An Organozinc Hydrazide-Thiolate Aggregate with a $Zn_3N_4S_2$ Core

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The first organometallic zinc hydrazide-thiolate cluster, $[(MeZn)_2(PhSZn)(HNNMe_2)(H_2N–NMe_2)(SPh)_2]_2$ (**1**) has been prepared by alkane elimination from dimethylzinc solutions upon treatment with *N*,*N*-dimethylhydrazine and thiophenol and characterised by NMR spectroscopy, elemental analysis and single crystal X-ray diffraction. Compound **1** forms asymmetric aggregates containing a $Zn_3N_4S_2$ core. The core features rings with different connectivities. A seven-membered ZnSZnNNZnS ring comprises three five-membered rings, two of a ZnSZnNN and one of a ZnNZnNN atom sequence. Intermolecular S···H bonding is observed in the crystal.

Key words: Zinc, Hydrazide, Thiolate, Crystal Structure, Aggregate

Introduction

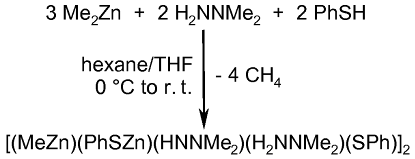
With the aim of providing new molecular precursor compounds for the synthesis of nitrogen-containing zinc oxide or zinc oxynitride, we recently reported on the synthesis and structural characterisation of novel organometallic aggregates with zinc-alkyl units and hydrazide [1] and hydroxylaminato-κ-*O* units [2], but also mixed aggregates with both anionic groups [3]. Further investigations concerned such hydrazide aggregates with some of the hydrazide units replaced by hydroxide [1], alkoxide [1, 4] and silanolate groups [5]. Without the inclusion of hydroxylaminato-κ-*O* units, the aggregates are predominantly tetranuclear, while with hydroxylaminato-κ-*O* units they are generally based on penta-nuclear motifs [1 – 5]. In almost all cases the zinc atoms adopt the coordination number four, the only exception being $[Zn(EtZn)_4(ONEt_2)_6]$ with a central Zn atom of coordination number six. These pentanuclear structures are highly dynamic as has also been shown for analogous cadmium hydroxylaminato aggregates [6].

Replacement of alkoxide by homologous sulphur units can be expected to lead to changes in the structures due to the softer nature of the thiolate ligands. However, while a large range of zinc alkoxides [7] and silanolates is known [8], only few zinc thiolate aggregates have been described so far. These include the pentameric $[MeZnS^tBu]_5$ [9], the octameric $[MeZnS^iPr]_8$ [10] and the dimeric $[MeZnS^tBu·C_6H_5N]_2$ and $[MeZnS^tBu·$*trans*$\text{-}C_6H_{15}N_3]_2$ [11]. Cluster aggregates containing both, thiolate and hydrazide groups, have so far only been reported from the chemistry of molybdenum: $[Cp_2Mo_2(\eta^2\text{-}\mu\text{-}NHNPh)(\mu\text{-}SMe)_3]·BF_4$ [12].

We report herein the first organometallic mixed hydrazide-thiolate aggregate of zinc and discuss its coordination behaviour.

Result and Discussion

Dropwise addition of dimethylzinc to a mixture of *N*,*N*-dimethylhydrazine and thiophenol in an *n*-hexane/THF (1:1) solvent mixture at ambient temperature leads to the formation of the mixed zinc hydrazide-thiolate $[(MeZn)_2(PhSZn)(HNNMe_2)(H_2NNMe_2)(SPh)_2]$ (**1**), a trinuclear zinc aggregate (Scheme 1).



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Scheme 1.

Compound **1** is only sparingly soluble in *n*-hexane, but dissolves completely in the presence of a small amount of THF. The compound was identified by single crystal X-ray diffraction (where it contains half an equivalent of THF per formula unit) and by elemental analysis.

