

Cadmium Carboxylate Chemistry: Preparation, Crystal Structure, and Thermal and Spectroscopic Characterization of the One-dimensional Polymer $[\text{Cd}(\text{O}_2\text{CMe})(\text{O}_2\text{CPh})(\text{H}_2\text{O})_2]_n$

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In dedication to the late Professor John M. Tsangaris for his important contributions to Inorganic Chemistry

Compound $[\text{Cd}(\text{O}_2\text{CMe})(\text{O}_2\text{CPh})(\text{H}_2\text{O})_2]_n$ (**1**) was initially obtained in a serendipitous way during efforts to prepare a $\text{Cd}^{\text{II}}/\text{PhCO}_2^-/\text{bepy}$ complex (bepy = 2-benzoylpyridine). With the identity of **1** established by single-crystal X-ray crystallography, a rational preparative route to this complex was designed and carried out by reacting $\text{Cd}(\text{O}_2\text{CMe})_2 \cdot 2\text{H}_2\text{O}$ with a slight excess of PhCOOH in MeCN under reflux. The crystal structure of **1** consists of isolated zig-zag chains. The Cd^{II} atom is coordinated to five carboxylate and two aqua oxygen atoms creating a distorted, capped trigonal prismatic coordination polyhedron. The acetate group exhibits the $\eta^1:\eta^2:\mu_2$ coordination mode, while the benzoate ligand is chelating. There is an extensive hydrogen-bonding network which reinforces the chains and also links them generating sheets. The new complex was characterized by IR, far-IR, Raman, CP MAS and solution ^{113}Cd NMR spectroscopy. The spectroscopic data are discussed in terms of the nature of bonding and the known structure. An anhydrous compound with the empirical formula $\text{Cd}(\text{O}_2\text{CMe})(\text{O}_2\text{CPh})$ was isolated during the thermal decomposition of **1**; the vibrational study of this thermally stable intermediate supports an 1D polymeric structure with 6-coordinate Cd^{II} ions.

Key words: Cadmium Carboxylate Complexes, ^{113}Cd NMR Spectroscopy, Mixed Acetate-benzoate Complexes, Thermogravimetry, Vibrational Spectroscopy

Introduction

Simple carboxylate anions are ubiquitous and versatile ligands in coordination chemistry [1–4]. Numerous complexes with a variety of metals have been synthesized, many of which have played key roles in the conceptual development of modern inorganic chemistry. Perhaps most striking in terms of their impact are the so called dinuclear “paddlewheel”, the trinuclear “basic” carboxylate and the tetranuclear “butterfly” complexes (Fig. 1). Extensive physicochemical and structural studies of these compounds have been crucial for increasing our understanding of bonding and magnetic interactions between proximate metal centres, topics with implications ranging from industrial catalysis to metalloprotein structure and function. The versatility of the RCO_2^- ligand is reflected

by the variety of metal binding modes it can adopt. Up to three transition metal ions have been shown to bind to a single carboxylate ligand [1]; however, more common is the coordination of one or two metal ions in structurally distinct ways to one or more of the four available electron lone pairs of the carboxylate anion.

In contrast to the great number of studies concerning $3d^n$, $4d^n$, $5d^n$ ($n = 1 - 9$) and $4f$ metal carboxylate chemistry, relatively little is known about the group 10 metal carboxylate complexes; this is especially true for cadmium and mercury. One reason for this is the existence of only a limited number of Cd^{II} and Hg carboxylate starting materials; in Cd^{II} chemistry, for example, only cadmium(II) acetate dihydrate, $\text{Cd}(\text{O}_2\text{CMe})_2 \cdot 2\text{H}_2\text{O}$, is readily available in the market. Restricting further discussion to Cd, it is known [5]

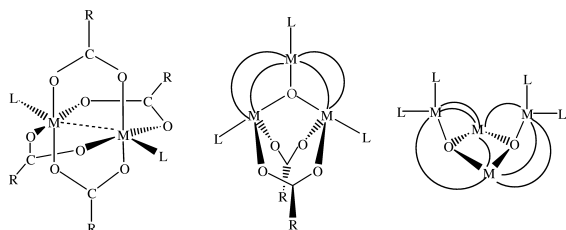


Fig. 1. Paddlewheel (left), trinuclear basic carboxylate (middle) and tetranuclear “butterfly” carboxylate (right) complexes. Curved lines represent bridging carboxylate groups. The paddlewheel structural type is associated with a variety of metal-metal interactions ranging from no interactions, weak spin-pairing, various orders of metal-metal bonding, to the “super-short” metal-metal bonds. The L groups are often monodentate ligands but they may represent intercluster association into polymeric structures or (only in the case of the “butterfly” complexes) one donor atom of a bidentate chelating ligand.

that the maximum deviation of the Cd^{II} atom from the carboxylate plane can reach up to 1.5 Å, whereas most 3d metal ions (Mn^{II} , Mn^{III} , Fe^{II} , Fe^{III} , Co^{II} , Co^{III} , Ni^{II} , Cu^{I} , Cu^{II}) and Zn^{II} tend to lie in the carboxylate plane. This means that the Cd^{II} ion is much more accommodating to the arrangement of the carboxylate anions, a fact which in combination with the stereochemical adaptability of this d^{10} metal ion favours structural variations [5–7]. It should be noted at this point that there has been an increasing interest in the coordination chemistry of cadmium(II) due to the recognition of its role in biological systems [8–11], as well as in molecule-based materials [12–17]. In search for molecule-based materials with interesting physical properties, much attention has been given to one- (1D), two- (2D) and three-dimensional (3D) coordination polymers of cadmium(II).

