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# Evidence for Charge−Dipole Effects in the Rubredoxin Model Compound $[(CH_3)_4N]_2Fe[SCH_2CON(CH_3)_2]_4$

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## Introduction

The role of hydrogen bonds in determining the electronic structure and redox properties of iron−sulfur (Fe−S) proteins has been a topic of much speculation.[1−16] In spite of an invariance in both metal ligation and hydrogen-bonding geometry at the active site, the $Fe_4S_4$ ferredoxins differ greatly in their redox potentials.[2] Similar observations have been made for other classes of iron−sulfur proteins. The focus has therefore shifted away from hydrogen-bonding effects. Recent reports on computational results suggest that redox potential variations may be explained by simple noncovalent electrostatic interactions, with hydrogen bonding as only one of several factors.[17,18] This view is supported by spectroscopic and electrochemical data from our laboratory, acquired on a series of molybdenum complexes, $[TpMo(NO)(SCH_2R)_2]$, where R $= CH_3$, $CONHCH_3$, $CON(CH_3)_2$, $(CH_2)_2CH_3$, $CH_2CONHCH_3$, and $CH_2CON(CH_3)_2$.[19]

Numerous studies of charge−dipole (C−D) interactions in organic compounds have provided accurate models of reactivity in polar molecules.[20−22] Analogous studies of metal complexes would be helpful in explaining trends in the redox potentials of electron transfer proteins, but such approaches have been few. The work described here is designed to examine the C−D influence of a non-hydrogen bonding amide on the redox potential of a model compound of the rubredoxin (Rd) active site. The active site and models thereof consist of a single iron atom coordinated by four thiolate sulfur atoms in approximately tetrahedral geometry.[3] As part of this work we have synthesized the tetrahedral complex anion $[Fe\{SCH_2CON(CH_3)_2\}_4]^{2-}$ (**1**), whose redox potential we compare with those of two other iron alkanethiolate model compounds, $[Fe(SC_2H_5)_4]^{2-}$ (**2**) and $[Fe(S_2\text{-}o\text{-}xyl)_2]^{2-}$ (**3**).[23,24] In order to correlate the redox potentials of complexes **1**−**3** with familiar and easily measurable ligand properties, we undertook studies of the ligand p$K_a$ values and the carbonyl frequencies of the corresponding thiol ester ($SCOCH_3$) derivatives. Our experimental approach was designed to test the hypothesis that ligand p$K_a$ values, thiol ester bond order, and the redox potentials of complexes **1**−**3** would be determined by a C−D field effect which we expected to predominate over the competing influence of induction through $\sigma$ bonds.

The synthesis and isolation of iron(II,III) alkanethiolate complexes is challenging because of the tendency of the complexes to form oligomers.[25] Benzenethiolate metal complexes,[26−29] by contrast, are relatively stable, but the benzenethiolate ligand is a poor cysteine analog because of conjugation between sulfur and the phenyl ring. Moreover, ring substituents exert a $\pi$-inductive effect on sulfur.[20,26] In order to avoid this $\pi$-induction we limited our study to alkanethiolate complexes.

## Experimental Section

All syntheses were carried out under an inert atmosphere. Compounds **2** and **3** were synthesized by standard methods.[23,24]

For the synthesis of $[(CH_3)_4N]_2Fe[SCH_2CON(CH_3)_2]_4$, (**1**), tetramethylammonium chloride, $(CH_3)_4NCl$, (1.32 g, 12.1 mmol) and sodium *N*,*N*-dimethylmercaptoacetamide, $NaSCH_2CON(CH_3)_2$ (1.65 g, 14.0 mmol) were combined in absolute EtOH (50 mL) and the mixture was stirred for 1 h. The solvent was removed under vacuum, and $CH_3CN$ (80 mL) was added, forming a slurry, to which anhydrous $FeBr_2$ (0.47 g, 2.18 mmol) was added. The resulting light yellow-brown solution was stirred overnight, filtered, and concentrated under vacuum to a volume of about 20 mL. Ether (10 mL) was added, and the solution temperature was lowered and maintained at −20 °C for several days, resulting in the formation of needle-shaped, off-white crystals. These were collected by filtration and washed with a cold solution of 1:1 $CH_3CN/Et_2O$ (yield: 1.30 g, 88%).

