

# A Detailed Mechanistic Study of the Substitution Behavior of an Unusual Seven-Coordinate Iron(III) Complex in Aqueous Solution

Ivana Ivanovic-Burmazovic,<sup>†</sup> Mohamed S. A. Hamza,<sup>‡</sup> and Rudi van Eldik<sup>\*</sup>

*Institute for Inorganic Chemistry, University of Erlangen-Nürnberg, Egerlandstrasse 1, 91058 Erlangen, Germany*

Received January 28, 2002

A detailed mechanistic study of the substitution behavior of a 3d metal heptacoordinate complex, with a rare pentagonal-bipyramidal structure, was undertaken to resolve the solution chemistry of this system. The kinetics of the complex-formation reaction of  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]\text{ClO}_4$  ( $\text{H}_2\text{dapsox} = 2,6\text{-diacetylpyridine-bis(semioxamizide)}$ ) with thiocyanate was studied as a function of thiocyanate concentration, pH, temperature, and pressure. The reaction proceeds in two steps, which are both base-catalyzed due to the formation of an aqua-hydroxo complex ( $\text{p}K_{\text{a}1} = 5.78 \pm 0.04$  and  $\text{p}K_{\text{a}2} = 9.45 \pm 0.06$  at 25 °C). Thiocyanate ions displace the first coordinated water molecule in a fast step, followed by a slower reaction in which the second thiocyanate ion coordinates trans to the N-bonded thiocyanate. At 25 °C and  $\text{pH} < 4.5$ , only the first reaction step can be observed, and the kinetic parameters ( $\text{pH} 2.5$ :  $k_{\text{r}(0)} = 2.6 \pm 0.1 \text{ M}^{-1} \text{ s}^{-1}$ ,  $\Delta H_{\text{r}(0)}^\ddagger = 62 \pm 3 \text{ kJ mol}^{-1}$ ,  $\Delta S_{\text{r}(0)}^\ddagger = -30 \pm 10 \text{ J K}^{-1} \text{ mol}^{-1}$ , and  $\Delta V_{\text{r}(0)}^\ddagger = -2.5 \pm 0.2 \text{ cm}^3 \text{ mol}^{-1}$ ) suggest the operation of an  $\text{I}_\text{a}$  mechanism. In the pH range 2.5 to 5.2 this reaction step involves the participation of both the diaqua and aqua-hydroxo complexes, for which the complex-formation rate constants were found to be  $2.19 \pm 0.06$  and  $1172 \pm 22 \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C, respectively. The more labile aqua-hydroxo complex is suggested to follow an  $\text{I}_\text{d}$  or D substitution mechanism on the basis of the reported kinetic data. At  $\text{pH} \geq 4.5$ , the second substitution step also can be monitored ( $\text{pH} 5.5$  and 25 °C:  $k_{\text{r}(0)} = 21.1 \pm 0.5 \text{ M}^{-1} \text{ s}^{-1}$ ,  $\Delta H_{\text{r}(0)}^\ddagger = 60 \pm 2 \text{ kJ mol}^{-1}$ ,  $\Delta S_{\text{r}(0)}^\ddagger = -19 \pm 6 \text{ J K}^{-1} \text{ mol}^{-1}$ , and  $\Delta V_{\text{r}(0)}^\ddagger = +8.8 \pm 0.3 \text{ cm}^3 \text{ mol}^{-1}$ ), for which an  $\text{I}_\text{d}$  or D mechanism is suggested. The results are discussed in terms of known structural parameters and in comparison to relevant structural and kinetic data from the literature.

## Introduction

Heptacoordinate 3d metal complexes are rather rare and have so far mostly been studied in terms of their solid-state crystal structure.<sup>1</sup> Their solution chemistry remains largely undefined and there is limited information available on the substitution behavior of such complexes,<sup>2–4</sup> making the solution chemistry of these species an especially challenging area.

There are two experimental ways to approach the substitution behavior of 3d metal heptacoordinate species in solution. One is to investigate the formation of such species as reaction intermediates or transition states in substitution reactions of hexacoordinate complexes, and the other is to study the substitution behavior of such complexes directly by using them as starting material. At present, more data obtained through the first approach are available in the literature. However, it has been shown that water exchange reactions of  $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  follow an associative mechanism with heptacoordinate intermediate and transition states, respectively.<sup>5–7</sup> The reaction of  $\text{H}_2\text{O}_2$  with dioxovanadate(V) proceeds through a heptacoordinate transition

\* Author to whom correspondence should be addressed. E-mail: vaneldik@chemie.uni-erlangen.de.

