

## 二核遷移金属錯体の設計・開発による低分子の活性化状態および磁氣的相互作用の研究

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# 1989 Fiscal Year Final Research Report Summary

## Studies on the Preparation of Dinuclear Transition Metal Complexes, and the Activation-states of Small Molecules and the Magnetic Interactions involved therein

Research Project

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無機・錯塩・放射化学

### Research Institution

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### Research Abstract

(1) Dinuclear Iron Complexes: dinuclear mixed-valence iron(II,III) centers have been known to be involved in the iron proteins such as semi-methemerythrin and pink uteroferrin. We designed two new dinucleating ligands, 2,6- bis[bis(2-pyridylmethyl and 2-benzimidazolylmethyl)aminomethyl]-4-methylphenol, which have bilaterally bisymmetric structures. The dinuclear iron(II,II), (II,III) and (III,III) complexes containing the above ligands and carboxylate ions

were newly prepared. From the results of electronic, ESR and Mossbauer spectra, and magnetic susceptibilities, it was found that (1) the iron(II,III) complex is much more stabilized than the iron(II,II) and (III,III) complexes; (2) the iron(II,III) complex belongs to the so-called Class II mixed-valence complex; and (3) a weak antiferromagnetic interaction it exerted between the two iron ions.

(2) Dinuclear and Tetranuclear Manganese Complexes: the dinuclear and tetranuclear manganese centers in photosystem II (PS II) in green plants have been shown to play an essential role for the catalytic oxidation of water to molecular oxygen ( $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ ). We newly prepared the dinuclear manganese(II,II), (II,III), (III,IV), and (IV,IV) complexes with 2,6-bis[bis(2-pyridylmethyl)aminomethyl]-4-methylphenol and the tetranuclear manganese(II,III,III,II) complexes with tris(2-pyridylmethyl)amine (N<sub>4</sub>-py).















The structures of the complexes were clarified by means of X-ray crystallography. Among these complexes, the N<sub>4</sub>-py complex showed the sign of possibility of the catalytic oxidation of water, but we have not yet obtained good enough evidences. The study in this category has great potentialities for future development.

(3) We succeeded in isolating the dinuclear cobalt(II,II) complexes which bind reversibly molecular oxygen. A weak antiferromagnetic interaction was recognized in the dinuclear chromium(III,III) complexes which contain a linear cyanide ion as the bridging ligand.

## Research Products (16 results)

All Other

All Publications (16 results)

- [Publications] M.Suzuki,H.Oshio,A.Uehara,K.Endo,M.Yanaga,S.Kida,and K.Saito: "Syntheses and Characterization of Dinuclear High-Spin Iron(II,III)and(III,III)Complexes with 2,6-Bis[bis(2-benzimidazolylmethyl)-aminomethyl]-4-methylphenolate(1-)." Bull.Chem.Soc.Jpn. 61. 3907-3913 (1988) 
- [Publications] M.Suzuki,H.Senda,Y.Kobayashi,H.Oshio,and A.Uehara: "Synthesis and Characterization of the Di(μ-oxo)Dimanganese(III,IV)Complexes with Carboxylate Groups as a Terminal Ligand." Chem.Lett.1763-1766 (1988) 
- [Publications] M.Kaneda,M.Suzuki,and A.Uehara: "Thermal Reactions of Metal Complexes under Quasi-isothermal and -isobaric Conditions.5.Thermal Behavior of Molybdenum(O)Dinitrogen Complexes in the Solid State." Thermochem.Acta. 138. 161-166 (1989) 
- [Publications] M.Johda,M.Suzuki,and A.Uehara: "Preparation of μ-Cyano Dinuclear Chromium(III)Complexes  $\text{M}^{\text{I}}[\text{F}(\text{en or tn})_2\text{Cr}(\text{CN})\text{Cr}(\text{CN})_5]$  from the Doubly Complexed Salts of the Form  $\text{M}^{\text{I}}[\text{CrF}(\text{H}_2\text{O})(\text{en or tn})_2][\text{Cr}(\text{CN})_6]$ ." Bull.Chem.Soc.Jpn.62. 738-744 (1989) 
- [Publications] M.Suzuki,T.Sugisawa,H.Senda,H.Oshio,and A.Uehara: "Synthesis and Characterization of a Novel Tetranuclear Manganese(II,III,III,II) Mixed Valence Complex." Chem.Lett.1091-1094 (1989) 
- [Publications] M.Suzuki,T.Sugisawa,and A.Uehara: "Dinuclear Cobalt(II) Complexes Containing 1,3-(or 1,5-)Bis[bis(2-pyridylmethyl)amino]-2-propanolate(or -3-pentanolate): Preparation and Reaction with Molecular Oxygen." Bull.Chem.Soc.Jpn.(in press). 63. (1990) 
- [Publications] M. Suzuki, A. Uehara, H. Oshio, M. Yanaga, S. Kida, and K. Saito.: "Syntheses and Characterization of Dinuclear Iron(II, II) and Iron(II, III) Complexes with a Dinucleating Ligand, 2,6-Bis[bis(2-pyridylmethyl)aminomethyl]-4-methylphenolate(1)" Bull. Chem. Soc. Jpn., 60, 3547-3555 (1987). 
- [Publications] M. Suzuki, M. Mikuriya, S. Murata, A. Uehara, H. Oshio, S. Kida, and K. Saito.: "Syntheses and Characterization of Dinuclear Manganese(II, II) and Manganese(II, III) Complexes with Phenolate and Two Carboxylate Bridges." Bull. Chem. Soc. Jpn., 60, 4305-4312 (1987). 
- [Publications] M. Suzuki, S. Tokura, M. Suhara, and A. Uehara.: "Dinuclear Manganese(III, IV) and Manganese(IV, IV) Complexes with Tris(2-pyridylmethyl)amine." Chem. Lett., 1988, 477-480. 
- [Publications] M. Fushimi, M. Suzuki, and A. Uehara.: "Thermal cis-trans Isomerization of Dihalogenobis[trialkyl(of aryl)phosphine]-platinum(II) in the Solid State." Bull. Chem. Soc. Jpn., 61, 1809-1811 (1988). 
- [Publications] M. Suzuki, H. Oshio, A. Uehara, K. Endo, M. Yanaga, S. Kida, and K. Saito.: "Syntheses and Characterization of Dinuclear High-Spin Iron(II, III) and (III, III) Complexes with 2,6-Bis[bis(2-benzimidazolylmethyl)aminomethyl]-4-methylphenolate(1-)." Bull. Chem. Soc. Jpn., 61, 3907-3913 (1988). 
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[Publications] M. Suzuki, T. Sugisawa, H. Senda, H. Oshio, and A. Uehara.: "Synthesis and Characterization of a Novel Tetranuclear Manganese(II, III, III, II) Mixed Valence Complex." Chem. Lett., 1989, 1091-1094. ▼

[Publications] M. Suzuki, T. Sugisawa, and A. Uehara.: "Dinuclear Cobalt(II) Complexes Containing 1,3-(or 1,5-)Bis[bis(2-pyridylmethyl)amino]-2-propanolato (or -3-pentanolato): Preparation and Reaction with Molecular Oxygen." Bull. Chem. Soc. Jpn., (1990). ▼

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