The thioacetate compounds were synthesized from their corresponding halides by reaction with thiolacetic acid.[19] 2-(*N*,*N*-Dimethylamino)-2-oxoethyl thioacetate, $(CH_3)COSCH_2CON(CH_3)_2$, was obtained from

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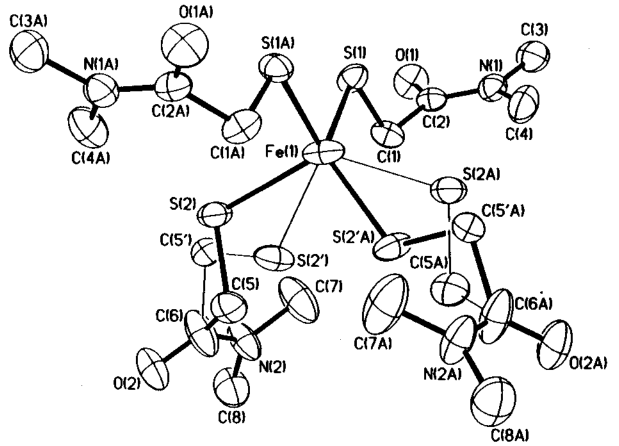

**Figure 1.** ORTEP diagram of complex **1** showing 30% probability ellipsoids. The S(2)-thiolate arm is equally disordered over two positions.

**Table 1.** Crystallographic Data for $[(CH_3)_4N]_2Fe[SCH_2CON(CH_3)_2]_4$ (**1**)

| | |
|---|---|
| empirical formula | $C_{20}H_{44}FeN_5O_4S_4$ |
| formula wt | 602.7 |
| space group | $C2/c$ |
| $a$, Å | 18.329(2) |
| $b$, Å | 18.538(2) |
| $c$, Å | 11.066(1) |
| $\beta$, deg | 101.53(1) |
| $V$, Å$^3$ | 3684.3(7) |
| $Z$ | 4 |
| $T$, K | 296 |
| $\rho_{calcd}$, g cm$^{-3}$ | 1.087 |
| $\mu$, cm$^{-1}$ | 6.63 |
| $R(F)$ (obs data), % | 5.56 |
| $R_w(F)$ (all data), % | 10.09 |

*N,N*-dimethylchloroacetamide (yield: 65%); benzyl thioacetate, $(CH_3)COSCH_2C_6H_5$, from benzyl chloride (yield: 78%); and butyl thioacetate, $(CH_3)COSC_4H_9$, from bromobutane (yield: 70%).

For chemical and X-ray analysis, crystals of **1** were obtained by the dissolution of the sample in a minimum amount of warm $CH_3CN$, followed by filtration and the gradual cooling of the filtrate to −20 °C. After several days, the resulting crystals were collected by filtration and washed with a cold solution of 1:1 $CH_3CN$/THF. Anal. Calcd for $C_{24}H_{56}FeN_6O_4S_4\cdot 0.5CH_3CN$: C, 43.06; H, 8.31; N, 13.05. Found: C, 43.49; H, 8.78; N, 12.71. IR (cm$^{-1}$) (KBr): 1621.5 (CO). $^1$H-NMR (ppm) ($CD_3CN$): 2.84 $[(CH_3)_4N]^+$, 6.99 $[N(CH_3)_2]$, 215.5 ($-CH_2-$).

Data on p$K_a$ values were obtained by the method of Kurz.[30] All solutions were handled under a nitrogen atmosphere at room temperature. The following absorption bands were observed: $HSCH_2CON(CH_3)_2$, $\lambda_{max} = 204$ nm, $[SCH_2CON(CH_3)_2]^-$, $\lambda_{max} = 244$ nm. The optical densities of the conjugate base ($OD_A$), the undissociated acid ($OD_{HA}$), and the solution (OD) were measured at pH 10.00, 1.00, and 8.13, respectively. The total concentration $C = [HA] + [A^-]$ was constant. The p$K_a$ of $HSCH_2N(CH_3)_2$ was estimated by means of the formula $pK_a = pH + \log[(OD_A - OD)/(OD - OD_{HA})]$.