<sup>†</sup> On leave from the Department of Chemistry, University of Belgrad, Belgrad, Yugoslavia.

<sup>‡</sup> On leave from the Department of Chemistry, Faculty of Science, Ain Shams University, Cairo, Egypt.

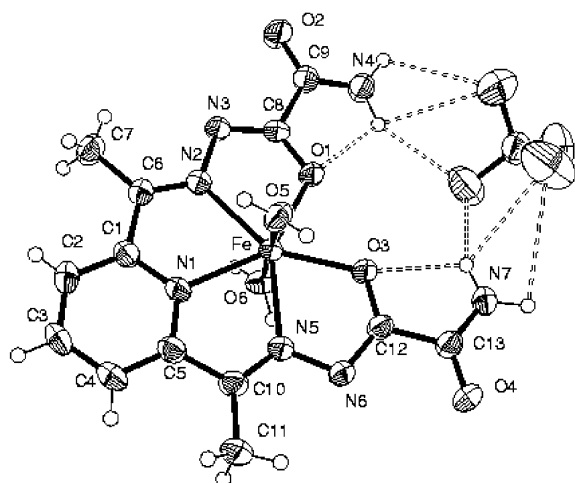
- (1) Ivanovic-Burmazovic, I.; Bacchi, A.; Pelizzi, G.; Leovac, V. M.; Andjelkovic, K. *Polyhedron* **1998**, *18*, 119 and references therein.
- (2) Dellert-Ritter, M.; van Eldik, R. *J. Chem. Soc., Dalton Trans.* **1992**, 1037.
- (3) Mizuno, M.; Funahashi, S.; Nakasuka, N.; Tanaka, M. *Inorg. Chem.* **1991**, *30*, 1550.

(4) Schnepfensieper, T.; Seibig, S.; Zahl, A.; Tregloan, P.; van Eldik, R. *Inorg. Chem.* **2001**, *40*, 3670.

(5) van Eldik, R., Ed. *High-Pressure Inorganic Chemistry: Kinetics and Mechanisms*; Elsevier: Amsterdam, The Netherlands, 1986.

(6) Merbach, A. E. *Pure Appl. Chem.* **1987**, *59*, 161.

(7) Hartmann, M.; Clark, T.; van Eldik, R. *J. Phys. Chem. A* **1999**, *103*, 9899.



**Figure 1.** ORTEP view of the  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]\text{ClO}_4$  complex including hydrogen bond interaction between the complex cation and perchlorate anion (dashed lines).<sup>10</sup>

state,<sup>8</sup> which is also true for the reaction between  $[\text{Cr}(\text{Hedta})\text{-H}_2\text{O}]$  and thiocyanate.<sup>9</sup> In all these cases the reactants have an octahedral structure. Only a few kinetic studies on substitution reactions of heptacoordinate complexes have been reported. The substitution behavior of polyaminocarboxylate Fe(III) complexes with respect to ligand displacement<sup>2</sup> and water exchange reactions have been studied.<sup>3,4</sup> These heptacoordinate complexes are significantly more labile than hexaquaairon(III), with the result that water exchange proceeds much faster and more dissociatively than in the case of hexaquaairon(III). This has been interpreted as a consequence of the 19 VE character of the heptacoordinate complex that will favor a dissociative substitution mechanism.

In light of the fact that the above-mentioned results seem to be the only ones available on the substitution behavior of heptacoordinate 3d metal complexes, the questions arise as to what extent the lability of these complexes results from the increase in coordination number (from 6 to 7), and to what extent it is a consequence of the electronic environment of the selected chelate. In more general terms, it remains to be seen whether the heptacoordinate 3d metal complexes are always more labile than their corresponding octahedral species.

