Spontaneous Assembly of a Novel Tetranuclear Ni–Fe Complex by Complete Reshuffling of Ligands and Oxidation States

Elisabeth Bouwman,*[a] Richard K. Henderson,[a] Anthony L. Spek,[b] and Jan Reedijk[a]

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Upon reaction of the mononuclear nickel dithiolate complex [Ni(dsdm)] (H_2dsdm = *N*,*N*′-dimethyl-*N*,*N*′-bis(2-sulfanylethyl)ethylenediamine) with K[HFe$(CO)_4$] in ethanol a unique reshuffling of ligands and of oxidation states takes place. This results in the formation of a novel tetranuclear complex [Fe^{II}(dsdm)$Ni^0(CO)_3]_2$, in which a linear array of Ni–Fe–Fe–Ni is formed. The inner core of this complex consists of the dinuclear $[Fe(dsdm)]_2$, and two $Ni(CO)_3$ groups are bound at the periphery through one of the thiolate sulfurs.

The [NiFe] hydrogenases consist of enzymes, which, apart from iron, also contain nickel in the active site. The first crystal structure of a [NiFe] hydrogenase enzyme, extracted from *Desulfovibrio gigas*, has been published by Volbeda et al. in 1995.[1] The active site was shown to contain an unexpected disulfur-bridged heterobimetallic Ni−Fe core. There are two further cysteine groups bound to the nickel and three small non-protein ligands bound to the iron. These diatomic ligands are nowadays considered to be one carbon monoxide and two cyanide molecules, based on isotopic enrichment experiments and FT-IR measurements.[2] The publication of the crystal structure has renewed interest in the chemical modelling of the active site of [NiFe] hydrogenases. A large amount of modelling chemistry had already been reported prior to the publication of the X-ray structure,[3][4] when it was believed that the active site contained mononuclear nickel.

The compound described in the present paper was synthesised as part of research in modelling the heterodinuclear Ni−Fe active site of hydrogenases. It was decided that ligands containing mixed N/S donor groups would be used preferentially to provide greater synthetic control. In view of the new structural information, the ligand *N*,*N*′-dimethyl-*N*,*N*′-bis(2-sulfanylethyl)ethylenediamine (H_2dsdm) was considered useful in our synthetic modelling studies. The mononuclear [Ni(dsdm)] and trinuclear $[Ni_3(dsdm)_2]Cl_2$ complexes with this ligand have previously been reported from this laboratory.[5] The mononuclear nickel compound was reinvestigated as it contains two *cis* sulfur atoms from thiolate groups, which have potential in forming heterodimetallic complexes in which sulfur bridges to iron compounds.[6]

The complex $[Fe(dsdm)Ni(CO)_3]_2$ (**1**) was prepared from a reaction of the mononuclear dithiolate complex [Ni(dsdm)] with K[HFe$(CO)_4$], and was characterised by IR spectroscopy, elemental analysis and single-crystal X-ray crystallography. A fully labelled representation of the molecular structure of the tetranuclear compound **1**, is given in Figure 1. The asymmetric unit contains one half of the molecule, the other half is generated by a centre of symmetry. The compound is built up in an array of $Ni^0-Fe^{II}-Fe^{II}-Ni^0$. The ligand dsdm is folded around the Fe^{II} ion, and one of the thiolate groups of the dsdm ligand bridges to the second (symmetry generated) iron ion, thus forming the dinuclear $[Fe(dsdm)]_2$ core of the complex. The other thiolate group of the ligand is bridging to a Ni^0 tricarbonyl group, thus forming the tetranuclear complex.

Initially, the structure was refined as "[Ni(dsdm)Fe$(CO)_3]_2$", in view of the composition of the starting materials. However, substitution of Fe^{II} for Ni^{II}, thus giving a tetranuclear Fe_4 cluster, resulted in significantly better *R* values and lower residual electron densities in the refinement of the structure, and substitution of the peripheral iron by nickel resulted in even better refinement of the crystal data. Ultimately, this also explained the "16-electron" count for the, initially, Fe^0 moieties, which can now be rationalised as 18-electron Ni^0 species. The coordination around the iron is distorted trigonal bipyramidal, and the nickel atoms are in a tetrahedral geometry. The Fe−N and the Fe−S distances in this unique tetranuclear compound are significantly longer than the Ni−N and Ni−S distances observed in the Ni-dsdm trinuclear species characterised by Turner et al.[5] Instead, the Fe−N and Fe−S bond distances and angles in **1** are comparable to those found in $[Fe(dsdm)]_2$,[7] deviating by less than 0.04 Å and 5.6° from this "parent" compound.

