Cadmium Peroxides

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O_2 Insertion into a Cadmium–Carbon Bond: Structural Characterization of Organocadmium Peroxides**

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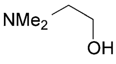
Insertion of oxygen into a metal–carbon bond is one of the oldest known reactions in organometallic chemistry. The early experiments of Frankland over 150 years ago,[1] which relate to the extreme sensitivity of ZnR_2 ($R = Me$, Et) in air, initiated a series of studies on the outcome of the R_2Zn/O_2 reaction that are still ongoing. The products of this reaction have been reported as being the alkoxides RZn(OR), $Zn(OR)_2$ or the peroxides RZn(OOR), $Zn(OOR)_2$[2] involving insertion of O_2 into either one or both Zn–C bonds. In more recent years, heterocubanes $[\{RZn(OR)\}_4]$ and bis(heterocubane) structures $[(RZn)_6Zn(OR)_8]$ have been structurally authenticated from these reactions, in which the presence or absence of water plays a role in determining the outcome.[3] Despite this historical and contemporary interest, the first organozinc peroxide was only isolated and structurally characterized as recently as 2003 by Lewiński,[4] and since then some of the mechanistic insights and synthetic procedures required to form and isolate these highly reactive species have emerged. Thus, a labile ligand is initially required to afford a three-coordinate $R_2Zn(L)$ species in situ,[5] as the four-coordinate $R_2Zn(L)_2$ are less reactive to O_2 insertion. The resulting RZnOOR then needs to be stabilized by appropriate donor groups, which now include both *N,O*[4a] and *N,N* chelating ligands.[4b,6]

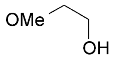
The chemistry of organocadmium peroxides is considerably less well explored than the related zinc system. $CdMe_2$ is known to smoke on exposure to air and the limited reports available suggest that autoxidation of this species affords MeCdOOMe and/or $Cd(OOMe)_2$ depending on the ratio $Me_2Cd{:}O_2$,[2d,7] though neither species has been characterized to any extent, either spectroscopically or structurally; MeCdOO*t*Bu has been suggested as a tetramer on the basis of cryoscopy in benzene, though the analytical data for the sample studied bring its purity into question.[8] We are aware of only limited attempts to understand the mechanistic aspects of the Me_2Cd/O_2 reaction, and those that have been carried out are largely kinetic in nature,[8,9] with the identity of the species formed based on the amounts of O_2 consumed. The speculative formation of an initial $R_2Cd{\cdot}O_2$ adduct, claimed in the case of Et_2Cd,[10] has been disputed for Me_2Cd,[9] and rearrangements of the type MeCdOOR→$(MeO)_2Cd$ were also ruled out.[8]

There appear to have been no studies of the structural chemistry of any intermediates formed in this reaction, and unequivocal evidence for the formation of organocadmium alkylperoxides central to this chemistry is still outstanding. Thermal decomposition of MeCdOO*t*Bu has been claimed to produce the alkoxides MeCdO*t*Bu, MeOCdO*t*Bu, and the formate $MeCdO_2CH$.[11]

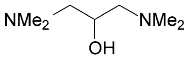
Indeed, only a limited number of organocadmium alkoxides RCdOR' have themselves been reported, including tetrameric heterocubanes $[\{RCdOR'\}_4]$ ($R' = Me$, Et, *i*Pr, *t*Bu, moe), and our work utilizing aminoalcohols has given dimeric $[\{MeCd(tdmap)\}_2]$, trimeric $[\{MeCd(bdmap)\}_3]$, and tetrameric $[\{MeCd(dmae)\}_4]$.[12]



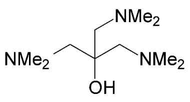
Hdmae



Hmoe



Hbdmap



Htdmap

Our own interest in the autoxidation of Group 12 dialkyls has stemmed from the $ZnMe_2$/Hbdmap/O_2 reaction, which has allowed us to isolate $[(MeZn)_3(bdmap)_2(OOMe)]$, $[(MeZn)_3(bdmap)_2(OH)]$, and a product likely to be a result of peroxide decomposition, $[(MeZn)_5(bdmap)_3O]$.[13] We now present the outcome of the analogous organocadmium chemistry, which has furnished the first structurally characterized examples of organocadmium organoperoxides.

