Research paper

Influence of cadmium(II) source upon the formation of a discrete monomer $[\text{Cd}(\kappa^2\text{-OC}(\text{O})^t\text{Bu})_2(\text{H}_2\text{O})_2]$ and a trinuclear heterobimetallic 1D CP, $\{\text{Na}_2[\text{Cd}(\mu_5\text{-}\kappa^3\text{:}\kappa^3\text{-OAc})(\mu_3\text{-}\kappa^2\text{:}\kappa^3\text{-OC}(\text{O})^t\text{Bu})(\mu_3\text{-}\kappa^1\text{:}\kappa^2\text{-OC}(\text{O})^t\text{Bu})_2]\cdot 2^t\text{BuC}(\text{O})\text{OH}\}_\infty$

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ABSTRACT

The reaction of $\text{CdCl}_2\cdot 2.5\text{H}_2\text{O}$ with two equiv of aq. NaOH followed by treatment of the resulting solution with two equiv of pivalic acid gave $[\text{Cd}(\kappa^2\text{-OC}(\text{O})^t\text{Bu})_2(\text{H}_2\text{O})_2]$ (**1**) in 83% yield while the aforementioned reaction with $\text{Cd}(\text{OAc})_2\cdot 2\text{H}_2\text{O}$ as Cd^{2+} source afforded a trinuclear heterobimetallic 1D-CP, $\{\text{Na}_2[\text{Cd}(\mu_5\text{-}\kappa^3\text{:}\kappa^3\text{-OAc})(\mu_3\text{-}\kappa^2\text{:}\kappa^3\text{-OC}(\text{O})^t\text{Bu})(\mu_3\text{-}\kappa^1\text{:}\kappa^2\text{-OC}(\text{O})^t\text{Bu})_2]\cdot 2^t\text{BuC}(\text{O})\text{OH}\}_\infty$ (**2**) in 90% yield. Complexes **1** and **2** were characterized by elemental analyses, IR spectroscopy, solution ^1H and ^{13}C $\{^1\text{H}\}$ NMR spectroscopy and solid state CP-MAS $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy, TG-DTA analyses and single crystal X-ray diffraction. The phase purity of **2** was also verified by powder X-ray diffraction. Complex **1** represents the first structurally characterised discrete mononuclear cadmium(II) carboxylate complex which is known to contain a pair of chelating carboxylate ligand, while **2** represents the first structurally characterized trinuclear heterobimetallic 1D-CP formed through aggregation via covalent coordinate bond.

1. Introduction

Cadmium(II) carboxylates are useful precursors for discrete Lewis base coordinated cadmium(II) carboxylate complexes, coordination polymers (CPs), metal organic frameworks (MOFs) and cadmium chalcogenides. Cadmium(II) monocarboxylate complexes are known to exist as discrete monomers, dimers, aggregates formed through covalent coordinate bond depending upon the substituent at the carboxylate ligand [1–6]. Mixed cadmium(II) mono carboxylate complexes are also known to exist as an aggregate formed through covalent coordinate bond [7]. Factors that dictate the degree of aggregation/nuclearity of cadmium(II) carboxylate complexes remain unknown presently.

Molecular structures of discrete $\text{Zn}(\text{OAc})_2\cdot 2\text{H}_2\text{O}$ and $\text{Zn}(\text{OC}(\text{O})^t\text{Bu})_2\cdot 2\text{H}_2\text{O}$ have been reported via single crystal X-ray diffraction (SCXRD; [8a,b]). Further, molecular structures of anhydrous polymeric $\text{Zn}(\text{OAc})_2$ and anhydrous polymeric $\text{Zn}(\text{OC}(\text{O})^t\text{Bu})_2$ have been determined by SCXRD and powder X-ray diffraction (PXRD; [9,10]) respectively. However, no information is available on the molecular and crystal structures of anhydrous cadmium(II) pivalate or its hydrated version. Hence, we wanted to isolate and structurally

characterize cadmium(II) pivalate hydrate in order to understand how the increased size of the *tert*-butyl substituent in the pivalate ligand compared with the methyl substituent in $\text{Cd}(\text{OAc})_2\cdot 2\text{H}_2\text{O}$ influences the molecular and crystal structures of the former complex. The results obtained from our endeavor are outlined in this manuscript.

