DOI: 10.1002/zaac.201100543

Crystal and Molecular Structure of the *trans*-Hyponitrite Compounds $Ph_3E(\mu\text{-}ONNO)EPh_3$ (E = Ge, Pb)

Tobias Mayer[a] and Hans-Christian Böttcher*[a]

Dedicated to Professor Wolfgang Beck on the Occasion of His 80th Birthday

Keywords: Hyponitrite; Germanium; Lead; Crystal Structure; DFT calculations

Abstract. The synthesis of the *trans*-hyponitrite compounds Ph_3E(μ-ONNO)EPh_3 [E = Ge (**1**), Pb (**2**)] as well as their crystal and molecular structure are reported. Compound **1** crystallized from toluene/pentane in the trigonal space group $R\bar{3}$ with a = 29.7969(18), b = 29.7969(18), c = 11.8465(6) Å; γ = 120°; V = 9108.8(9) Å^3; Z = 12, ρ = 1.461 g·cm^{-3}, T = 173(2) K. Compound **2** crystallized from toluene/*iso*-hexane in the triclinic space group $P\bar{1}$ with a = 10.0330(2), b = 11.0615(2), c = 24.2080(4) Å; α = 97.3730(10), β = 95.8550(10), γ = 115.3940(10)°; V = 2369.69(7) Å^3; Z = 3, ρ = 1.970 g·cm^{-3}, T = 173(2) K.The crystal structure determination revealed that two conformational isomers exist in the row of related group 14 element compounds. Whereas the species of tin and lead exhibit a S-shaped arrangement of the hyponitrite group between the two EPh_3 fragments, the corresponding germanium compound shows instead of a N-shape within the hyponitrite group. DFT calculations revealed that S-shaped conformers should be in all three cases the more stable ones. This stands in contrast to the observed N conformation of **1** in the crystal.

Introduction

Recently we reported the crystal and molecular structure of the hyponitrite compound Ph_3Sn(μ-ONNO)$SnPh_3$.[1] During the last years compounds containing hyponitrite groups got more and more in the focus of bioinorganic investigation because they offer the possibility to serve as model compounds of active intermediates in enzymatic processes of nitric oxide reductases (NORs).[2–7] In the field of transition metal hyponitrito complexes we reported recently[8] the synthesis and the X-ray crystal structures of some new compounds [$Ru_2(CO)_4$(μ-H)(μ-P*t*Bu)$_2$(μ-L_2)(μ-η^2-ONNO)] (L_2 = bisphosphane or aminobisphosphane). In contrast to the synthesis of the title species reported therein, the latter compounds were formed by a direct reaction of nitric oxide with the corresponding coordinatively unsaturated precursor complexes. Very recently the chemistry of reductive N–N coupling of NO on transition metal complexes affording nitrous oxide was reviewed.[9] In the field of main group element compounds containing hyponitrite groups only few species were described in the literature. In 1968, *Beck* et al. reported compounds of the formula Ph_3E(μ-ONNO)EPh_3 (E = Sn, Pb), which were characterized by IR spectroscopy and elemental analysis.[10] A second report in this area was represented by the synthesis and characterization of the bis(trimethylsilyl) hyponitrite, Me_3Si(μ-ONNO)$SiMe_3$, by *Wiberg* et al.[11] Furthermore the X-ray crystal structures of some organic hyponitrites were reported.[12] In this paper we describe the synthesis and the crystal and molecular structures of the title compounds Ph_3E(μ-ONNO)EPh_3 [E = Ge (**1**), Pb (**2**)].

Results and Discussion

As described by *Beck* et al.,[10] the compound Ph_3Pb(μ-ONNO)$PbPh_3$ (**2**) was prepared by the reaction of triphenylplumbyl iodide with silver hyponitrite (molar ratio 2:1) in toluene by stirring at room temperature overnight. Compound **2** was obtained by this way in satisfactory yields as a colorless microcrystalline powder. Beside the known spectroscopic data,[10] compound **2** was additionally characterized by NMR spectroscopy (^{1}H and ^{13}C). Thus the ^{1}H NMR spectrum of **2** in [D_8]toluene showed the expected signals for the phenyl protons in the range of δ = 7.68–7.33 ppm. In a similar manner we used also the above mentioned synthesis for the preparation of the new compound Ph_3Ge(μ-ONNO)$GePh_3$ (**1**). Thus the reaction of triphenylgermyl bromide with $Ag_2N_2O_2$ (2:1) in toluene by stirring overnight at room temperature afforded the latter species as colorless crystals in yields of about 53 %. The new compound **1** was characterized by elemental analysis, ^{1}H and ^{13}C NMR spectroscopy, and an X-ray crystal structure analysis. In the ^{1}H NMR spectrum of **1** ([D_8]toluene) the phenyl protons resonate at δ = 7.67–7.51 ppm. The IR spectrum of **1** (as solid) showed a band at 964 cm^{-1} corresponding to the hyponitrite group ν(NO).