In the last several years, we have developed a strong interest in 3d metal carboxylate chemistry, as it has become apparent that this area represents a rich source of high-nuclearity (polynuclear) and polymeric products with interesting structural, spectroscopic and magnetic properties [18–30]. We have recently extended our interests to Cd^{II} , believing that Cd^{II} carboxylate chemistry would encompass a range of novel structural types and products with unusual physical properties. This paper describes the preparation and characterization of an interesting 1D coordination polymer of cadmium(II) possessing both acetate and benzoate ligands; this compound can be considered as a

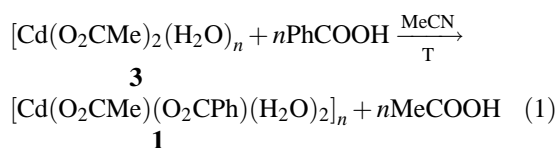
useful starting material for further Cd^{II} carboxylate chemistry.

Results and Discussion

Synthetic comments

We initially came across complex $[\text{Cd}(\text{O}_2\text{CMe})(\text{O}_2\text{CPh})(\text{H}_2\text{O})_2]_n$ (**1**) during our efforts to prepare a $\text{Cd}^{\text{II}}/\text{PhCO}_2^-/\text{bepy}$ complex (bepy = 2-benzoylpyridine). The 1:1 reaction between bepyp and a starting material believed to be “ $\text{Cd}(\text{O}_2\text{CPh})_2 \cdot x\text{H}_2\text{O}$ ” in MeCN under reflux gave a homogeneous solution; slow evaporation of this solution at room temperature gave a mixture of well-formed, prism-shaped colourless crystals and pale yellow plates. Their not-too-dissimilar solubility prevented chemical separation. The difference in colour and the rather large size of the prismatic crystals allowed manual separation of the two materials. The prismatic crystals proved to be complex **1** by single-crystal X-ray crystallography. Unfortunately, we were not able to obtain crystals of appropriate quality for the X-ray study required for the elucidation of the structure of the pale yellow product; analytical data and IR spectroscopy indicated the formulation $[\text{Cd}_3(\text{O}_2\text{CPh})_6(\text{bepy})_2]$ (**2**). The IR spectra of **1** and “ $\text{Cd}(\text{O}_2\text{CPh})_2 \cdot x\text{H}_2\text{O}$ ” are identical, indicating that **1** was, in fact, unreacted starting material in the reaction that leads to product **2**. The “ $\text{Cd}(\text{O}_2\text{CPh})_2 \cdot x\text{H}_2\text{O}$ ” starting material had been isolated from the reaction between $\text{Cd}(\text{O}_2\text{CMe})_2 \cdot 2\text{H}_2\text{O}$ and two equivalents of benzoic acid, PhCOOH , in MeCN.

With the identity of **1** established, a rational preparative procedure was devised by reacting $\text{Cd}(\text{O}_2\text{CMe})_2 \cdot 2\text{H}_2\text{O}$ (**3**) with one equivalent of PhCOOH in MeCN under reflux as summarized in eq. (1):



Such a reactivity pattern is consistent with the known acidities of the RCOOH molecules as reflected in their pK_a values (4.75 for MeCOOH , 4.19 for PhCOOH) and the probable mechanism [31] involves protonation of a bound acetate by the more acidic PhCOOH , followed by its displacement by generated PhCO_2^- . Such ligand substitution reactions have been widely used in metal carboxylate chemistry [31–33]. A slight excess of Ph-

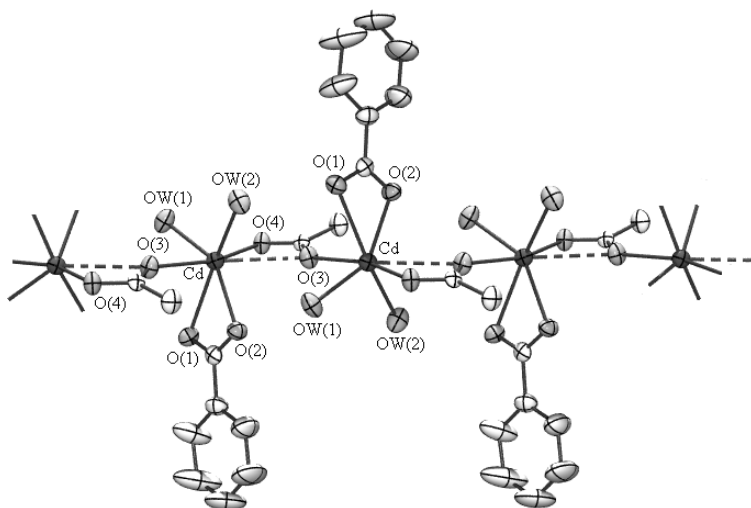


Fig. 2. A partially labelled, small section of the polymeric chain of complex **1**. The dashed line indicates the weak Cd-O(3) $[1/2 - x, 1/2 + y, -z]$ bond.

