

## Simple Methylcadmium Alkoxides

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The reaction of dimethylcadmium with alcohols R-OH in equimolar ratio leads to the formation of tetrameric methylcadmium alkoxides with molecular formula [(MeCd)<sub>4</sub>(OR)<sub>4</sub>] [R = Me (**1**), Et (**2**) and <sup>i</sup>Pr (**3**)]. These compounds have been characterised by <sup>1</sup>H, <sup>13</sup>C NMR and IR spectroscopy, by mass spectrometry, elemental analyses and by X-ray crystallography (for **2** and **3**). The solid state structures show distorted cubane-type aggregates with Cd<sub>4</sub>O<sub>4</sub> cores. The structural aspects and the spectroscopic characterisations of these compounds are discussed.

**Key words:** Alkoxide, Cadmium, Crystal Structure

### Introduction

The alkoxides of group 12 elements are well known in the literature. Zinc alkoxides have been known since the early work of Frankland in 1849, who obtained these compounds by oxygenation of zinc alkyls [1]. For more than 150 years this chemistry has been continuously extended [2]. Very recently, we published a way to cubane- and bis-cubane-type zinc alkoxides by oxidation of dialkylzinc precursors with dioxygen, which can be switched between the aggregates by the presence or absence of water [3].

In contrast to the rich zinc alkoxide chemistry, only few cadmium alkoxides are known, including [MeCdOMe]<sub>4</sub> [4], [MeCdOEt]<sub>4</sub> [4], [MeCdO<sup>i</sup>Pr]<sub>4</sub> [4], [MeCdO<sup>n</sup>Pr]<sub>4</sub> [5], [MeCdO<sup>n</sup>Bu]<sub>4</sub> [6], [MeCdOPh]<sub>4</sub> [7], [MeCdO<sup>i</sup>Bu]<sub>4</sub> [8], and [MeCdOCPh<sub>3</sub>]<sub>4</sub> [9]. Among these alkoxides of cadmium, only [MeCdO<sup>i</sup>Bu]<sub>4</sub> [8] has been structurally characterised and was found to form a distorted cubane-type structure. Cadmium alkoxides can be used as cadmium oxide source in the preparation of II–VI compound semi-

conductor materials and nanometer semiconductor particles. Recently, Boyle *et al.* have shown heteroleptic “Cd(OR)(NR<sub>2</sub>)” and homoleptic “Cd(OR)<sub>2</sub>” complexes to be applicable as precursors to CdO nanocrystals [10]. It should also be noted that besides the typical alkoxide chemistry, the chemistry of cadmium siloxides was established by Schmidbaur and Schindler already in 1965 [11].

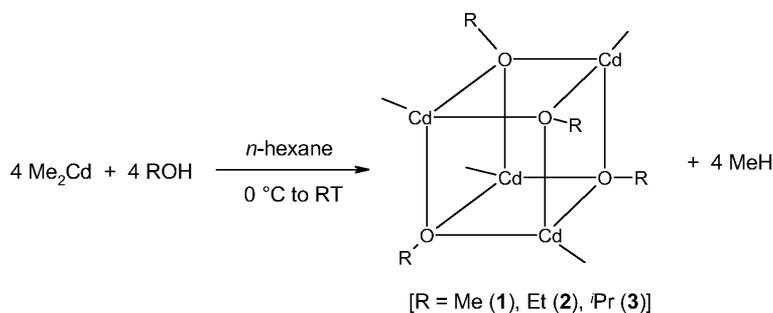
On this basis, it is now interesting to explore the chemistry of cadmium alkoxides in more detail, which includes the study of their solid state structures. Herein we report some structural aspects of cadmium alkoxides.