To develop and enhance our understanding of the solution chemistry of the 3d metal heptacoordinate complexes, we have studied the substitution behavior of the pentagonal-bipyramidal (PBP) diaqua complex of Fe(III),  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]^+$  ( $\text{H}_2\text{dapsox} = 2,6\text{-diacetylpyridine-bis}(\text{semioxamazide})$ ), with an anionic planar pentadentate ligand in the equatorial plane<sup>10</sup> (see the structure in Figure 1). There are several reasons for having chosen this particular complex. First, the coordinated chelate has completely different stereochemical and electronic properties than the polyaminocarboxylates, which enables a comparison of the

influence of different chelate systems on the mechanistic behavior of 3d PBP complexes (the Fe(III) polyaminocarboxylate complexes also have an almost PBP shape).<sup>3,4</sup> In addition, the conjugation-stabilized planar dianionic nature of the pentadentate chelate makes the heptacoordinate structure of the complex comparable with octahedral Fe(III) porphyrins, which enables a comparison of the change in coordination number from 6 to 7 on the nature of the substitution process. Second, in the presence of two axial ligands it is possible to obtain mechanistic information on the two-step displacement of the trans positioned solvent molecules. In this respect it is interesting that even in the case of *trans*-diaquaairon(III) octahedral complexes, the underlying two-step substitution mechanism has not yet been completely clarified.<sup>11,12</sup> Furthermore, kinetic studies on the substitution reactions of  $[\text{Fe}(\text{salen})(\text{H}_2\text{O})_2]^+$  ( $\text{salen}^{2-}$  is a  $\text{N}_2\text{O}_2$  tetradentate ligand), which is probably the most suitable octahedral system for a comparison with our  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]^+$  complex, have not been possible since in basic medium a  $\mu$ -oxo dimer is formed, whereas in acidic medium a hydrolytic decomposition process occurs.<sup>13</sup> It is of fundamental interest to separate the two stages of the substitution reactions of diaquaairon(III) complexes kinetically, to obtain data on which basis their intimate mechanisms can be defined. For that reason we have also performed high-pressure kinetic measurements, since the volume of activation allows a clearer picture of the transition state to be visualized.<sup>5</sup>

A study of the ligand substitution mechanism of  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]^+$  is also of interest from another point of view, since it has been found that Fe(III) PBP complexes with pentaaza macrocyclic ligands exhibit an excellent superoxide dismutase (SOD) activity and offer considerable promise as SOD catalysts for pharmaceutical applications.<sup>14</sup> In these systems, the  $[\text{Fe}(\text{L})(\text{H}_2\text{O})\text{OH}]$  form of the complex is responsible for the catalytic properties, and a condition for the high activity of the complexes is their existence in mostly this form under physiological pH conditions. With  $\text{p}K_{\text{a}1}$  and  $\text{p}K_{\text{a}2}$  values of the investigated pentaaza complexes being  $\sim 3.5$  and  $\sim 7.5$ , respectively, it would be logical to study another system that would have significantly higher  $\text{p}K_{\text{a}}$  values to improve the catalytic action under physiological pH conditions. The dianionic nature of the chelate in our  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]^+$  complex as compared to the neutral nature of the pentaaza chelates may be ideal for obtaining the desired reduction in acidity of the water molecules coordinated to the Fe(III) center.

On the basis of the arguments outlined above, we have performed a detailed investigation of the substitution behavior of the pentagonal-bipyramidal complex,  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]^+$ , with thiocyanate as entering nucleophile as a function of the

(8) Funahashi, S.; Ishiara, K.; Tanaka, M. *Inorg. Chem.* **1981**, *20*, 51.  
 (9) Beswick, C. L.; Shalders, R. D.; Swaddle, T. W. *Inorg. Chem.* **1996**, *35*, 991.  
 (10) Andjelkovic, K.; Bacchi, A.; Jeremic, D.; Ivanovic-Burmazovic, I. *J. Coord. Chem.* **2002**, in press.

(11) Cheng, S. H.; Chen, Y. S.; Su, Y. O. *J. Chin. Chem. Soc.* **1991**, *38*, 15.  
 (12) Beck, M. J.; Gopinath, E.; Bruce, T. C. *J. Am. Chem. Soc.* **1993**, *115*, 21.  
 (13) Lloret, F.; Julve, M.; Mollar, M.; Castro, I.; LaTorre, J.; Faus, J.; Solans, W.; Morgenstern-Badarau, I. *J. Chem. Soc., Dalton Trans.* **1989**, 729.  
 (14) Zhang, D.; Busch, D. H.; Lennon, P. L.; Weiss, R. H.; Neumann, W. L.; Riley, D. P. *Inorg. Chem.* **1998**, *37*, 956.

nucleophile concentration, pH, temperature, and pressure, which resulted in a complete elucidation of the underlying two-step reaction mechanism.

