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Polymer-Bonded Iron-Molybdenum-Sulphur Clusters

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Dedicated to Prof. C.I. Simionescu's 60th birthday

INTRODUCTION

The nature of the molybdenum sites in the various molybdoenzymes continues to attract attention. Recently, the isolation of an iron-molybdenum cofactor (Fe-Mo-co) (1) has been described, and Molybdenum-K-edge X-ray absorption fine structure (EXAFS) analysis of the Fe-Mo-co (2), and synthetic models (3,4) was reported. The recent EXAFS data suggest an attractive model of Fe-Mo-co composed of two cubane-type cores joined by a common Mo atom ($MoFe_6S_8$) (4). A priori it seems difficult to obtain a complex with the core ($MoFe_6S_8$) by a spontaneously self-assemble from simple reactants under homogeneous conditions.

We have now achieved the synthesis of the ($MoFe_6S_8$) core attached to a polymer and we describe here our preliminary results.

The formation of the ($MoFe_6S_8$) cluster was achieved according to a reaction sequence wich involves the $(MoFeS_4)^{2-}$ and $(MoFe_3S_4)^{2-}$ intermediates as shown in Scheme 1.

EXPERIMENTAL

All operations were performed in a purified dry argon atmosphere in a Schlenck-type glassware; all solvents and reagents were thoroughly degassed prior to use. Experimental procedures for the synthesis of macromolecular styrene-divinylbenzene copolymers, chloromethylation procedure (5), and the addition of -SH groups to these chloromethylated resins (6) are described in previous publications and, therefore, will not be reported here.

1. Preparation of ($MoFeS_4$)-attached Resin

To a stirred suspension of 4 g of resin I (3% divinylbenzene; 0.3 mequiv/g S) in 50 ml of anhydrous methanol, a solution of 0.8 g of sodium methoxide in 75 ml of anhydrous methanol was added. After stirring for 24 h at 25°C, the suspension was decanted, and the resin was extracted with 200-ml portions of anhydrous methanol until the phenolphtaleine in water gave a negative test for sodium hydroxide. The resin

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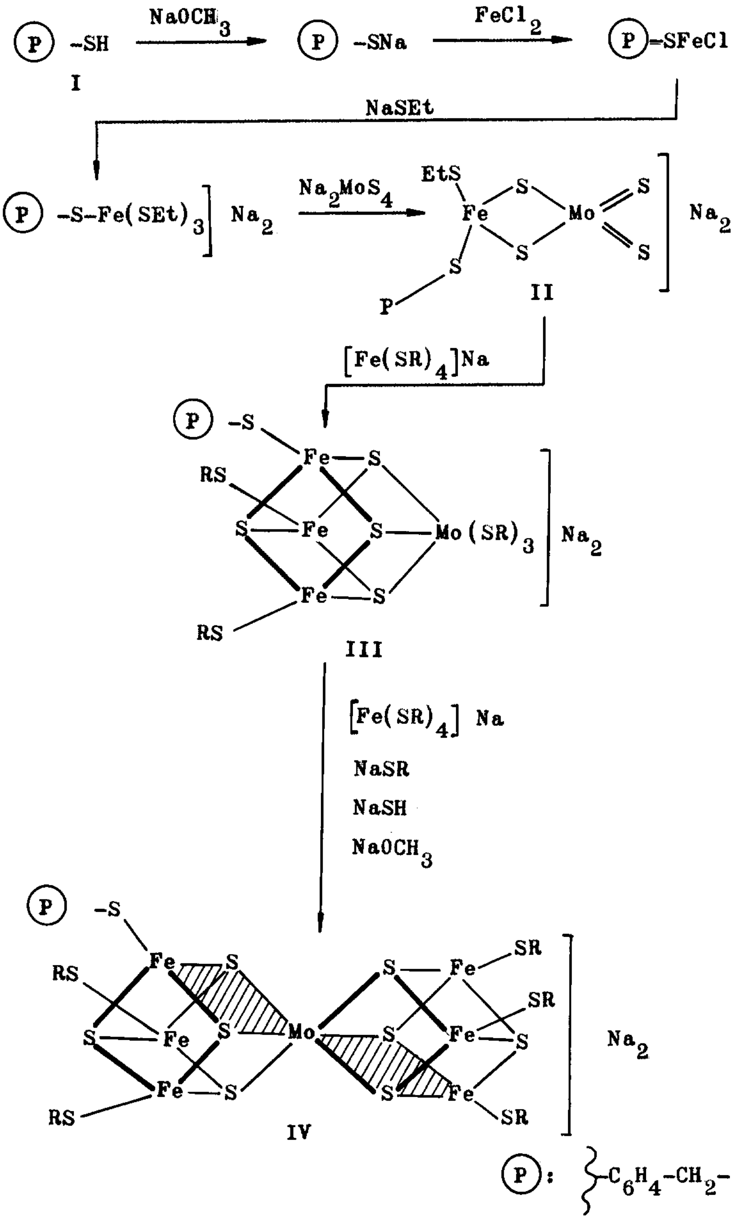

