CHEMISTRY LETTERS, pp. 1185-1188, 1994.

Preparation of Oxo-Bridged Dinuclear Iron(III) Complexes with One or Two O,O'-Bridged Optically Active Amino Acids

Yoichi SASAKI,* Keisuke UMAKOSHI, Shuji KIMURA, Chang-Eon OH,[††]
Mikio YAMAZAKI,[†] and Takashi SHIBAHARA[†]
Department of Chemistry, Faculty of Science, Hokkaido University, Kita-ku, Sapporo 060
[†] Department of Chemistry, Faculty of Science, Okayama University of Science, Ridai-Cho, Okayama 588

Amino-acid bridged diiron complexes, $[Fe_2(\mu\text{-}O)(\mu\text{-}L)_2(tacn)_2]^{4+}$ (tacn = 1,4,7-triazacyclononane; L = (*S*)-valine or (*S*)-proline) and $[Fe_2(\mu\text{-}O)(\mu\text{-}L)(tpa)_2]^{4+}$ (tpa = tris(2-pyridylmethyl)amine; L = (*S*)-valine, (*S*)-proline, or (*S*)-alanine) have been prepared. Crystal structures of the two tacn complexes were determined. Electronic absorption spectra and redox properties of these complexes are similar to the corresponding μ-acetate complexes.

X-Ray structural study of the azidomethemerythrin and methemerythrin disclosed the existence of the μ-oxo-di-μ-carboxylato-diiron unit in the active center.1-3) Similar structural unit but one μ-carboxylate bridge was also found in the active center of the ribonucleotide reductase by the X-ray structural determination.4) Many structural model compounds of these binuclear iron centers have been reported,5-15) but, in spite of the fact that the bridging carboxylate groups are provided by the optically active amino acid residue of the surrounding proteins, no model compounds with bridging amino acids have ever been prepared. We wish to report here new dinuclear Fe(III) structural model compounds with μ-O,O'-bridging amino acids (as zwitter ionic forms) for both types of the metallo enzymes. Very recently, Tokii and coworkers reported a highly relevant hexairon(III) complexes, $[Fe_6(O)_4(OH)_2(\text{amino-acid})_4(phen)_8]^{9+}$ (amino acid = β-alanine or glycylglycine; phen = 1,10-phenanthroline), in which a μ-hydroxo analog of amino-acid bridged structural model of hemerythrin active center, $Fe_2(\mu\text{-}OH)(\mu\text{-amino-acid})_2(phen)_2$, is found as a structural unit.16)

Newly prepared complexes are $[Fe_2(\mu\text{-}O)(\mu\text{-amino-acid})_2(tacn)_2]^{4+}$ (tacn = 1,4,7-triazacyclononane; amino

---

[††] On leave from the Department of Chemistry, Yengnam University, Gyongsam, Korea, in 1992-1993.

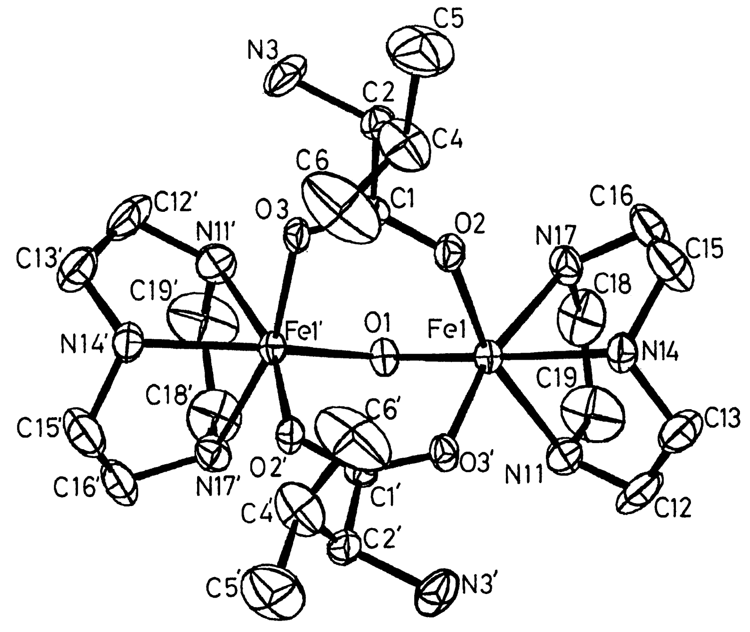

Fig. 1. Molecular structure of **1a**. Selected bond distances (Å) and angles (°): Fe(1)··· Fe(1') 3.115(2), Fe(1)-O(1) 1.787(3), Fe(1)-O(2) 2.044(4), Fe(1)-O(3') 2.073(4), Fe(1)-N(11) 2.160(6), Fe(1)-N(14) 2.176(6), Fe(1)-N(17) 2.132(6), Fe(1)-O(1)-Fe(1') 121.2(3).