Based on earlier results for the above mentioned organozinc aggregates with hydrazide and hydroxylaminato-κ-*O* groups [1 – 5] and on the frequent observation of complicated aggregation isomerism and molecular dynamics, it was expected that

^1H and ^{13}C NMR spectra of compound **1** would be complicated and difficult to assign. In the ^1H NMR spectrum, a sharp singlet at -0.50 ppm, along with four smaller singlets at -0.66, -0.59, -0.55 and -0.52 ppm, is observed for the protons of the zinc-bound methyl groups. In the light of the constitution in the solid state, this points to the expected dynamics in solution. Spectra recorded at lower temperature led to some changes, but did not allow a better assignment or any interpretation of the molecular dynamics. Nevertheless, the integrals of the groups of signals belonging to the Zn-methyl, the hydrazide-methyl and the phenyl groups are found to adopt the ratio consistent with the above formula finally derived from crystal structure determination and elemental analysis.

A similar observation is made for the ^{13}C NMR spectrum of **1**. It has also to be mentioned that no proton or carbon signals for the THF molecule were found in the ^1H or ^{13}C NMR spectra. This is probably due to a weak binding of the THF molecule and its evaporation under the reduced pressure, which was applied to dry the compound before dissolving it for the NMR experiments. This loss of THF upon drying in vacuum was also confirmed by the results of the elemental analysis.

A single crystal of **1** was obtained from an *n*-hexane/THF (3 : 1) solution upon storage at -26 °C. Compound **1** crystallises in the monoclinic space group *C*2/*c*. There are two independent molecules in the unit cell (Fig. 1), one being linked to a THF molecule *via* hydrogen bonding to one of the N–H functions of the complex. The molecules are chiral, but are present as a racemate with the enantiomers being related by space group symmetry. The bond lengths and angles of both molecules differ only slightly from each other. Since the aggregation motifs of both independent molecules are the same, only one of them is discussed here.

The aggregates consist of two Zn–CH_3 units and one $(H_5C_6)S$–Zn unit. All three zinc atoms are four-coordinate. The inorganic $(H_5C_6)S$-bound zinc atom (Zn(3)) is further linked to a phenylthiolate S atom (S(4)), the amide part of an *N*,*N*-dimethylhydrazide anion $[Me_2NN(H)]$ (N(1)) and the NH_2 group of a non-deprotonated *N*,*N*-dimethylhydrazine unit (N(3)). These zinc atoms are obviously the harder coordination centres as compared to the other two methyl-bound zinc atoms. The first of these (Zn(1)) is linked to two phenylthiolate S atoms (S(2) and S(4)) and the neutral NMe_2 group (N(2)) of the *N*,*N*-dimethylhydrazide anion $[Me_2NN(H)]$ besides the methyl group. The other zinc atom (Zn(2)) is linked to one phenylthiolate S atom (S(2)), an NMe_2 group (N(2)) of the neutral *N*,*N*-dimethylhydrazine unit $[Me_2NNH_2]$ and the amide NH group (N(1)) of the *N*,*N*-dimethylhydrazide anion $[Me_2NN(H)]$ besides the methyl group.