### Results and Discussion

The reaction of a solution of dimethylcadmium with alcohols R-OH (R = Me, Et, <sup>i</sup>Pr) in an equimolar ratio at ambient temperature leads to the formation of methylcadmium alkoxides with the formula [(MeCd)<sub>4</sub>(OR)<sub>4</sub>] [R = Me (**1**), Et (**2**), <sup>i</sup>Pr (**3**)] (Scheme 1). The syntheses of these compounds have already been reported in the early literature [4], but at that time only elemental analyses and molecular weight determinations by cryoscopy were documented. The methoxide derivative **1** is only sparingly soluble in hydrocarbon solvents, but reasonably soluble in THF. Compounds **2** and **3** are soluble in most hydrocarbons and ethereal solvents. Due to the decomposition above 200 °C, compound **1** cannot be molten up to a temperature of 300 °C. Compound **3** melts at 214–215 °C without decomposition. Compounds **1–3** have been characterised by NMR and infrared spectroscopy, by mass spectrometry and – for compounds **2** and **3** – by elemental analyses.

The <sup>1</sup>H NMR spectrum of **1** shows a singlet at –0.66 ppm with a coupling constant <sup>2</sup>J<sub>Cd–H</sub> = 40.1 Hz for the methyl groups at cadmium and a singlet at 3.65 ppm for the methoxy protons. The integral ratio is 1:1 for the protons of the methyl groups at cadmium and those of the alkoxy groups, which is consistent with the stoichiometric ratio of the formula [(MeCd)<sub>4</sub>(OR)<sub>4</sub>]. The EI-mass spectra of **1** show the highest mass peak at *m/z* = 619, which corresponds to the molecular mass of the cation diminished by that of one methyl group.

For **2** and **3**, the NMR characteristics are similar to those of **1**. In the case of **2**, two broad and overlapping



Scheme 1.

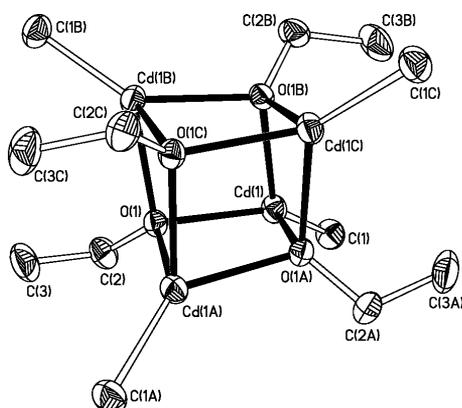


Fig. 1. Molecular structure of  $[(\text{MeCd})_4(\text{OEt})_4]$  (**2**) as determined by X-ray crystallography (hydrogen atoms are omitted for clarity).

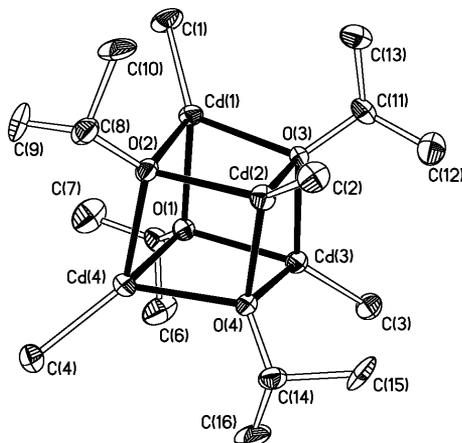


Fig. 2. Molecular structure of  $[(\text{MeCd})_4(\text{O}^i\text{Pr})_4]$  (**3**) as determined by X-ray crystallography (hydrogen atoms omitted for clarity).

singlets at  $-0.05$  and  $-0.02$  ppm have been detected in the  $^1\text{H}$  NMR spectrum (intensity ratio about 1 : 2), whereas in the  $^{13}\text{C}$  NMR spectrum only one resonance was found to correspond to the protons of the Cd bound Me groups. Reversely, the ethyl groups cause two res-

Table 1. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for **2** and **3** as determined by X-ray crystallography.