2. Results and discussion

2.1. Syntheses

The reaction of $\text{CdCl}_2\cdot 2.5\text{H}_2\text{O}$ with two equiv of aq. NaOH in MeOH followed by treatment of the resulting solution with two equiv of pivalic acid afforded a discrete mononuclear complex **1** in 83% yield (see Scheme 1). Analogously, the use of $\text{Cd}(\text{OAc})_2\cdot 2\text{H}_2\text{O}$ instead of $\text{CdCl}_2\cdot 2.5\text{H}_2\text{O}$ as Cd(II) source in the above mentioned reaction afforded a trinuclear heterobimetallic 1D-CP, **2** in 90% yield (see Scheme 2). The presence of an acetate moiety in **2** indicates that it is difficult to hydrolyse this moiety completely from $\text{Cd}(\text{OAc})_2\cdot 2\text{H}_2\text{O}$ during the course of preparation of the former complex, while $\text{CdCl}_2\cdot 2.5\text{H}_2\text{O}$ can be hydrolyzed completely to afford **1**. Stamatatos *et al* have isolated a 1D-CP,

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Scheme 1. Synthesis of complex 1.

Scheme 2. Synthesis of complex 2.

$[\text{Cd}(\text{OC}(\text{O})\text{Me})(\text{OC}(\text{O})\text{Ph})(\text{H}_2\text{O})_2]_\infty$ from the mixture consisting of $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ and benzoic acid in acetonitrile and the 1D-CP has been structurally characterized [7]. The reason for incomplete removal of the acetate from $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ by the benzoate during the course of the formation of the aforementioned 1D-CP was not discussed. Based on the work of Stamatis *et al.*, we presume the formation of “ $\text{Cd}(\text{OH})_2$ ” and “ $\text{Cd}(\text{OH})(\text{OAc})$ ” as possible intermediates during the course of the syntheses of **1** and **2**, respectively.

2.2. Diffraction studies

Molecular structures of **1** and **2** have been determined by SCXRD and are shown in Figs. 1 and 2 respectively. Selected bond parameters are listed in Tables 1 and 2. Complex **1** is a mononuclear complex wherein the $\text{Cd}(\text{II})$ atom is surrounded by a pair of oxygen atoms of two chelating (κ^2) pivalate moieties and the oxygen atoms of two water molecules and the $\text{Cd}(\text{II})$ atom is thus six-coordinated. The $\text{Cd}(\text{II})$ atom in **1** adopts a distorted trigonal prism geometry. The discrete nature of **1** as compared to the polymeric nature of cadmium(II) formate dihydrate [3] and cadmium acetate dihydrate [4] is ascribed to the greater steric bulk of the *tert*-butyl substituent in the former complex.

There are two types of $\text{Cd}-\text{O}_{(\text{piv})}$ bond distances in **1** (2.377(5)/2.219(5) Å and 2.371(6)/2.289(6) Å) as analogously found in cadmium acetate dihydrate (2.597(3)/2.294(4) Å and 2.546(4)/2.304(4) Å [4]). The average $\text{Cd}-\text{O}_{(\text{piv})}$ distance in **1** (2.314(11) Å) is shorter than the average $\text{Cd}-\text{O}_{(\text{acetate})}$ distance observed in cadmium acetate dihydrate (2.408(8) Å) and this difference is not only due to the lower coordination number of $\text{Cd}(\text{II})$ atom but also due to greater inductive effect of the pivalate in the former complex. However, the $\text{Cd}-\text{O}_{(\text{water})}$ bond distances, 2.218(7) Å and 2.317(9) Å, found in **1** are somewhat comparable with the corresponding distances of 2.299(3) Å and 2.325(4) Å found in $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ within the 3σ cut off limit. The zinc (II) atom is tetracoordinated in $\text{Zn}(\text{OC}(\text{O})^t\text{Bu})_2 \cdot 2\text{H}_2\text{O}$ while the

Fig. 1. Molecular structure of **1** at 30% probability level. Fig. 2. Molecular structure of **2** at 30% probability level.

