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SYNTHESIS OF AND CATALYSIS BY DEXTRAN-BOUND Mo-CYSTEINE COMPLEX

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Cysteine was bound to the dextran polymer. The dextran-bound cysteine formed with Mo^{5+} a binuclear complex, which had a similar structure to free Mo-Cys complex. The dextran-bound Mo(V)-Cys complex exhibited a much higher catalytic activity for the reduction of acetylene with $NaBH_4$ compared with the free Mo-Cys complex.

The metal complexes containing biologically important moieties have an abiding interest as models of metallo-enzyme systems with active sites or metal binding sites.[1)] As most of enzyme, coenzyme and other biologically active substances have polymer structures, the functions of the polymer structure would be studied by examining the behavior of the synthetic models of biopolymer.[2)] On the other hand, when homogeneous catalysts are immobilized to have heterogeneous catalytic systems, we can not only separate the reactants and products from catalysts, but also control the reaction conditions more readily than in homogeneous systems.[3)] It has been demonstrated by Schrauzer and his coworkers that Mo-Cys complex exhibits an activity for a nitrogenase model reaction.[4-7)] In the present communication we wish to report that Mo^{5+} and dextran-bound cysteine form a stable complex similar to free Mo-Cys complex and also this polymer-bound Mo(V)-Cys exhibits a catalytic activity for the reduction of acetylene to ethylene and ethane.

Cysteine was attached to dextran according to the Curtius azide method.[8,9)] CM-Sephadex C-25 (Pharmacia Fine Chemicals) was used as dextran. The -SH group of cysteine was protected by a benzyl group and was released by Na/NH_3 after the reactions. Elementary analyses were done at each step of the reactions. Cysteine 1.05 mmol was contained in 1.0 g of the obtained dextran-bound cysteine. Dextran-cysteine was oxidized gradually to dextran-cystine in air. Dextran-cystine was reduced by $NaBH_4$ to dextran-cysteine and was filtered and washed repeatedly until ammonia was not detected by Nesslar's reagent. Molybdenum was incubated according to the same method as free Mo-Cys complex synthesis.[10)] Orange brown complex was obtained after filtration, washing and drying up. This complex was stable in dry air.

The infrared spectra of the dextran-bound cysteine and its Mo complex are shown in Fig. 1. The bands of the cysteine moiety of S-H stretching (2500 cm^{-1}) disappeared. The band of C=O stretching (1730 cm^{-1}) was shifted to 1590 cm^{-1} after the addition of Mo. These changes are in accordance with the fact that Mo is bound to -S and -C=O.[11,12)] The strong band of C=O stretching of cysteine was shifted without any residues, which followed that all of the polymer- bound cysteine

Fig. 1.

Infrared Spectra of Dextran-bound Cysteine (----) and its Mo Complex (———).

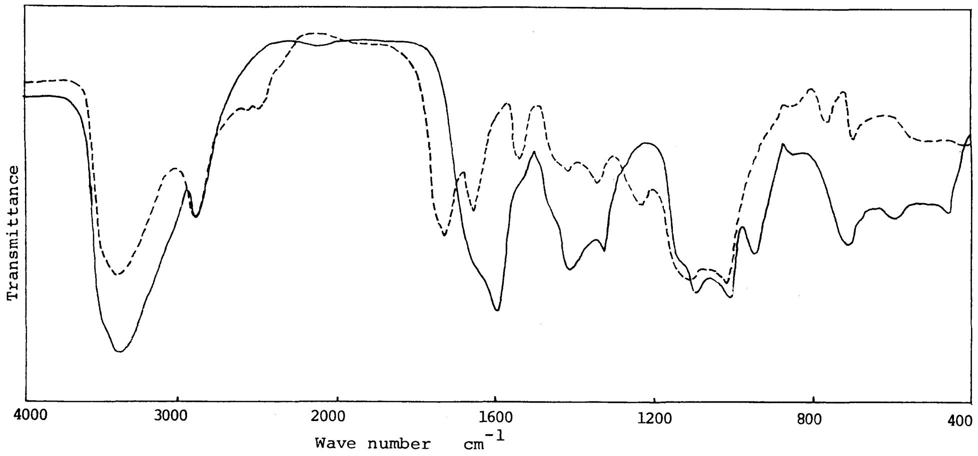


Table 1. Infrared frequencies and assignment of Mo-Cys complex (cm^{-1})

	NH_2 str.	C=O (or COO)	NH_2 bend.	Mo=O	Mo-O-Mo antisym.	 sym.
Mo-Cys complex[a)]	3210	1580	- 1630	970 945 925	730	425
Dextran-bound Mo-Cys complex[b)]	3100 - 3300	1580	- 1630	940 - 950	720 - 740	455

a) Taken from the data in ref. 13. b) This work.