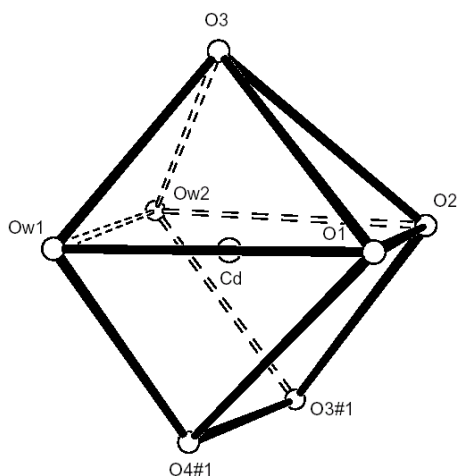


Fig. 3. The monocapped trigonal stereochemistry about the Cd^{II} atom in complex **1**.

COOH seems beneficial to the preparation increasing the yield of the reaction.

Description of structure

A drawing of the molecular structure of complex **1** is shown in Fig. 2; the coordination polyhedron of the Cd^{II} ion is depicted in Fig. 3. Selected bond distances and angles are given in Table 1.

The compound contains zig-zag chains of repeating $\{Cd(O_2CMe)(O_2CPh)(H_2O)_2\}$ units. The polymeric chains extend along the *b* axis. In each chain the Cd^{II} atoms are bridged by $\eta^1:\eta^2:\mu_2$ acetate groups. Seven-coordination at each metal is completed by one chelat-

Table 1. Selected bond lengths (Å) and angles (°) relevant to the cadmium coordination sphere for complex **1**.^a

Cd-O(1)	2.494(3)	Cd-O(2)	2.298(3)
Cd-O(3)	2.307(4)	Cd-O(3)#1	2.728(5)
Cd-O(4)#1	2.279(4)	Cd-OW(1)	2.284(4)
Cd-OW(2)	2.270(4)		
O(1)-Cd-O(2)	54.3(1)	O(1)-Cd-O(3)	81.8(1)
O(1)-Cd-O(3)#1	109.7(1)	O(1)-Cd-O(4)#1	98.8(1)
O(1)-Cd-OW(1)	94.8(1)	O(1)-Cd-OW(2)	162.4(1)
O(2)-Cd-O(3)	86.4(1)	O(2)-Cd-O(3)#1	76.6(1)
O(2)-Cd-O(4)#1	109.0(1)	O(2)-Cd-OW(1)	147.9(1)
O(2)-Cd-OW(2)	110.8(2)	O(3)-Cd-O(3)#1	146.3(2)
O(3)-Cd-O(4)#1	161.7(1)	O(3)-Cd-OW(1)	80.0(1)
O(3)-Cd-OW(2)	88.2(2)	O(3)#1-Cd-O(4)#1	50.6(1)
O(3)#1-Cd-OW(1)	128.2(1)	O(3)#1-Cd-OW(2)	71.6(2)
O(4)#1-Cd-OW(1)	81.8(1)	O(4)#1-Cd-OW(2)	95.2(2)
OW(1)-Cd-OW(2)	97.8(2)		

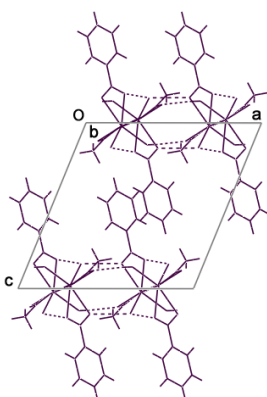
^a Symmetry transformation used to generate equivalent atoms: #1 $1/2 - x, 1/2 + y, -z$.

ing benzoate ligand and two terminal aqua ligands. The Cd-O_{aqua} bond lengths [2.270(4), 2.284(4) Å] are similar and agree well with values found for other 7-coordinate cadmium(II) complexes [34, 35]; for example, the Cd-O_{aqua} bond length in the 7-coordinate polymer $[Cd(mal)(H_2O)]_n$, where mal²⁻ is malonate(-2), is 2.272(7) Å [34]. The Cd-O_{carboxylate} bond distances are in the wide range 2.279(4)-2.728(5) Å. The Cd-O_{benzoate} distances are asymmetric [2.298(3), 2.494(3) Å]. There are three distinct Cd-O_{acetate} bond distances due to the $\eta^1:\eta^2:\mu_2$ coordination mode of the acetate ligand. The bridging Cd-O_{acetate} distances are also asymmetric [2.307(4), 2.728(5) Å]. The Cd-O bond distance for the bridging acetate oxygen atom

Table 2. Dimensions of the established and possible hydrogen bonds (distances in Å and angle in °) for complex **1**.