Table 1

Selected bond distances (Å) and bond angles (deg) for **1**.

$\text{Cd}(1)-\text{O}(1)$	2.377(5)	$\text{O}(2)-\text{Cd}(1)-\text{O}(3)$	129.0(2)
$\text{Cd}(1)-\text{O}(2)$	2.219(5)	$\text{O}(2)-\text{Cd}(1)-\text{O}(4)$	132.7(2)
$\text{Cd}(1)-\text{O}(3)$	2.289(6)	$\text{O}(2)-\text{Cd}(1)-\text{O}(5)$	106.8(2)
$\text{Cd}(1)-\text{O}(4)$	2.371(6)	$\text{O}(2)-\text{Cd}(1)-\text{O}(6)$	89.5(2)
$\text{Cd}(1)-\text{O}(5)$	2.317(9)	$\text{O}(3)-\text{Cd}(1)-\text{O}(4)$	54.3(2)
$\text{Cd}(1)-\text{O}(6)$	2.218(7)	$\text{O}(3)-\text{Cd}(1)-\text{O}(5)$	123.5(3)
$\text{O}(1)-\text{Cd}(1)-\text{O}(2)$	54.8(2)	$\text{O}(3)-\text{Cd}(1)-\text{O}(6)$	90.1(2)
$\text{O}(1)-\text{Cd}(1)-\text{O}(3)$	105.8(2)	$\text{O}(4)-\text{Cd}(1)-\text{O}(5)$	95.8(3)
$\text{O}(1)-\text{Cd}(1)-\text{O}(4)$	78.2(2)	$\text{O}(4)-\text{Cd}(1)-\text{O}(6)$	135.3(2)
$\text{O}(1)-\text{Cd}(1)-\text{O}(5)$	113.5(2)	$\text{O}(5)-\text{Cd}(1)-\text{O}(6)$	81.8(3)
$\text{O}(1)-\text{Cd}(1)-\text{O}(6)$	143.4(2)		

cadmium(II) atom in **1** is hexacoordinated. This difference can be ascribed to the larger ionic radius of the $\text{Cd}(\text{II})$ atom compared with that of $\text{Zn}(\text{II})$ atom (1.09 Å versus 0.88 Å [11]). Complex **1** is the first crystallographically characterized discrete mononuclear complex devoid of aggregation in the cadmium(II) monocarboxylate complex series, primarily due to the steric factor associated with the *tert*-butyl substituent in the pivalate moiety.

SCXRD analysis of **2** revealed that this complex is a 1D-CP (see Fig. 3). The cadmium(II) atom is surrounded by three pairs of oxygen atoms with one pair originating from one acetate ($\mu_5-\kappa^3:\kappa^3$), one pair originating from one pivalate ($\mu_3-\kappa^2:\kappa^3$) and one pair originating from two distinct pivalate moieties ($\mu_3-\kappa^1:\kappa^2$). The pair of oxygen atoms of the acetate moiety not only chelates the $\text{Cd}(\text{II})$ atom but also bridges two pairs of $\text{Na}(\text{I})$ atoms. On two sides the $\text{Na}(1)-\text{Cd}(01)-\text{Na}(2)$ unit is held together by a pair of pivalate moieties in a $\mu_3-\kappa^1:\kappa^2$ coordination mode and on one side it is held together by a pivalate moiety which exhibits a $\mu_3-\kappa^2:\kappa^3$ coordination mode. The sixth coordination site around $\text{Na}(1)$ and $\text{Na}(2)$ is fulfilled by the carbonyl oxygen atom of a pivalic acid. Thus, both $\text{Cd}(\text{II})$ atoms and the two crystallographically distinct $\text{Na}(\text{I})$ atoms are six-coordinated with the former exhibiting a distorted trigonal prism geometry while the latter exhibit a severely distorted octahedral geometry. The coordination polyhedra around the $\text{Cd}(\text{II})$ and $\text{Na}(\text{I})$ atoms are illustrated in Fig. 4. The repeat unit is linked with the neighboring repeat unit through a pair of bridging pivalates ($\mu_3-\kappa^1:\kappa^2$) and one chelating bridging acetate ($\mu_5-\kappa^3:\kappa^3$) to afford a 1D CP. The three types of carboxylate coordination modes present in **2** are illustrated in Fig. 5. $\text{Na}-\text{Cd}$ containing CPs wherein the carboxylate

