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[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**

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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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A projection of the structure of the dinuclear iron(II) compound is shown in Figure 1. The structure consists of two octahedrally coordinated iron(II) atoms, each with different ligand environments. Fe(1) is coordinated to the ligand dsdm and the two thiolate sulfur atoms from bmes, resulting in an FeN_2S_4 chromophore. Fe(2) is bound to the ligand bmes, to two terminally coordinating carbon monoxide groups, and to one of the thiolate sulfur atoms from dsdm, resulting in a FeC_2S_4 chromophore. The two octahedra face-share through three asymmetric μ_2-thiolato bridges. The dinuclear molecule is electronically neutral, and therefore both irons should be divalent.

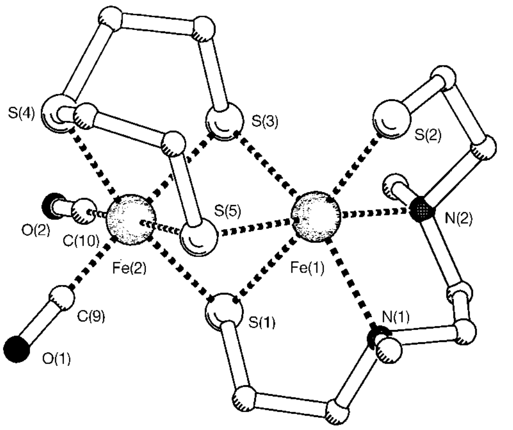

Figure 1. Schematic representation of the structure of **1** in the crystal (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Fe(1)–S(1) 2.5451(8), Fe(1)–S(2) 2.3658(8), Fe(1)–S(3) 2.5002(8), Fe(1)–S(5) 2.5053(8), Fe(1)–N(1) 2.279(2), Fe(1)–N(2) 2.307(2), Fe(2)–S(1) 2.3158(8), Fe(2)–S(3) 2.3517(8), Fe(2)–S(4) 2.2553(8), Fe(2)–S(5) 2.3387(8), Fe(2)–C(9) 1.772(3), Fe(2)–C(10) 1.771(3), O(1)–C(9) 1.145(4), O(2)–C(10) 1.145(3); S(1)-Fe(1)-S(2) 174.97(3), S(1)-Fe(1)-S(3) 75.32(3), S(1)-Fe(1)-S(5) 78.22(2), S(2)-Fe(1)-S(3) 100.33(3), S(2)-Fe(1)-S(5) 99.16(3), S(3)-Fe(1)-S(5) 86.60(3), S(1)-Fe(2)-S(3) 82.67(3), S(1)-Fe(2)-S(4) 169.21(3), S(1)-Fe(2)-S(5) 86.40(3), S(3)-Fe(2)-C(9) 175.74(10), Fe(2)-C(9)-O(1) 177.9(3), Fe(2)-C(10)-O(2) 178.7(3).

The bond lengths of approximately 2.50 Å between the bridging thiolate ligands and Fe(1) are considerably longer than those to Fe(2), which are in the order of 2.35 Å. These differences probably originate from the different spin states of the Fe^{II} atoms: Fe(1) is high-spin and Fe(2) is low-spin. The bond lengths are comparable to those in the trinuclear complex $[(OC)_3Fe^{II}(SPh)_3Fe^{II}(SPh)_3Fe^{II}(CO)_3]$.[6] The low-spin state of Fe(2) is a result of the influence of the strong CO ligands, which generally invoke a low-spin state. The Fe(1)–Fe(2) distance of 3.0747(7) Å implies no direct metal–metal bonding between the iron atoms,[7] which is confirmed by magnetic susceptibility measurements.[8]

Compared to the starting material, the high-spin complex $[Fe(dsdm)]_2$,[9] the coordination sphere of Fe(1) in **1** has changed from trigonal bipyramidal to octahedral geometry by addition of an extra bridging dithiolato ligand. The Fe(2)–C distances of 1.771(3) and 1.772(3) Å and the C–O distances of 1.145 Å with Fe-C-O angles of 177.9(3)° and 178.7(3)° are comparable to those found in the octahedral complex $[Fe^{II}(CO)_2(tddt)]$ (tddt = 2,3,8,9-dibenzo-1,4,7,10-tetrathiadecane).[10]

The IR spectrum of the compound in the solid state reveals strong absorption bands for the carbonyl ligands at 2011 and 1957 cm^{-1}, well within the range observed for [Fe]-only hydrogenases. The postulated spin states of the iron(II) atoms were verified by Mössbauer spectroscopy. A Mössbauer spectrum recorded at room temperature showed two doublets of equal intensity but with different isomer shifts and quadrupole splittings, and confirmed the presence of two distinct Fe^{II} atoms (Figure 2). An isomer shift of 0.308 $mm\,s^{-1}$ (ΔE_Q = 0.637 $mm\,s^{-1}$) is observed for the low-spin iron(II) atom, while an isomer shift of 1.083 $mm\,s^{-1}$ (ΔE_Q = 3.368 $mm\,s^{-1}$) is observed for the high-spin iron(II) atom. Similar results have also been reported for other mixed-spin iron complexes.[6a, 11]

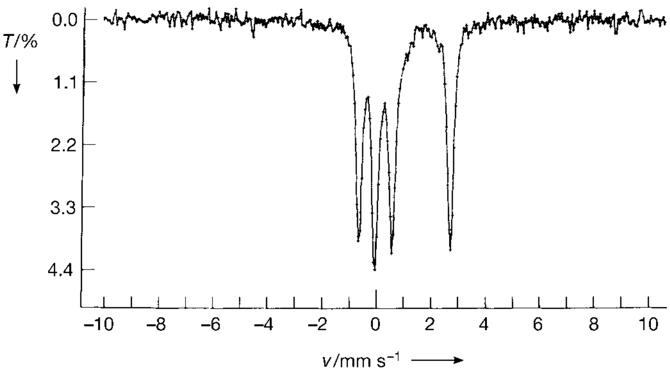

Figure 2. Zero-field Mössbauer spectrum of **1** at room temperature.

