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Partially Oxidized Zintl Ions? The Characterization of $[(\mu_3\text{-OH})(\mu_3\text{-O})_3(\text{OEt})_3\{(\text{CO})_5\text{W}\}_7\text{Sn}_7]^{2-}$**

Peter Kircher, Gottfried Huttner,* Laszlo Zsolnai, and Alexander Driess

Dedicated to Professor Heribert Offermanns on the occasion of his 60th birthday

The characterization of mixed-valent and subvalent compounds is an important key principle in the search for solid phases with unusual material properties.[1] Molecular analogues of such subvalent phases are only found in rare cases in the chemistry of main group elements in the homoatomic aggregates $[E_x]^{m-}$[2] denoted as Zintl ions and in the isopolycations $[E_y]^{n+}$.[3] Subvalent compounds are also known in the form of partially oxidized derivatives of molecular element modifications (e.g. P_4/P_4S_3). A new class of compounds of this type would be generated if Zintl ions $[E_x]^{m-}$ could be partially oxidized, in which case—as in P_4S_3—some of the element–element bonds would be retained. However, a direct transformation of Zintl ions in this sense has not been achieved so far.

The characterization of $[\{(CO)_5Cr\}_6Sn_6]^{2-}$ had shown that a de novo synthesis of Zintl ions from mononuclear precursors may be achieved by using organometallic protective groups.[4] Furthermore, the preparation of $[(\mu_3\text{-OH})_4(\mu_3\text{-O})_4\{(CO)_5Cr\}_6Sn_6]$[5] showed that by analogous syntheses compounds are accessible that can be considered formally as completely oxidized derivatives of Zintl ions. Therefore it seemed appropriate to attempt, under modified conditions, to construct cage compounds that contain within the same molecule building blocks in which the main group elements, as in Zintl ions, are linked directly and building blocks in which the main group elements are bridged by oxygen.

In analogy to the preparation of $[(\mu_3\text{-OH})_4(\mu_3\text{-O})_4\{(CO)_5Cr\}_6Sn_6]$ from $K_2[Cr(CO)_5]$, $SnCl_2$, and H_2O in THF,[5] $SnCl_2$ was treated with $Na_2[W_2(CO)_{10}]$ in the hope that the $[(CO)_5W]$ derivatives of the desired cage compounds and clusters would be more stable than their $[(CO)_5Cr]$ analogues. We finally obtained a few crystals of the compound $[(\mu_3\text{-OH})_4(\mu_3\text{-O})_4\{(CO)_5W\}_6Sn_6]$ (**1**), the $[(CO)_5Cr]$ analogue of which is already known (Scheme 1).[5]

An aggregate, which, unlike the tin(II) compound **1**, also contains tin in a lower oxidation state, was first obtained when the orange solution of $Na_2[W_2(CO)_{10}]$ in ethanol was treated with $SnCl_2$. This led spontaneously to a red solution, from which, after the addition of a solution of $[Ph_4P]Cl$ in ethanol, the phosphonium salt of $[(\mu_3\text{-OH})(\mu_3\text{-O})_3(OEt)_3\{(CO)_5W\}_7Sn_7]^{2-}$ (**2**) precipitated as an orange solid (Scheme 2).

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[*] Prof. Dr. G. Huttner, Dipl.-Chem. P. Kircher, Dr. L. Zsolnai, Dipl.-Chem. A. Driess
Anorganisch-chemisches Institut der Universität
Im Neuenheimer Feld 270, D-69120 Heidelberg (Germany)
Fax: (+49) 6221-545707