## Experimental Section

**Materials.** All chemicals used were of p.a. grade and were used as received without any further purification. Bis-Tris buffer was purchased from Sigma.  $\text{HClO}_4$ ,  $\text{NaClO}_4$ ,  $\text{NaSCN}$ ,  $\text{HCOOH}$ ,  $\text{HCOONa}$ ,  $\text{CH}_3\text{COOH}$ , and  $\text{CH}_3\text{COONa}$  were purchased from Merck. Ultrapure water was used in all the kinetic and thermodynamic measurements.

**[Fe(dapsox)(H<sub>2</sub>O)<sub>2</sub>]ClO<sub>4</sub>.** The complex was prepared and characterized as described previously.<sup>10</sup>

**[Fe(dapsox)(H<sub>2</sub>O)(NSC)].** To 20 cm<sup>3</sup> of a 0.2 M [Fe(dapsox)(H<sub>2</sub>O)<sub>2</sub>]ClO<sub>4</sub> solution was added 0.8 g of solid NaSCN. After 5 min of heating and mixing a microcrystalline brown product precipitated and was separated by filtration. Yield: 87%. Anal. Calcd (found) for C<sub>14</sub>H<sub>15</sub>FeN<sub>8</sub>O<sub>5</sub>S: C 36.30 (35.89); H 3.24 (3.15); N 24.20 (23.93); S 6.91 (6.89). IR (KBr pellet  $\nu$ , cm<sup>-1</sup>): 3456 (s), 3420 (s), 3370 (s), 2065 (vs), 1701 (vs), 1614 (s), 1551 (vs), 1510 (s), 1300 (s), 1150 (m), 1063 (m), 759 (m), 540 (m), 452 (m).

**Instrumentation and Measurements.** IR spectra were recorded on a Mattson FTIR Infinity spectrophotometer with KBr pellets, as well as a KBr cell for samples in DMSO and water solutions. IR spectra of aqueous solutions were also recorded with the use of a two-mirror ATR cell. The reflection instrument utilized a Ge crystal as an internal reflection plate with a size of 50 × 10 × 2 mm and a 45° angle of incidence. Diffuse reflectance spectra were recorded on a Shimadzu UV-2401 PC spectrophotometer, using BaSO<sub>4</sub> powder as a reference. Reflectance spectra were transformed to absorbance spectra according to the Kubelka–Munk theory. The pH of the solutions was measured on a Mettler Delta 350 pH meter with a combined glass electrode that was calibrated with standard buffer solutions at pH 4.0, 7.0, and 10.0. The reference electrode was filled with NaCl instead of KCl to prevent precipitation of KClO<sub>4</sub>. UV–vis spectra were recorded on Shimadzu UV-2101 and Hewlett-Packard 8452A spectrophotometers.

Kinetic measurements were carried out on a Biologic stopped-flow instrument for which data were analyzed with use of the OLIS KINFIT program and on an Applied Photophysics SX 18MV stopped-flow instrument coupled to an online data acquisition system. At least 10 kinetic runs were recorded under all conditions, and the reported rate constants represent the mean values. All kinetic measurements were carried out under pseudo-first-order conditions, i.e., the ligand concentration was in excess (complex concentrations in the range of 5 × 10<sup>-5</sup> to 5 × 10<sup>-4</sup> M, and [SCN<sup>-</sup>] in the range of 0.02 to 1 M). The reactions were studied at an ionic strength of 2.0 M (NaClO<sub>4</sub>) and within a pH range from 2.0 to 6.4. The pH was adjusted with HClO<sub>4</sub> and NaOH in the range 2–3, with formate buffer at pH 3.5, with acetate buffer at pH 4–5.2, and with Bis-tris buffer at pH 5.5 and 6.4, respectively. Measurements under high pressure were carried out with use of a homemade high-pressure stopped-flow instrument.<sup>15</sup>

The UV–vis spectrophotometers and stopped-flow instruments were thermostated to the desired temperature ±0.1 °C. Values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  were calculated from the slopes and intercepts, respectively, of plots of  $\ln(k/T)$  versus  $1/T$ , and values of  $\Delta V^\ddagger$  were calculated from the slope of plots of  $\ln(k)$  versus pressure.