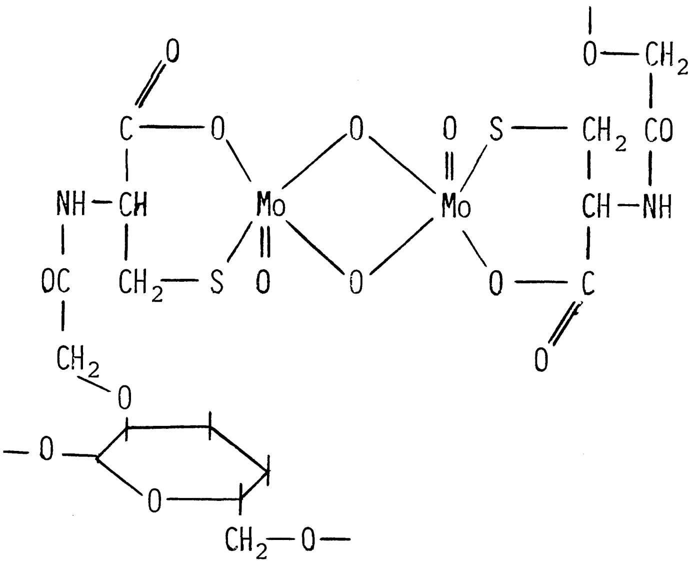
formed complexes with Mo and free cysteine moieties were not remained. The polymer-bound Mo-cysteine complex exhibited remarkably similar infrared spectrum except for the absorption of the polymer chain, which is shown in Table 1. Consequently it was demonstrated that the structures of the Mo-Cys complexes were almost similar in both cases, namely, two Mo ions formed a binuclear complex with two cysteine moieties bound to polymer. The uv absorption spectrum of dextran-bound Mo-Cys complex (λ_{max} = 305 nm) was also similar to that of the free complex (λ_{max} = 308 nm). It was reported that the free Mo-Cys complex was dissociated to the mono nuclear complex with the weak band at 580 nm in its spectrum,[4)] and the dextran-bound Mo-cys complex, however, have not any band in this region. Moreover the esr spectrum of this complex in alkaline buffer solution had no signals for the dissociated complex in the literature.[10)] These facts show that the dextran-bound Mo-Cys complex is hardly dissociated. The features of the dextran-bound Mo-Cys, such as the close similarity of infrared spectrum to that of the free complex, the complex formation of cysteine with Mo without any residues and difficulties to dissociate, might be associated with the polymer backbone of dextran which had no effect on the strains of polymer chain, but had assisted for the binuclear complex formation. It was supposed that OH groups of dextran form hydrogen bonds with other polymer chain. These hydrogen bonds might play an important role in stabilizing the complex.

Reduction of acetylene catalyzed by the dextran-bound Mo-Cys complex was carried out in pH 9.5 borate buffer solution, employing $NaBH_4$ as a reducing agent. The catalyst 80mg was dispersed in 15ml buffer solution and 20cmHg of C_2H_2 was admitted and 80mg of $NaBH_4$ was added. The volume of reaction vessel was 130ml. The products were analyzed by gas chromatography. The comparison of the catalytic activity between the free Mo-Cys complex and dextran-bound Mo-Cys complex in the reduction of C_2H_2 to C_2H_4 are shown in Table 2. The initial rate of C_2H_4 formation by the dextran-bound Mo-Cys complex was much higher than by the free complex, although it was far behind that of the nitrogenase.[4)] The products ratio of C_2H_4/C_2H_6 was 1.5 at 27°C. Its ratio was rather small compared with that in the case of free Mo-Cys complex. This behavior coincided with the result of free Mo-Cys complex that more ethane was formed in the presence of non-dissociated Mo-Cys complex.[4)] In the buffer solution of pH 7.5 H_2 evolution was only observed, no reductions of C_2H_2 taking place. Mo ion was readily released at pH 5.5. The activation energy of C_2H_4 formation was 17 kcal/mol, which was similar to nitrogenase.[4)] When temperature was raised, C_2H_6 formation increased in parallel with H_2 evolution from the decomposition of $NaBH_4$.

Table 2. Characteristics of the reduction of acetylene by nitrogenase and its model systems

	catalyst (mmol)	reducing agent	products ratio (C_2H_4/C_2H_6)	activation energy (kcal/mol)	initial rate[c)]
Nitrogenase[a)]		$Na_2S_2O_4$	10000	14	150 - 200
Mo-Cys complex[a)]	0.07	$NaBH_4$	18	13	0.048
Dextran-bound Mo-Cys complex[b)]	0.07	$NaBH_4$	2	17	1.3

a) Taken from the data in ref. 4. b) This work. c) mol/mol(catalyst)·min.



Reference

1) R.J.P. Williams, Inorg. Chem. Acta Rev., 5, 137(1971).
2) J.H. Wang, Accounts Chem. Res., 3, 90(1970).
3) C.V. Pittman, Jr. and G.O. Evans, CHEMTECH 560(1973).
4) G.N. Schrauzer and P.A. Doemeny, J. Amer. Chem. Soc., 93, 1608(1971).
5) G.N. Schrauzer, G.N. Kiefer, K. Tano, and P.A. Doemeny, ibid., 96, 641(1974).
6) M. Ichikawa and S. Meshitsuka, ibid., 95, 3411(1973).
7) M. Ichikawa, R. Sonoda, and S. Meshitsuka, Chem. Lett., 1973, 709.
8) F. Micheel and J. Ewers, Makromol. Chem., 3, 200(1949).
9) M.A. Mitz and J. Summaria, Nature, 189, 576(1961).
10) T.J. Huang and G.P. Haight, Jr., J. Amer. Chem. Soc., 92, 2336(1970).
11) K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds 2nd ed., p232, John Wiley & Sons, Inc.
12) A. Kay and P.C.H. Mitchell, Nature, 219, 267(1968).
13) L.R. Melby, Inorg. Chem., 8, 349(1969).

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