First mixed hydrazide/hydroxylamide metal aggregates†

Surajit Jana,∗a Raphael J. F. Berger,∗a Roland Fröhlichb and Norbert W. Mitzel∗∗a

Received (in Berkeley, CA, USA) 7th June 2006, Accepted 25th July 2006

First published as an Advance Article on the web 10th August 2006

DOI: 10.1039/b608135e

The first organometallic clusters of mixed hydrazide/hydroxylamide clusters of zinc, [Zn(MeZn)4(HNNMe)22(OEt)2]4 and [Zn(OCZn)4(HNN(CH3)2)24(OEt)2]4 were synthesized in one-pot synthesis protocols from dialkylzinc solutions, substituted hydrazines and N,N-diethylhydroxylamine; competing for the Zn atoms, the different binding properties of hydrazide and hydroxylamide ligands in these heteroleptic clusters are discussed.

Realising different stoichiometries of metal : non-metal atoms is a crucial requirement for the rational design of new molecular precursor compounds for many areas of material synthesis. The so far unknown zinc oxynitrides or nitrogen containing zinc oxide are promising but so far hardly accessible semiconductor materials.1 Thus, a chemical synthesis route via thermolysis of molecular precursors compounds with suitable Zn : N : O stoichiometries would be highly desirable, but so far lack the accessibility of molecular precursor compounds. Recent contributions to this field are novel organometallic hydrazide and mixed hydrazide/alkoxide clusters of zinc having different core moieties such as Zn2N8, Zn2N2O, Zn2N2O2, Zn2N2O2.2-4 The use of hydrazides for nitride material generation has been demonstrated earlier for Al and Ga,5 and the hydrazide chemistry of these elements has recently been reviewed.6

Besides hydrazides, hydroxylamide units are interesting components for the simultaneous introduction of N and O atoms into such metal compounds, and the weak N–N and N–O bonds provide predetermined breaking points for their thermal decomposition chemistry. In addition, both, hydrazide and hydroxylamide groups, introduce relatively low carbon contents. However, in contrast to the meanwhile well established hydroxylamide7 (and oximato8) compounds of Al and Ga, hydroxylamine compounds of zinc are almost unknown so far and the neutral hydroxylamine complex (H2NHOH)2ZnCl2, Chrsimer’s salt,9 is the best known example.

Combining the properties of hydrazine, N–N, and hydroxylamine units, N–O, in one metal compound is a concept which has so far not been realised and so we report here the first organometallic zinc compounds, containing both, hydrazide and hydroxylamide ligands.

As outlined in Scheme 1, dimethylzinc reacts cleanly with N,N-dimethylhydrazine and N,N-diethylhydroxylamine in a 2 : 1

ratio in n-hexane at ambient temperature to afford the pentazinc cluster 1.† Compound 1 was isolated as air-sensitive colourless plates (ca. 87% yield) and was characterised by 1H and 13C NMR spectroscopy, by elemental analysis, mass spectrometry and single-crystal X-ray diffraction.§ The 1H NMR spectrum of 1 shows two signals for the methyl protons at zinc with equal intensity at −0.40 and −0.27 ppm. The chemical shifts of the protons of the ethylene groups at the hydroxylamine and the methyl groups at the hydrazine units appear almost in the same region. In the 1H VT-NMR at 200 K, eight sets of ethylene protons of N,N-diethylhydroxylamine and two singlets for methyl protons on hydrazine units were observed. These data are fully consistent with molecular C2 symmetry. The highest mass observed in the mass spectrum corresponds to the mass of the molecule diminished by that of one methyl group. A signal at 3184 cm−1 in the IR spectrum identified the NH functions.

Analogously to the synthesis of 1, compound 2 was prepared by reacting Et2Zn with 1-aminopiperidine and Et2NOH in a 2 : 1 : 1 ratio in a one-pot-synthesis protocol (ca. 77% yield, Scheme 1).‡ Compound 2 was characterised by NMR spectroscopy, elemental analysis and X-ray crystallography.‡ The 1H NMR signals of the hydroxylamine and hydrazine substituents and the ethyl groups at zinc overlap with one another and are thus difficult to assign even in a spectrum recorded at 200 K. The same scenario was also observed in the 13C NMR. The compound melts at 195 °C with decomposition. The IR signal at 3177 cm−1 confirms the presence of N–H bonds in the cluster.