acid = (*S*)-valine (**1a**) or (*S*)-proline (**1b**)) and $[Fe_2(\mu\text{-}O)(\mu\text{-amino-acid})(tpa)_2]^{4+}$ (tpa = tris(2-pyridylmethyl)amine; amino acid = (*S*)-valine (**2a**), (*S*)-proline (**2b**), or (*S*)-alanine (**2c**)). Preparation of these complexes is straight forward. The complex cations **1a** and **1b** were obtained by adding $FeCl_3$(tacn) (100 mg) to an aqueous solution of (*S*)-valine (900 mg/20 mL) and (*S*)-proline (500 mg/10 mL), respectively, at 50 °C. Subsequent addition of KPF_6 or NaI gave crystals of the corresponding salts. The perchlorate salts of **2** were obtained by adding amino acids (0.5 mmol/4 mL) to a methanol solution (10 mL) containing $Fe(ClO_4)_3 \cdot 10H_2O$ (1 mmol) and tpa (1 mmol).

Structures of $[\mathbf{1a}](PF_6)_4 \cdot 4H_2O$ and $[\mathbf{1b}]I_4 \cdot H_2O$ were determined by the X-ray crystallography.[17,18) Figure 1 shows the ORTEP drawing of the complex cation **1a**. The O(1) atom in both complex cations lies on a crystallographically imposed two-fold axis perpendicular to the Fe(1)··· Fe(1') axis. Structural characteristics of **1b** (Fe··· Fe, 3.101(5) Å; Fe-O-Fe, 120(1) °) are very similar to those of **1a** (Fe··· Fe, 3.115(2) Å; Fe-O-Fe, 121.2(3)°), and to those of the corresponding acetate-bridged complex, $[Fe_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2(tacn)_2]^{2+}$ (Fe··· Fe, 3.063(2) Å; Fe-O-Fe, 118.7(4) °).19) Preliminary structural determination of **2a** and **2b** disclosed similar structures to $[Fe_2(\mu\text{-}O)(\mu\text{-}CH_3COO)(tpa)_2]^{3+}$ with asymmetric coordination geometry of the two tpa ligands.5)

Electronic absorption spectral characteristics of the two types of complexes in acetonitrile are very similar to each other and to those of corresponding acetate analogs.[20)] Circular dichroism spectra show weak features corresponding to the absorption bands and confirm that the structure with coordinated optically active amino acids is retained in solution. The di-μ-amino-acid complexes showed an irreversible reduction wave at around -0.7 V vs Ag/Ag^+ in acetonitrile. The reduction potential shifted to positive direction by ca. 0.4 V as compared with corresponding acetate-bridged complex.[21)] The trend is consistent with the observation of a linear correlation between the redox potentials and the basicities of the bridging ligands for the series of μ_3-oxo trinuclear Fe(III) complexes with bridging amino-acids and carboxylates (the corresponding difference in the redox potentials is ca. 0.45 V).[22)]

This work was supported by a Grant-in-Aid for Scientific Research (No. 05225201) on Priority Area of "New Development of Organic Electrochemistry" and a Grant-in Aid for Scientific Research (No. 05403008) from the Ministry of Education, Science, and Culture, Japan. We are grateful to a research grant from Suhara Memorial Foundation. We thank professor K. Wieghardt of Ruhr University, Germany, for kindly providing us with a sample of tacn.

References

1) R. E. Stemcamp, L. C. Siecker, and L. H. Jensen, *Nature*, **291**, 263 (1981).
2) R. E. Stemcamp, L. C. Siecker, and L. H. Jensen, *Acta Crystallogr., Sect. B, Struct. Sci. Cryst. Struct. Chem.*, **B39**, 697 (1983).
3) R. E. Stemcamp, L. C. Siecker, and L. H. Jensen, *J. Am. Chem. Soc.*, **106**, 618 (1984).
4) P. Nordlund, B.-M. Sjoberg, and H. Eklund, *Nature*, **345**, 593 (1990).
5) L. Que, Jr. and A. E. True, *Progr. Inorg. Chem.*, **38**, 98 (1990).
6) S.-H. Cho, D. Whang, K.-N. Han, and K. Kim, *Inorg. Chem.*, **31**, 519 (1991).
7) K. J. Oberhausen, J. F. Richardson, R. J. O'Brien, R. Buchanan M,, J. K. McCusker, R. J. Webb, and D. N. Hendrickson, *Inorg. Chem.*, **31**, 1123 (1992).
8) R. H. Beer and S. J. Lippard, *Inorg. Chem.*, **32**, 1030 (1993).
9) S. Yan, D. D. Cox, L. L. Pearce, C. Juarez-Garcia, L. Que, Jr., J. H. Zhang, and C. J. O'Connor, *Inorg. Chem.*, **28**, 2507 (1989).
10) R. E. Norman, S. Yan, L. Que, Jr., G. Backes, J. Ling, J. Sanders-Loehr, J. H. Zhang, and C. J. O'Connor, *J. Am. Chem. Soc.*, **112**, 1554 (1990).
11) S. Menage and L. Que, Jr., *New. J. Chem.*, **15**, 431 (1991).
12) H. G. Jang, M. P. Hendrich, and L. Que, Jr., *Inorg. Chem.*, **32**, 911 (1993).

