An Organocadmium Hydroxylamide

Surajit Jana,[†,‡] Roland Fröhlich,[§] Alexander Hepp,[†] and Norbert W. Mitzel*[,‡,||]

NRW Graduate School of Chemistry, Institut für Anorganische and Analytische Chemie, and
Organisch-chemisches Institut, University of Münster, Münster, Germany, and Fakultät für Chemie,
Universität Bielefeld, Universitätsstrasse 25, 33615 Bielefeld, Germany

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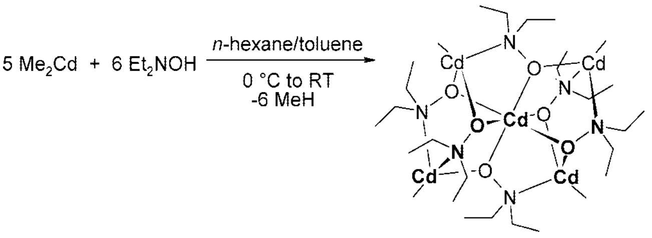
*Summary: The first organometallic cadmium hydroxylamide [Cd(MeCd)$_4$(ONEt$_2$)$_6$] (***1***) has been prepared by alkane elimination from dimethylcadmium upon treatment with N,N-diethylhydroxylamine and characterized by variable-temperature NMR spectroscopy (^{1}H, ^{13}C, ^{113}Cd), single-crystal X-ray diffraction, and elemental analysis. In the solid state compound* **1** *comprises an Cd$_5$N$_6$O$_6$ backbone with a central octahedral coordinate Cd atom, while all 12 donor atoms are attached to the 5 Cd nuclei whereas in solution it is of highly dynamic nature.*

Introduction

The chemistry of the hydroxylamides of the trivalent group 13 elements with their different structural motifs is well established.[1] The high coordination flexibility of the hydroxylamide ligands has been demonstrated in Al and Ga organometallics (e.g., in the readily fluctuating tetracyclic trinuclear Al$_3$ aggregate [{(Me$_2$Al)[ONMe]$_2$CH$_2$}$_2$(AlMe)][2]). It can be expected that this allows for the construction of highly dynamic Zn or Cd based multinuclear aggregates. This is because compared with trivalent group 13 elements, group 12 atoms require further contacts to a donor atom to achieve coordination number four due to their divalent nature. Hydroxylamine derivatives of the elements Zn and Cd were unknown, except the neutral hydroxylamine complex (H$_2$NOH)$_2$ZnCl$_2$ (Chrismer's salt),[3] until recently some of us reported on hydroxylamide complexes of zinc,[4] which show highly dynamic behavior in solution. We have also succeeded in the preparation of the first mixed hydroxylamide−hydrazide aggregates of zinc of the type [Zn(RZn)$_4$(NHNR′$_2$)$_2$(ONEt$_2$)$_4$].[5] However, up to now no cadmium hydroxylamine compounds are known, despite cadmium having a rich alkoxide chemistry.[6] Such an organocadmium aggregate compound with hydroxylamide substituents is reported in this contribution.

Scheme 1



[Cd(MeCd)$_4$(ONEt$_2$)$_6$] **1**

Results and Discussions

The reaction of dimethylcadmium with *N*,*N*-diethylhydroxylamine in an equimolar ratio leads to the formation of the cadmium hydroxylamide complex [Cd(MeCd)$_4$(ONEt$_2$)$_6$] (**1**) (Scheme 1), the first hydroxylamide of cadmium. Compound **1** is sparingly soluble in pentane and hexane, but well soluble in toluene and ethereal solvents. The compound was characterized by NMR spectroscopy, elemental analysis, and also X-ray crystal structure determination.

Single crystals of **1** were obtained from a solvent mixture of *n*-hexane/toluene (2:1) upon prolonged times of keeping concentrated solutions at –26 °C. Compound **1** crystallizes in the triclinic system, space group $P\bar{1}$. Toluene molecules fill the voids in the crystal structure, but have no significant contacts with any of the atoms of **1**.