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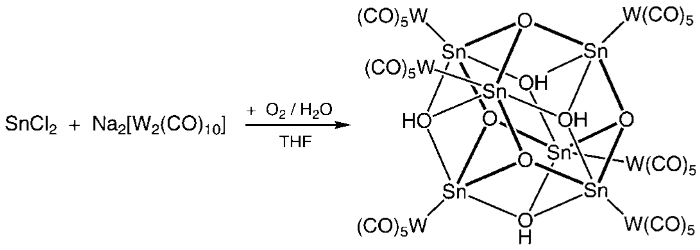
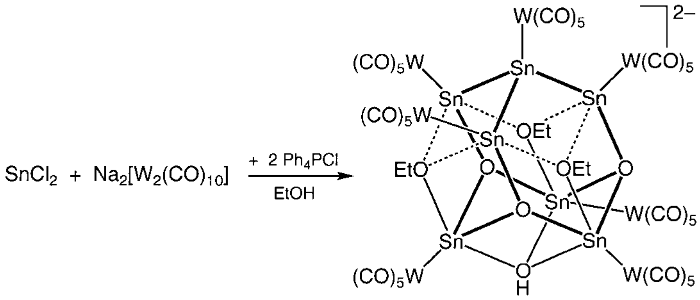


1

Scheme 1. Synthesis of **1**.



2

Scheme 2. Synthesis of **2**.

The structure of **1** closely resembles that of known structures of different derivatives of $[(\mu_3\text{-OR})_4(\mu_3\text{-O})_4Sn_6]$.[5–7] The structure of **2**[6, 7] is a modification of that of the known structure of **1**, in which an μ_3-O building block is replaced by a μ_3-Sn{W(CO)$_5$} unit. At the same time the charge of the cage **2** is -2, so that formally the oxygen atom with its six electrons is replaced by the isoelectronic Sn^{2-} ion. Thus, the cage comprises an Sn_4 unit in the top half (Sn_a and Sn_b)[8] and a $[(\mu_3\text{-OH})(OEt)_3\{Sn_3O_3\}]$ unit in the bottom half (Sn_c).

Owing to the different bonding of the tin centers in the cage of **2**, different Sn–W distances are displayed for Sn_a–W_a (280 pm) and for Sn_b–W_b/Sn_c–W_c (272–275 pm, Figure 1). Whereas in cage **1** six chemically equivalent tin(II) centers are present whose electron requirement is compensated by symmetrical μ_3-OH and μ_3-O bridges, the electron requirement and Lewis acidic character of the three kinds of tin centers in **2** differ because of the different oxidation states. Compound **1** contains four μ_3-OH groups, in contrast, **2** contains one μ_3-OH and three OEt groups. The μ_3-OH group in the bottom half of the cage of **2** symmetrically bridges the three tin centers in this part of the cage. In contrast the OEt groups are almost terminally bound (Figure 1). The interactions to the tin centers in the top half of the compound (Sn_b) can, on the basis of the longer Sn–O distances, be considered as comparatively weak (Figure 1). The frameworks of **1** and **2** are very similar, are drumlike in form[9] and can, as the formulas show, be delineated to an adamantane structure. On the basis of the Zintl–Klemm concept this is expected for the replacement of μ_3-O (**1**) by μ_3-Sn^{2-} (**2**).[10] The mixed-valent aggregate **2** (average oxidation state $+8/7$ for Sn) can be considered as the first in a series of compounds that can be derived by partial oxidation of Zintl ions protected by organometallic groups.