Crystallographic data for **1** are listed in Table 1. The S(2)-thiolate arm was found to be disordered over two positions as shown in Figure 1. The refined occupancies of the two orientations are equal within their esd's. The asymmetric unit consists of one $Me_4N^+$ cation and half of the Fe complex, which is situated on a crystallographic 2-fold axis. With all non-hydrogen atoms anisotropic and all hydrogen atoms idealized, $R(F) = 5.56\%$ for the observed data. The acentric space group *Cc* was considered for **1** but was rejected in favor of the *C*2/*c* space group. Attempted refinements in using the *Cc* space group produced a high correlation between the two independent molecules, whereas refinement using the *C*2/*c* space group produced a chemically reasonable result.

**Table 2.** Selected Bond Lengths and Angles for $[(CH_3)_4N]_2Fe[SCH_2CON(CH_3)_2]_4$ (**1**)[a]

| | | | |
|---|---|---|---|
| | Bond Distances (Å) | | |
| Fe−S(1) | 2.310 (2) | S(1)−C(1) | 1.822 (6) |
| Fe−S(2′) | 2.202 (3) | S(2)−C(5) | 1.813 (11) |
| Fe−S(2) | 2.576 (3) | S(2′)−C(5′) | 1.790 (11) |
| | Bond Angles (deg) | | |
| S(1)−Fe−S(2) | 104.2(1) | S(2)−Fe−S(2′A) | 98.6(1) |
| S(2)−Fe−S(1A) | 103.2(1) | S(1)−Fe−S(1A) | 100.2(1) |
| S(1)−Fe−S(2′A) | 117.0(1) | S(1A)−Fe−S(2′A) | 130.1(1) |
| | | Fe−S(1)−C(1) | 103.7(2) |
| | | Fe−S(2)−C(5) | 105.3(4) |
| | | Fe−S(2′)−C(5′) | 109.3(4) |

[a] Bond lengths and angles were presented for one of the disordered molecules that comprise the crystal structure.

**Table 3.** Correlation of p$K_a$ with Redox Potential for Iron Tetrathiolate Complexes $[Fe(SR)_4]^{2-}$ [a]

| | | DMF | | $CH_3CN$ | |
|---|---|---|---|---|---|
| RSH | p$K_a$ | $E_{1/2}$, V | $\Delta E$, mV | $E_{1/2}$, V | $\Delta E$, mV |
| $(CH_3)_2NCOCH_2SH$ (**1**) | 8.2 | −0.63 | 180 | −0.71 | 95 |
| $o$-$C_6H_4(CH_2SH)_2$ (**3**) | 9.4[b] | −1.03[c] | | −1.06 | 180 |
| $CH_3CH_2SH$ (**2**) | 10.6 | | | −1.10 | 100 |

[a] p$K_a$ values are for the neutral ligands. $E_{1/2}$ values are for the metal complexes, **1**, **2**, and **3**. Cyclic voltammetry was carried out with a Pine Instruments AFRDF4 potentiostat. The measurements were made in dry acetonitrile and DMF under $N_2$. Scan rate: 50 mV/s for **1** and **2**; 200 mV/s for **3**. Concentration of sample: 1.6 mM. Electrolytes: 0.10 M $Et_4NClO_4$ ($CH_3CN$); 0.20 M $Bu_4NBF_4$ (DMF). Reference electrode: saturated calomel. Working electrodes: glassy carbon ($CH_3CN$); Pt wire (DMF). Auxiliary electrode: Pt wire. [b] Estimated from the published data on benzyl mercaptan ref. 33. [c] Reference 24.