Reaction of $CdMe_2$ with Hbdmap (2:1)[14] affords crystals of $[\{MeCd(bdmap)\}_3{\cdot}2\,CdMe_2]$ (**1**) (Figure 1).[15] One $CdMe_2$ moiety is coordinated to the $\{MeCd(bdmap)\}_3$ trimer by *N,O* chelation from a bdmap ligand, in the same manner as reported for $[\{MeZn(bdmap)\}_3{\cdot}ZnMe_2]$.[13] Remarkably, an additional, uncoordinated $CdMe_2$ is also present in the lattice with its closest neighbor being another uncomplexed $CdMe_2$ (Cd⋯Cd: 3.90 Å); we are unaware of any previously published examples of this structural feature.[16] When the reaction is repeated in 4:3 ratio, **1** still crystallizes from solution, but solution-state NMR data are consistent with formation of $[\{MeCd(bdmap)\}_3{\cdot}CdMe_2]$ (**2**), lacking the uncomplexed $CdMe_2$ moiety. ^1H NMR (238 K) data for **1** shows resolvable signals for MeCd (3H and 6H; −0.34, −0.48 ppm) and $CdMe_2$ (12H: −0.58 ppm), and a splitting of the NMe_2 signal, resolving $Me_2N{:}\rightarrow CdMe_2$ (6H, 1.86 ppm) from the remaining NMe_2 groups (30H, 1.89 ppm). In the ^{113}Cd NMR (298 K) there are broad signals at about −26 and 290 ppm that resolve at 198 K to sharp signals at −8

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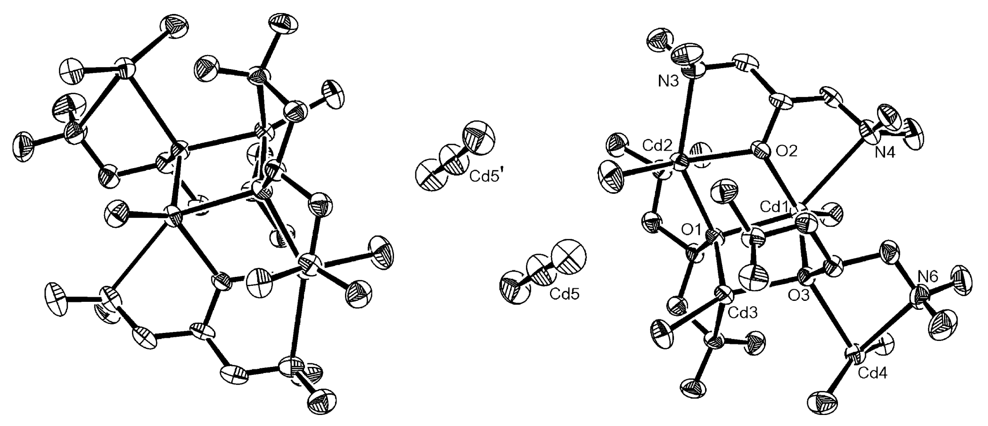


Figure 1. The structure of **1** with labeling of selected atoms; ellipsoids set at 50% probability, hydrogen atoms omitted for clarity. Selected bond lengths [Å]: Cd1–O2 2.211(3), Cd1–O3 2.298(3), Cd1–O1 2.360(3), Cd2–O2 2.199(3), Cd2–O1 2.375(3), Cd2–N2 2.421(4), Cd2–N3 2.512(4), Cd3–O3 2.226(3), Cd3–O1 2.264(3), Cd3–N1 2.617(4), Cd4–O3 2.542(3), Cd4–N6 2.561(4) Å; symmetry operation: 1−*x*, −*y*, −*z*.