H bond	D...A H...A	D-H...A	Operator of A	
OW(2)-H(OW2)-O(4) ^a	2.690	1.921	165.8	$1-x, -y, -z$
OW(1)...O(1) ^a	2.800	c	c	$-x, -y, -z$
OW(1)...O(2) ^b	2.794	c	c	$1/2-x, -1/2+y, -z$
OW(2)...O(1) ^b	2.920	c	c	$1/2-x, 1/2+y, -z$

^a Interchain hydrogen bonds; ^b intrachain hydrogen bonds; ^c hydrogen atoms were not located in the difference map; A = acceptor, D = donor.

Fig. 4. Hydrogen bonding and packing viewed down the *b* axis for complex **1**.

is longer than the distance exhibited by the terminal oxygen atom to the same Cd^{II} atom [2.728(5) versus 2.279(4) Å]. The increase in bond length upon bridging relative to terminal ligation has been observed previously [5] in many complexes containing carboxylate ligands with one bridging oxygen atom. Based on theoretical and experimental studies which have indicated that the *syn* lone pairs of the carboxylate group are more basic than the *anti* lone pairs [1, 36, 37], one might expect the Cd-O(3)#1 distance to be shorter than the Cd-O(3) distance; however, the reverse relation holds for **1** (see Table 1). This result, which is in accordance with results obtained for many cadmium carboxylate complexes [5], suggests that the Cd-O bond lengths involving $\eta^1:\eta^2:\mu_2$ RCO₂⁻ ligands are mainly influenced by geometrical factors rather than the electronic properties of the carboxylate group. The intrachain Cd...Cd distance is 4.639(1) Å.

Since even the more symmetrical of the possible 7-coordinate geometries [38, 39] differ only slightly from one another and conformational interconversions require relatively slight angular changes, the geometry observed for any actual structure may be largely a reflection of constraints placed on the complex by ligand

steric requirements and packing considerations. In the present instance the coordination polyhedron of oxygen atoms about the central metal ion is best described as a distorted capped trigonal prism, the capping atom being O(3).

The compound is extensively hydrogen bonded. Fig. 4 shows the hydrogen bonding (broken lines) and packing arrangement viewed down the *b* axis, while metric parameters for the hydrogen bonds are listed in Table 2. Both water oxygen atoms are involved as donors, while both benzoate and the terminally ligated acetate oxygen atoms [O(4)] act as acceptors. There are both intra- and interchain hydrogen bonds; the latter generate 2D sheets parallel to *ab*.

The structure of complex **1**, as detailed in the above discussion and in Table 1, shows a remarkable similarity with that of cadmium diacetate dihydrate [35], whose correct formulation is [Cd(O₂CMe)₂(H₂O)₂]_n (**3**). The latter is a 7-coordinate, 1D polymer containing one $\eta^1:\eta^2:\mu_2$ acetate, one chelating acetate and two aqua ligands per Cd^{II}. Thus, complex **1** can be considered as derived from **3** after substitution of one chelating acetate by one chelating benzoate, see also eq. (1).

Spectroscopic characterization

The IR and Raman spectra of complex **1** are shown in Figs. 5a and 6, respectively. Vibrational assignments for some diagnostic bands are discussed below. Assignments have been given in comparison with the data obtained for NaO₂CMe and NaO₂CPh (assumed to contain a 'free' carboxylate group), by taking into account the structure of the complex and by studying literature reports for cadmium(II) carboxylate complexes [6, 17, 40, 41].

The IR spectrum of **1** exhibits a broad band of medium intensity at ~ 3440 cm⁻¹, assignable [41, 42] to $\nu(\text{OH})_{\text{coord. water}}$. The broadness and relatively low frequency of this band are both indicative of hydrogen bonding. This band is absent from the IR spectrum of the dehydrated complex (Fig. 5b), as expected.

Three bands and three shoulders appear in the 1620–1350 cm⁻¹ range; the corresponding Raman region contains six to seven bands. Contributions from RCO₂⁻ (R= Me, Ph) $\nu_{\text{as}}(\text{CO}_2)$ and $\nu_{\text{s}}(\text{CO}_2)$ vibrations would be expected in this region, but overlap with the stretching vibrations of the aromatic ring and $\delta(\text{CH}_3)$ renders detailed assignments difficult. Owing to the presence of two different types of carboxylate groups in **1**, two $\nu_{\text{as}}(\text{CO}_2)$ and two $\nu_{\text{s}}(\text{CO}_2)$ bands might be ex-