Figure 1 depicts the molecular structure of **1**. The central Cd atom of the hydroxylamide aggregate [Cd(MeCd)$_4$(ONEt$_2$)$_6$] (**1**) adopts an octahedral coordination sphere by binding to the O atoms of all six O−N ligands. Formally an anionic fragment [Cd(ONEt$_2$)$_6$]$^{4-}$ can be assigned to constitute the center. The charge of this is compensated by four formally cationic MeCd$^+$ groups. As all O and N atoms are coordinated to Cd atoms, two possible modes of connectivity with the MeCd fragments are observed: N,O,O or N,N,O. Consequently, aggregate **1** is one of the limited examples of Cd species that exhibit mixed coordination numbers.[7] A similar structural type of aggregation was recently reported for an analogous zinc compound

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* Corresponding author. E-mail: mitzel@uni-bielefeld.de.

[†] Institut für Anorganische and Analytische Chemie, Universität Münster, Corrensstrasse 30, D-48149 Münster.

[‡] NRW Graduate School of Chemistry, Universität Münster, Corrensstrasse 30, D-48149 Münster.

[§] Organisch-chemisches Institut, Universität Münster, Correnssstrasse 40, D-48149 Münster.

[||] Fakultät für Chemie, Universität Bielefeld, Universitätsstrasse 25, D-33615 Bielefeld.

(1) (a) Hausen, H. D.; Schmöger, G.; Schwarz, W. *J. Organomet. Chem.* **1978**, *153*, 271. (b) Mitzel, N. W.; Lustig, C.; Woski, M. *Dalton Trans.* **2004**, 397.

(2) (a) Mitzel, N. W.; Lustig, C. *Angew. Chem.* **2001**, *113*, 4521. (b) Angew. Chem., Int. Ed. 2001, *40*, 4390.

(3) (a) Chrismer, A. *Bull. Soc. Chim.* **1890**, *3*, 119. (b) Walker, J. E.; Howell, D. M. *Inorg. Synth.* **1967**, *9*, 2 and references cited therein.

(4) Ullrich, M.; Berger, R. J. F.; Lustig, C.; Fröhlich, R.; Mitzel, N. W. *Eur. J. Inorg. Chem.* **2006**, 4219.

(5) Jana, S.; Berger, R. J. F.; Fröhlich, R.; Mitzel, N. W. *Chem. Commun.* **2006**, 3993.

(6) (a) Coates, G. E.; Lauder, A. *J. Chem. Soc.* **1966**, A264. (b) Maciel, G. E.; Borzo, M. *J. Chem. Soc., Chem. Commun.* **1973**, 394. (c) Maciel, G. E. *NMR Spectroscopy of nuclei other than protons*; Axenrod, T., Webb, G. A., Eds.; Wiley: New York, 1974; p 347. (d) Holmes, J. R.; Kaesz, H. D. *J. Am. Chem. Soc.* **1961**, *83*, 3903. (e) Nöth, H.; Thomann, M. *Chem. Ber.* **1995**, *128*, 923. (f) Ramsey, N. F. *Phys. Rev.* **1950**, *78*, 699. (g) Jana, S.; Pape, T.; Mitzel, N. W. *Z. Naturforsch., B: Chem. Sci.* **2007**, *62b*, 1339.

(7) Boyle, T. J.; Bunge, S. D.; Alam, T. M.; Holland, G. P.; Headley, T. J.; Avilucea, G. *Inorg. Chem.* **2005**, *44*, 1309.

10.1021/om7012343 CCC: $40.75

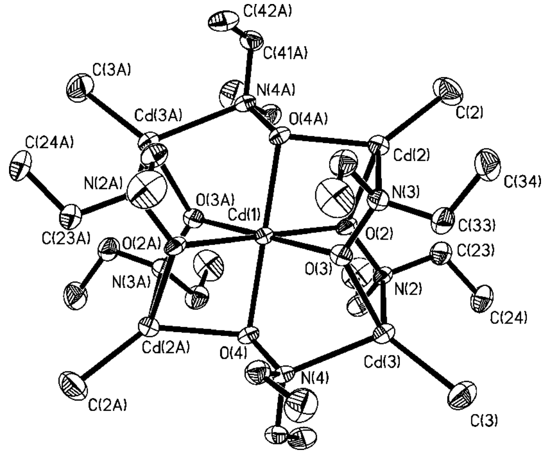
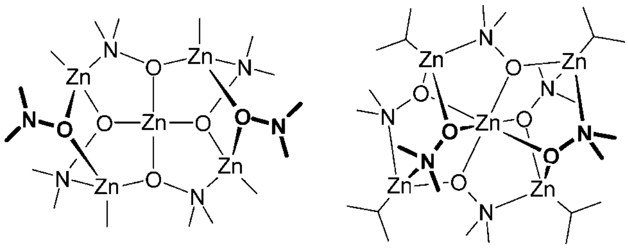