(uncoordinated $CdMe_2$) and −253 (four-coordinate *N*,*O*-chelated $CdMe_2$), and −285 and −303 ppm assignable to five-coordinate MeCd centers in the six-membered Cd_3O_3 ring. The NMR spectra of **2** are essentially the same apart from a change in the ^1H MeCd/$CdMe_2$ region (now 9H; −0.62 ppm; 6H: −0.55 ppm) and the lack of a ^{113}Cd signal at about 0 ppm, which are both consistent with the loss of lattice $CdMe_2$ present in **1**.

Cooling a solution of **2**, prepared in situ, to −78 °C, adding an atmosphere of dry O_2 for 5 min, and then evacuating and replacing this with dry N_2 yields the novel double-peroxide species [{MeCd(bdmap)}$_4$Cd(OOMe)$_2$] (**3**) arising from controlled insertion of O_2 into the Cd–Me bond. Compound **3** comprises two [MeCd(bdmap)]$_2$ rings joined by a {Cd(OOMe)$_2$} unit (Figure 2),[17] with each peroxide acting as a μ_2-bridge. The O–O distances (1.461(5), 1.436(8) Å) are similar to those reported for zinc alkyl peroxides.[4,13] The central cadmium is six-coordinate within a CdO_4N_2 ligand sphere, while the five-coordinate MeCd centers are either $MeCdO_2N_2$ (Cd3, Cd5) or $MeCdO_3N$ (Cd2, Cd4); the bdmap bridges either two terminal metals or a terminal and the central metal, both in a μ_2-mode. The peroxide appears as a 6H singlet at 3.58 ppm in the ^1H NMR spectrum, superimposed on three overlapping signals for the CH groups of the bdmap, while the four MeCd groups appear as three signals at −0.51 (3H), −0.58 (6H), and −0.65 ppm (3H). The ^{113}Cd NMR spectrum has two closely spaced signals at −279 and −282 ppm, which are consistent with the similar $MeCdO_2N_2$ and $MeCdO_3N$ metal environments, and a weak signal at −536 assignable to the CdN_2O_4 center.

Repeating the same reaction that formed **3** but at room temperature leads to the formation of the triple peroxide [(MeCd)$_5$(bdmap)$_2$(OOMe)$_3$] (**4**). Compound **4** incorporates four essentially equivalent five-coordinate metals, each in a $MeCdO_3N$ environment, and a central six-coordinate $MeCdO_5$ moiety (Figure 3).[18] Of the three peroxides in **4**, two each cap a Cd_3 triangle, while the remaining peroxide bridges in both μ_3 and μ_2-modes.

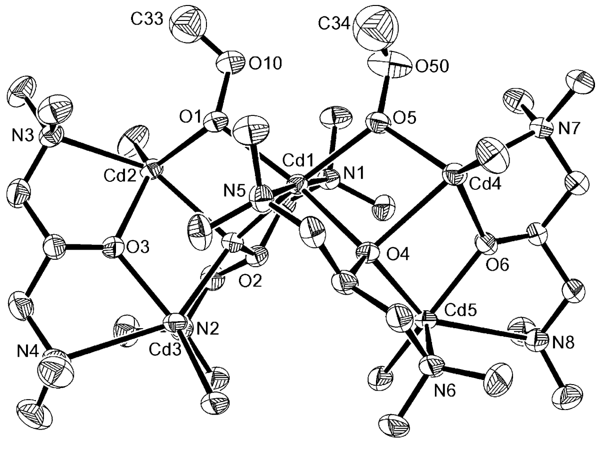


Figure 2. The structure of **3** with labeling of selected atoms; ellipsoids set at 40% probability, hydrogen atoms omitted for clarity. Selected bond lengths [Å]: Cd1–O1 2.274(2), Cd1–O2 2.324(2), Cd1–O4 2.327(2), Cd1–O5 2.249(2), Cd1–N1 2.436(3), Cd1–N5 2.430(3), Cd2–O1 2.209(2), Cd2–O2 2.498(2), Cd2–O3 2.216(2), Cd2–N3 2.597(3), Cd3–O2 2.324(2), Cd3–O3 2.168(2), Cd3–N2 2.457(3), Cd4–O4 2.523(2), Cd4–O5 2.198(2), Cd4–O6 2.220(2), Cd4–N7 2.558(3), Cd5–O4 2.330(2), Cd5–O6 2.158(2), Cd5–N6 2.452(3), O1–O10 1.461(5), O5–O50 1.436(8) Å.