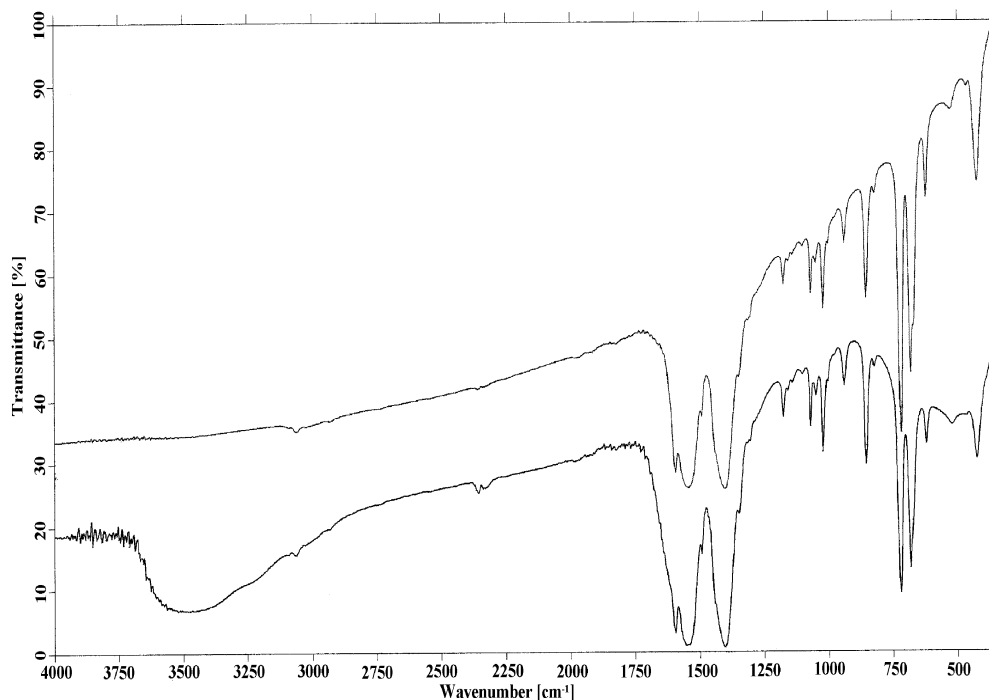


Fig. 5. The IR spectrum of complex **1** (a) and its dehydrated form (b).

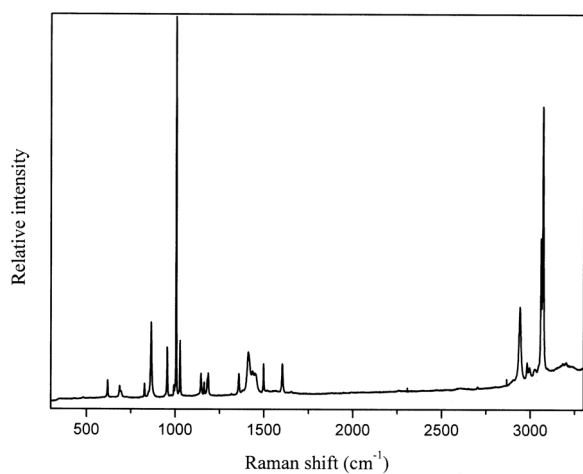


Fig. 6. The Raman spectrum of complex **1** in the 3300–300 cm^{-1} region.

pected. It seems that the IR frequencies of the $\nu_{\text{as}}(\text{CO}_2)$ and $\nu_{\text{s}}(\text{CO}_2)$ bands of the two different carboxylate ligands coincide at 1557 and 1404 cm^{-1} , respectively; the broadness of these bands supports the view of an overlapping character of each band. The difference $\Delta[\Delta = \nu_{\text{as}}(\text{CO}_2) - \nu_{\text{s}}(\text{CO}_2)]$ is 154 cm^{-1} , less than the

corresponding values for NaO_2CPh (184 cm^{-1}) and NaO_2CMe (164 cm^{-1}), as expected from the bidentate coordination modes of both carboxylate groups [43]. In the Raman spectrum, two $\nu_{\text{s}}(\text{CO}_2)$ lines are clearly observed at 1411 and 1437 cm^{-1} [43, 44], whereas the $\nu_{\text{as}}(\text{CO}_2)$ vibrations appear weak (as expected [43]) and are probably masked under the aromatic stretch at 1610 cm^{-1} .

The bands at 286, 277, 255, 244, 222 and 201 cm^{-1} in the far-IR spectrum of **1** are tentatively assigned [41] to $\nu(\text{Cd-O})$ modes; the bands at 222 and 201 cm^{-1} should contain a $\nu(\text{Cd-O}_{\text{water}})$ character since their intensities are significantly decreased after dehydration.

The CP MAS ^{113}Cd NMR spectroscopic study was carried out on finely ground crystals of **1**. The spectrum shows a single resonance at $\delta -41$ corresponding to a single type of Cd^{II} atom. ^{113}Cd NMR is a very useful tool for the study of cadmium(II) complexes due to the sensitivity of the ^{113}Cd chemical shift to the nature of donor atoms, their coordination geometry and bond lengths [46]. The coordination number of Cd^{II} in complexes with exclusively oxygen ligation is normally six, seven or eight, while the isotropic chemical shifts span the range δ 140 to -115 [46]. From sys-