Table 2
Selected bond distances (Å) and bond angles (deg) for **2**.

Cd(1)–O(2)	2.244(2)	O(5)–Cd(1)–O(7)	96.52(8)
Cd(1)–O(3)	2.591(2)	O(5)–Cd(1)–O(8)	109.78(7)
Cd(1)–O(4)	2.315(2)	O(7)–Cd(1)–O(8)	55.21(8)
Cd(1)–O(5)	2.247(2)	O(1)–Na(2)–O(3)	97.72(8)
Cd(1)–O(7)	2.237(3)	O(1)–Na(2)–O(8)	82.63(8)
Cd(1)–O(8)	2.460(2)	O(1)–Na(2)–O(9)	83.5(1)
Cd(1)–O(2)	2.244(2)	O(1)–Na(2)–O(4)	165.97(9)
Na(1)–O(2)	2.399(2)	O(1)–Na(2)–O(5)	118.87(9)
Na(1)–O(3)	2.552(3)	O(3)–Na(2)–O(8)	74.91(8)
Na(1)–O(4)	2.489(2)	O(3)–Na(2)–O(9)	177.9(1)
Na(1)–O(6)	2.419(2)	O(3)–Na(2)–O(4)	83.53(8)
Na(1)–O(8)	2.409(2)	O(2)–Na(1)–O(4)	75.57(8)
Na(1)–O(11)	2.336(3)	O(2)–Na(1)–O(11)	103.03(9)
Na(1)–O(2)	2.399(2)	O(2)–Na(1)–O(3)	77.64(8)
Na(2)–O(1)	2.422(2)	O(2)–Na(1)–O(6)	119.06(9)
Na(2)–O(3)	2.552(2)	O(2)–Na(1)–O(8)	147.60(9)
Na(2)–O(4)	2.496(2)	O(4)–Na(1)–O(11)	94.29(9)
Na(2)–O(5)	2.411(3)	O(4)–Na(1)–O(11)	83.66(8)
Na(2)–O(8)	2.413(2)	O(4)–Na(1)–O(11)	165.31(9)
Na(2)–O(9)	2.324(3)	O(4)–Na(1)–O(11)	84.45(8)
Na(2)–O(1)	2.422(2)	O(11)–Na(1)–O(3)	177.6(1)
O(2)–Cd(1)–O(3)	100.37(7)	O(11)–Na(1)–O(6)	83.87(9)
O(2)–Cd(1)–O(4)	82.16(8)	O(11)–Na(1)–O(8)	103.67(9)
O(2)–Cd(1)–O(5)	138.58(8)	O(3)–Na(1)–O(6)	97.82(8)
O(2)–Cd(1)–O(7)	98.27(8)	O(3)–Na(1)–O(8)	74.98(8)
O(2)–Cd(1)–O(8)	110.45(7)	O(6)–Na(1)–O(8)	81.85(8)
O(3)–Cd(1)–O(4)	53.06(7)	O(3)–Na(2)–O(5)	77.70(8)
O(3)–Cd(1)–O(5)	100.00(7)	O(8)–Na(2)–O(9)	103.6(1)
O(3)–Cd(1)–O(7)	128.63(8)	O(8)–Na(2)–O(4)	84.23(8)
O(3)–Cd(1)–O(8)	73.44(7)	O(8)–Na(2)–O(5)	147.24(9)
O(4)–Cd(1)–O(5)	81.92(8)	O(9)–Na(2)–O(4)	94.9(1)
O(4)–Cd(1)–O(7)	178.00(8)	O(9)–Na(2)–O(5)	103.2(1)
O(4)–Cd(1)–O(8)	126.50(7)	O(4)–Na(2)–O(5)	75.09(8)