	$[(\text{MeCd})_4(\text{OEt})_4]$ ( <b>2</b> )	$[(\text{MeCd})_4(\text{O}^i\text{Pr})_4]$ ( <b>3</b> )	
Cd(1)–C(1)	2.123(4)	Cd(1)–C(1)	2.131(5)
Cd(1)–O(1)	2.246(2)	Cd(1)–O(1)	2.285(3)
O(1)–C(2)	1.436(4)	O(1)–C(5)	1.431(6)
C(1)–Cd(1)–O(1)	137.4(2)	C(1)–Cd(1)–O(1)	132.2(2)
O(1)–Cd(1)–O(1B)	80.7(1)	O(1)–Cd(1)–O(2)	79.5(2)
O(1)–Cd(1)–O(1C)	80.1(1)	O(1)–Cd(1)–O(3)	81.3(2)
C(2)–O(1)–Cd(1)	120.1(2)	C(2)–O(1)–Cd(1)	118.8(3)
Cd(1)–O(1)–Cd(1A)	98.3(1)	Cd(1)–O(1)–Cd(3)	97.3(2)
Cd(1)–O(1)–Cd(1B)	99.3(1)	Cd(1)–O(1)–Cd(4)	99.8(2)

onances in the  $^1\text{H}$  NMR spectrum for the  $\text{CH}_3$  and  $\text{CH}_2$  units, whereas a double set of close lying signals is observed in the corresponding  $^{13}\text{C}$  NMR spectrum. This indicates some varieties of aggregates in solution, but we have no detailed explanation for these facts at present. Moreover, for compound **3** a  $^{113}\text{Cd}$  NMR experiment provided a resonance at  $-272$  ppm.

Compounds **2** and **3** were further characterised by single crystal X-ray diffraction. These compounds were crystallised from *n*-hexane by keeping the solutions at  $-26^\circ\text{C}$  for several days. Compound **2** crystallises in the tetragonal space group  $I4_1/a$ . The solid state molecular structure is shown in Fig. 1. The compound is a cubane-shaped tetramer. Cadmium and oxygen atoms occupy the vertices of a distorted cube. The molecule possesses a crystallographic  $S_4$  axis and is in total of  $D_{2d}$  symmetry. The methyl groups at the cadmium atoms and the ethyl groups at the oxygen atoms point away from the center of the cube. This cube is distorted, as is clearly indicated by bond angles (O–Cd–O) at the cadmium corners at approximately  $80^\circ$  and by the Cd–O–Cd angles at the oxygen corners at approximately  $99^\circ$ .

Compound **3** crystallises in the tetragonal space group  $P4_3$ . The molecular structure is similar to that of **2**, *vic.* a distorted cubane-shaped cluster. The molecular structure is shown in Fig. 2. Selected bond lengths

and angles for **2** and **3** are listed in Table 1, and crystallographic data are listed in Table 2. The Cd–O distances of **3** fall over a range from 2.267(3) (Cd2–O2) to 2.298(6) Å (Cd4–O1). This is longer than in **2**, which bears less bulky substituents at the oxygen atoms, and thus shows the influence of such comparatively subtle changes in the substituent pattern. The Cd–O–Cd and O–Cd–O angles in **3** adopt values comparable to that of **2** with deviations of about 1°. Bond lengths and angles of **2** and **3** are also – with small deviations – matching those of the few available structural data for the cadmium compounds [(MeCdOtBu)<sub>4</sub>] [8], [(F<sub>5</sub>C<sub>6</sub>CdOH)<sub>4</sub>] [12] and [(μ<sup>3</sup>-9-BBN-9-O)CdMe]<sub>4</sub> [13].

## Experimental Section

**General Consideration:** All manipulations of air-sensitive compounds were carried out under a dry nitrogen atmosphere with standard Schlenk and high-vacuum techniques using double manifolds or a glovebox operated under argon. Solvents were purified and dried by standard methods immediately prior to use. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker AM200 and Bruker Avance 400 spectrometers. All spectra were referenced internally to residual protiosolvent (<sup>1</sup>H) or solvent (<sup>13</sup>C) resonances. For <sup>113</sup>Cd NMR δ values refer to Me<sub>2</sub>Cd as the standard, negative signs correspond to frequencies smaller than standard. IR spectra were measured with a Bruker IFS (103 V) instrument using Nujol mulls prepared in the glove box. Elemental analyses were performed using a Vario EL III CHNS elemental analyser.

