_2O) solution; *i.e.* for 0.1 mol dm^{-3} $Cd(ClO_4)_2$ at I = 4.5 mol dm^{-3} and solid $Cd(ClO_4)_2 \cdot 6H_2O$, δ −15. These and other cadmium–oxo compounds have been examined, but the data were found to be insufficiently discriminating to allow for the correlation of structure and chemical shift. This may be because there are too many factors that can influence the chemical shift values (*e.g.* bond length, local site symmetry, and co-ordination number). For example, bis[diaquabis(*o*-hydroxybenzoato)cadmium(II)][10] and diaquasuccinatocadmium(II) hemihydrate[10] have similar seven-co-ordinated pentagonal-bipyramidal structures, but their observed chemical shifts are δ −31 and −52; the more basic ligand (succinate) seems to have a higher shielding ability for cadmium atom.

The six-, seven- and eight-co-ordinated cadmium atoms of compounds **1**–**3** reported herein represent interesting examples where the cadmium is co-ordinated only by carboxyl oxygens of malonate and water. There seems to be a good correlation between the chemical shift and number of co-ordinating oxygens. The chemical shift (δ 18) of the six-co-ordinated cadmium (see Fig. 2) of **1** lies within the range δ 25 to −5 reported for other six-co-ordinated cadmium atoms. The chemical shifts of seven-co-ordinated cadmium atoms of **2** (see Fig. 4, δ −47) and **3** (see Fig. 6, δ −53) are in good agreement with those of other examples of seven-co-ordinated cadmium atoms (range δ −31 to −58). An interesting comparison can be made of the co-ordinations of the cadmium atoms of **2** and **3** which are both close to pentagonal bipyramidal. The Cd atom of **2** is co-ordinated to one water molecule, one six-membered and two four-membered chelated carboxy-groups; **3** is formed when carboxyl oxygens forming a six-membered chelate ring are substituted by two water molecules, but such displacement results in only a small upfield shift from δ −47 to −53. The eight-co-ordinated cadmium atom [see Cd(1) in Fig. 2] of **1** has two water molecules and is found at unusually upfield value of δ −107. This atom seems to be more shielded than those in cadmium(II) calcium(II) acetate hexahydrate (δ −29) or cadmium(II) maleate dihydrate (δ −22). This site shows an isotropic chemical shift that lies within the range observed for the metalloproteins concanavaline A and parvalbumin. The only other example of an eight-co-ordinated cadmium atom that appears in such an upfield region is that in cadmium nitrate tetrahydrate (δ −115).[32] The upfield shift of the latter has been discussed in terms of the shielding of weak ligands with weak bonding interactions. Other examples of eight-co-ordinated cadmium are needed to understand this ususual upfield shift.

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References

1 Y. Boulanger, I. M. Armitage, K.-A. Miklossy and D. R. Winge, *J. Biol. Chem.*, 1982, **257**, 13717.
2 P. Gettins and J. E. Coleman, *Fed. Proc., Fed. Am. Soc. Exp. Biol.*, 1982, **41**, 2966.
3 B. R. Bobsein and R. J. Myers, *J. Am. Chem. Soc.*, 1980, **102**, 2454.
4 D. B. Bailey, P. D. Ellis and J. A. Free, *Biochemistry*, 1980, **19**, 591.
5 J. D. Otoves and I. M. Armitage, *Biochemistry*, 1980, **19**, 4031.
6 J. L. Evelhoch, D. F. Bocian and J. L. Sudmeier, *Biochemistry*, 1981, **20**, 4951.
7 A. J. M. S. Uiterkamp, I. M. Armitage and J. E. Coleman, *J. Biol. Chem.*, 1980, **255**, 3911.
8 R. S. Honkonen and P. D. Ellis, *J. Am. Chem. Soc.*, 1984, **106**, 5488.
9 P. F. Rodesiler and E. L. Amma, *J. Chem. Soc., Chem. Commun.*, 1982, 182.
10 N. G. Charles, E. A. H. Griffith, P. F. Rodesiler and E. L. Amma, *Inorg. Chem.*, 1983, **22**, 2717.
11 E. A. H. Griffith, N. G. Charles, K. Lewinski, E. A. Amma and P. F. Rodesiler, *Inorg. Chem.*, 1987, **26**, 3983.
12 R. M. H. Banda, I. G. Dance, T. D. Bailey, D. C. Craig and M. L. Scudder, *Inorg. Chem.*, 1989, **28**, 1682.
13 P. F. Rodesiler, N. G. Charles, E. A. H. Griffith and E. L. Amma, *Acta Crystallogr., Sect. C*, 1987, **43**, 1058.
14 E. Rivera, M. A. Kennedy, R. D. Adams and P. D. Ellis, *J. Am. Chem. Soc.*, 1990, **112**, 1400.
15 S. Nishikiori, C. I. Ratcliffe and J. A. Ripmeester, *J. Am. Chem. Soc.*, 1992, **114**, 8590.

16 D. B. Bailey, A. D. Cardin, W. D. Behnke and P. D. Ellis, *J. Am. Chem. Soc.*, 1978, **100**, 5236.

17 P. S. Marchetti, P. D. Ellis and R. G. Bryant, *J. Am. Chem. Soc.*, 1985, **107**, 8191.

18 T. Drakenberg, B. Lindman, A. Cave and J. Parello, *FEBS Lett.*, 1978, **92**, 346.

19 A. Cave, J. Parello, T. Drakenberg, E. Thulin and B. Lindman, *FEBS Lett.*, 1979, **100**, 148.

20 E. A. H. Griffith, N. G. Charles, P. F. Rodesiler and E. L. Amma, *Acta Crystallogr.*, *Sect. B*, 1982, **38**, 262.

21 A. L. Swain and E. L. Amma, *Inorg. Chim. Acta*, 1989, **163**, 5.

22 K. H. Chung and C. H. Moon, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 75.

23 M. L. Post and J. Trotter, *J. Chem. Soc.*, *Dalton Trans.*, 1974, 674.

24 B. H. O'Connor and E. N. Maslen, *Acta Crystallogr.*, 1966, **20**, 824.

25 K. H. Chung, E. Hong, Y. Do and C. H. Moon, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 2333.

26 J. L. de Boer and A. J. M. Duisenburg, *Acta Crystallogr.*, *Sect. A*, 1984, **40**, C410.

27 G. M. Sheldrick, SHELXS 86, Program for crystal structure determination, University of Göttingen, 1986.

28 G. M. Sheldrick, SHELXL 93, Program for crystal structure refinements, University of Göttingen, 1993.

29 D. A. Langs and C. R. Hare, *Chem. Commun.*, 1967, 890.

30 M. L. Post and J. Trotter, *J. Chem. Soc.*, *Dalton Trans.*, 1974, 1922.

31 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

32 P. G. Mennitt, M. P. Shatlock, V. J. Bartuska and G. E. Maciel, *J. Phys. Chem.*, 1981, **85**, 2087.

33 P. D. Ellis, *Science*, 1983, **221**, 1141.

34 M. F. Summers, *Coord. Chem. Rev.*, 1988, **86**, 43.

35 P. F. Rodesiler, E. A. H. Griffith, N. G. Charles and E. L. Amma, *Acta Crystallogr.*, *Sect. C*, 1985, **41**, 673.

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