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Polymer-Supported Iron–Sulfur Clusters

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Synthetic iron–sulfur cluster complexes have been extensively studied as analogues of redox active sites of ferrodoxin-type proteins [1–5]. However, the iron–sulfur cluster embedded in the native protein and their homologous clusters in the crystalline or solvated form can present a different chemical reactivity. This different reactivity causes problems in the use of soluble synthetic complexes as models for the protein active sites: it is usually associated with the stability of the active species incorporated in the protein chain, whereas the soluble species are highly air-sensitive.

The fixation of synthetic iron–sulfur clusters on flexible polymer should bring more stability to these species and should provide better models for the protein active sites. The potential for such a fixation has been examined in the present work on two synthetic iron-sulfur cluster anions.

$$[Fe_4(\mu_3 - S_4)(StBu)_4]^{2-} \qquad \text{(I)}$$

$$[Fe_4(\mu_3 - S_4)(SBz)_4]^{2-} \qquad \text{(II)}$$

The clusters I and II were incorporated in an anion-exchange resin. The fixation involved the formation of an ionic bonding between the supported cationic ligand and the cluster. This type of fixation has recently been reported in the literature for an ionic triiron carbonyl cluster [6]. The cluster II was also incorporated in a thiol-functionalized polymer. This fixation produced covalently-bonded clusters, and has been reported in the literature with -PPh_2 groups as supported ligands [7]. The reaction of I with thiol groups of the modified synthetic resin yields a new type of ferrodoxin analogue material.

The poly(styrene-divinylbenzene) support used for the ionic bonding was a commercial resin (Dowex) incorporating ammonium groups Ⓓ–CH_2–$N(CH_3)_3$, Cl^-. The support used for incorporating covalently-bonded clusters was purchased chloromethylated poly(styrene-divinylbenzene) beads which were modified according to a described procedure to produce the thiol functionalization [8] Ⓟ–CH_2SH. Membranes have also been prepared for a styrene and divinylbenzene copolymerization and functionalization according to described procedures [8].

Preparation procedures described in the literature have been applied, yielding shiny sheets of well-formed crystals of NEt_4^+ salts of I and II recrystallized from acetonitrile [10]. (Fe%: I cal: 23.06; Fd: 23.00; II cal: 20.21; Fd: 20.38). The usual spectral properties (vis UV Mössbauer) have been checked and the stability of the solutions tested in the operating conditions (degased solvents, argon atmosphere).

Dowex beads were added to the black solution of cluster I or II and kept under argon for 2 h (1 g resin for 5 mmol in 300 ml of MeOH) with continuous stirring. The formation of solids incorporating iron-sulfur species (samples 1 and 2) was obtained from a ligand exchange between a cationic ligand on the molecular cluster and an analogous attached ligand. The identification of the species attached on samples 1 and 2 was done by far-infrared spectroscopy (Table I and Fig. 1). Comparing the attached species spectra with those of I an II clearly shows that the cluster structures have been preserved during the fixation. Furthermore, our IR data for II in the soluble state are in good accordance with recently reported Raman data for the same compound [10, 11] (Table I). As expected, samples 1 and 2 showed poor stability in the presence of oxygen. The Fe_4S_4 centers decomposed promptly when samples 1 and 2 were brought into contact with air: the IR bands showed in Fig. 1 disappeared completely. The iron content of samples 1 and 2 are reported in Table I.

In an attempt to produce a ferrodoxin-analogue, polymers incorporating thiol groups were brought into contact with an acetonitrile solution of I (1 g resin for 5 mmol of I in 300 ml of DMF). The formation of covalently-bonded clusters was obtained from a ligand exchange between thiol groups on I and -SH groups on the polymer. Sample 3 was obtained when beads were used as support (S wt.%: 5.1), whereas sample 4 was obtained using a membrane as support (S wt.%: 2.1). The species in samples 3 and 4 were identified by far-infrared spectroscopy, by comparing their infrared spectra with that of II (Table I, Fig. 2). In spite of some blurring, this comparison demonstrates that the thiol exchange reaction has taken place. The iron content of samples 3 and 4 are reported in Table I.

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TABLE I. Observed Absorption Band Frequencies (cm^{-1}) and Assignments of I and II Clusters and of Supported Material.