Reactivity studies of nickel thiolate complexes in binding with other metal ions have been reported for several years. In particular mononuclear nickel complexes with *cis* dithiolate groups are regarded as very reactive in forming thiolate bridged polynuclear compounds. Reactions of such nickel complexes with $FeCl_2$,[8] $Fe(ClO_4)_2$,[9] $Fe_2(CO)_9$,[10] or (norbornadiene)M$(CO)_4$ (with M = Cr, Mo, W)[6] have been carried out at room temperature with stirring only.

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[a] Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University,
P. O. Box 9502, 2300 RA Leiden, The Netherlands
E-mail: bouwman@chem.leidenuniv.nl
[b] Bijvoet Center for Biomolecular Research, Crystal and Structural Chemistry, Utrecht University,
Padualaan 8, 3584 CH Utrecht, The Netherlands

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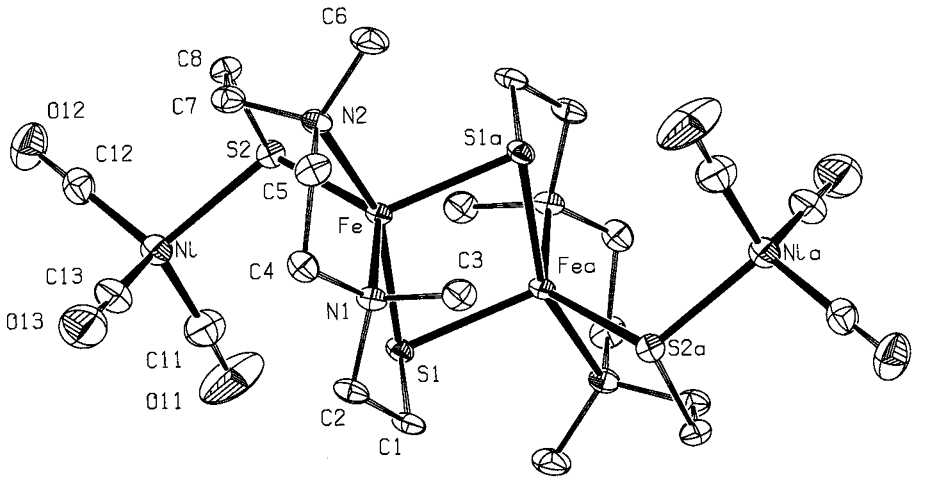

Figure 1. ORTEP view at 50% probability level of the molecular structure of **1** with the atomic labelling. Hydrogen atoms have been omitted for clarity; selected bond lengths [Å] and angles [°]: Ni−Fe 3.899(1), Fe−Fea 3.098(1), Ni−S2 2.317(1), Ni−C11 1.789(6), Ni−C12 1.773(4), Ni−C13 1.786(5), Fe−S1 2.444(1), Fe−S2 2.346(1), Fe−N1 2.168(3), Fe−N2 2.330(3), Fe−S1a 2.363(1), S2−Ni−C11 103.9(2), S2−Ni−C12 104.5(2), S2−Ni−C13 110.8(2), C11−Ni−C12 110.8(2), C11−Ni−C13 113.7(2), C12−Ni−C13 112.5(2), S1−Fe−S2 97.79(4), S1−Fe−N1 83.58(9), S1−Fe−N2 156.20(8), S1−Fe−S1a 99.75(4), S2−Fe−N1 132.48(10), S2−Fe−N2 82.98(8), S2−Fe−S1a 115.56(4), N1−Fe−N2 78.7(1), N1−Fe−S1a 110.87(9), N2−Fe−S1a 101.32(8)

These reactions resulted in various heteropolynuclear complexes, in which the original nickel thiolate complexes act as monodentate or didentate ligands towards the newly introduced metal ion. In our hands, the mononuclear compound [Ni(dsdm)] did not react with either $Fe_2(CO)_9$ or $Fe(CO)_5$ under similar mild reaction conditions. However, more severe conditions such as described above, leads to complete scrambling of the reactants.