Scheme 1 R : tert-C_4H_9

was then stirred at room temperature in 100 ml of dioxane containing 0.4 g $FeCl_2$ for 24 h, filtered, and extracted with 200 ml-portions of dioxane until the extract was no longer colored. The resulting green-gray resin was then suspended in a solution prepared from 0.75 g of ethanethiol and 0.56 g of sodium methoxide in 50 ml of anhydrous methanol. This suspension was stirred for 24 h at room temperature. After filtration, the dark green resin beads were extracted with 200-ml portions of acetonitrile until silver nitrate in acetonitrile gave a negative test for mercaptan. To a stirred suspension of this resin in 60 ml of DMF, a solution of 0.6 g of Na_2MoS_4 in 80 ml of DMF was added. The reaction mixture was stirred for 18 h at room temperature. The resulting dark red beads were washed with five portions of 200 ml acetonitrile-dimethylformamide (1:1) and dried in vacuo at 70°C. The elemental analysis of this resin suggests the composition $P\text{-}S\text{-}(EtS)FeS_4MoNa_2$.(Anal. Calcd. for $P\text{-}C_2H_5FeMoS_6Na_2$: S 5.35; Mo 2.67; Fe 1.55 %. Found: S 5.21; Mo 2.45; Fe 1.35 %). (P = polymer core).

2. Preparation of ($MoFe_3S_4$)-attached Resin.III.

Two solutions of reactants were prepared as follows: (i) 1.2 g of anhydrous $FeCl_3$ were dissolved in 50 ml of anhydrous methanol and the solution was filtered through a Celite pad; (ii) 3 g of tert-butyl-mercaptan were added to a stirred solution of 1.8 g of sodium methoxide in 50 ml of anhydrous methanol. The solution (i) was added dropwise in approximately 0.5 h to the stirred solution (ii). The resulting reaction mixture was filtered, and 4 g of resin II were added to filtrate. After 18 h of stirring, the suspension was filtered, and the resin beads were extracted with 200 ml-portions of acetonitrile until silver nitrate in acetonitrile gave a negative test for mercaptan. The product was dried in vacuo at 60°C to give 4.2 g (92-93%). The elemental analysis of this resin suggests the composition $P\text{-}S\text{-}MoFe_3MoS_4(SBu^t)_5Na_2$. (Anal.Calcd. for $P\text{-}C_{20}H_{45}Fe_3MoS_{10}Na_2$: S 7.83; Fe 4.1; Mo 2.35 %. Found : S 7.57; Fe 3.85; Mo 2.19 %). (P = polymer core).

3. Preparation of ($MoFe_6S_8$)-attached resin.IV.

Two solutions of reactants were prepared as follows : (i) 2.35 g of anhydrous $FeCl_3$ were dissolved in 50 ml of anhydrous methanol and the solution was filtered through a Celite pad; (ii) 7.8 g of tert-butyl-mercaptan were added to a stirred solution of 4.5 g of sodium methoxide in 150 ml of anhydrous methanol. The solution (i) was added dropwise in approximately 0.5 h to solution (ii) under continous stirring. After complete addition of solution (i), the reaction mixture was filtered and 2 g of resin III were added to filtrate. This suspension was stirred for 5 h at room temperature and a solution prepared from 1 g of NaSH and 0.9 g of sodium methoxide was then added. After 18 h of stirring, the suspension was filtered and the resin was extracted with 100 ml-portions of acetonitrile until the extract was no longer colored. Repeating this workup for three times, provided a black resin which was well washed with acetonitrile and dried in vacuo at 70°C for 18 h. The elemental analysis of this resin suggests the composition: $P{-}S{-}MoFe_6S_8(SBu^t)_5Na_2$. (Anal. Calcd. for $C_{20}H_{45}Fe_6MoS_{14}Na_2$: S 10.23; Fe 7.65; Mo 2.19 %. Found : S 9.9 Fe 7.47; Mo 2.15 %).(P = polymer core).