13) Y. Dong, S. Menage, B. A. Brennan, T. E. Elgren, H. G. Jang, L. L. Pearce, and L. Que, Jr., *J. Am. Chem. Soc.*, **115**, 1851 (1993).

14) B. Mauerer, J. Crane, J. Schuler, K. Wieghardt, and B. Nuber, *Angew. Chem., Int. Ed. Engl.*, **32**, 289 (1993).

15) R. C. Holz, T. E. Elgren, L. L. Pearce, J. H. Zhang, C. J. O'Connor, and L. Que, Jr., *Inorg. Chem.*, **32**, 5844 (1993).

16) T. Tokii, K. Ide, M. Nakashima, and M. Koikawa, *Chem. Lett.*, **1994**, 441.

17) Crystal data for $[\mathbf{1a}](PF_6)_4{\cdot}4H_2O$: $C_{22}H_{60}F_{24}Fe_2N_8O_9P_4$, FW=1272.32, orthorhombic, space group $P2_12_12$, $a = 11.932(2)$ Å, $b = 19.468(4)$ Å, $c = 11.091(2)$ Å, $V = 2576.2(6)$ Å^3, $Z = 2$, $d_{calcd} = 1.64$ g cm^{-3}. The structure was solved by direct method using SHELXS-86.[23] Full matrix least-squares refinement yielded the final R value of 0.071 ($R_w = 0.086$) for 2094 independent reflections with $|F_o| \geq 6\sigma|F_o|$ measured on a Mac Science MXC18 diffractometer up to $2\theta = 50°$ (Mo Kα radiation, $\lambda = 0.71073$ Å).

18) Crystal data for $[\mathbf{1b}]I_4 \cdot H_2O$: $C_{22}H_{52}Fe_2I_4N_8O_6$, FW=1144.02, monoclinic, space group $I2$; $a = 16.831(1)$ Å, $b = 10.658(2)$ Å, $c = 14.487(2)$ Å, $\beta = 95.71(1)°$, $V = 2586.0(6)$ Å^3, $Z = 2$, $d_{calcd} = 1.47$ g cm^{-3}. The structure was solved by heavy atom method using UNICS III.[24] The final R value was 0.077 ($R_w = 0.090$) for 1749 reflections with $|F_o| \geq 3\sigma|F_o|$ measured on a RIGAKU AFC-5R diffractometer up to $2\theta = 55°$ (Mo Kα radiation, $\lambda = 0.71073$ Å).

19) A. Spool, I. D. Williams, and S. J. Lippard, *Inorg. Chem.*, **24**, 2156 (1985).

20) Electronic absorption data in acetonitrile: λ_{max}/nm (ε_{max}/mol^{-1}dm^{3}cm^{-1} per dimer), **1a**; 772 (140), 556 sh, 516 sh, 477 (1330), 426 sh, 378 sh, 334 (8660). **1b**; 772 (134), 561 sh, 519 sh, 477 (1250), 381 sh, 331 (8050), 292 (6490). **2a**; 694 (146), 503 sh, 489 (1027), 459 (1193).

21) In the case of the mono-μ-amino-acid complexes, **2a**, **2b**, and **2c**, an irreversible reduction wave was observed at -0.41 V vs Ag/$AgNO_3$ in the presence of equi-molar of 2,4,6-trimethylpyridine, more positive by ca. 0.03 V than that of the mono-μ-acetato complex. The reduction wave was observed at -0.2 V in the presence of equi-molar of *para*-toluenesulfonic acid. In the absence of both 2,4,6-trimethylpyridine and *para*-toluenesulfonic acid, splitted reduction wave was observed for all the three complexes at around -0.2 and -0.4 V.

22) K. Nakata, A. Nagasawa, Y. Sasaki, and T. Ito, *Chem. Lett.*, **1989**, 753.

23) G. M. Sheldrick, **SHELXS-86**, A computer program for crystal structure determination. University of Göttingen, Federal Republic of Germany, 1986.

24) T. Sakurai and K. Kobayashi, *Rikagaku Kenkyuusho Hokoku (Rep. Inst. Phys. Chem. Res.)*, **55**, 69 (1979).

(Received April 8, 1994)