## Results and Discussion

The crystal structure of **1**, shown in Figure 1, comprises two disordered molecules in equal proportions. The tetrahedral core of the first molecule is designated by the numbering scheme Fe(1), S(1), S(1A), S(2), and S(2′A). For the second molecule, S(2) and S(2′A) are replaced by S(2′) and S(2A), respectively. The Fe atom resides on a crystallographic 2-fold axis. When the structures of the two disordered molecules are superimposed, the disorder of the two molecules is manifested by the appearance of the S(2)-thiolate arm in two equally probable positions (Figure 1). Because of this disorder, the individual Fe−S(2) and Fe−S(2′) distances and associated angles are chemically unreasonable, but the unperturbed Fe−S(1) distance of 2.310(2) (Table 2) Å is similar to the mean Fe−S bond length of 2.356(5) Å found in the iron(II) *o*-xylenedithiolate complex anion of **3**.[24] Furthermore, if all Fe−S distances are used to compute a mean, with each of the two Fe−S(2) distances appropriately weighted, the value is 2.350(3) Å, which is indistinguishable from the value obtained in the anion of **3**. Subtle differences are expected between complexes **1** and **3** regarding their electronic and steric characteristics. However, as the only monomeric Fe(II) alkanethiolate complexes to have been characterized by X-ray crystallography, complexes **1** and **3** merit comparison. Proton NMR data on complex **1** in $CD_3CN$ includes the methylene peak, at 215.5 ppm, whose large isotropic shift corresponds to the 196 ppm resonance peak of the simple tetrahedral ion complex $[Fe(SEt)_4]^{2-}$.[23] The NMR data confirms that complex **1** maintains its structural integrity in solution.

Complex **1** exhibits quasi-reversible Fe(II)/Fe(III) redox couples, with $E_{1/2}$ equal to −0.712 V ($\Delta E = 95$ mV) in $CH_3CN$ and −0.628 V ($\Delta E = 180$ mV) in DMF (Table 3). The $E_{1/2}$ value of **2**, measured in $CH_3CN$ under the same conditions,

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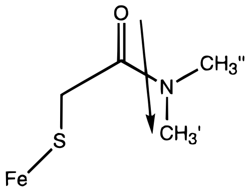
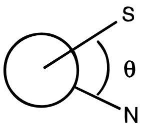
is −1.10 V ($\Delta E$ = 100 mV). Compound **3** has been reported to have a redox potential of −1.03 V in DMF [24] and was determined by us to have a redox potential of −1.06 V ($\Delta E$ = 180 mV) in $CH_3CN$. In $CH_3CN$ solution, the redox potential of complex **1** is larger than those of complexes **2** and **3** by 390 and 350 mV, respectively. On the basis of differences, it appears that the redox potential is strongly influenced by polar amide groups adjacent to the metal−ligand redox center.[19,21,31]

The relatively positive redox shift observed in **1** is likely due to a decrease in the effective valence electron density of sulfur, caused by the combined effects of the electrostatic potential of a dipolar neighbor (field effect) and by induction through $\sigma$ bonds. A C−D field effect induced positive redox shift would require an average ligand conformation in which sulfur is situated near the positive end (arrow head) of an amide dipole. A positive redox potential shift would result from this conformation because the sulfur electron density near the iron atom would be reduced by the electrostatic potential of the amide.

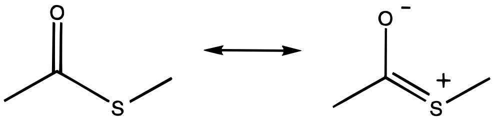




We investigated the plausible conformations of the *N*,*N*-dimethylmercaptoacetamide ligand by means of MM2 molecular mechanics (CS Chem3D Pro, Ver. 3.2). The steric energy of the amide was minimized as a function of the N−C−C−S dihedral angle, $\theta$, which was increased from −180° to +180° in 10° steps, with 1° steps around the minima. Two energy minima occurred at approximately ±82°, with the sulfur, as expected, inclined toward the positive end of the amide dipole. A van der Waals repulsion between sulfur and $CH_3'$ prevents a closer approach of sulfur to the amide plane. The corresponding dihedral angles in **1** are N(1)−C(2)−C(1)−S(1), 80.7°, and N(2)−C(6)−C(5)−S(2), 90.8°. The series of compounds **1**−**3** affords us no means of testing for the influence of $\sigma$ induction. This issue, however, has been addressed in the literature (vide infra).

