
Constantinus F. Martens, Henk L. Blonk, Thijs Bongers, Johannes G. M. van der Linden, Gezina Beurskens, Paul T. Beurskens, Jan M. M. Smits and Roeland J. M. Nolte

Department of Organic Chemistry, Department of Inorganic Chemistry and Department of Crystallography, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

An Fe4S4-cluster, partly encapsulated by a concave, tetratdentate ligand, mimics certain electrochemical properties of metalloproteins.

Current efforts in the design of iron–sulphur protein analogues focus on the use of cavitands and other macroyclic ligand systems to coordinate the Fe4S4-core. Recent examples include modified cyclodextrines, macrocycles and cavitands based on hexa-substituted benzenes. A variety of goals are being pursued, inter alia the improvement of the aqueous solubility of the formed cluster, the creation of a specific iron-subsite, and the mimicking of the hydrophobicity in the protein pocket.

As part of our programme aimed at the development of metalloclohosts from the building block diphenylglycuril we describe a novel concave, tetratdentate thiol ligand system 1, which forms a 1:1 complex with an Fe4S4-cluster 2. In the cluster complex the Fe4S4-core is partly shielded from its concave and its convex side is shielded by two phenyl rings. The overall shape is being pursued, inter alia the improvement of the aqueous solubility of the formed cluster, the creation of a specific iron-subsite, and the mimicking of the hydrophobicity in the protein pocket.

As part of our programme aimed at the development of metalloclohosts from the building block diphenylglycuril we describe a novel concave, tetratdentate thiol ligand system 1, which forms a 1:1 complex with an Fe4S4-cluster 2. In the cluster complex the Fe4S4-core is partly shielded from its concave and its convex side is shielded by two phenyl rings. The overall shape is being pursued, inter alia the improvement of the aqueous solubility of the formed cluster, the creation of a specific iron-subsite, and the mimicking of the hydrophobicity in the protein pocket.

An Fe4S4-cluster, partly encapsulated by a concave, tetratdentate ligand, mimics certain electrochemical properties of metalloproteins.

Current efforts in the design of iron–sulphur protein analogues focus on the use of cavitands and other macroyclic ligand systems to coordinate the Fe4S4-core. Recent examples include modified cyclodextrines, macrocycles and cavitands based on hexa-substituted benzenes. A variety of goals are being pursued, inter alia the improvement of the aqueous solubility of the formed cluster, the creation of a specific iron-subsite, and the mimicking of the hydrophobicity in the protein pocket.

As part of our programme aimed at the development of metalloclohosts from the building block diphenylglycuril we describe a novel concave, tetratdentate thiol ligand system 1, which forms a 1:1 complex with an Fe4S4-cluster 2. In the cluster complex the Fe4S4-core is partly shielded from its concave and its convex side is shielded by two phenyl rings. The overall shape is being pursued, inter alia the improvement of the aqueous solubility of the formed cluster, the creation of a specific iron-subsite, and the mimicking of the hydrophobicity in the protein pocket.

An Fe4S4-cluster, partly encapsulated by a concave, tetratdentate ligand, mimics certain electrochemical properties of metalloproteins.
Theoretical value for a reversible one-electron process (ca. 65 mV) is observed. This might indicate that the complex is monomeric. The reduction at the platinum working electrode is diffusion controlled as can be concluded from the linear response of \( i_{pc} \) on \( v^{1/2} \) (see Fig. 2). The redox potential of the 2\(-/3\(- reduction process of the newly formed cluster 2 is close to that of the known \([Fe_4S_4(SEt)_4]^{2-}\) cluster supporting the formation of the former compound. The UV-VIS spectra of both clusters are very similar.