**Equilibrium Measurements.** A 5 × 10<sup>-5</sup> M [Fe(dapsox)(H<sub>2</sub>O)<sub>2</sub>]ClO<sub>4</sub> solution was made in a suitable buffer and placed in a 1.0 cm path length cuvette in the thermostated cell block of the spectrophotometer for 20–30 min (25 °C). This solution was titrated by addition of small volumes of a concentrated stock solution of sodium thiocyanate, using a Hamilton syringe. The thiocyanate solution was prepared in the same buffer, and the ionic strength was adjusted to 0.1 or 2 M with NaClO<sub>4</sub>. The titrations were carried out in duplicate and were monitored at several wavelengths where the largest change in absorbance occurred. The values of the equilibrium constant,  $K$ , were obtained by fitting the absorbance versus concentration curve, after correction for dilution (see the Results for further details).

## Results and Discussion

**Spectroscopic Data.** The synthesis, IR spectral features, and X-ray data for [Fe(dapsox)(H<sub>2</sub>O)<sub>2</sub>]ClO<sub>4</sub>·3H<sub>2</sub>O were reported before.<sup>10</sup> Due to the limited solubility of the complex in water and the low intensity of the relevant bands, the IR spectrum of a DMSO solution was recorded to investigate a possible change in the PBP geometry or ring-opening of any of the four five-membered chelate rings. The IR spectrum in DMSO showed that during dissolution of the solid complex, there was no disruption of the dapsox<sup>2-</sup> pentadentate chelate nature. This suggests that there are no changes in the symmetrical coordination of the two side chains, which would have resulted in the appearance of new bands in the 1600–1720 cm<sup>-1</sup> range.<sup>16</sup> It was found that not only the number of bands remains the same, but also the position of the band corresponding to a coordinated C=O hydrazide group of both chains is identical, both in the solid and in the solution spectrum. The band corresponding to the uncoordinated C=O amide groups is shifted by 10 cm<sup>-1</sup> toward higher frequencies in the solution spectrum. The strengthening of these bonds is most probably related to the inability to form hydrogen bonds with DMSO molecules, whereas in the solid state these groups are involved in intermolecular contacts with crystal and coordinated water molecules.<sup>10</sup> In addition, the UV–vis spectrum of the solid [Fe(dapsox)(H<sub>2</sub>O)<sub>2</sub>]ClO<sub>4</sub> complex is in very good agreement with its solution spectrum, confirming the heptacoordinate structure of the complex in aqueous solution.

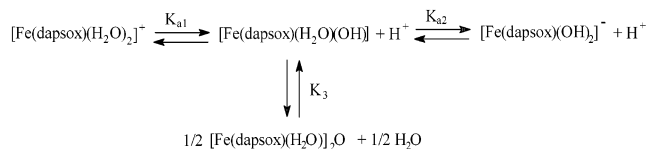
In this study it was possible to isolate the monothiocyanato complex by addition of solid NaSCN to the [Fe(dapsox)(H<sub>2</sub>O)<sub>2</sub>]<sup>+</sup> complex solution. Almost instantaneously, a poorly soluble brown microcrystalline product precipitated. Elemental analysis and IR spectra for the complexes isolated at pH 2.5 and 4.5 suggest the formation of the same monothiocyanato product. The poor solubility of the 1:1 complex, which leads to its rapid precipitation from solution at higher concentrations, and the very low formation constant for the 1:2 complex make it almost impossible to isolate the dithiocyanato complex. Although some dithiocyanato PBP complexes are known, viz. [Fe(B)(NCS)<sub>2</sub>]ClO<sub>4</sub><sup>17,18</sup> and [Fe(C)(NCS)<sub>2</sub>]ClO<sub>4</sub>,<sup>18</sup> it appears that they can only be

(15) (a) van Eldik, R.; Palmer, D. A.; Schmidt, R.; Kelm, H. *Inorg. Chim. Acta* **1981**, *50*, 131. (b) van Eldik, R.; Gaede, W.; Wieland, S.; Kraft, J.; Spitzer, M.; Palmer, D. A. *Rev. Sci. Instrum.* **1993**, *64*, 1355.