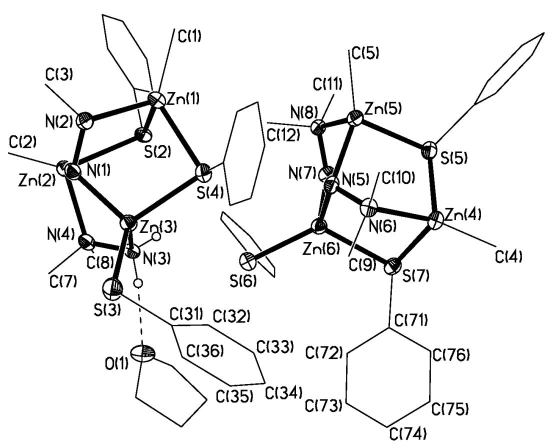

Fig. 1. Molecular structure of $[(MeZn)_2(PhSZn)(HNNMe_2)(H_2NNMe_2)(SPh)_2]_2\cdot THF$ (**1**) as determined by X-ray crystallography. The thermal displacement ellipsoids are drawn at the 50 % probability level. Carbon atoms are shown in stick mode; hydrogen atoms have been omitted for clarity (apart from those at the NH_2 group involved in H bonding to a THF molecule). Selected bond lengths (Å) and bond angles (deg): Zn(1)–N(2) 2.152(2), Zn(1)–C(1) 1.968(2), Zn(2)–N(1) 2.058(2), Zn(2)–N(4) 2.151(2), Zn(2)–S(2) 2.411(2), Zn(3)–N(3) 2.107(2), Zn(3)–S(3) 2.257(1), N(1)–N(2) 1.460(2), N(3)–N(4) 1.464(2), N(5)–N(6) 1.468(2), Zn(5)–N(8) 2.184(2); C(2)–Zn(2)–N(1) 129.2(2), N(1)–Zn(2)–N(4) 93.0(1), N(1)–Zn(2)–S(2) 94.5(1), N(1)–N(2)–Zn(1) 107.7(2), Zn(3)–N(1)–Zn(2) 107.1(1), N(1)–Zn(3)–N(3) 98.2(1), N(1)–Zn(3)–S(3) 117.7(1), N(1)–Zn(3)–S(4) 103.5(1), S(3)–Zn(3)–S(4) 121.2(1), N(2)–N(1)–Zn(3) 112.1(2), S(2)–Zn(1)–S(4) 93.8(1), N(5)–Zn(6)–S(6) 120.9(1).

Fig. 2 shows the $Zn_3N_4S_2$ core of **1** and its constitution. It contains one seven-membered ZnSZnNNZnS ring comprising two five-membered rings of the atom sequence ZnSZnNN and one five-membered ring of the atom sequence ZnNZnNN. All bond lengths are within the expected ranges defined by related compounds named above.

The components of the crystal structure are held together by hydrogen bonding, which link the aggregate units into endless chains by N–H···S bridges, as is displayed in Fig. 3. The average intermolecular S···H distance is 2.67 Å. Every second molecule is further linked to a THF molecule by an N–H···O bridge with the O···H distance being 2.02 Å.

In essence we have established the existence of a mixed hydrazide/thiolate aggregate of zinc. The

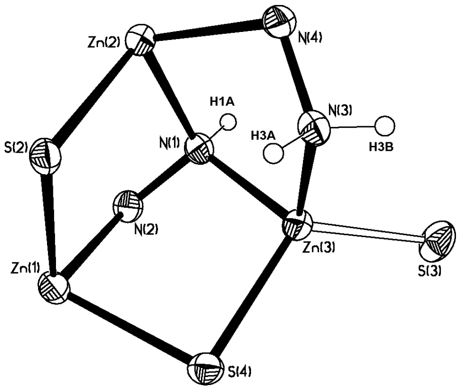

Fig. 2. $Zn_3N_4S_2$ core of **1**. The carbon and hydrogen atoms are omitted except for the hydrogen atoms of the N–H functions.

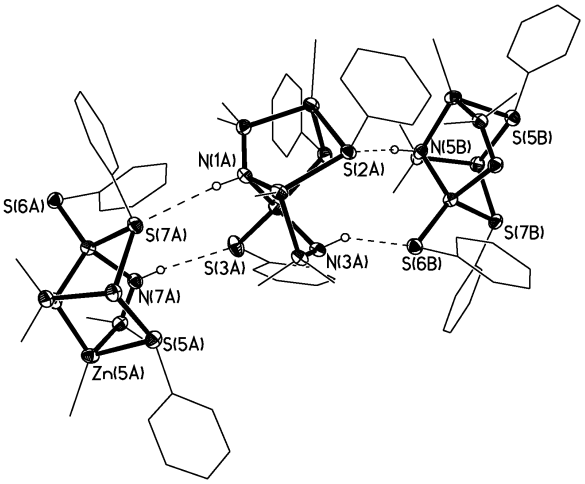

Fig. 3. Aggregation of **1** into endless chains $[(MeZn)_2(PhSZn)(HNNMe_2)(H_2NNMe_2)(SPh)_2]_\infty$ by intermolecular S···H bonding. Carbon atoms are shown in stick mode; hydrogen atoms have been omitted for clarity (apart from those involved in H bonding to S).