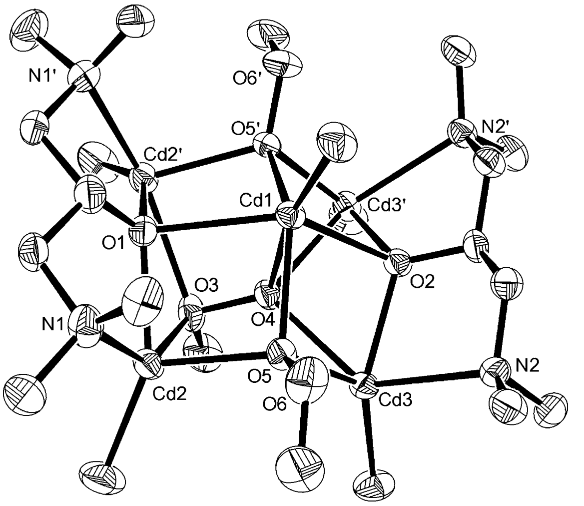
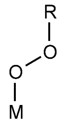
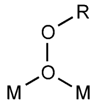


Figure 3. The structure of **4** with labeling of selected atoms; ellipsoids set at 40% probability, hydrogen atoms omitted for clarity. Selected bond lengths [Å]: Cd1–O1 2.514(5), Cd1–O2 2.525(5), Cd1–O3 2.544(10), Cd1–O5 2.353(3), Cd1–O5′ 2.353(3), Cd2–O1 2.245(3), Cd2–O4 2.584(6), Cd2–O5 2.303(3), Cd2–N1 2.526(5), Cd3–O2 2.237(3), Cd3–O5 2.254(4), Cd3–N2 2.550(4), O3–O4 1.472(13), O5–O6 1.463(5) Å; symmetry operation: *x*, *y*, 0.5−*z*.

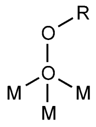
Data for metal alkylperoxides is scarce beyond the relatively common linear (**I**) or μ_2-bridging modes (**II**), with only very limited examples of the μ_3- (**III**), η^2- (**IV**), and combined μ_3,η^2-variations (**V**).[19] In this respect, the peroxide in **4** involving O3/O4, which links five separate metal centers (**VI**), is unprecedented; the O−O distances (1.472(13), 1.463(5) Å) are consistent with those in **3**.



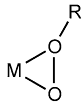
(I)



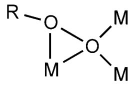
(II)



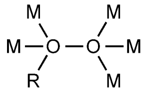
(III)



(IV)



(V)



(VI)

However, when $CdMe_2$ and Hbdmap are reacted in a 2:1 ratio (that is, 6:3 rather than 4:3), which generates **2** along with excess $CdMe_2$ in solution, and subsequently treated with O_2 as above, the outcome differs. At −78 °C, **3** is again the observed product, but when O_2 insertion occurs at room temperature, the bis(cubane) $[(MeCd)_6Cd(bdmap)_2(OMe)_6]$ (**5**) is now produced (Figure 4).[20] Compound **5** can be viewed as containing two $\{(MeCd)_3(bdmap)\}$ moieties linked by a central $\{Cd(OMe)_6\}$ unit and can only be compared with $[(C_6F_5)_6Cd_7(moe)_8]$.[12d] Within the $[(MeCd)_3(bdmap)]$ fragment there is one four-coordinate $CCdO_3$ (Cd2) which appears at −246 ppm in the ^{113}Cd NMR spectrum (298 K) and two five-coordinate $CCdO_3N$ ($\delta(^{113}Cd)$: −312 ppm). Any signal owing to the six-coordinate CdO_6 center is extremely weak, as with the CdN_2O_4 signal in **3**, but is tentatively assigned at −525 ppm. For comparison, the six-coordinate CdO_6 environment appears at −478 ppm for $Cd(bdmap)_2$ (**6**),[21] while CdO_3N_3 signals appear at −460m and −453 ppm in $Cd(bdmap)_2$ and $Cd(tdmap)_2$,[12c] respectively. The presence of OMe groups are confirmed by the 18H singlet at $\delta(^1H) = 3.82$ ppm and $\delta(^{13}C) = 55.7$ ppm.

