Intramolecular NH···S Hydrogen Bond in *o*-Acylamino Substituted Benzenethiolate Iron(II) and Cobalt(II) Complexes

Norikazu Ueyama, Taka-aki Okamura and Akira Nakamura*

Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

The crystal structures of $(NEt_4)_2[Fe^{II}(o\text{-pabt})_4]$ (*o*-pabt = *o*-pivaloylaminobenzenethiolato) and $(NEt_4)_2[Co^{II}(o\text{-pabt})_4]$ show the presence of NH···S hydrogen bonds which contribute to the positive shift of redox potential and the through-bonding isotropic-contact shift.

The presence of NH···S hydrogen bonds in the metal centre of metalloproteins, *e.g.* rubredoxin,[1] plant-type ferredoxin,[2] bacterial ferrodoxin[3] and high potential iron protein,[4] has been proposed on the basis of crystallographic analyses and Raman spectroscopy. We have demonstrated that the hydrogen bonding in a ferredoxin model complex contributes to the positive shift of redox potential in low dielectric solvents. A rubredoxin model complex, $[Fe^{II}(\text{Z-Cys-Pro-Leu-Cys-Gly-Val-OMe})_2]^{2-}$, exhibits the highly contact-shifted ^2H NMR signals of an amide group in the region of δ 50 to −20.[5] The observed contact shifts of these signals provide direct evidence for the NH···S hydrogen bonding as shown in Fig. 1(*a*). However, there is still a possibility that the dipolar shift of the amide NH groups by Fe^{II} ions contributes to the large up- or down-field shift of the N^2H signals in the ^2H NMR spectrum since most of the NH groups direct towards the Fe^{II} ions. Here novel simple model Fe^{II} and Co^{II} complexes were synthesized using *o*-acylamino substituted benzenethiolate ligands that were designed to have an intramolecular NH···S hydrogen bond as illustrated in Fig. 1(*b*). Recently, simple model complexes of rubredoxin were used to demonstrate the presence of NH···S hydrogen bonds between thiolate anions and amide cations in the solid state for $[Me_3NCH_2-CONH_2]_2[Co^{II}(SPh)_4]$.[6]

This paper reports the presence and chemical properties of NH···S hydrogen bonds in $(NEt_4)_2[Fe^{II}(o\text{-pabt})_4]$ (*o*-pabt = *o*-pivaloylaminobenzenethiolato) **1** and $(NEt_4)_2[Co^{II}(o\text{-}$

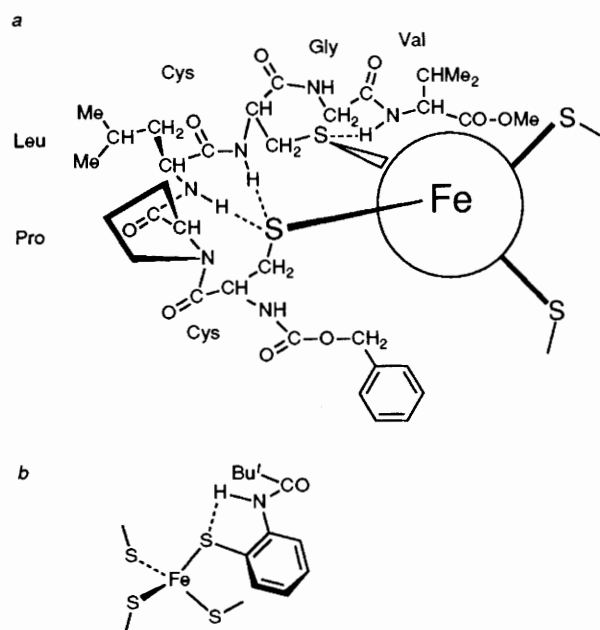**Fig. 1** (*a*) Proposed NH—S hydrogen bonds in $[Fe^{II}(\text{Z-Cys-Pro-Leu-Cys-Gly-Val-OMe})_2]^{2-}$. (*b*) Designed NH···S hydrogen bonds in *o*-acylamino substituted benzenethiolate complex.
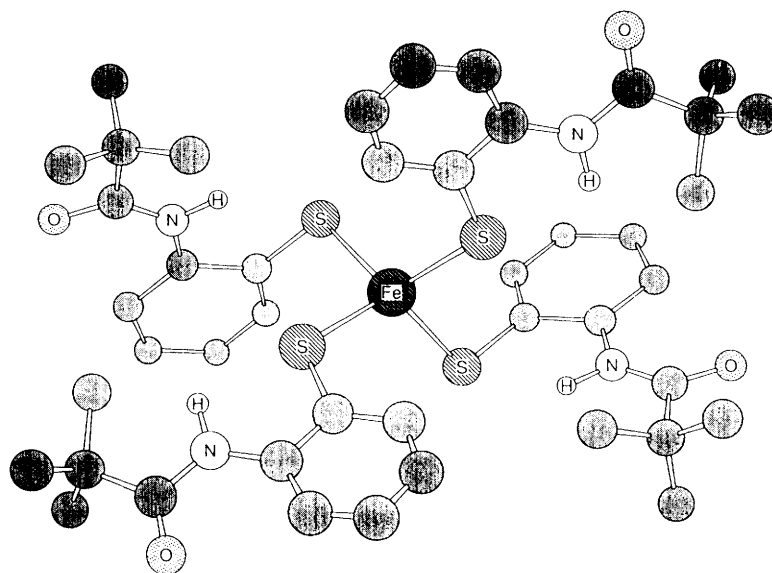
Fig. 2 Molecular structure of **1** viewed down along the C_2 axis