### Synthesis of [(MeCd)<sub>4</sub>(OMe)<sub>4</sub>] (**1**)

Me<sub>2</sub>Cd (4.0 mL of a 1 M solution in *n*-hexane; 4.0 mmol) was added dropwise *via* a syringe to a stirred solution of MeOH (0.20 mL, 4.0 mmol) in a 1:1 mixture of *n*-hexane/THF (20 mL) at 0 °C. The reaction mixture was gradually warmed to r.t. and stirred for 6 h. After removal of the solvent under reduced pressure, the resulting residue was dissolved in THF and filtered. The clear, colourless filtrate, when stored at r.t. using an H-tube (one side containing pure *n*-hexane and the other side the compound in THF), afforded colourless needle-shaped crystals of **1** suitable for X-ray diffraction experiments. Yield: 75% (476 mg, 0.75 mmol). – M. p. > 300 °C (decomp.). – <sup>1</sup>H NMR (200 MHz, [D<sub>6</sub>]DMSO): δ = –0.66 [s, J<sub>Cd–H</sub> = 40.1 Hz, 12 H; CH<sub>3</sub>Cd], 3.65 [s, 12 H; OCH<sub>3</sub>]. – <sup>13</sup>C {<sup>1</sup>H} NMR (50 MHz, [D<sub>6</sub>]DMSO): δ = –17.43 [CH<sub>3</sub>Cd], 55.26 [OCH<sub>3</sub>]. – IR (Nujol): ν = 3188 (s), 2725 (s), 2667 (s), 1462 (w), 1454 (w), 1446 (w), 1363 (w), 1313 (w), 1155 (s), 1008 (s), 962 (s), 580 (vs) cm<sup>–1</sup>. – EI-MS: *m/z* (%) = 619 (24) [M–CH<sub>3</sub>]<sup>+</sup>.

Table 2. Crystallographic details of compounds **2** and **3**.

Compound	[(MeCd) <sub>4</sub> (OEt) <sub>4</sub> ] ( <b>2</b> )	[(MeCd) <sub>4</sub> (O <sup><i>i</i></sup> Pr) <sub>4</sub> ] ( <b>3</b> )
Formula	C <sub>12</sub> H <sub>32</sub> O <sub>4</sub> Cd <sub>4</sub>	C <sub>16</sub> H <sub>40</sub> O <sub>4</sub> Cd <sub>4</sub>
Cryst. system	tetragonal	tetragonal
Space group	<i>I</i> <sub>4</sub> / <i>a</i>	<i>P</i> <sub>4</sub> <sub>3</sub>
<i>a</i> , Å	14.578(2)	9.635(1)
<i>c</i> , Å	19.789(2)	27.995(1)
<i>V</i> , Å <sup>3</sup>	2080.4(4)	2598.9(5)
ρ <sub>calc.</sub> , g · cm <sup>–3</sup>	2.203	1.907
<i>Z</i>	4	4
<i>M</i> , mm <sup>–1</sup> (MoK <sub>α</sub> )	4.039	3.241
<i>T</i> , K	153(2)	153(2)
2θ <sub>max.</sub> , deg	60.08	60.04
Measured refl.	11579	29291
Unique refl.	1520	7500
Observed refl.	1330	7128
<i>x</i> (Flack)	–	0.45(6)
<i>R</i> <sub>int</sub>	0.036	0.026
Refined param.	48	230
<i>R</i> [ <i>I</i> ≥ 2σ( <i>I</i> )]/ <i>wR</i> <sup>2</sup>	0.034/0.077	0.033/0.074
Δρ <sub>fin</sub> (max/min), eÅ <sup>–3</sup>	1.840/–0.461	1.084/–0.541