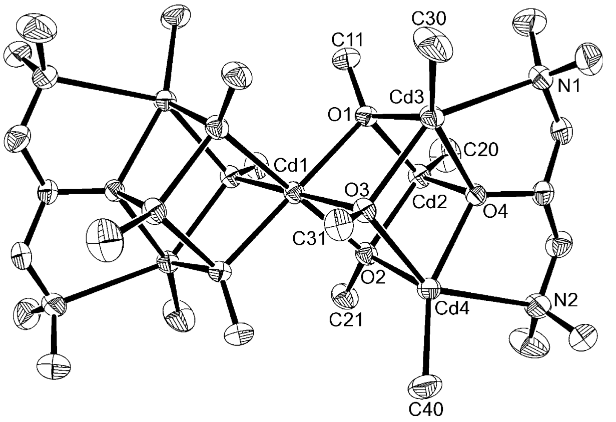


Figure 4. The structure of **5** with labeling of selected atoms; ellipsoids set at 40% probability, hydrogen atoms omitted for clarity. Selected bond lengths [Å]: Cd1–O1 2.322(3), Cd1–O2 2.356(3), Cd1–O3 2.235(3), Cd1–O1′ 2.322(3), Cd1–O2′ 2.356(3), Cd1–O3′ 2.235(3), Cd2–O1 2.248(3), Cd2–O2 2.228(3), Cd2–O4 2.310(3), Cd3–O1 2.293(3), Cd3–O3 2.357(3), Cd3–O4 2.270(3), Cd3–N1 2.712(5), Cd4–O2 2.298(4), Cd4–O3 2.359(3), Cd4–O4 2.274(3), Cd4–N2 2.699(5) Å; symmetry operation: 1−*x*, 1−*y*, 1−*z*.

Both **3** and **4** appear to be intermediates in the formation of **5**. The ^{113}Cd NMR spectrum of **3** shows the emergence of a weak signal at −311 ppm typical of **5**, while the evolution of **4** to **5** is more rapid, in that the ^{113}Cd NMR spectrum of **4** shows minor signals at −281 and −559 ppm (**4**) and a major signal at −312 ppm (**5**), which we assume is due to rapid decomposition in solution to **5**.[22]

In summary, the first structurally authenticated cadmium organoperoxides, obtained by the controlled insertion of O_2 into the Cd−Me bond and stabilized by the presence of donor NMe_2 groups, have been reported. $[\{MeCd(bdmap)\}_4Cd(OOMe)_2]$ (**3**) incorporates two μ_2-OOMe ligands similar to the arrangement in $[t$BuOOZn(pyr-pyrl)$]_2[$Zn(pry-pyrl)$_2]$ (pyr-pyrl = 2,2′-(1-pyrrolyinyl)pyrrole),[6b] while $[(MeCd)_5(bdmap)_2(OOMe)_3]$ (**4**) reveals a unique pentadentate peroxy ligand in which the preference of cadmium for a higher coordination number (in comparison to zinc) probably plays a role. Like the zinc analogues, these cadmium peroxides degrade to oxo clusters, typified by the bis(cubane) structural motif (**5**) common in zinc chemistry; the stability of the cadmium peroxides, however, seems lower than that of the zinc peroxides.

Experimental Section

Full experimental and crystallographic details can be found in the Supporting Information. CCDC 862652 (**6**), CCDC 862653 (**1**), CCDC 862654 (**3**), CCDC 862655 (**4**), CCDC 862656 (**5**), and CCDC 862657 (**7**) 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.