Figure 1. Molecular structure of $[Cd(MeCd)_4(ONEt_2)_6]\cdot C_7H_8$ (**1**) as determined by X-ray crystallography. The toluene molecule and the hydrogen atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms labeled with A: $-x + 1$, $-y + 2$, $-z$. Selected bond lengths (Å) and bond angles (deg): Cd(1)−O(4) 2.281(2), Cd(1)−O(2) 2.305(2), Cd(1)−O(3) 2.349(2), Cd(2)−C(2) 2.146(2), Cd(2)−O(2) 2.269(2), Cd(2)−N(3) 2.386(2), O(2)−N(2) 1.446(2); O(2)−Cd(1)−O(4) 100.8(1), O(3)−Cd(1)−O(4) 88.9(1), O(2)−Cd(1)−O(3) 78.8(1), C(2)−Cd(2)−O(2) 124.0(2), C(2)−Cd(2)−N(3) 126.3(2), O(2)−Cd(2)−N(3) 89.5(1), O(3)−Cd(3)−N(4) 82.1(1), N(2)−Cd(3)−N(4) 106.8(1), N(2)−O(2)−Cd(2) 121.0(2), Cd(1)−O(2)−Cd(2) 92.1(1), Cd(1)−O(3)−Cd(3) 98.7(1).

Scheme 2



2 3

$[Zn(ZnR)_4(ONMe_2)_6]$

2: R = Me; **3**: R = *i*Pr

$[Zn(iPrZn)_4(ONMe_2)_6]$ (**3**, see Scheme 2).[4] However, other compounds of a similar composition but different substituents at both zinc and nitrogen atoms like $[Zn(MeZn)_4(ONMe_2)_6]$ (**2**, Scheme 2), $[Zn(EtZn)_4(ONMe_2)_6]$, and $[Zn(MeZn)_4(ONEt_2)_6]$ (which is the exact zinc analogue of **1**) adopt an isomeric aggregation mode with an open chalice-like fenestrane-type structure, which leaves the central Zn atom only four coordinate and involves two dangling NR_2 units, not involved in coordination to metal atoms.

Figure 2 shows the $Cd_5N_6O_6$ core of the cluster **1** to demonstrate the inversion center of the molecule. The shortest Cd1−O bond, Cd1−O4, is found at 2.281(2) Å and the longest Cd1−O3 at 2.349(2) Å. The peripheral Cd−O bond lengths are approximately 0.1 Å shorter than that of the central Cd−O lengths.

In the ^1H NMR spectrum of **1** in C_6D_6 solution, a single peak at –0.13 ppm with the corresponding satellites ($^2J_{CdH} = 36.8$ Hz) is observed for methyl groups at cadmium. In d_8-toluene solution the same resonance is recorded at −0.27 ppm ($^2J_{CdH} = 36.9$ Hz), both at ambient temperature. However, the appearance of the spectrum changes upon cooling. Two equal intensity peaks at –0.18 ($J_{CdH} = 35.1$ Hz) and 0.06 ppm ($^2J_{CdH} = 35.6$ Hz) are recorded for the methyl groups in d_8-toluene solution at 200 K, which is in accordance with two different connectivities at the MeCd units observed in the solid-state structure. Broad peaks are obtained for the protons of the hydroxylamine substituents even at 200 K.