Although the initial aim of the reaction was to form a heterodinuclear NiFe compound as a model for hydrogenase, such as the one reported by Darensbourg et al.,[10] the tetranuclear complex which was obtained instead is interesting by itself for other research areas. Numerous examples are known of iron carbonyl compounds, which are bridged by thiolates to other transition metals, but to our knowledge such compounds have not been reported with nickel carbonyl groups. The tetranuclear **1** is the first compound in which a $Ni(CO)_3$ group is bound to a transition metal thiolate complex. Only a few organometallic clusters with bridging inorganic sulfide, in which the nickel monocarbonyl is part of the cluster core, have been reported.[11]

The observation and characterisation of this reshuffled complex may draw the attention to the fact that a tetradentate chelating ligand may not be enough to hold on and stabilize a divalent metal ion. The reshuffling of ligands and oxidation states may have been triggered by the strong reducing power of $K[HFe(CO)_4]$ species, leading to "$[Ni(0)(dsdm)]^{2-}$", which then falls apart and causes a cascade of other reactions. Another scrambled compound which could be isolated from the reaction mixture is the dinuclear $[Fe(dsdm)Fe(dmes)(CO)_2]$ (H_2dmes = bis(sulfanylethyl)sulfide).[12]

Experimental Section

General: Infrared spectra (KBr pellets) were recorded in the range 4000−400 cm^{-1} using a Perkin−Elmer FT-IR Paragon spectrophotometer controlled by a PC using PE Grams Analyst software.

Synthesis: All experiments were performed in an argon atmosphere. Solvents were dried according to standard procedures. The ligand H_2dsdm was synthesised according to a literature procedure.[13] [Ni(dsdm)] was synthesized by reaction of $Ni(acac)_2$ with H_2dsdm in toluene.

Iron pentacarbonyl (1 mmol, 0.131 mL) was added to an ethanolic solution of potassium hydroxide (2 mmol, 0.112 g in 5 mL of absolute ethanol) and stirred overnight until a red solution of $K[HFe(CO)_4]$ was obtained.[14] The solution was filtered to remove precipitated $KHCO_3$, which was washed with 10 mL of absolute ethanol. To the red solution was added solid [Ni(dsdm)] (1 mmol, 0.26 g) and the mixture was heated under reflux for 2 hours during which time the solution became very dark. After cooling the reaction mixture was filtered to remove any precipitated solids, and the resulting solution was left to crystallize. Orange-brown crystals suitable for X-ray diffraction were obtained after a few days. − Infrared Spectrum (KBr pellet): 3443 (br) 2919 (m), 2861 (m), 2048 (vs), 1968 (vs), 1949 (vs), 1648 (m,br), 1465 (m), 1295(m), 1273(m), 1079 (m), 1046 (m), 1029 (m), 939 (s), 882 (w), 764 (m), 740 (w), 668 (w), 519 (w), 450 (m) cm^{-1}. The compound gets slightly sticky when in contact with air. Satisfactory elemental analysis was obtained for $[C_{22}H_{36}Fe_2N_4Ni_2O_6S_4] \cdot 3\ H_2O$.

X-ray Crystal Structure Analysis: Crystal data for $[Fe(dsdm)Ni(CO)_3]_2$: $[C_{22}H_{36}Fe_2N_4Ni_2O_6S_4]$, $M = 809.89$, orange-brown needle (0.12 × 0.12 × 0.55 mm), triclinic, space group $P-1$ with $a = 8.2339(17)$, $b = 8.3530(15)$, $c = 12.729(3)$ Å, $\alpha = 79.683(18)$, $\beta = 74.661(18)$, $\gamma = 75.532(16)°$, $U = 811.5(3)$ Å^3, $Z = 1$, $D_c = 1.657$ $g \cdot cm^{-3}$, $F(000) = 416$, $\mu(Mo\text{-}K_\alpha) = 23.2$ cm^{-1}, 7392 reflections measured, 3717 independent ($R_{av} = 0.05$). Mo-K_α radiation, graphite monochromator, $\lambda = 0.71073$ Å, $\theta_{max} = 27.5°$, $T = 150$ K, CAD4T diffractometer on rotating anode. Data were corrected for absorption (analytical). The structure was solved by Patterson techniques (DIRDIF)[15] and refined on F^2 using SHELXL96.[16] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located at calculated positions and refined riding on their carrier atoms. Convergence was reached at $R_1 = 0.0415$ [for 2653 reflections with $I > 2\sigma(I)$] and $wR_2 = 0.0892$ ($S = 0.98$). A final difference map did not show any features outside $-0.54 < \Delta\rho < 0.70$ e·Å^{-3}. Structure graphics and checking for higher symmetry were performed with the program PLATON.[17]

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102783. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44(1223) 336-033, E-mail: deposit@ccdc.cam.ac.uk].

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