$[(MeCdbdmap)_4Cd(OOMe)_2]$ (**3**): Dimethylcadmium (1 mL, 2.0 M solution in hexane, 2.0 mmol) was diluted with toluene (6 mL). Hbdmap (0.22 g, 1.5 mmol, 4:3 ratio) was added to this mixture with stirring. The mixture was then cooled to −78 °C whereby the Schlenk headspace was replaced by O_2 and stirred for 5 min. The headspace was then replaced by N_2 and the sample was allowed to warm to room temperature. The sample was then concentrated until 1 mL of solution remained. Placing the solution in a freezer (−20 °C) gave crystals of **3** (m.p. 110 °C). Elemental analysis (%) calcd for $C_{34}H_{86}Cd_5N_8O_8$: C 31.3, H 6.65, N 8.6; found: C 31.3, H 6.61, N 8.42. NMR spectroscopy (298 K, $[D_8]$toluene): ^{1}H: $\delta = 3.83$ (br s, 2 H, CH), 3.74 (br s, 1 H, CH), 3.68 (br s, 1 H, CH), 3.58 (br s, 6 H, $OOCH_3$), 1.99 (br s, 16 H, CH_2N) 1.87 (s, 48 H, CH_3N), −0.51 (s, 3 H, $CdCH_3$), −0.58 (s, 6 H, $CdCH_3$), −0.65 ppm (s, 3 H, $CdCH_3$). $^{13}C\{^1H\}$: $\delta = 67.3$ (CO), 64.5 (CH_2N), 46.0 (OOMe), 45.7 (CH_3N), −16.4 (CH_3Cd). $^{113}Cd\{^1H\}$: $\delta = -279, -282, -536$ ppm.

$(MeCd)_5(bdmap)_2(OOMe)_3$ (**4**): Dimethylcadmium (1 mL, 2.0 M solution in hexane, 2.0 mmol) was added to toluene (4 mL). Hbdmap (0.22 g, 1.5 mmol, 4:3 ratio) was added to this mixture with stirring. The Schlenk headspace was replaced by dry O_2 and stirred for 5 min. The headspace was then replaced by dry N_2 and the sample volume was then reduced by half. Placing the solution in the freezer (−20 °C) gave crystals of **4**. Elemental analysis (%) calcd for $C_{22}H_{58}Cd_5N_4O_8$: C 24.7, H 5.47, N 5.24; found C 24.7, H 5.60, N 5.17. NMR spectroscopy (298 K, $[D_8]$toluene): ^{1}H: $\delta = 3.76$ (br s, 2 H, CH), 3.60 (br s, 3 H, OOCH$_3$), 3.57 (br s, 3H, OOCH$_3$), 3.49 (br s, 3H, OOCH$_3$), 1.86 (br m, 4H, CH$_2$N), 1.82 (br s, 24H, CH$_3$N), 1.76 (br m, 4H, CH$_2$N), −0.43 ppm (br s, 15H, CdCH$_3$). ^{13}C{^{1}H}: $\delta = 66.6$ (CH$_2$N), 64.5 (CO), 55.7 (OOMe), 46.1 (CH$_3$N), −17.4 ppm (CH$_3$Cd). ^{113}Cd{^{1}H}: $\delta = -281, -559$ ppm.