Further information that 2 had been formed, comes from IR spectroscopy, which showed the disappearance of the intense Fe-Cl vibration at

<table>
<thead>
<tr>
<th>[Ba(CIO_4)_2] ( \text{mmol dm}^{-3} )</th>
<th>( E_{1/2} \text{V} \text{ vs. Fc}^+/\text{Fc} )</th>
<th>( i_{pc} )</th>
<th>( i_{pa} )</th>
<th>( i_{pc}/i_{pa} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-1.70</td>
<td>1.15</td>
<td>2.3</td>
<td>0.85</td>
</tr>
<tr>
<td>5</td>
<td>-1.67</td>
<td>2.7</td>
<td>3.5</td>
<td>0.60</td>
</tr>
<tr>
<td>10</td>
<td>-1.66</td>
<td>4.2</td>
<td>3.2</td>
<td>0.76</td>
</tr>
<tr>
<td>25</td>
<td>-1.64</td>
<td>5.2</td>
<td>4.1</td>
<td>0.79</td>
</tr>
<tr>
<td>50</td>
<td>-1.63</td>
<td>4.7</td>
<td>2.9</td>
<td>0.62</td>
</tr>
</tbody>
</table>

* 2\(-/3\(- Reduction at ca. 25°C in DMF using a PGE-working electrode, a platinum auxiliary electrode, a Ag/AgCl reference electrode and 0.1 mol dm\(^{-3}\) tetrabutylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. * Potentials vs. Fe\(^{3+}/\text{Fe}^0 \) in DMF. * Arbitrary units.

\[ \text{UV-VIS (DMF)} I_{\text{max}}/\text{nm} \text{ for } [\text{Fe}_4\text{S}_4(\text{SEt})_4]^{2-} : 297 (23 200), 412 (17 200); I_{\text{max}}/\text{nm} \text{ found for [Fe}_4\text{S}_4\text{Cl}_4]^{2-} : 295 (25 500), 412 (13 100). * H NMR revealed the presence of two sets of the CH\(_3\)S-protons in complex 2, viz. at \( \delta 13.25 \) (6H) and 14.25 (2H), respectively. This suggests that one of the corners of the Fe\(_2\)S\(_2\)-cube points towards the cavity as indicated schematically in drawing Fig. 2.
The Use of a High Surface Area Silicon Oxynitride as a Solid, Basic Catalyst
Peter W. Lednor* and René de Ruitter
Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research BV), PO Box 3003, 1003 AA Amsterdam, The Netherlands

High surface area silicon oxynitride is shown to be a basic catalyst through its ability to catalyse Knoevenagel condensations when suspended in toluene at 50 °C; the activity is due to the presence of surface nitrogen.

Silicon oxynitride is shown to be capable of acting as a solid, basic catalyst. This is of interest because, (i) it extends the range of inorganic solids that find application as heterogeneous catalysts, such materials being mainly represented by oxides, and (ii) catalysis by solid bases, while less developed than catalysis by solid acids, is of growing importance.1-3

The application of non-oxide ceramics in catalysis is facilitated by their increasing availability in high surface area forms,4 and by surfaces that are kinetically stable to oxidation and hydrolysis. We have previously described the synthesis of a high surface area silicon oxynitride.5 The presence and stability of surface nitrogen6 suggested that the surface might show basic properties; some evidence for the presence of basic sites on the surface of silicon nitride was provided by IR spectroscopy in conjunction with the use of probe molecules.7 To test the possibility of basic catalysis we have investigated the Knoevenagel condensation over silicon oxynitride. This reaction, illustrated in eqn. (1), is usually catalysed by amines in which the nitrogen functions as a basic site.

\[
\text{PhCHO} + \text{CH}_2(\text{CN})\text{COEt} \rightarrow \text{PhCH} = (\text{CN})\text{COEt} + \text{H}_2\text{O} \\
\]

Initial experiments were carried out in toluene (25 ml) at 50 °C with 0.5 g of silicon oxynitride [23 %wt. surface nitrogen, determined by X-ray photoelectron spectroscopy (XPS): 155 m² g⁻¹] and 10 mmol of each of the reactants depicted in eqn. (1). The conversion was measured by GLC and confirmed by ¹H NMR measurements. After 4 h the conversion to the product was 89%; 70 h 97%. Addition of more reactants (10 mmol) showed that the catalyst maintained its activity, giving 97 and 90% conversions after second and third experiments of 20 h each. After these three experiments the total number of product molecules formed per unit of surface area was 230 nm⁻², clearly indicating a catalytic process. The surface area had decreased only very slightly, to 210 m² g⁻¹.

Fig. 1 The activity of silicon oxynitride catalysts in a Knoevenagel condensation as a function of surface nitrogen concentration

References