ligand is derived from trimesic acid [12] and 4,4'-oxydiphthalic acid [13] are known in the literature. Complex **2** is the first crystallographically characterised trinuclear heterobimetallic 1D-CP that contains a monocarboxylate ligand to be reported in the literature.

The phase purity of **2** was verified by powder X-ray diffraction (PXRD). This pattern resembles the XRD pattern generated from SCXRD data which suggest that the bulk material obtained after crystallization consists of only **2** (see Fig. S1 in the Supplementary data).

2.3. Spectroscopic studies

The solid state CP-MAS $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy was shown to be one of the useful techniques used to distinguish various types of carboxylate coordination modes in metal carboxylates [8b,11,14] and hence we measured $\delta(^{13}\text{C})$ for complexes **1** and **2**. Complex **1** revealed three signals for all three types of carbons namely CH_3 ($\delta = 26.1, 27.6$, and 28.4 ppm), CMe_3 ($\delta = 39.1, 40.0$, and 42.4 ppm) and OC(O) ($\delta = 185.6, 187.8$, and 189.7) of the pivalate moieties in contrast to one signal anticipated for all three carbons mentioned above. The greater number of $^{13}\text{C}\{^1\text{H}\}$ NMR signals observed than anticipated is ascribed to the presence of three crystallographically distinct molecules in the unit cell in the solid state (symmetries = identity, 2-fold screw axis and glide plane; see Fig. 6). The solid state $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of anhydrous zinc(II) acetate was shown to reveal two types of signals for both the Me and OC(O) carbon nuclei and this observation was explained by invoking the presence of two crystallographically distinct molecules in the unit cell [9a,14b].

^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **2** in solution revealed only one type of signal for the pivalate moiety although it contains two types of pivalate moieties and one pivalic acid. The apparently simple NMR spectra of **2** mentioned above indicate that the sample dissociates in solution [14a]. Metal carboxylates are prone to undergo 'carboxylate shift' in solution and the rate of the 'carboxylate shift' could be faster than the NMR time scale [15]. Thus, one cannot completely rule out the 'carboxylate shift' process for the observance of simpler solution NMR pattern for **2**. The solid state CP-MAS $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2** showed three signals at $\delta = 22.0, 27.7$ and 29.0 ppm for the CH_3 carbon atom of acetate, pivalic acid and the pivalate moieties. Further, two distinct signals were observed at $\delta = 38.4$, and 39.8 ppm for the CMe_3 carbon of pivalic acid and the pivalate moieties as anticipated. In the carbonyl region, four signals were observed at $\delta = 183.0, 184.1, 187.2$, and 188.0 ppm which could arise due to the OC(O) carbon of the acetate, two pivalate moieties ($\mu_3\text{-}\kappa^2\text{:}\kappa^3$ and $\mu_3\text{-}\kappa^1\text{:}\kappa^2$) and pivalic acid.

2.4. Thermal studies

Complexes **1** and **2** were subjected to TGA and DTA studies to understand their mode of decomposition. The TGA and DTA thermograms

Fig. 3. 1D polymeric structure of complex **2**.