(MeCd)$_6$Cd(bdmap)$_2$(OMe)$_6$ (**5**): Dimethylcadmium (1 mL, 2.0 M solution in hexane, 2.0 mmol) was diluted with toluene (6 mL). Hbdmap (0.15 g, 1.0 mmol, 2:1 ratio) was added to this mixture with stirring. The Schlenk headspace was replaced by dry O$_2$ and stirred for 5 min. The headspace was then replaced by dry N$_2$ and the sample volume was then reduced by half. Placing the solution in the freezer (−20 °C) yielded crystals of **5**. Elemental analysis (%) calcd for $C_{26}H_{70}Cd_7N_4O_8$: C 22.9, H 5.17, N 4.1; found C 22.7, H 5.12, N 4.4. NMR spectroscopy (298 K, [D$_8$]toluene): ^{1}H: $\delta = 3.82$ (br s, 18H, OMe), 3.38 (br s, 2H, CHO), 2.04 (br m, 4H, CH$_2$N), 1.94 (br s, 24H, Me$_2$N), 1.71 (br m, 4H, CH$_2$N), −0.31 ppm (br s, 18H, CdCH$_3$). ^{13}C{^{1}H}: $\delta = 67.3$ (CH$_2$N), 66.6 (CO), 55.7 (OMe), 46.1 (Me$_2$N), −17.4 ppm (CH$_3$Cd). ^{113}Cd{^{1}H}: $\delta = -247, -312, -525$ ppm.

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[14] See the Supporting Information for details.

[15] Crystallographic data for **1**: M_r 1146.00, triclinic, $P\bar{1}$, $a = 11.1209(2)$, $b = 11.6055(2)$, $c = 19.0887(4)$ Å, $\alpha = 106.905(1)$, $\beta = 101.735(1)$, $\gamma = 90.517(1)°$, $V = 2301.81(7)$ Å^3, $Z = 2$, $\rho_{\text{calcd}} = 1.653\ \text{mg m}^{-3}$, $\mu(\text{Mo}\,k_\alpha) = 2.304\ \text{mm}^{-1}$, $F(000) = 1142$, final R_1, wR_2 ($I > 2\sigma(I)$) = 0.0436, 0.1076, GOF = 1.051.

[16] [{MeCd(tdmap)}·3 CdMe$_2$] (**7**) also contains this feature; see the Supporting Information.

[17] Crystallographic data for **3**: $C_{34}H_{86}Cd_5N_8O_8$, M_r 1297.11, triclinic, $P\bar{1}$, $a = 10.5248(1)$, $b = 14.1084(2)$, $c = 18.5883(3)$ Å, $\alpha = 75.975(1)$, $\beta = 78.394(1)$, $\gamma = 85.626(1)°$, $V = 2622.01(6)$ Å^3, $Z = 2$, $\rho_{\text{calcd}} = 1.643\ \text{mg m}^{-3}$, $\mu(\text{Mo}\,k_\alpha) = 2.041\ \text{mm}^{-1}$, $F(000) = 1300$, final R_1, wR_2 ($I > 2\sigma(I)$) = 0.0341, 0.0755, GOF = 1.074.

[18] Crystallographic data for **4**: $C_{22}H_{59}Cd_5N_4O_8$, M_r 1069.73, orthorhombic, $Pbnm$, $a = 11.9031(2)$, $b = 15.5711(2)$, $c = 20.4938(4)$ Å, $V = 3798.41(11)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.871\ \text{mg m}^{-3}$, $\mu(\text{Mo}\,k_\alpha) = 2.794\ \text{mm}^{-1}$, $F(000) = 2092$, final R_1, wR_2 ($I > 2\sigma(I)$) = 0.0431, 0.0917, GOF = 1.075.

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[20] Crystallographic data for **5**: $C_{26}H_{70}Cd_7N_4O_8$, M_r 1353.66, triclinic, $P\bar{1}$, $a = 10.5736(4)$, $b = 14.6987(5)$, $c = 15.7768(5)$ Å, $\alpha = 84.5583(18)$, $\beta = 71.2310(19)$, $\gamma = 82.0554(17)°$, $V = 2296.01(14)$ Å^3, $Z = 2$, $\rho_{\text{calcd}} = 1.958\ \text{mg m}^{-3}$, $\mu(\text{Mo-k}_\alpha) = 3.218\ \text{mm}^{-1}$, $F(000) = 1308$, final R_1, wR_2 ($I > 2\sigma(I)$) = 0.0385, 0.0911, GOF = 1.060.

[21] See the Supporting Information for details of the synthesis and X-ray structure of **6**.

[22] The ^{1}H NMR spectrum of a solution of **4** also shows a multiplicity of broad signals which integrate more closely to **5** than **4**.