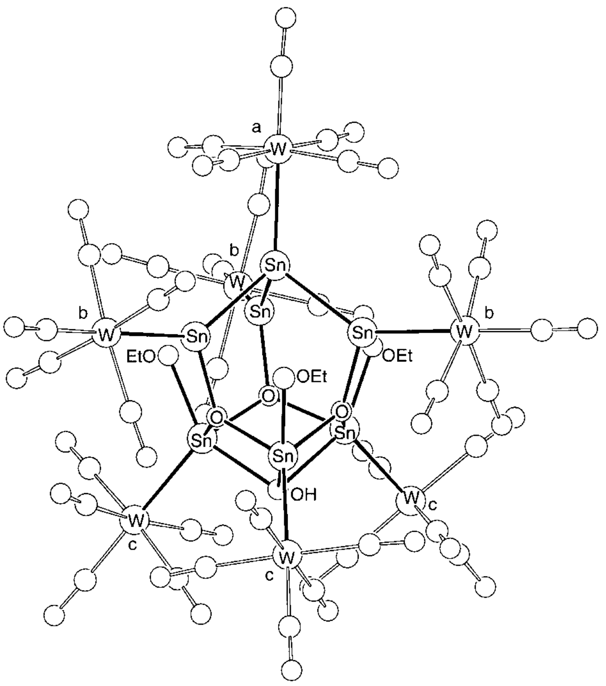


Figure 1. View of the structure of **2** in the crystal. The labeling of the tin centers follows the symbolic designation (a–c) of the tungsten centers. Selected distances [pm]: Sn_a–W_a 279.6(1), Sn_b–W_b 274.2–275.2(2), Sn_c–W_c 271.7–274.0(1), Sn_a–Sn_b 279.1–280.1(2), Sn_c–(μ_3-OH) 228.6–234.0(9), Sn_b–(μ_3-O) 205–208(1), Sn_c–(μ_3-O) 203–207(1), Sn_b–(OEt) 257–322, Sn_c–(OEt) 208–214(1).

Experimental Section

All experiments were carried out with Schlenk techniques under an argon atmosphere with exclusion of moisture and oxygen. NMR: Bruker-Avance-DPX-200, $T = 298$ K, ^{1}H NMR (200.13 MHz), ^{13}C{^{1}H} NMR (50.323 MHz), the solvent was used as internal standard, TMS as external standard: [D$_6$]acetone ($\delta(^1H) = 2.04$, $\delta(^{13}C) = 206.18$ and 29.8); ^{31}P{^{1}H} NMR (81.015 MHz), external standard 85% H_3PO_4. IR: Bruker-FT-IR-IFS-66, CaF_2 cells. C,H analysis: Mikroanalytisches Labor, Organisch-chemisches Institut der Universität Heidelberg.

1: Compound **1** was prepared analogously to $[(\mu_3\text{-OH})_4(\mu_3\text{-O})_4\{(CO)_5Cr\}_6Sn_6]$.[5a] Single crystals suitable for X-ray structure analysis were obtained only on one occasion. The yield of crystalline material was about 60 mg (2%); IR (THF): $\tilde{\nu}_{CO} = 2071$ m, 1953 vs, 1932 vs cm^{-1}.

2: $SnCl_2$ (190 mg; 1 mmol) was added under stirring to a solution of $Na_2[W_2(CO)_{10}]$ (694 mg, 1 mmol) in ethanol (50 mL). The solution spontaneously turned dark red. After 30 min, it was filtered through Kieselgur. Addition of a solution of [Ph$_4$P]Cl (150 mg, 0.4 mmol) in ethanol (5 mL) to the resulting clear, dark red solution led to the immediate formation of an intense orange precipitate of **2**$\cdot$[Ph$_4$P]$_2$, which was separated on a frit (G4), washed with diethyl ether (3 × 10 mL), and dried in high vacuum. The Ph$_4$P salt of **2** was dissolved in THF (3 mL) on the frit and layered with ethanol (50 mL). Orange single crystals were obtained that were suitable for crystal structure analysis. Yield of crystalline material: 360 mg (9%). ^{1}H NMR: 7.95–7.87 (m, 40 H, H$_{arom.}$), 4.27 (q, 6 H, OCH$_2$), 1.56 (t, 9 H, CH$_3$); ^{13}C NMR: 136.52 (s, C$_{para}$), 135.8 (d, C$_{ortho}$, $^2J_{C,P} = 9$ Hz), 131.5 (d, C$_{meta}$, $^3J_{C,P} = 13$ Hz), 61.9 (s, OCH$_2$), 19.8 (s, CH$_3$); ^{31}P NMR: 24.3 (s); IR (THF): $\tilde{\nu}_{CO} = 2066$ w, 2054 w, 2044 w, 1941 vs, 1918 vs cm^{-1}; CH analysis: calcd: C 26.88, H 1.42; found C 25.02, H 1.55.

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[7] Structure solution and refinement: G. M. Sheldrick, SHELXS 86, Universität Göttingen, **1986**; SHELXL 93, Universität Göttingen, **1993**; graphical data processing: L. Zsolnai, G. Huttner, XPMA, Universität Heidelberg, **1998**; http://www.rzuser.uni-heidelberg.de/~v54/xpm.html.