In order to obtain higher hydrazide : hydroxylamide ratios, zinc alkyls, hydrazine and hydroxylamine were employed in different ratios from 2 : 1 : 1 to 2 : 2 : 1 to 2 : 3 : 1 under the same reaction conditions. However, the resulting products have the same composition and constitution as 1 and 2, but lower yields were obtained.


‡ Crystallographic data for 1 and 2 have been deposited with the Cambridge Crystallographic Data Centre and are available under numbers CCDC 666810 for 1 and CCDC 684125 for 2.

aInstitut für Anorganische und Analytische Chemie and NRW Graduate School of Chemistry, Westfälische Wilhelms-Universität Münster, Corrensstrasse 30, D-48149, Münster, Germany.
E-mail: Mitzel@uni-muenster.de; Fax: Int+49 251 8336007

bOrganisch-chemisches Institut, Westfälische Wilhelms-Universität Münster, Corrensstrasse 40, D-48149, Münster, Germany.


COMMUNICATION www.rsc.org/chemcomm | ChemComm

Single crystals of both compounds were grown from n-hexane solutions upon cooling and used for structure determination by X-ray diffraction. Compound 1 (Fig. 1) consists of a chalice shaped aggregate comprising six fused rings. Fig. 2 shows the molecular core of compound 1 and the C2 axis passing through the atom Zn1 and bisecting the angle O(21)–Zn1–O(41). The central Zn atom, Zn(1), is connected to the anionic ends of two hydroxylamide and two hydrazide units. The “anionic” O and N binding sites of this formally dianionic [Zn(ONEt2)2(NHNMe2)2]2– unit bind further four organometallic ZnMe units, while the neutral N atoms of these ONEt2 and NHNMe2 substituents form rings by binding to these ZnMe moieties. As all zinc atoms of this formal [Zn(ONEt2)2(NHNMe2)2(ZnMe)4]2+ unit are only three-coordinate, their fourth coordination site is saturated by two further hydroxylamide units, each μ2-O-bridging two peripheral Zn atoms. This leaves one NEt2 group non-coordinated.

All six rings are five-membered, but have different constitution: two ZnONZnN rings include the central Zn atom and endocyclic NO units, two ZnNNZnO rings the central Zn atom and endocyclic NN units and the two peripheral ZnNNZnO rings also include an endocyclic NN unit.

This aggregation motif is entirely new and the closest relationship is to a few pentanuclear species found e.g. in bioinorganics,10 but those contain square-planar coordinated central metal ions and contain no N–N bonds.

Zn–N bonds of different lengths are observed: the distance of Zn(1)–N(11) at 1.987(4) Å is shorter than the Zn(5)–N(11) bond to the peripheral Zn atom at 2.093(4) Å and is also about 0.1 Å shorter than Zn–N distance in tetrameric zinc hydrazide clusters.2,3 The same pattern is observed for the Zn–O bonds, where also those to the central Zn(1) are shortest at 1.961(4) Å, while there is a slightly longer Zn(5)–O(51) bond at 1.989(4) Å and two longer bonds, Zn(2)–O(21) and Zn(2)–O(51) at 2.023(4) Å.

The structure of 2 is shown in Fig. 3 and similar to that of 1. The bulkiness of the substituents at the hydrazine unit and zinc do not alter the constitution and the aggregation motif.

An interesting feature of both compounds is that hydroxylamide rather than hydrazide units adopt the peripheral positions of the pentanuclear aggregate with one non-coordinate N atom. Obviously—and explainable through the more electron-withdrawing bonding partner oxygen—these hydroxylamides are weaker donors at these N atoms than the hydrazide ligands. In order to estimate the relative energies of the two isomeric forms, calculations on the relative energies (Table 1) of the isomers of...
Table 1 Relative energies of the isomers 3, 4a, 4b and 4c of [Zn(ZnMe)4(HNNMe2)2(ONMe2)4] (Scheme 2) as calculated at the DFT(BP)/SV(P) level of theory

<table>
<thead>
<tr>
<th>Isomer</th>
<th>3</th>
<th>4a</th>
<th>4b</th>
<th>4c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative energy/kJ mol⁻¹</td>
<td>0</td>
<td>36</td>
<td>42</td>
<td>50</td>
</tr>
</tbody>
</table>

Notes and references