Suitable crystals for an X-ray diffraction study of **1** were obtained by slow diffusion of pentane into a toluene solution

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* Prof. Dr. H.-C. Böttcher
E-Mail: hans.boettcher@cup.uni-muenchen.de
[a] Department Chemie
Ludwig-Maximilians-Universität
Butenandtstr. 5–13
81377 München, Germany

of the compound at room temperature. The crystal structure determination revealed that crystals of **1** belong to the trigonal space group $R\bar{3}$ with two crystallographically independent molecules in the asymmetric unit. The second molecule of **1** is disordered in the crystal resulting in a high value wR_2. The molecular structure of **1** as a selected ORTEP view of one molecule is shown in Figure 1. The molecule consists of two Ph_3Ge units bridged by a *trans*-hyponitrite group. The molecule of **1** is related to that of the *trans*-hyponitrite compound $Ph_3Sn(\mu\text{-}ONNO)SnPh_3$ (**3**).[1] In both molecules the hyponitrite group was found in the more stable *trans* configuration and the following bonding characteristics were observed for **3**: d(Sn–O) = 2.062(2)–2.069(2), d(N–N) = 1.231(6)–1.240(5), d(N–O) = 1.365(3)–1.372(3) Å, and angles N–N–O = 110.8(3)–111.6(3), N–O–Sn = 115.6(3)–117.0(2)°[1] (the corresponding data for **1** see caption in Figure 1).

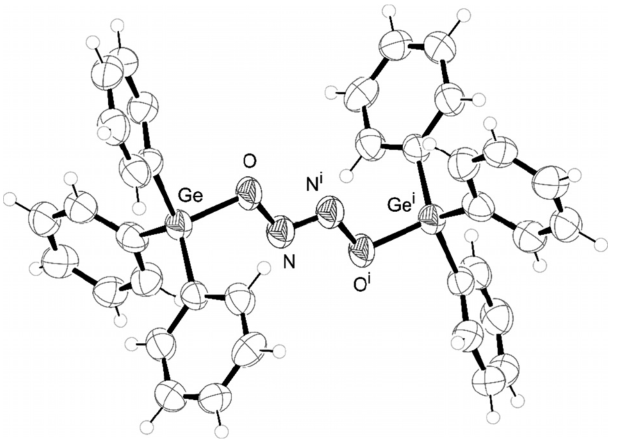

Figure 1. Molecular structure of $Ph_3Ge(\mu\text{-}ONNO)GePh_3$ (**1**) in the crystal (ORTEP drawing with 50 % probabilityl ellipsoids) For clarity only one molecule of the asymmetric unit is shown, whereby the asymmetric unit contains only a half of the molecule of **1**. Selected distances /Å and angles /°: Ge–O 1.824(5), N–O 1.388(8), N–N^i 1.225(8); Ge–O–N 110.6(4), N^i–N–O 108.5(6). Atoms are generated by symmetry operation *i*: 1/3–*x*, 2/3–*y*, 2/3–*z*.

The crystal structure determination of compound **2** afforded that crystals of **2** belong to the triclinic space group $P\bar{1}$ crystallizing with three molecules in the unit cell. As observed for **1** and **3**, respectively, also in **2** the hyponitrite group is found in the more stable *trans* configuration. A selected ORTEP view of one molecule of **2** is shown in Figure 2, important bond lengths and angles are given in the caption. The molecular structure of **2** is closely related to that of **1** and **3**, respectively. However a remarkable difference with respect to the conformation of these molecules in the solid was found and should be briefly discussed.