Fig. 4. Coordination environments around the Cd(II) and Na(I) atoms in **2**. Fig. 5. Coordination modes of carboxylate moieties in **2**. Fig. 6. Packing diagram illustrating three distinct molecules in a unit cell of **1**. Fig. 7. TGA and DTA thermograms of **1**.

are depicted in Figs. 7 and 8, respectively. The modes of decomposition of **1** and **2** were determined from the weight loss observed in the TGA pattern as outlined in Fig. 9. The TGA data of **1** showed an initial weight loss of 10.27% (Calc: 10.02%) between 95 °C and 218 °C for the loss of two water molecules to afford $\text{Cd}(\text{OC}(\text{O})^t\text{Bu})_2$. Anhydrous $\text{Cd}(\text{OC}(\text{O})^t\text{Bu})_2$ decomposes above 200 °C to afford Cd metal (Found: 32.05% and Calc: 32.20% for the loss of CO_2 ; Found: 57.70% and Calc:

Fig. 8. TGA and DTA thermograms of **2**.

56.03% for the loss of $\text{Me}_3\text{C-CMe}_3$). The DTA pattern showed that the second step of decomposition is an endothermic process.

TGA and DTA thermograms of **2** showed the loss of CO and one pivalic acid between 98 and 194 °C (Found: 17.04% and Calc: 17.95%). CP **2** undergoes a weight loss between 194 °C and 365 °C due to the loss of 2,3-dimethylethanol (Found: 10.90% and Calc: 10.22%) to afford $\text{Na}_2[\text{Cd}(\text{OC}(\text{O})^t\text{Bu})_3(\text{OAc})]$. Between 400 °C and 450 °C, $\text{Na}_2[\text{Cd}(\text{OC}(\text{O})^t\text{Bu})_3(\text{OAc})]$ loses di-*t*-butyl-cadmium and two molecules of CO_2 through a decarboxylation process (Found: 43.34% and Calc: 43.40%) to afford $\text{Na}_2(\text{OC}(\text{O})^t\text{Bu})(\text{OAc})$. Above 500 °C, $\text{Na}_2(\text{OC}(\text{O})^t\text{Bu})(\text{OAc})$ undergoes decarboxylation and decarbonylation with the additional loss of CMe_4 to afford Na_2O as the end product.

Complexes **1** and **2** were separately calcined at 500 °C for 3 h in air that yielded CdO and Na_2O , respectively as deduced from the PXRD pattern (see Figs. S2 and S3 in the Supplementary data). The PXRD pattern of CdO and Na_2O obtained from decomposition studies in the present investigation matched well with the authentic PXRD patterns of CdO (JCPDS-780653) and Na_2O (JCPDS-770210).

3. Conclusion

One discrete complex **1** and one trinuclear heterobimetallic 1D-CP **2** were isolated in good yields. The two new complexes have been characterized by elemental analyses, IR and solution and solid state NMR spectroscopic and diffraction techniques. The precursor $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ is completely hydrolysed while the precursor $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ is incompletely hydrolysed under basic conditions before forming **1** and **2**, respectively. Complex **2** represents the first trinuclear heterobimetallic 1D-CP aggregated through covalent coordinate bonds. The phase purity of **2** was verified by powder X-ray diffraction. Complexes **1** and **2** upon thermolysis afforded Cd and Na_2O as revealed by TGA/DTA analyses while complexes **1** and **2** upon calcination at 500 °C afforded CdO and Na_2O respectively as revealed by PXRD.

Fig. 9. Decomposition patterns of **1** and **2**. The numbers within the parenthesis indicate calculated weight loss.