[8] The Sn_a–Sn_b distances (Figure 1) are significantly shorter than the Sn–Sn distances in $[\{(CO)_5Cr\}_6Sn_6]^{2-}$ (294 pm).[4] They are similar to those in $[Sn(SnPh_3)_3]^-$ (282 pm) and in $[(\mu_3\text{-}Sn)_2(SnPh_2)_3]$ (286 pm). Shorter distances are present in $[Sn(SnPh_3)_3]^+$ (263 pm). a) L. N. Bochkarev, O. V. Grachev, S. F. Ziltsov, L. N. Zakharov, Y. T. Struchkov, *J. Organomet. Chem.* **1992**, *436*, 299–311; b) L. R. Sita, R. D. Bickerstaff, *J. Am. Chem. Soc.* **1989**, *111*, 6454–6456, c) M. Nardelli, C. Pelizzi, G. Pelizzi, P. Tarasconi, *Z. Anorg. Allg. Chem.* **1977**, *431*, 250–260.

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A Structural Model for [Fe]-Only Hydrogenases[**]

Vincent E. Kaasjager, Richard K. Henderson, Elisabeth Bouwman,[*] Martin Lutz, Anthony L. Spek, and Jan Reedijk

Hydrogenases are enzymes that are capable of catalyzing the reversible oxidation of dihydrogen. They can be divided into two main groups, based on the metals in the enzyme: [Fe]-only hydrogenases and [NiFe]-hydrogenases.[1] FTIR spectroscopy in combination with a crystal structure determination of the enzyme isolated from *Desulfovibrio gigas* has shown that the active site of [NiFe]-hydrogenases contains the dinuclear unit $[(Cys\text{-}S)_2Ni(\mu_2\text{-}S\text{-}Cys)_2Fe(CO)(CN)_2]$.[2, 3] The publication of the structure of this novel heterodinuclear active site with the biologically uncommon ligands CO and CN[2, 3] has been an incentive for the synthesis of new compounds that could serve as structural models for hydrogenases.[4] The [Fe]-only hydrogenases contain only iron as the metal constituent. Unfortunately the structure of an [Fe]-only hydrogenase has not yet been determined, and also the composition of the H_2-activating site is still unknown: the reported iron contents vary between three and six Fe atoms per molecule.[5] Interestingly, a similar architecture has been proposed for the active site of both [NiFe]- and [Fe]-hydrogenases.[3, 5]

We now report the first dinuclear iron(II) compound, which can be regarded as a promising first generation structural model for [Fe]-only hydrogenases. The synthesis and crystallographic characterization of this mixed-spin, dinuclear iron(II) complex, which contains sulfur bridges and terminal carbon monoxide ligands, is described. The compound was synthesized from a mixture of $[\{Fe^{II}(dsdm)\}_2]$ (H_2dsdm = *N*,*N*′-dimethyl-*N*,*N*′-bis(2-sulfanylethyl)ethylenediamine) and $K[HFe(CO)_4]$ in the presence of 2-bis(sulfanylethyl)sulfide (H_2bmes), which was heated under reflux. X-ray quality crystals of the product $[Fe^{II}(dsdm)(bmes)Fe^{II}(CO)_2]$ (**1**) were readily obtained by addition of diethyl ether to a solution of the complex in toluene/ethanol.

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[*] Dr. E. Bouwman, V. E. Kaasjager, Dr. R. K. Henderson,
Prof. Dr. J. Reedijk
Leiden Institute of Chemistry, Gorlaeus Laboratories
Leiden University
P.O. Box 9502, NL-2300 RA Leiden (The Netherlands)
Fax: (+31)71-5274451
E-mail: bouwman@chem.leidenuniv.nl

Dr. M. Lutz, Dr. A. L. Spek
Laboratory of Crystal and Structural Chemistry
Bijvoet Center for Biomolecular Research
Utrecht University (The Netherlands)

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