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Preparation and Crystal Structure of Binuclear Manganese(II) Complex Exhibiting Multiline ESR Signal

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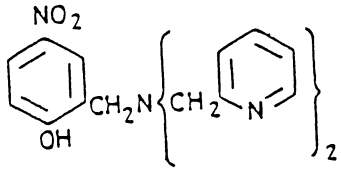
Binuclear manganese(II) complex with 2-[bis(2-pyridylmethyl)-aminomethyl]-4-nitrophenol, which exhibits a multiline ESR signal, was prepared, and its crystal structure was determined by X-ray diffraction method.

S-Adenosylmethionine synthetase(ATP:L-methionine S-Adenosyltransferase) catalyzes the formation of the sulfonium compound S-Adenosylmethionine. This reaction is unusual in that the entire tripolyphosphate chain is cleaved from the ATP molecule, and is further degraded to PP_i and P_i before the products are released.[1,2] The enzyme requires both monovalent(e.g., K^+) and divalent cations (e.g., Mg(II) and Mn(II)) for maximal activity. The enzyme·Mn(II) complex shows the six hyperfine lines in its ESR spectrum. When methionine, AMP derivative, Mn(II) and K^+ are added to the enzyme, a large number of lines appear[3] (21 peaks are distinguished at higher gain), suggesting that two manganese(II) ions are bound very close to each other. However, there is no binuclear manganese(II) complex which shows a multiline ESR signal. In this article we will report the preparation of the first manganese(II) complex exhibiting a multiline ESR signal.

The ligand, HL, 2-[bis(2-pyridylmethyl)aminomethyl]-4-nitrophenol was obtained by the published method.[4] Addition of NH_4NCS to the methanol solution of Mn(II) acetate and ligand gives yellow crystals of Mn(L)NCS.[5] The same compound was also obtained by adding NH_4NCS to the methanol solution of $Mn(CH_3COO)_3 \cdot 2H_2O$ and the ligand. The crystal used for X-ray analysis was obtained by the latter method.[6] The ORTEP drawing of the compound is shown in Fig. 1. The complex contains a centrosymmetric binuclear Mn(II) unit bridged by the phenoxide with Mn-Mn distance of 3.422 Å. The manganese ions are of a distorted octahedral geometry.



Chemical structure of HL

In Fig. 2, the ESR spectrum of Mn(L)NCS(77 K, X-band) is shown. It is clear that a multiline ESR siganl is observed in the range 250-350 mT, suggesting that the complex exists as the dimer also in solution. Average peak-to-peak separation around 300 mT is 4.2 mT, which is very close to that(4.5 mT) observed for the native enzyme.[3] It has been proposed that two metal ions may be coordinated to the phosphory group of the nucleotide in the native enzyme,[3] and preparation of such compounds is now in progress.

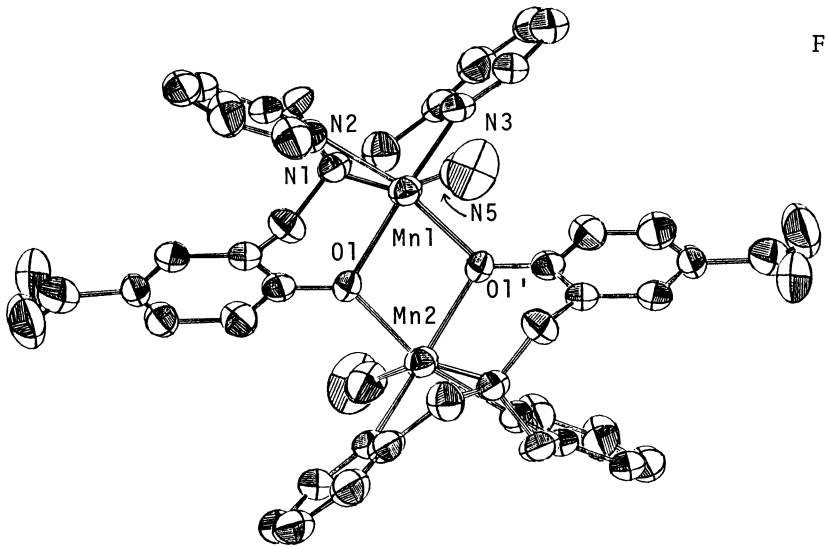


Fig. 1. ORTEP drawing of Mn(L)NCS. Selected bond distances(Å) and angles(°): Mn1-Mn2, 3.422(2); Mn1-N1, 2.354(8); Mn1-N2, 2.250(8); M1-N3, 2.269(8); Mn1-O1, 2.168(6); Mn1-O1', 2.171(6); Mn1-N5(NCS), 2.143(8). Mn1-O1-Mn2, 104.1(3); O1-Mn1-O1', 75.9(2).

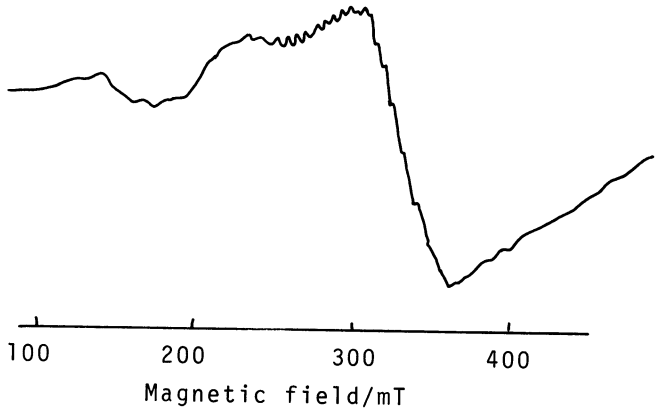


Fig. 2. ESR spectrum of Mn(L)NCS(in dmf, 77 K, X-band).

References

1) S. H. Mudd, "The Enzymes," ed by P. D. Boyer, Academic Press, New York(1973), Vol. 8.
2) G. D. Markham, E. W. Hafner, C. W. Tabor, and H. Tabor, J. Biol. Chem., 255, 9082(1980).
3) G. D. Markham, J. Biol. Chem., 256, 1903(1981).
4) Y. Nishida, H. Shimo, and S. Kida, J. Chem. Soc., Chem. Commun., 1984, 1611.
5) Analytical data: Found; C, 51.53; H, 3.80; N, 15.51; Mn, 12.0%. Calcd for $MnC_{20}H_{17}N_5O_3S$: C, 51.95; H, 3.71; N, 15.15; Mn, 11.88%.
6) Crystal data: MW=462.4, monoclinic space group $P2_1/n$, a=12.338(5), b=16.929(10), c=10.010(4) Å, β=97.83(3)°, T=294 K. The structure was solved by direct method, and refined by block-diagonal least-squares. A total of 3706 reflections with $Fo > 3\sigma(Fo)$ were refined to a conventional value of R=0.082.

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