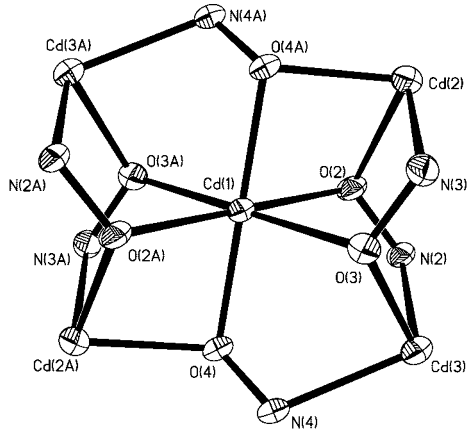


Figure 2. Core structure of the $Cd_5N_6O_6$ unit in **1**.

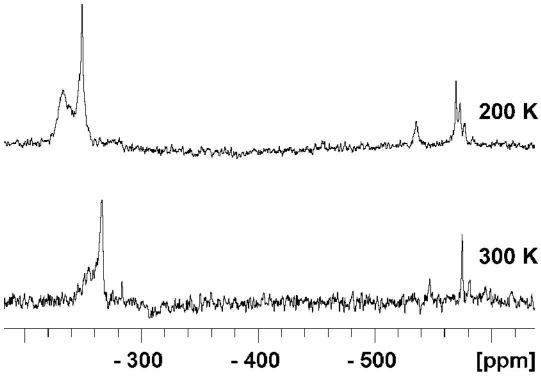


Figure 3. ^{113}Cd NMR spectra of **1** in d_8-toluene at 300 and 200 K in inset.

A ^{113}Cd NMR spectrum recorded at 300 K in d_8-toluene shows two resonances at –575.3 and –266.8 ppm corresponding to the central cadmium atom and the four peripheral cadmium atoms, respectively. Heating to 320 K causes no significant changes to the spectrum. At 200 K in d_8-toluene solution two broad signals at −249.2 and −233.0 ppm are observed for the peripheral cadmium atoms (Figure 3). This is in the same range as for other four-coordinate Cd atoms as in $[(MeCd)_4(O^iPr)_4]$, where the resonance was found at −272 ppm.[6g] Besides this, there are further smaller signals, which indicate the presence of even more aggregation isomers, which we could not assign structures on the basis of the limited data available.

These VT-NMR spectra confirm that the central cadmium atom in the hydroxylamide complex is attached to all six O atoms of the hydroxylamide units in this inversion-symmetric complex. Due to the highly fluxional behavior, the ^1H NMR of the methyl group at the peripheral cadmium atom and ^{113}Cd NMR of the peripheral cadmium gave only one set of signals at room temperature, i.e,. they rapidly exchange places and coordination pattern.

Experimental Section

Materials and Methods. All manipulations were carried out under a dry nitrogen atmosphere with standard Schlenk and high-vacuum techniques with double manifolds or in a glovebox operated under an argon atmosphere. All solvents were purified by standard procedures immediately prior to use. Et_2NOH (Aldrich) was purified by fractional distillation. **Note:** Care must be taken in the handling and storage of cadmium-containing compounds, as well as the subsequent waste due to the high toxicity associated with compounds of this element, in particular if they are volatile like Me_2Cd.