pabt)$_4$] **2** which were synthesized by the reaction of bis(*o*-pivaloylaminobenzene) disulfide, (NEt$_4$)BH$_4$ and (NEt$_4$)$_2$-[M^{II}Cl$_4$] (M^{II} = Fe^{II}, Co^{II}) in 1,2-dimethoxyethane.† Compounds **1** and **2** have a T_d structure of the MS$_4$ core with a relatively short Fe–S (mean 2.329 Å) and Co–S (mean 2.296 Å),‡ compared with those (means 2.353 and 2.329 Å) of [M(SPh)$_4$]$^{2-}$ (M = Fe^{II}) and Co^{II} reported,[7] respectively. Fig. 2 shows the molecular structure of **1**. Location of all NH groups close to the sulfur atom indicates the presence of NH$\cdots$S hydrogen bonds. The IR spectrum of **2** in the solid state indicates an NH band at 3281 cm^{-1} and a free C=O stretching at 1667 cm^{-1} due to the formation of NH$\cdots$S hydrogen bonds.

The isotropic ^{1}H NMR shifts§ of amide NH in **1** and **2** are observed at $(\Delta H/H_o)^{iso}$ = −15.0 and −12.9 ppm, respectively, in [^{2}H$_3$]acetonitrile at 30 °C. On the other hand, the cobalt(II) *p*-pivaloylaminobenzenethiolate complex, (NEt$_4$)$_2$[Co^{II}(*p*-pabt)$_4$] **3**, exhibits an NH ^{1}H NMR signal at $(\Delta H/H_o)^{iso}$ = 5.3 ppm. *o*-Methylbenzenethiolate cobalt(II) complex, (NEt$_4$)$_2$[Co^{II}(*o*-methylbenzenethiolato)$_4$] **4**, shows a methyl ^{1}H NMR signal at $(\Delta H/H_o)^{iso}$ = 24.5 ppm under the same conditions. The down-field shift of the amide NH signal of the *p*-acylamino substituted complex, **3**, exhibits the same sign of the isotropic shift due mainly to the Fermi contact by the conjugated benzene double bonds. However, the opposite sign in the up-field shift of the amide NH protons of **1** and **2** is

clearly ascribed to the isotropic shift through the NH$\cdots$S hydrogen bond. The results strongly suggest that the contribution of the dipolar shift is not significant in the substituted benzenethiolate Fe^{II} and Co^{II} complexes. The positive sign of the isotropic shift in **4**, although the protons locate at similar position to those of the acylamino of **1** and **2**, indicates that the Fermi contact predominantly contributes to the down-field shift in the same trend as that of the *p*-substituted benzenethiolate complex, **3**.

The positive-shifted redox potential [−0.29 V *vs.* SCE (SCE = saturated calomel electrode)] for **1** was found in acetonitrile compared with that (−0.53 V *vs.* SCE) of [Fe^{II}(SPh)$_4$]$^{2-}$.[8] The shift is ascribed to the NH$\cdots$S hydrogen bonding as concluded from the data of the peptide model complexes.[5]

Thus, the contribution of the NH$\cdots$S hydrogen bond to both the positive shift of redox potential and the isotropic-contact shift through the hydrogen bond has been demonstrated by the novel simple thiolate model complexes having an *o*-acylamino substituted benzenethiolate ligand.

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† All of the complexes showed satisfactory microanalyses.

‡ *Crystal data* for **1**: C$_{66}$H$_{106}$N$_8$O$_4$S$_4$Fe, M = 1259.70, tetragonal, space group $P4_12_12$, a = 14.477(5), c = 35.221(4) Å, V = 7381(5) Å^3, Z = 4, D_c = 1.133 g cm^{-3}, F(000) = 2720, μ(Mo-Kα) = 3.57 cm^{-1}, R = 0.077 (R_w = 0.076) using 1094 observed data [I>3σ(I)].

For **2**: C$_{66}$H$_{106}$N$_8$O$_4$S$_4$Co, M = 1262.79, tetragonal, space group $P4_12_12$, a = 14.475(8), c = 35.14(1) Å, V = 7363(8) Å^3, Z = 4, D_c = 1.139 g cm^{-3}, F(000) = 2724, μ(Mo-Kα) = 3.86 cm^{-1}, R = 0.077 (R_w = 0.089) using 1925 observed data [I>3σ(I)].

Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ Isotropic shift is defined as $(\Delta H/H_o)^{iso}$ = $(\Delta H/H_o)^{obsd}$ − $(\Delta H/H_o)^{dia}$. Diamagnetic reference is disulfide for **1, 2** or free thiol for **3, 4**.

References

1 K. D. Watenpaugh, L. C. Sieker and L. H. Jensen, *J. Mol. Biol.*, 1979, **131**, 509.

2 T. Tsukihara, K. Fukuyama, M. Nakamura, Y. Katsube, N. Tanaka, M. Kakudo, T. Hase, K. Wada and H. Matsubara, *J. Biochem.*, 1981, **90**, 1763.

3 E. Adman, K. D. Watenpaugh and L. H. Jensen, *Proc. Natl. Acad. Sci. USA*, 1975, **72**, 4854.

4 C. W. Carter, *J. Biol. Chem.*, 1977, **252**, 7802.

5 W.-Y. Sun, N. Ueyama and A. Nakamura, *Inorg. Chem.*, 1991, **30**, 4027.

6 M. A. Walters, J. C. Dewan, C. Min and S. Pinto, *Inorg. Chem.*, 1991, **30**, 2656.

7 D. Coucouvanis, D. Swenson, N. C. Baunziger, C. Murphy, D. G. Holah, N. Sfarnas, A. Simopoulos and A. Kostikas, *J. Am. Chem. Soc.*, 1981, **103**, 3350.

8 K. S. Hagen, J. G. Reynolds and R. H. Holm, *J. Am. Chem. Soc.*, 1981, **103**, 4054.