4. Experimental

4.1. Complex 1

$\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (200 mg, 0.876 mmol) was dissolved in methanol (15 ml) and stirred. To this solution, an aq. solution of NaOH (70.1 mg, 1.75 mmol) was added and the resulting solution cooled to RT. Subsequently, pivalic acid (138.6 mg, 1.752 mmol) was added to the above mentioned solution and the resulting clear solution was stored at RT for several days to afford **1** as colorless crystals. Yield = 83% (256 mg, 0.731 mmol). Mp 138 °C. FT-IR (KBr, cm^{-1}): $\nu(\text{OH})$ 3369 (m); $\nu_s(\text{OCO})$ 1550, 1384, 1228. Anal. Calcd for $\text{CdC}_{10}\text{H}_{22}\text{O}_6$ (Mw: 350.683): C, 34.25; H, 6.32. Found: C, 34.00; H, 6.33. ^1H NMR (CD_3OD , 400 MHz): δ 1.18 (s, 18H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3OD , 100.5 MHz): δ 28.76 (CH_3), 39.77 ($\text{C}(\text{CH}_3)_3$), 188.37 (OC(O)). Solid state CP-MAS $^{13}\text{C}\{^1\text{H}\}$ NMR (150.9 MHz) δ 26.1, 27.6, 28.4 (CH_3), 39.1, 40.0, 42.4 (each br, $\text{C}(\text{CH}_3)_3$), 185.6, 187.8, 189.7 (each br, OC(O)).

4.2. Complex 2

Complex **2** was prepared from $\text{Cd(OAc)}_2 \cdot 2\text{H}_2\text{O}$ (200 mg, 0.751 mmol), an aq. solution of NaOH (60.1 mg, 1.50 mmol) and pivalic acid (153.3 mg, 1.50 mmol) in methanol (15 ml) following the procedure outlined previously for **1**. The clear solution obtained was stored at RT for several days to afford **2** as colorless crystals. Yield = 90% (490 mg, 0.675 mmol). Mp (DSC) 145.92 °C. FT-IR (KBr, cm^{-1}): $\nu(\text{OH})$ 2980 (m); $\nu_s(\text{OCO})$ 1708, 1604, 1492, 1436. Anal. Calcd for $\text{Na}_2\text{CdC}_{27}\text{H}_{50}\text{O}_{12}$ (Mw: 725.067): C, 44.73; H, 6.95. Found: C, 44.35; H, 7.04. ^1H NMR (D_2O , 400 MHz): δ 1.12 (s, $15 \times 3\text{H}$, CH_3), 1.94 (s, 3H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (D_2O , 100.5 MHz): δ 22.11, 27.09 (CH_3), 38.99 ($\text{C}(\text{CH}_3)_3$), 180.43, 187.43 (OC(O)). Solid state CP-MAS $^{13}\text{C}\{^1\text{H}\}$ NMR (150.9 MHz) δ 22.0, 27.7, 29.0 (CH_3), 38.4, 39.8 (each br, $\text{C}(\text{CH}_3)_3$), 183.0, 184.1, 187.2, 188.0 (OC(O)).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ica.2019.02.012>. These data include MOL files and InChIKeys of the most important compounds described in this article.