Synthesis of $[Cd(MeCd)_4(ONEt_2)_6]\cdot C_7H_8$ (1). Me_2Cd (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 Et_2NOH (0.30 mL, 4.0 mmol) in a 2:1 mixture of *n*-hexane/toluene (15 mL) at 0 °C. The reaction mixture was gradually warmed to room temperature and stirred for 6 h. The color of the reaction mixture turned yellowish. After removal of the solvent under reduced pressure, the resulting residue was dissolved in a mixture of *n*-hexane/toluene and filtered. The clear, colorless filtrate stored at –26 °C in a freezer for 2–3 weeks afforded colorless blocks of **1**. Yield 50% (518 mg, 0.50 mmol) (with respect to hydroxylamine); mp 245 – 246 °C; ^{1}H NMR (400.1 MHz, C_6D_6) δ –0.13 (s, $J_{CdH} = 36.8$ Hz, 12 H; $\mathrm{CdC}H_3$), 1.03 (t, $^3J = 7.0$ Hz, 36 H; $\mathrm{NCH_2C}H_3$), 2.95, 3.07 (2 br s, 24 H; $\mathrm{NC}H_2\mathrm{CH_3}$), 2.09, 6.97, 6.99, 7.01, 7.10 (toluene); ^{1}H NMR (400 MHz, d_8-toluene, 300 K) δ –0.27 (s, $^2J_{CdH} = 36.9$ Hz, 12 H; $\mathrm{CdC}H_3$), 0.98 (t, $^3J = 6.8$ Hz, 36 H; $\mathrm{NCH_2C}H_3$), 2.87, 2.99 (2 br s, 24 H; $\mathrm{NC}H_2\mathrm{CH_3}$); ^{1}H NMR (400.1 MHz, d_8-toluene, 200 K) δ –0.18 (s, $^2J_{CdH} = 35.1$ Hz, 6 H; $\mathrm{CdC}H_3$), 0.06 (s, $^2J_{CdH} = 35.7$ Hz, 6 H; $\mathrm{CdC}H_3$), 0.94, 1.09 (2 br, 36 H; $\mathrm{NCH_2C}H_3$), 2.41, 2.82, 2.94, 3.84 (4 br s, 24 H; $\mathrm{NC}H_2\mathrm{CH_3}$); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6) δ –11.6 ($^1J_{^{111}CdC} = 472$ Hz, $^1J_{^{113}CdC} = 494$ Hz; $\mathrm{Cd}C\mathrm{H_3}$), 12.1 (br, $\mathrm{NCH_2}C\mathrm{H_3}$), 54.4 (br, $\mathrm{N}C\mathrm{H_2CH_3}$), 21.4, 125.7, 128.5, 129.3, 137.8 (toluene); ^{13}C{^{1}H} NMR (100.6 MHz, d_8-toluene, 200 K) δ –11.31 (br, $\mathrm{Cd}C\mathrm{H_3}$), 12.8, 13.8 (br s, $\mathrm{NCH_2}C\mathrm{H_3}$), 50.4, 51.5, 55.7, 62.1, 62.1 (br s, $\mathrm{N}C\mathrm{H_2CH_3}$); ^{113}Cd NMR (88.8 MHz, d_8-toluene, 300 K) δ –575.3 (central *Cd*), –266.8 (peripheral *Cd*); ^{113}Cd NMR (88.8 MHz, d_8-toluene, 200 K, δ –577.4, −573.6, −569.8, −536.1 (central *Cd*), –249.2, –233.0 (br, peripheral *Cd*); $C_{28}H_{72}N_6O_6Cd_5$ (1150.97 g mol^{-1}) calcd C 29.22, H 6.31, N 7.30; found C 29.90, H 6.26, N 7.22.

Crystallographic data for **1**: $C_{28}H_{72}N_6O_6Cd_5\cdot C_7H_8$, $M = 1243.05$ g$\cdot$mol^{-1}, colorless block shape, size $0.25 \times 0.25 \times 0.10$ mm^3, triclinic, space group $P\bar{1}$, $a = 10.401(1)$ Å, $b = 11.508(1)$ Å, $c = 12.431(1)$ Å, $\alpha = 68.66(1)°$, $\beta = 66.65(1)°$, $\gamma = 68.36(1)°$, $V = 1227.7(2)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.681$ g$\cdot$cm^{-3}, $\mu = 2.172$ mm^{-1}, 12717 reflections collected on a Nonius Kappa CCD four-circle diffractometer [ω-scan, $2\theta_{max} = 56.22°$, Mo Kα radiation, $\lambda = 0.71073$ Å, $T = 198(2)$ K] merged to 5825 unique ($R_{int} = 0.035$) refining to $R_1 = 0.029$ for 5100 data [$F_o > 4\sigma(F_o)$] and $wR_2 = 0.072$ for all data. All thermal displacement parameters for non-H-atoms were refined anisotropically, and for H-atoms isotropically.[8] For crystallographic data in CIF of other electronic format see DOI: XX.

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Supporting Information Available: Crystallographic information files (CIF) of compound **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[8] (a) *SHELXTL 6.10*; Bruker-AXS X-Ray Instrumentation Inc.: Madison, WI, 2000. (b) Sheldrick, G. M. *SHELXL-93: Program for crystal structure refinement*; Universität Göttingen: Göttingen, Germany, 1993.