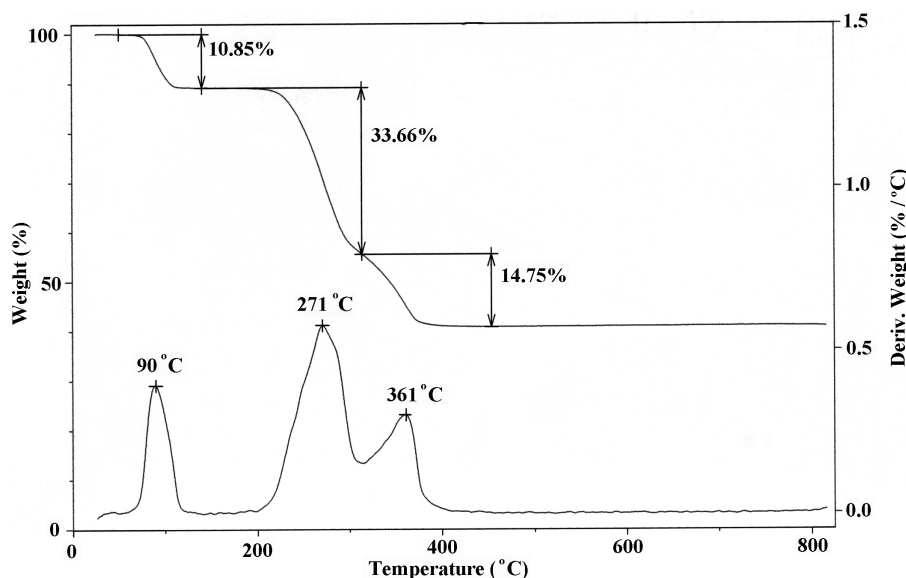


Fig. 7. Thermogravimetric (up) and differential thermogravimetric data (down) for complex **1**.

tematic studies, a pattern has emerged [46,47] showing that 6-coordinate Cd^{II} has a chemical shift ranging from δ 140 to -70 , 7-coordinate Cd^{II} spans the range δ 0 to -70 , and 8-coordinate Cd^{II} a range δ 0 to -115 . Few spectroscopic studies on 7-coordinate cadmium compounds with Cd^{II} atoms coordinated only to carboxylate oxygens and aqua ligands have been reported. These include $[\text{Cd}(\text{O}_2\text{CMe})_2(\text{H}_2\text{O})_2]_n$ (δ -58) [48], $[\text{Cd}(\text{suc})(\text{H}_2\text{O})_2]_n$ (δ -52) [49], where suc^{2-} is succinate(-2), $[\text{Cd}_2(\text{salH})_4(\text{H}_2\text{O})_4]$ (δ -31) [49], where salH^- is salicylate(-1), $[\text{Cd}(\text{mal})(\text{H}_2\text{O})]_n \cdot n\text{H}_2\text{O}$ (δ -47) [50] and $[\text{Cd}(\text{mal})(\text{H}_2\text{O})_3]_n \cdot n\text{H}_2\text{O}$ (δ -53) [50], where mal^{2-} is malonate(-2). The chemical shift (δ -41) of the 7-coordinate Cd^{II} of **1** lies within the range δ -31 to -58 reported for other 7-coordinate Cd^{II} atoms with exclusively carboxylate and aqua ligation.

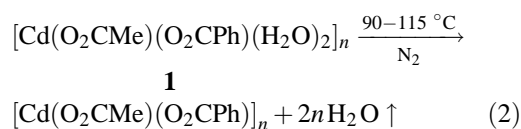
The ^{113}Cd NMR spectrum of **1** in D_2O solution shows a single resonance at δ 46, also corresponding to a single type of Cd^{II} atom. Based on the above mentioned data, this chemical shift is assigned to a 6-coordinate Cd^{II} atom, indicating that the solid-state structure does not persist in solution. It is well-established that the decrease of coordination number leads to more deshielded δ values [49, 50].

Thermal decomposition

The thermal decomposition of complex **1** was studied using thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal analysis

(DTA) techniques under nitrogen. TG and DTG data are shown in Fig. 7.

Complex **1** decomposes *via* an anhydrous stable intermediate. The data show an initial, endothermic weight loss between 90 and 115 °C, which corresponds exactly to the release of all the water content (found: 10.85; calc.: 10.96%). A clear plateau is reached at about 120 °C up to 200 °C, suggesting that the anhydrous species is thermally stable. The anhydrous product, obtained after a TG experiment up to 140 °C by keeping the heating rate at 1 °C min^{-1} or by keeping the sample at 110 °C for 24 h, was isolated (temperature-arrest technique [51, 52]) and studied by IR (Fig. 5b), far IR and Raman spectroscopic methods (see below). The anhydrous intermediate decomposes above 200 °C with a rather simple degradation mechanism, as revealed by the appearance of two rather broad DTG maxima at 271 and 361 °C, and without the formation of a new stable intermediate. A brown amorphous residue of CdO [53] (found: 40.79; calc. 39.08%) is obtained at ~ 380 °C. The formation of the thermally stable, anhydrous intermediate is summarized by eq. (2). It is a matter of interest that the species with the empirical formula $\text{Cd}(\text{O}_2\text{CMe})(\text{O}_2\text{CPh})$ has been isolated in pure form from a solid-state reaction



[eq. (2)], whilst attempts for its preparation from solution have been unsuccessful.

