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An Fe₄S₄-cluster, partly encapsulated by a concave, tetradeutate 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 macrocyclic ligand systems to coordinate the Fe₄S₄-core. Recent examples include modified cyclodextrines, 1 macrocyclics 2 and cavitands based on hexa-substituted benzenes. 3 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 metallohosts 4 from the building block diphenylglycoluril we describe a novel concave, tetradeutate 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 environments giving rise to electrode phenomena previously encountered with proteins.

The protected tetra thiol ligand 1a was synthesised using previously described procedures. 4 Its structure (see stereo-view; Fig. 1) was determined by X-ray crystallography. 5 Host 1a has a cavity formed by two fused 2-imidazolidone rings, which are flanked by two α-xylylene units. Its overall shape is concave and its convex side is shielded by two phenyl substituents.

Quantitative deprotection of 1a into 1b was easily achieved using sodium methanolate. Exchange reactions of (Bu₄N)₂[Fe₄S₄Cl₁₄] 7 with a suspension of 1b in dimethylformamide (DMF) were conducted under a nitrogen atmosphere in very dilute solutions to avoid the formation of polymeric products, eqn. (1).

\[ \text{[Fe₄S₄Cl₄]}⁺ + L(Na) → [Fe₄S₄(L)]⁺ + 4NaCl \]

During the course of the reaction a colour change was observed from purple-black to brown-black. The progress of the exchange reaction was followed with cyclic voltammetry (CV) and differential pulse polarography (DPP) by monitoring the disappearance of the 2⁻/3⁻ wave of the Fe₄S₄Cl₁₄²⁻ reduction at −1.34 V (vs. Fe⁺/²⁺) and the simultaneous appearance of the 2⁻/3⁻ reduction wave of the newly formed product at −1.70 V in samples, obtained from the reaction mixture. The complex 2 was isolated through precipitation with diethyl ether or evaporation of the solvent. The samples thus obtained were characterised further using various physical methods.

First of all CV was used to identify the nature of our product. Remarkably, the current response of the new wave was very small, a phenomenon noted earlier for the electrochemical reduction of a variety of redox-active metalloproteins in water. 8 With the addition of a modulator (Ba²⁺ or Na⁺) a considerable increase in the current response was noted in the CV and DPP of 2. This was observed for all four electrodes we used, viz. Au, Pt, pyrolytic graphite edge (PGE) and pyrolytic graphite basal (PGB), indicating that not only the electrode material, but also the modulator plays an important role in the 2⁻/3⁻ reduction process. We believe that association and dissociation processes of cluster 2 with the Ba²⁺ ions occurring in the interfacial electrode layer (probably through coordination at the ether and carbonyl oxygen atoms present in our ligand system) enhance the electron transfer rate considerably. This can be concluded from the 70 mV redox potential shift from −1.70 to −1.63 V that is observed when Ba²⁺ is added, while no potential shift is noted for the ferrocene oxidation or for the reduction of other simple thiolate cluster compounds under the same conditions. As with the natural systems, a maximum response was observed when the Ba²⁺ concentration is approximately 25 mmol dm⁻³ (Table 1). Similarly, like with the metalloproteins, α monovalent cations did not improve the current response to the same extent as did divalent cations. With the modulator present a nearly chemically reversible wave was obtained with \( i_0/i_º = 0.80 \) and a cathodic-anodic peak separation close to the...
Table 1. Electrochemical properties of cluster compound 2.

<table>
<thead>
<tr>
<th>[Ba(ClO\textsubscript{4})\textsubscript{2}]\textsuperscript{2-}</th>
<th>E\textsubscript{1/2}/V\textsuperscript{b}</th>
<th>i\textsubscript{pc}/mA</th>
<th>i\textsubscript{pa}/mA</th>
<th>i\textsubscript{pa}/i\textsubscript{pc}</th>
</tr>
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<tbody>
<tr>
<td>0.0 mmol dm\textsuperscript{-3}</td>
<td>-1.70</td>
<td>1.15</td>
<td></td>
<td></td>
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<tr>
<td>5.0 mmol dm\textsuperscript{-3}</td>
<td>-1.67</td>
<td>2.7</td>
<td>2.3</td>
<td>0.85</td>
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<tr>
<td>10.0 mmol dm\textsuperscript{-3}</td>
<td>-1.66</td>
<td>4.2</td>
<td>3.2</td>
<td>0.76</td>
</tr>
<tr>
<td>25.0 mmol dm\textsuperscript{-3}</td>
<td>-1.64</td>
<td>5.2</td>
<td>4.1</td>
<td>0.79</td>
</tr>
<tr>
<td>50.0 mmol dm\textsuperscript{-3}</td>
<td>-1.63</td>
<td>4.7</td>
<td>2.9</td>
<td>0.62</td>
</tr>
</tbody>
</table>

\* 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\textsuperscript{-3} tetrabutylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. \* Potentials vs. Fc\textsuperscript{-}/Fc in DMF. c Arbitrary units.

352 cm\textsuperscript{-1} (solid CsI, comparison of 2 with [Fe\textsubscript{4}S\textsubscript{4}Cl\textsubscript{4}]\textsuperscript{2-}). 1H NMR revealed the presence of two sets of the CH\textsubscript{3}S-protons in complex 2, viz. at \(\delta\) 1.25 (6H) and 1.45 (2H), respectively. This suggests that one of the corners of the Fe\textsubscript{4}S\textsubscript{4}-cube points towards the cavity as indicated schematically in drawing.
2. Corey–Pauling–Koltun models show that in this way the cluster and ligand are well matched. A temperature-dependence shift experiment ([{H}_4]DMSO, temperature range 25–50 °C) showed that each of the two sets of CH_2S-protons in 2 shift 0.75 ppm downfield when the temperature is increased by 25 °C. This shift value is in good agreement with values reported for other iron–sulphur clusters. It suggests that the Fe_4S_4-core in 2 is intact. The same conclusion was drawn from a core extrusion experiment: addition of a slight excess of PhSH to 2 generated the cluster [Fe_4S_4(S-Ph)_4]^2−, which was detected by ¹H NMR [measured ([²H_6]DM SO), lit.10 (CD_3CN) 5.50, 5.28 (p-PhH); 5.80, 5.88 (o-PhH); 8.20, 8.18 (m-PhH)].

In summary, we may conclude that we have synthesised a new semi-encapsulated iron–sulphur cluster, which displays electrochemical behaviour previously only encountered in metalloproteins. Currently, our research is being focused on the synthesis of diphenylglycoluril ligand systems capable of fully encapsulating an Fe_4S_4-core.

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References


The Use of a High Surface Area Silicon Oxynitride as a Solid, Basic Catalyst

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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, and by surfaces that are kinetically stable to oxidation and hydrolysis. We have previously described the synthesis of a high surface area silicon oxynitride. The presence and stability of surface nitrogen4 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. 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.

PhCHO + CH_2(CN)CO_2Et → PhCH=C(CN)CO_2Et + H_2O (1)

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 220 m² g⁻¹. The conversion was found to be 97% after 20 h, 90% after 40 h, and 89% after 60 h; the conversion is thus linear with reaction time (fig. 1).

![Fig. 1 The activity of silicon oxynitride catalysts in a Knoevenagel condensation as a function of surface nitrogen concentration](image-url)