References

- [1] (a) G.B. Gavioli, L. Menabue, M. Saladini, M. Sola, A.B. Corradi, L.P. Battaglia, J. Chem. Soc., Dalton Trans. (1989) 1345–1349; (b) Q. Miao, M.-L. Hu, Acta Crystallogr. Sect. E: Struct. Rep. Online 61 (2005) m2083–m2085; (c) Y. Liu, Acta Crystallogr. Sect. E: Struct. Rep. Online 61 (2005) m669–m670; (d) H. Fang, S.W. Ng, Acta Crystallogr. Sect. E: Struct. Rep. Online 63 (2007) m1523–m1524; (e) H.A. Habib, J. Sanchiz, C. Janiak, Dalton Trans. (2008) 4877–4884; (f) C.-Y. Zhang, Q. Gao, Y. Cui, Y.-B. Xie, Acta Crystallogr., Sect. E: Struct. Rep. Online 65 (2009); (g) Z.L. Zhang, L. Huang, C.F. Wang, Y.L. Wang, Koord. Khim. (Russ.) (Coord. Chem.) 38 (2012) 620–622; (h) J. Yang, L. Shen, G.-W. Yang, Q.-Y. Li, W. Shen, J.-N. Jin, J.-J. Zhao, J. Dai, J. Solid State Chem. 186 (2012) 124–133; (i) B. Mohapatra, S. Verma, Cryst. Growth Des. 16 (2016) 696–704; (j) S.-C. Xia, S.M. Hu, J.J. Zhang, X.-T. Wu, J.-C. Dai, Z.-Y. Fu, W.-X. Du, Inorg. Chem. Commun. 7 (2004) 271–273.
- [2] H. Chen, L. Zhang, B. Hu, X.-L. Wu, T. Wang, G. Huang, Y.-Q. Wang, C.-Z. Liu, J. Struct. Chem. 55 (2014) 89–95.
- [3] M.L. Post, J. Trotter, Acta Cryst. B30 (1974) 1880–1882.
- [4] W. Harrison, J. Trotter, J. Chem. Soc., Dalton Trans. (1972) 956–960.
- [5] R. Kruszynski, A. Turek, J. Coord. Chem. 57 (2004) 1089–1098.
- [6] W.-D. Song, C.-S. Gu, J.W. Liu, X.-M. Hao, Acta Cryst. E62 (2006) m2397–m2399.
- [7] T.C. Stamatatos, E. Katsoulakou, V. Nastopoulos, C.P. Raptopoulou, E. Manessi Zoupa, S.P. Perlepes, Z. Naturforsch. B Chem. Sci. 58 (2003) 1045–1054.
- [8] (a) T. Ishioka, Y. Shibata, M. Takahashi, I. Kanekasa, Y. Kitagawa, K.T. Nakamura, Spectrochim. Acta Part A 54 (1998) 1827–1836; (b) U. Kumar, J. Thomas, M. Agarwal, N. Thirupathi, Inorg. Chim. Acta 370 (2011) 122–131.
- [9] (a) W. Clegg, I.R. Little, B.P. Straughan, Acta Cryst. C42 (1986) 1701–1703; (b) H. He, Acta Cryst. E62 (2006) m3291–m3292.
- [10] I.G. Fomina, V.V. Chernyshev, Yu.A. Velikodnyi, M.A. Bykov, I.P. Malkerova, A.S. Alikhanyan, Yu.S. Zavorotnyi, Zh.V. Dobrokhotova, I.L. Eremenko, Russ. Chem. Bull. Int. Ed. 62 (2013) 427–434.
- [11] P. Saxena, N. Thirupathi, Polyhedron 98 (2015) 238–250.
- [12] J.-X. Chen, S.-X. Liu, E.-Q. Gao, Polyhedron 23 (2004) 1877–1888.
- [13] X.-L. Chen, B. Zhang, H.-M. Hu, F. Fu, X.-L. Wu, T. Qin, M.-L. Yang, G.L. Xue, J.-W. Wang, Cryst. Growth Des. 8 (2008) 3706–3712.
- [14] (a) U. Kumar, J. Thomas, N. Thirupathi, Inorg. Chem. 49 (2010) 62–72;

- (b) P.A. Hunt, B.P. Straughan, A.A.M. Ali, R.K. Harris, B.J. Say, J. Chem. Soc., Dalton Trans. (1990) 2131–2135;
- (c) B.-H. Ye, X.-Y. Li, I.D. Williams, X.-M. Chen, Inorg. Chem. 41 (2002) 6426–6431;
- (d) H.A. Habib, A. Hoffmann, H.A. Höppe, C. Janiak, Dalton Trans. (2009) 1742–1751;
- (e) U. Kumar, M. Singh, N. Thirupathi, Polyhedron 55 (2013) 233–240;
- (f) S.-J. Lin, T.-N. Hong, J.-Y. Tung, J.-H. Chen, Inorg. Chem. 36 (1997) 3886–3891;
- (g) U. Kumar, J. Thomas, R. Nagarajan, N. Thirupathi, Inorg. Chim. Acta 372 (2011) 191–199.
- [15] R.L. Rardin, W.B. Tolman, S.J. Lippard, New J. Chem. 15 (1991) 417–430.