The IR spectrum of the anhydrous product (which appears slightly hygroscopic) is identical to that of **1**, except for the fact that the former does not contain the band of coordinated water at $\sim 3440\text{ cm}^{-1}$ (Fig. 5). The identical frequencies of the $\nu_{\text{as}}(\text{CO}_2)$ and $\nu_{\text{s}}(\text{CO}_2)$ modes in the spectra of **1** and its anhydrous form may suggest that the coordination modes of acetate and benzoate ligands remain the same in the latter.

Concluding Comments

Compound $[\text{Cd}(\text{O}_2\text{CMe})(\text{O}_2\text{CPh})(\text{H}_2\text{O})_2]_n$ (**1**), initially obtained serendipitously and subsequently isolated using a rational synthetic scheme, is one-dimensional coordination polymer possessing interesting structural and physical/spectroscopic properties. Its mixed-carboxylate character and good solubility properties make this complex a useful starting material in the area of cadmium carboxylate chemistry. Complex **1** occupies the third apex of a triangle in $\text{Cd}^{\text{II}}/\text{RCO}_2^-$ chemistry ($\text{R} = \text{Me}, \text{Ph}$); the other two apices are occupied by the structurally characterized homocarboxylate species $[\text{Cd}(\text{O}_2\text{CMe})_2(\text{H}_2\text{O})_2]_n$ (**3**) [35] and $[\text{Cd}(\text{O}_2\text{CPh})_2(\text{H}_2\text{O})_2] \cdot 2\text{PhCOOH}$ (**4**) [54], which have 1D and monomeric structures, respectively. Complex **1** retains the $\eta^1:\eta^2:\mu_2\text{ MeCO}_2^-$ coordination mode observed for one acetate in **3** and the chelating PhCO_2^- character observed for both benzoate ligands in **4**. The anhydrous compound isolated by the solid-state thermal decomposition of **1** emphasizes further the versatility of cadmium carboxylate chemistry. Work is in progress in our laboratories to isolate and structurally characterize a PhCOOH -free cadmium benzoate complex.

Experimental Section

All manipulations were performed under aerobic conditions using starting materials (Merck) and solvents as received. Elemental analyses (C, H) were conducted by the University of Ioannina, Greece, Microanalytical Service. IR spectra ($4000 - 500\text{ cm}^{-1}$) were recorded on a Perkin-Elmer 16PC FT spectrometer with samples prepared as KBr pellets. Far-IR spectra ($500 - 100\text{ cm}^{-1}$) were recorded on a Bruker IFS 113v FT spectrometer with a DTGS detector using polyethylene pellets. The Raman spectrum has been measured in the micro-Raman backscattering geometry. The spectra were excited with the 441.6 nm line of an air-cooled HeCd laser of Kimmon Electric Co. (Dual, 325/442 nm, UV/blue, 20/80 mW, IK5651R-G model laser). A narrow-

bandpass interference filter was used for the elimination of the laser plasma lines. The excitation beam was directed to the sample compartment of a confocal open microscope attachment for punctual analysis. The microscope was used for the delivery of the excitation laser beam on the sample. The focusing objective was a Long Working distance (8 mm) 50x/0.55 Olympus lens. The spectrum was obtained using a $\sim 5\text{ mW}$ laser power on the specimen for a total integration time of 5 s. The Raman scattered radiation was focused on a confocal entrance slit (of $100\text{ }\mu\text{m}$ width) of an achromatic flat field spectrograph of 800 nm focal length. The integrated laser Raman system employed was the UV-vis Labram HR of the Jobin Yvon-Horiba group. The dispersion and the detection of the Raman photons were done by an 1800-grooves/mm grating and a 2D CCD detector (operating at 140 K), respectively. The spectral slit width was approximately 3 cm^{-1} . Thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal analysis (DTA) experiments were performed on the SDT-2960 module from TA Instruments in a dinitrogen gas flow; sample weights of 5–15 mg and heating rates of 1 and $5\text{ }^\circ\text{C min}^{-1}$ were used. The solid-state ^{113}Cd NMR spectrum of **1** was measured with the same single crystals used previously in crystallography, in a finely ground form. The spectrum was 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 solution (D_2O , $\sim 70\text{ mM}$) ^{113}Cd NMR spectrum was recorded on a Bruker WP200 spectrometer. For both solid-state and solution spectra chemical shifts are quoted relative to 0.1 M $\text{Cd}(\text{ClO}_4)_2$ aqueous (D_2O) solution as the reference with positive chemical shifts downfield.

Serendipitous isolation of complex 1

A colourless slurry of “ $\text{Cd}(\text{O}_2\text{CPh})_2 \cdot x\text{H}_2\text{O}$ ” ($\sim 0.11\text{ g}$, $\sim 0.3\text{ mmol}$, see *Synthetic comments*) and *bepy* (0.06 g, 0.3 mmol) in MeCN (20 ml) was refluxed for 20 min. The solids soon dissolved to give a clear, homogeneous solution. The reaction solution was refluxed for a further 10 min. Slow evaporation of the solution at room temperature gave a mixture of well-formed, prismatic colourless crystals and pale yellow plates. The products were carefully collected by filtration. The two crystalline materials were separated manually, dried in air and identified individually as complexes $[\text{Cd}(\text{O}_2\text{CMe})(\text{O}_2\text{CPh})(\text{H}_2\text{O})_2]_n$ (**1**) (by single-crystal X-ray crystallography) and $[\text{Cd}_3(\text{O}_2\text{CPh})_6(\text{bepy})_2]$ (**2**) (by elemental analyses and IR spectra). The yields for **1** and **2** were 15 and 45%, respectively (based on the total available cadmium).