In conclusion, the dinuclear iron complex presented here is the first example of a biomimetic iron compound, which can be regarded as a first generation model for the class of [Fe]-only hydrogenases. The complex incorporates both relevant carbon monoxide ligands, and three bridging thiolato ligands which could conceivably be present in the active site of these enzymes. Furthermore, the presence of a histidine group near to one of the iron(II) atoms in the H cluster in [Fe]-only hydrogenases is mimicked in complex **1** by the two amine nitrogen atoms in the dsdm ligand. Finally, the combination of two different, but related ligands might be useful as a new approach for the synthesis of other asymmetric dinuclear active sites, such as those in [NiFe]-hydrogenases, urease, and phosphatases.

Experimental Section

The compound $K[HFe(CO)_4]$ was prepared according to the literature,[12] the reaction time, however, was extended from 30 min to 16 h.

A solution of $K[HFe(CO)_4]$ (1.92 mmol) in EtOH (10 mL) was added to a suspension of $[\{Fe(dsdm)\}_2]$ (0.48 mmol) and bis(2-sulfanylethyl)sulfide (0.96 mmol) in toluene (10 mL).[13] The resulting mixture was then heated under reflux for 4 h. The solution was cooled and filtered to remove any impurities. Diethyl ether was carefully added without disturbing the solution, and the two-layer system was left to stand at room temperature. After several days, hexagonal orange-brown crystals were formed (yield 44%). Elemental analysis calcd for $C_{14}H_{26}Fe_2N_2O_2S_5$: C 31.95, H 4.98, N 5.32, S 30.45; found: C 31.32, H 4.98, N. 5.23, S 30.93; IR(KBr): $\tilde{\nu}$ = 2011 (C=O), 1957 (C=O) cm^{-1}; Vis-NIR (solid-state; D_2 lamp): λ = 308, 347, 764, 1066 nm.

X-ray structure analysis of **1**: $C_{14}H_{26}Fe_2N_2O_2S_5$, M_r = 526.37, monoclinic, $P2_1/c$, a = 12.502(2), b = 7.8709(5), c = 22.277(4) Å, β = 108.639(13)°, V = 2077.1(5) $Å^3$, Z = 4, ρ_{calcd} = 1.684 $g\,cm^{-3}$, T = 150(2) K, $(\sin\theta/\lambda)_{max}$ =

0.649 Å^{-1}, orange-brown hexagonal plates ($0.25 \times 0.5 \times 0.5$ mm^3), 8091 measured reflections, 4746 unique, ($R_{\mathrm{int}} = 0.030$), R values ($I > 2\sigma I$): $R1 = 0.0346$, $wR2 = 0.0640$, all data: $R1 = 0.0588$, $wR2 = 0.0713$. Diffractometer: Enraf-Nonius CAD4T with rotating anode (Mo$_{K\alpha}$, $\lambda = 0.71073$ Å). Structure solution with Patterson methods (DIRDIF-96).[14] Structure refinement with SHELXL-97 against F^2,[15] 330 parameters, no restraints. Non-hydrogen atoms were refined with anisotropic temperature parameters, hydrogen atoms were refined freely with isotropic temperature parameters. Absorption correction with Psi-scans ($\mu = 1.911$ mm^{-1}, 76–98% transmission). Structure graphics were performed with the program PLATON,[16] and the symmetry was checked. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101009. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Differences Between Gas-Phase and Solid-State Molecular Structures of the Simplest Phosphonium Ylide, $\mathrm{Me_3P = CH_2}$**

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Dedicated to Professor Hubert Schmidbaur

There is still no reliable structural determination of the simplest isolable phosphonium ylide $\mathrm{Me_3P{=}CH_2}$. This is surprising as ylides are very important reagents in chemistry,[1, 2] and $\mathrm{Me_3P{=}CH_2}$ was first prepared in a pure form by Schmidbaur and Tronich in 1968.[3] The main focus of structural investigations of ylides has been the coordination at the carbanion center, which is between tetrahedral and trigonal-planar geometries but not necessarily planar. The degree of flattening is dependent on the electronic nature of the substituents.[2] We have now observed substantial differences between the ab initio calculated geometry of trimethylmethylenephosphorane, $\mathrm{Me_3P{=}CH_2}$, and the structure determined by gas-phase electron-diffraction (GED) in 1977.[4] Moreover, a crystal structure determination has resulted in a geometry compatible with neither of these two structures.

The original GED geometry from 1977 was determined under the assumption of local C_3 symmetry for the $\mathrm{C{=}PMe_3}$ unit, whereas our new calculations employed theory up to the MP2/6-311G* level and consistently show a global minimum having C_s symmetry (Table 1). Assuming this symmetry for the model used in the GED analysis, we have reanalyzed the data collected in 1977[1] (see Figure 1 and Table 1). A refinement in the lower symmetry of C_s was feasible with our recently developed improved method of GED analysis (SARACEN,[5] which is a natural extension of Bartell's "predicate value" and Schäfer's MOCED method).[6] This avoids the use of simplifying, but unjustified fixed constraints, but instead employs information calculated by ab initio methods as flexible restraints. Thus, based on the sum of our experimental and theoretical knowledge, SARACEN provides us with improved geometries and better estimates of errors. The result for $\mathrm{Me_3P{=}CH_2}$ is a substantially improved fit on the experimental intensities relative to the old refinement,[1] and the agreement between refined and calculated

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