molecular structure obeys still the principle of tetracoordinate zinc atoms as has been found for all zinc hydrazides and their mixed alkoxy derivatives. Only for the hydroxylaminato-containing aggregates the higher coordination number six was found to be realised in some overcrowded pentanuclear aggregates. However, the nuclearity of **1** is lower than for the usual tetra- (all hydrazide aggregates) and pentanuclear aggregates (all hydroxylaminato aggregates). It is also here for the first time that a non-deprotonated hydrazine unit is included in the aggregate formation. It also has to be noted that in none of the mixed hydrazide/alkoxide and hydrazide/silanolate aggregates a two-coordinate oxygen atom is involved, whereas in **1** one of the phenylthiolate sulphur atoms is linked to only one zinc atom. Consequently, there are quite a few distinct differences in this area of chemistry between sulphur- and oxygen-containing hydrazide aggregates of zinc; there is no simple homologous behaviour.

Experimental Section

Synthesis of $[(MeZn)_2(PhSZn)(HNNMe_2)(H_2NNMe_2)(SPh)_2]_2 \cdot THF$ (1)

Me_2Zn (3.0 mL of a 2 M solution in toluene; 6.0 mmol) was added dropwise *via* a syringe to a stirred solution of H_2NNMe_2 (0.35 mL, 4.0 mmol) and PhSH (0.31 mL, 3.0 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 *n*-hexane/THF and filtered. The clear, colourless filtrate was kept in a −26 °C freezer to afford colourless block-type crystals of **1**. – ^1H NMR (200 MHz, C_6D_6): δ = −0.66, −0.59, −0.55, −0.52, −0.50 (5s, 6 H; $ZnCH_3$), 1.92, 1.96, 2.03, 2.10, 2.18 (5s, 16 H; NH, NMe_2), 6.84 – 7.13 (m, 12 H; *m*-, *p*-H of phenyl), 7.59 – 7.73 (m, 6 H; *o*-H of phenyl). – $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6): δ = −15.57 ($ZnCH_3$), 53.05, 53.35, 53.58, 53.88 (NMe_2), 123.82, 124.84, 125.11, 126.20, 128.87, 129.23, 129.52, 132.34, 132.66, 132.84, 133.16, 134.22, 134.89 (phenyl). – Elemental analysis (%) for $C_{52}H_{80}N_8OS_6Zn_6$: calcd. C 42.84, H 5.39, N 8.33, S 14.29; found C 42.85, H 5.45, N 8.20, S 13.79.

Crystallographic data for **1**: $C_{48}H_{72}N_8S_6Zn_6 \cdot C_4H_8O$, M = 1417.82 g mol^{-1}, colourless block, size 0.15 × 0.12 × 0.10 mm, monoclinic, space group $C2/c$, a = 35.907(12), b = 22.376(12), c = 24.955(12) Å, β = 132.54(2)°, V = 14774(11) Å^3, Z = 8, ρ_{calcd} = 1.275 g cm^{-3}, μ = 2.122 mm^{-1}, 57725 reflections collected on a Bruker APEX X-ray diffractometer [ω scans, $2\theta_{\max}$ = 50°, MoK_α radiation, λ = 0.71073 Å, T = 153(2) K] merged to 13025 unique (R_{int} = 0.037) refining to R_1 = 0.027 for 13025 data [$F_o \geq 4\sigma(F_o)$] and wR_2 = 0.068 for all data.

The structures were solved by Direct Methods and refined with full-matrix least-squares procedures against F^2 with the programs SHELXTL 6.10 or SHELXL-93 [13]. Non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms isotropically with a riding model.

CCDC 711846 contains 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.

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