4. Sodium Replacement Experiments.

Samples of resins II, III and IV were treated with an excces of tetramethylammonium chloride solution in methanol, well washed with methanol and acetonitrile, and dried in vacuo at 70°C for 18 h. Microanalyses for nitrogen were consistent with the replacement of 1.8 - 2.3 Na^+.

RESULTS AND DISCUSSION

To synthesize clusters of the general stoichiometry (Fe_6MoS_8), several reported experimental data were considered as suitable starting points: (i) formation of analogues of Fe_4S_4 clusters from their components proceeds trough the rubredoxine $(Fe(SR)_4)^{2-}$ species; (ii) formation of $MoFeS_4$ core by the reaccion of MoS_4^{2-} with $(Fe(SR)_4)^{2-}$ (7,8); (iii) when the $FeCl_3$-NaSR systems are treated with MoS_4^{2-} under homogeneous conditions, the only isolable species are of the type ($Mo_2Fe_6S_8$), ($Mo_2Fe_6S_9$) (4,9-13) , and ($Mo_2Fe_7S_8$) (13).

The scheme we have outlined for the preparation of $MoFe_6S_8$ cluster involves the following sequence: (i) preparation of the iron-molybdenum core $MoFeS_4$ via interaction of a resin-bonded $(Fe^{II}(SEt)_4)^{2-}$ complex with $(MoS_4)^{2-}$; (ii) preparation of the tetranuclear iron-molybdenum cluster $MoFe_3S_4$ by treating of the intermediate $P{-}S{-}Fe(SEt)MoS_4)^{2-}$ with an excces of $(Fe(SBu^t)_4)Na$ and $NaSBu^t$; (iii) preparation of the sevennuclear cluster $MoFe_6S_8$ via interaction of the $-Mo(SBu^t)_3$ group of the resin III with excces of $(Fe(SBu^t)_4)Na$ using NaSH as source of sulfide.

Additional research in progress is aimed toward the recovery of $MoFe_6S_8$ core from resin IV in the form of the well-characterized complex by reaction with C_2H_5COSH.

REFERENCES

1. V.K.Shah and W.J.Brill, Proc.Nat.Acad.Sci.USA,74,3249(1972)
2. S.P.Cramer, W.O.Gillum, K.O.Hodgson, L.E.Mortenson, E.I.Stiefel, J.R.Chisnell, W.J.Brill and V.K.Shah, J.Am. Chem.Soc.,100, 3814 (1978)
3. T.E.Wolff, J.M.Berg, C.Warrick, K.O.Hodgson, R.H.Holm and R.B.Frankel, J.Am.Chem.Soc., 100, 4630 (1978)
4. T.E.Wolff,J.M.Berg, K.O.Hodgson, R.B.Frankel,and R.H.Holm, J.Am.Chem.Soc., 101, 4140 (1979)

5. G.D.Jones, Ind.Eng.Chem., 11, 2686 (1952); K.W.Pepper, J.Chem.Soc., 4097 (1953); J.Černý, O.Wichterle, J.Polymer Sci., 30, 501 (1958)
6. A.K.Kun, J.Polymer Sci., A-1, 4, 847 (1966); C.L.Arcus and N.S.Solomons, J.Chem.Soc., 1175 (1963); A.B.Davancov and E.V.Zambrovskaya, Vysocomolecul.Soedin., 2, 1330 (1960)
7. G.Christou, B.Ridge and H.N.Rydon, J.C.S, Chem.Commun., 908 (1977)
8. D.Coucouvanis, E.D.Simhon, D.Swenson, and N.C.Baenziger, J.C.S., Chem.Commun., 361 (1979)
9. T.E.Wolff, J.M.Berg, C.Warrick, K.O.Hodgson, R.H.Holm, and R.B.Frankel, J.Am.Chem.Soc., 100, 4630 (1978)
10. G.Christou, C.D.Garner, and F.E.Mabbs, Inorg.Chim.Acta, 28, L 189 (1978)
11. G.Christou, C.D.Garner, F.E.Mabbs, and T.J.King, J.C.S., Chem.Commun., 740 (1978)
12. G.Christou, C.D.Garner, F.E.Mabbs, and M.G.B.Drew, J.C.S., Chem.Commun., 91 (1979)
13. T.E.Wolff, J.M.Berg, P.P.Power, K.O.Hodgson, and R.H.Holm, J.Am.Chem.Soc., 101, 5454 (1979)

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