### Synthesis of [(MeCd)<sub>4</sub>(OEt)<sub>4</sub>] (**2**)

Compound **2** was synthesised from EtOH (0.22 mL, 4.0 mmol) instead of MeOH in a procedure similar to that used for **1**. Instead of THF, *n*-hexane was used for dissolving the compound. Colourless crystals of **2** were obtained from an *n*-hexane solution at –26 °C after storing for several days. Yield: 65% (450 mg, 0.65 mmol). – M. p. 280 °C. – <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>): δ = –0.05, –0.02 [s, 12 H; CH<sub>3</sub>Cd], 1.24 [br, 12 H; OCH<sub>2</sub>CH<sub>3</sub>], 3.75 [br, 8 H; OCH<sub>2</sub>CH<sub>3</sub>]. – <sup>13</sup>C {<sup>1</sup>H} NMR (50 MHz, C<sub>6</sub>D<sub>6</sub>): δ = –19.91 [CH<sub>3</sub>Cd], 23.29, 23.56 [OCH<sub>2</sub>CH<sub>3</sub>], 63.32, 63.67 [OCH<sub>2</sub>CH<sub>3</sub>]. – EI-MS: *m/z* (%) = 675 (34) [M–CH<sub>3</sub>]<sup>+</sup>. – IR (Nujol) ν = 3167 (s), 2664 (s), 1476 (w), 1441 (w), 1376 (w), 1189 (s), 1019 (s), 954 (s) cm<sup>–1</sup>. – C<sub>12</sub>H<sub>32</sub>O<sub>4</sub>Cd<sub>4</sub>: calcd. C 20.89, H 4.67; found C 19.78, H 4.40.

### Synthesis of [(MeCd)<sub>4</sub>(O<sup>*i*</sup>Pr)<sub>4</sub>] (**3**)

Compound **3** was synthesised from <sup>*i*</sup>PrOH (0.26 mL, 4.0 mmol) instead of EtOH following a procedure similar to that used for **2**. Colourless crystals of **3** were obtained upon keeping an *n*-hexane solution at –26 °C for several days. Yield: 62% (463 mg, 0.62 mmol). – M. p. 214–215 °C. – <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ = 0.37 [s, J<sub>Cd–H</sub> = 39.7 Hz, 12 H; CH<sub>3</sub>Cd], 1.24 [d, *J* = 5.9 Hz, 24 H; OCH(CH<sub>3</sub>)<sub>2</sub>], 4.24 [sept, *J* = 5.9 Hz, 4 H; OCH]. – <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 0.20 [s, J<sub>Cd–H</sub> = 39.2 Hz, 41.0 Hz, 12 H; CH<sub>3</sub>Cd], 1.22 [d, *J* = 5.9 Hz, 24 H; OCH(CH<sub>3</sub>)<sub>2</sub>], 4.02 [sept, *J* = 5.9 Hz, 4 H; OCH]. – <sup>13</sup>C {<sup>1</sup>H} NMR (50 MHz, CDCl<sub>3</sub>): δ = –12.62 [CH<sub>3</sub>Cd], 29.18 [OCH(CH<sub>3</sub>)<sub>2</sub>], 67.99 [OCH]. – <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>): δ = –12.02 [J<sub>Cd–C</sub> = 495.5 Hz, 518.3 Hz; CH<sub>3</sub>Cd], 29.30 [OCH(CH<sub>3</sub>)<sub>2</sub>], 68.33 [OCH]. – <sup>113</sup>Cd NMR (88.8 MHz, C<sub>6</sub>D<sub>6</sub>): δ = –272.0. –

EI-MS:  $m/z$  (%) = 731(100)  $[M-CH_3]^+$ , 545 (74)  $[M-CH_3-CH_3CdOCH(CH_3)_2]^+$ . –  $C_{16}H_{40}O_4Cd_4$ : calcd. C 25.76, H 5.40; found C 25.34, H 5.36.

#### X-Ray structure determination

A Bruker Apex X-ray diffractometer ( $\lambda = 0.71073 \text{ \AA}$ ) was used to collect the scattering intensities for the single crystals of **2** and **3**. Single crystals of **2** and **3** were mounted under inert perfluoro-polyether at the tip of a glass fibre and cooled in a cryostream of the diffractometer. The structures were solved by Direct Methods and refined with the full-matrix least-squares procedure (SHELXTL) against  $F^2$  with the program SHELXTL 5.01 or SHELXTL 6.10 [14]. Non-hydrogen

atoms were refined with anisotropic displacement parameters and hydrogen atoms isotropically with a riding model.

CCDC 645304 (**2**) and 645303 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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