Just as complex **1** is distinct in its redox potential relative to **2** and **3**, so too is the p$K_a$ of its ligand, $HSCH_2CON(CH_3)_2$, relative to $C_2H_5SH$ and *o*-$C_6H_4(CH_2SH)_2$, the respective ligands of **2** and **3**. We measured a p$K_a$ value of 8.2, by UV spectroscopy for *N*,*N*-dimethylmercaptoacetamide.[31] The p$K_a$ of ethanethiol has been reported to be 10.6.[32] In dithio-*o*-xylene the p$K_a$ is influenced by the proximity of the *o*-mercaptomethyl groups and is not likely to correlate with the trend in redox potential. We estimate that for each of the thiol groups of this ligand the intrinsic p$K_a$ is 9.4, close to that of benzyl mercaptan.[33] In general, lower p$K_a$ values signify greater electron withdrawal from sulfur, which favors the reduced state of the metal complex and correlates with relatively positive redox potentials in the iron−thiolate complexes[34,35] (Table 1).

We prepared thiol ester derivatives of the ligands with the aim of observing shifts in the carbonyl vibrational frequency as a function of polar group influence.[36] In an early study of thiol esters, Nyquist and Potts explained trends in their infrared frequencies on the basis of the resonance structures:[37]



The left-hand resonance structure has a greater carbon−oxygen bond order and therefore a higher carbonyl frequency. Groups that reduce the electron density on sulfur favor the left-hand structure. We found that the carbonyl frequency of thiol esters varied as a function of the group proximal to sulfur. In the series of thiol acetate compounds $H_3CCOSR$, where R = $C_4H_9$, $CH_2C_6H_5$, and $CH_2CON(CH_3)_2$, the respective carbonyl frequencies, acquired at 2 $cm^{-1}$ resolution, are 1685, 1688, and 1691 $cm^{-1}$.[48] The interaction between sulfur and a polar group correlates with the high thiol ester carbonyl frequency for the compound $(CH_3)COSCH_2CON(CH_3)_2$. The frequency trend in this series of compounds is consistent with the redox and p$K_a$ values observed for complexes **1**−**3**.

In earlier work we observed polar group effects in the complexes $Mo[HB(Me_2pz)_3](NO)\{S(CH_2)_nCON(CH_3)_2\}_2$, whose redox potentials of −0.740 mV (*n* = 1) and −0.750 mV (*n* = 2) ($CH_3CN$) are approximately 200 mV higher than those of the simple alkanethiolate complexes, $Mo[HB(Me_2pz)_3](NO)(SR)_2$, R = $C_2H_5$, $C_4H_9$.[19] In that work we ascribed the positive redox potential shifts to the electrostatic potential (*field effect*) of the amide group. The effect appeared to be general and dependent on ligand conformation but not length, which eliminates the (through-bond) $\sigma$-inductive effect as an important factor.

In the present work, the trends in redox potentials, p$K_a$ values, and thiol ester carbonyl frequencies of complexes **1**−**3** are consistent with corresponding Taft constants and provide a qualitative measure of the inductive and field effects of the ligand substituents.[38−40] It follows that variations in the redox potentials of the iron−sulfur proteins and their model compounds may be attributed largely to the polarity and orientation of the groups adjacent to the metal−sulfur cores. Considerable experimental evidence from studies of aliphatic compounds has shown that polar substituent effects are transmitted predominantly through space (or solvent) and are designated as *field effects*.[31,41−43] This has been shown to be true, in particular, for p$K_a$ trends in substituted acetic acid $XCH_2COOH$ where the carbonyl group is separated from the substituent X by a methylene group. The p$K_a$ trends for these compounds suggest that $\sigma$-inductive interactions between the carboxylate and substituent are essentially quenched by the methylene group. The same likely holds for the amide−sulfur interactions in the ligand precursor, $HSCH_2CON(CH_3)_2$, of complex **1**.

## Conclusions

The amide−sulfur interaction in complex **1** results in a large redox shift, of approximately 370 mV, relative to simple

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alkanethiolate complexes **2** and **3**. Among Rd proteins whose active sites are structurally congruent, the redox potential range is +6 to −57 mV.[44] The narrow range of these potentials suggests that there is little variability in the polarity of the active sites of the Rd proteins.[45−47] The observed range of redox potentials can probably be adequately explained by small variations in the distance and orientation of polar groups that surround the protein redox site.

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**Supporting Information Available:** Tables of complete crystallographic data collection information, atomic coordinates, bond distances, bond angles, anisotropic thermal parameters, positional parameters of the H atoms, dihedral angles, and a cyclic voltammogram for **1** (12 pages). Ordering information is given on any current masthead page.

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