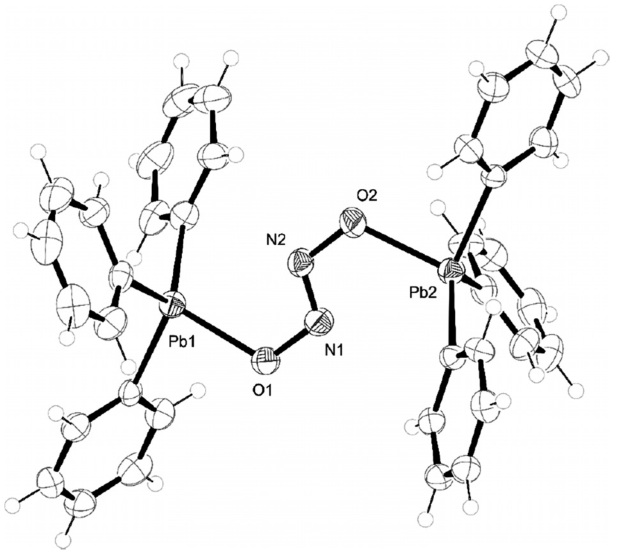

Figure 2. Molecular structure of $Ph_3Pb(\mu\text{-}ONNO)PbPh_3$ (**2**) in the crystal (ORTEP drawing with 50 % probabilityl ellipsoids). For clarity only one molecule of the asymmetric unit is shown, whereby the asymmetric unit contains one and a half molecule. Selected distances /Å and angles /°: Pb1–O1 2.198(4), Pb2–O2 2.188(5), N1–O1 1.368(8), N2–O2 1.355(8), N1–N2 1.246(9); Pb1–O1–N1 114.0(4), Pb1–O1–N1 114.0(4), O1–N1–N2 111.2(5), O2–N2–N1 112.4(5).

In crystals of **1** the *trans*-hyponitrite group connects the both $GePh_3$ fragments “horizontal” (N-shape), whereas in solid **2** and **3**, respectively, a “vertical” arrangement of this group between the EPh_3 (E = Sn, Pb) fragments (S-shape) was found. In this light DFT calculations were carried out affording that the S-shaped conformers should be the more stable ones in all three cases. However, whereas for **2** and **3**, respectively, the energy differences between E_S and E_N are significant (ΔE = 33.4 and 44.5 $kJ\cdot mol^{-1}$, respectively), for **1** only a small ΔE of 5.8 $kJ\cdot mol^{-1}$ was calculated. We assume that reasons of the crystal package could be responsible for the observation of the less stable N-shaped conformation in solid **1**. Moreover, DFT calculations on the hitherto unknown compounds $Ph_3E(\mu\text{-}ONNO)EPh_3$ [E = C (**4**), Si (**5**] were performed. For the latter two species energy differences between E_S and E_N afforded negative values (ΔE = –37.2 and –6.7 $kJ\cdot mol^{-1}$ respectively), therefore the N-shaped conformers should be the more stable ones in these cases. Unfortunately, the synthesis of the species **4** and **5**, respectively, failed till now in our hands to confirm these theoretical predictions. However, on the other hand, the crystal structure investigations of some organic hyponitrites confirmed the N-shaped conformation.[12]

Conclusions

The crystal and molecular structures of the *trans*-hyponitrite compounds $Ph_3E(\mu\text{-}ONNO)EPh_3$ [E = Ge (**1**), Pb (**2**)] were determined by single-crystal X-ray diffraction studies. The bonding characteristics of **1** and **2**, respectively, correspond well with the previous reported ones for the closely related compound $Ph_3Sn(\mu\text{-}ONNO)SnPh_3$. DFT calculations afforded that the compounds with E = C and Si should be arranged in the more stable N-shaped conformation, whereas the related analogues of germanium, tin, and lead should exhibit a S-shaped conformation. Interestingly for the germanium compound also the N-shaped arrangement was found, which could be presumably caused by reasons of the package in the crystal.

Experimental Section

General: All synthetic work was carried out under argon using standard Schlenk techniques. All chemicals were purchased from Sigma.

$Ag_2N_2O_2$ was synthesized according to the known procedure.[13] NMR spectra were recorded with a Jeol Eclipse 400 instrument operating at 400 MHz (^1H) and at 100 MHz (^{13}C). Chemical shifts are given in ppm relative to TMS (^1H, ^{13}C). Infrared spectra were recorded from solids with a JASCO FT/IR-460 plus spectrometer.