*Rational synthesis of $[\text{Cd}(\text{O}_2\text{CMe})(\text{O}_2\text{CPh})(\text{H}_2\text{O})_2]_n$ (**1**)*

A stirred colourless solution of $\text{Cd}(\text{O}_2\text{CMe})_2 \cdot 2\text{H}_2\text{O}$ (0.21 g, 0.8 mmol) in MeCN (15 ml) was treated with

Table 3. Summary of crystal data, data collection and structure refinement for X-ray diffraction study of complex **1**.

Chemical formula	C ₉ H ₁₂ O ₆ Cd
Formula weight	328.59
Colour, habit	colourless prisms
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>a</i>
<i>a</i> (Å)	11.816(1)
<i>b</i> (Å)	8.969(1)
<i>c</i> (Å)	12.065(1)
β (°)	112.27(1)
<i>V</i> (Å ³)	1183.3(2)
<i>Z</i>	4
<i>D</i> _{calc} (g cm ⁻³)	1.844
μ (mm ⁻¹)	14.921
<i>F</i> (000)	648
Radiation (Å)	Cu- <i>K</i> _α (λ = 1.54180)
Temperature (K)	298
Scan mode/speed (° min ⁻¹)	θ – 2 θ /4.5
θ Range (°)	6.33–62.02
<i>h</i> , <i>k</i> , <i>l</i> Ranges	–13 → 9, 0 → 10, 0 → 13
Measured reflections	1859
Unique reflections	1792 (<i>R</i> _{int} = 0.0457)
Reflections used [<i>I</i> > 2 σ (<i>I</i>)]	1725
Parameters refined	153
[Δ/σ] _{max}	0.013
<i>w</i> ^a	<i>a</i> = 0.1207; <i>b</i> = 1.2102
GoF (on <i>F</i> ²)	1.086
<i>R</i> 1 ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.0580
<i>wR</i> 2 ^c [<i>I</i> > 2 σ (<i>I</i>)]	0.1485
($\Delta\rho$) _{max} /($\Delta\rho$) _{min} (e Å ⁻³)	0.877/–0.868

^a $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = (\max(F_o^2, 0) + 2F_c^2)/3$;

^b $R1 = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$; ^c $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$.

PhCOOH (0.11 g, 0.9 mmol). The resulting white suspension was refluxed for 40 min; most of the solid dissolved during this time. The reaction mixture was filtered to remove a small quantity of undissolved material. The colourless filtrate was allowed to slowly concentrate at 25 °C. Well-formed, X-ray quality colourless crystals appeared after 24 h, which were collected by filtration, washed with Et₂O and dried in air. Typical yields were in the 75–85% range. IR (KBr pellet): $\nu = 3445, 1595, 1404, 1176, 1071, 1050, 1026, 954, 860, 720, 686, 620, 580, 535$ cm⁻¹. – Far-IR (polyethylene pellet): $\nu = 430, 332, 314, 286, 277, 255, 244, 222,$

201, 177, 157, 128, 120, 112, 107 cm⁻¹. – Main Raman lines: $\nu = 3076, 3060, 2940, 1610, 1498, 1437, 1411, 1187, 1127, 1005, 955, 866, 622$ cm⁻¹. – CP MAS ¹¹³Cd NMR (66.576 MHz): $\delta = -41$ (s). – ¹¹³Cd NMR (66.576 MHz, D₂O): $\delta = 46$ (s). – C₉H₁₂O₆Cd (328.59): calcd. C 32.90, H 3.69; found C 33.07, H 3.56.

Crystal structure determination

A colourless prismatic crystal of **1** (0.08 × 0.14 × 0.30 mm) was mounted in air. Diffraction measurements were made on a P2₁ Nicolet diffractometer upgraded by Crystal Logic using graphite monochromated Cu radiation. Crystal data and full details of the data collection and data processing are listed in Table 3. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centred reflections in the range 22 < 2 θ < 54°. Three standard reflections, monitored every 97 reflections, showed less than 3% intensity variation and no decay. Lorentz and polarization corrections were applied using Crystal Logic software.

The structure was solved by direct methods using SHELXS-86 [55] and refined by full-matrix least-squares techniques on *F*² with SHELXL-93 [56]. Almost all H atoms were introduced at calculated positions as riding on bonded atoms. Only one H atom of the two aqua ligands was located in the difference map and refined isotropically; the rest were not included in the refinement. All non-H atoms were refined using anisotropic displacement parameters. One X-ray crystallographic file for complex **1**, in CIF format, has been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, under the number 216776. A copy may be requested free of charge from the Director of CCDC (E-mail: deposit@ccdc.cam.ac.uk).

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