Sample number or reference	Supports	Fe wt.%	ν cm^{-1}
I		23.00	100w, 231s, 290s, 345s, 370s, 400s, 421s, 468w, 581s, 615w
II		20.4	81w, 134w, 246w, 320w, 330w, 354s, 381w, 471s, 552s
1	Ⓓ$-CH_2-(NCH_3)_3^{+a}$	4.1	100w, 231s, 290s, 345s, 370s, 400s, 421s, 468w, 581w, 581w
2	Ⓓ$-CH_2-(NCH_3)_3^{+a}$	0.84	81w, 134w, 246w, 320w, 330w, 354s, 381w, 471s, 552s
3	Ⓟ$-CH_2SH$, beads[a]	0.22	170w, 350s, 465w, 480s
4	Ⓟ$-CH_2SH$, membrane[a]	0.22	350w
II (10) Raman			330w, 354s, 381w, 471w

[a]Ⓟ,Ⓓ = poly(styrene-divinylbenzene).

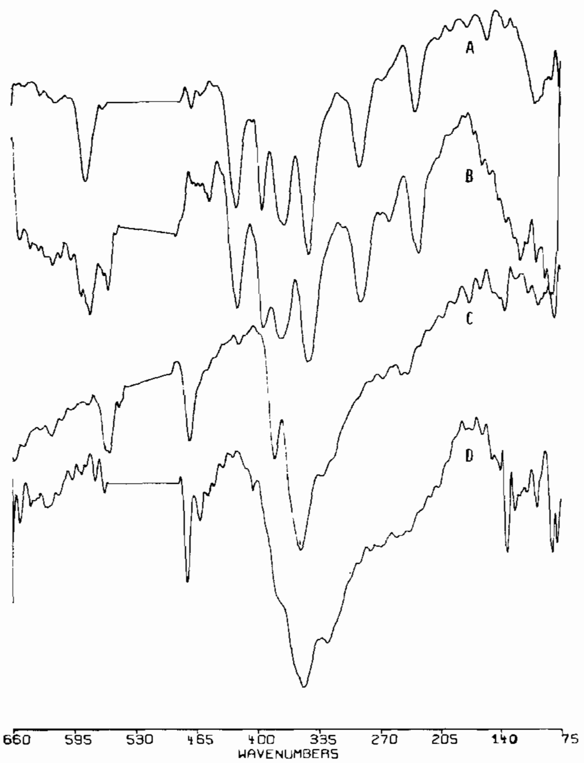

Fig. 1. Far IR spectra (cm^{-1}) of $Fe_4\mu_3\text{-}S_4SR_4^{2-}$ cluster anions in the solid state (dispersed in polythene). (A) IR = tBu;NEt_4^+ salt. (B) I supported on a NR_4^+ functionalized resin. (C) II R = Bz;NEt_4^+ salt. (D) II supported on a NR_4^+ functionalized resin.

Bowman and Burwell described the fixation of iron-sulfur cluster bonded to thiol-modified silica [12]. However, the authors did not give any spectroscopic evidence for the fixation. Furthermore, their choice of thiol-modified silica as a support is questionable, because it has been demonstrated that silica is not inert towards the fixed units [13]. Silica is also a poor model for the flexible polypeptide chain. To the best of our knowledge, samples 3 and 4 represent the first examples of covalently-bonded iron-sulfur clusters supported on polymers and identified by infrared spectroscopy in the domain of frequencies relevant to the Fe–S bonds.

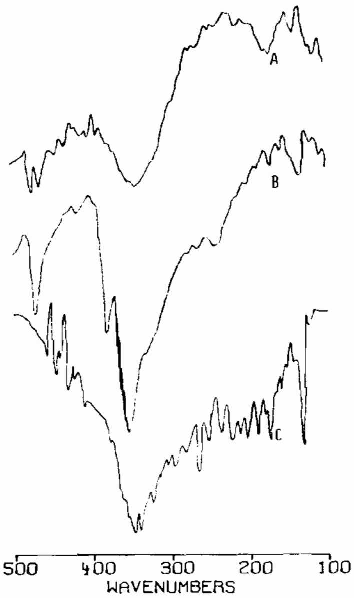

Fig. 2. Comparison of spectra of the reaction product of I with thiol functionalized polystyrenes: beads A), 11 μm thick membranes C) with the NEt_4^+ salt of II B).

Current investigations aim at testing samples 1–4 as catalysts for alkyne and alkene hydrogenation. Literature reports indicate that the soluble clusters I and II can activate such reactions [14]. Using a gas flow system will allow the simultaneous recording of the far IR spectum of the functioning catalyst and the conversion of reactant inter products.

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