Synthesis of $Ph_3Ge(\mu\text{-ONNO})GePh_3$ (1): Ph_3GeBr (364 mg, 0.95 mmol) was dissolved in toluene (10 mL). $Ag_2N_2O_2$ (154 mg, 0.56 mmol) was added and the resulting slurry was stirred for 20 h under exclusion of light. After filtration from the precipitated silver halide, the solvent was removed under reduced pressure. The remaining residue was recrystallized three times from toluene/*iso*-hexane (1:2) affording a colorless microcrystalline powder. Yield 168 mg (53 %). Mp 113 °C (dec.). $C_{36}H_{30}Ge_2N_2O_2$ (667.83): C 64.08 (calcd. 64.47); H 4.53 (4.51); N 4.45 (4.18) %. **IR**: ν(NO): 964 vs. cm^{-1}. **^1H NMR** ([D_8]toluene): δ = 7.67–7.51 (m, 30 H, C_6H_5). **$^{13}C\{^1H\}$ NMR** ([D_8]toluene): δ = 137.1, 135.2, 130.4, 128.7 (C_6H_5).

Synthesis of $Ph_3Pb(\mu\text{-ONNO})PbPh_3$ (2): Ph_3PbI (540 mg, 0.96 mmol) was dissolved in toluene (20 mL). $Ag_2N_2O_2$ (396 mg, 1.72 mmol) was added and the resulting slurry was stirred for 20 h under exclusion of light. After filtration from the precipitated silver halide, the solvent was removed under reduced pressure. The remaining residue was recrystallized once from toluene/*iso*-hexane (1:2) affording a colorless microcrystalline powder. Yield 184 mg (41 %). Mp 131 °C (dec.). $C_{36}H_{30}N_2O_2Pb_2$ (938.18): C 46.38 (calcd. 46.05); H 3.53 (3.22); N 2.85 (2.99) %. **IR**: ν(NO): 1015 vs. cm^{-1}. **^1H NMR** ([D_8]toluene): δ = 7.68–7.33 (m, 30 H, C_6H_5). **$^{13}C\{^1H\}$ NMR** ([D_8]toluene): δ = 137.9, 137.1, 130.5, 129.9 (C_6H_5).

Computational Details: The DFT calculations were performed with the Gaussian03 software package.[14] The structure and the energy of the model compounds were optimized at the B3LYP level[15] with basis sets: Ge, Pb: pseudopotential and basis set SDD. C, H, N, and O: 6-31G basis sets as implemented in the Gaussian program. A vibrational analysis was performed to confirm that the structure has no imaginary frequency.

Crystal Structure Determination and Refinement: Crystals of **1** and **2**, respectively, suitable for X-ray diffraction were obtained by diffusion of pentane into a toluene solution of the compound at room temperature. The crystals were selected by means of a polarization microscope, mounted on the tip of a class fiber, and investigated with a Nonius Kappa CCD diffractometer using Mo-K_α radiation (λ = 0.71073 Å). The structure was solved by direct methods (SHELXS-97)[16] and refined by full-matrix least-squares calculations on F^2 (SHELXL-97).[17] Anisotropic displacement parameters were refined for all non-hydrogen atoms. Details of crystal data, data collection, structure solution, and refinement parameters of **1** and **2**, respectively, are summarized in Table 1.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-855609 (**1**) and CCDC-855608 (**2**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Acknowledgement

The authors are grateful to the Department of Chemistry of the Ludwig Maximilian University Munich for supporting these investigations. T. M. thanks *Prof. P. Klüfers* for financial support. *A. Gallien* we thank for collecting the X-ray crystal data.

Table 1. Experimental details of the crystal structure determination of **1** and **2**.

	1	**2**
M	667.80	937.00
T /°C	–100	–100
Space group	$R\bar{3}$	$P\bar{1}$
a /Å	29.7969(18)	10.0330(2)
b /Å	29.7969(18)	11.0615(2)
c /Å	11.8465(6)	24.2080(4)
α /°	90	97.3730(10)
β /°	90	95.8550(10)
γ /°	120	115.3940(10)
V /Å^3	9108.8(9)	2369.69(7)
Z	12	3
Density /g·cm^{-3}	1.461	1.970
μ /mm^{-1}	2.015	10.677
2 θ_{max} /°	55	55
Reflections, collected	52392	18837
Reflections, independent	4732	10864
Refined parameters	266	568
wR_2 (all data)	0.1980	0.0809
R_1	0.0881	0.0373

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Received: December 19, 2011

*T. Mayer, H.-C. Böttcher** **1–5**

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