(16) Bacchi, A.; Ivanovic-Burmazovic, I.; Pelizzi, G.; Andjelkovic, K. *Inorg. Chim. Acta* **2001**, *313*, 109.

(17) Nelson, S. M.; Busch, D. H. *Inorg. Chem.* **1969**, *8*, 1859.

## Scheme 1

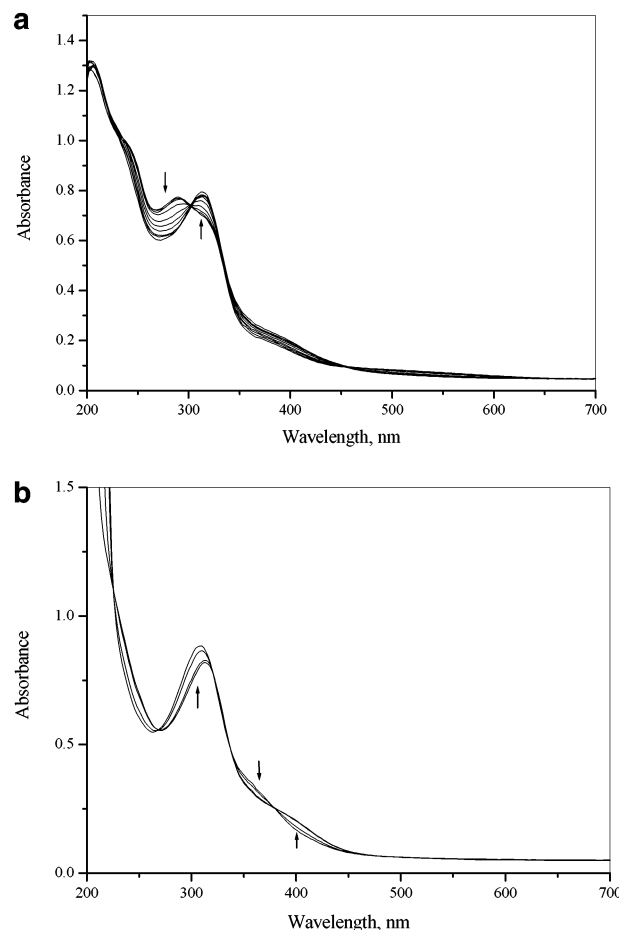


separated when a neutral pentadentate chelate is present in the coordination sphere, since the only other PBP Fe(III) complex with a deprotonated pentadentate chelate also only forms the monothiocyanato  $[\text{Fe}(\text{H}_2\text{daps})(\text{NCS})(\text{H}_2\text{O})]$  complex.<sup>19</sup>

The IR spectrum of  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})(\text{NCS})]$  exhibits a strong band at  $2065 \text{ cm}^{-1}$ , which corresponds to the C–N stretching mode and suggests that thiocyanate is N-bonded.<sup>20–22</sup> The position of this band is at the higher limit, whereas the C–S stretching frequency at  $759 \text{ cm}^{-1}$  is at the lower limit for such bands.<sup>18,20,22</sup> This suggests a somewhat stronger C–N and a weaker C–S bond, which leads to the linear coordination of thiocyanate as  $\text{N}=\text{C}-\text{S}^-$ . With the  $\text{dapsox}^{2-}$  chelate being completely planar and not causing any steric hindrance above and below the pentagon, a linear  $\text{SCN}^-$  coordination is very probable.<sup>21,23</sup> Besides the  $\text{SCN}^-$  bands and the absence of a band characteristic for the  $\text{ClO}_4^-$  ion, the IR spectrum of the monothiocyanato complex shows no additional differences as compared to the spectrum of the starting complex,  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]\text{ClO}_4$ .

The solid-state UV–vis spectrum of  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})(\text{NCS})]$  in comparison to the spectrum of solid  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]\text{ClO}_4$  shows the prominent increase in absorbance in the range 380–480 nm. Exactly the same spectral changes are observed during the spectrophotometric titrations of  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]\text{ClO}_4$  with  $\text{SCN}^-$  in aqueous solution, suggesting that in both the solid state and solution the same heptacoordinate complexes are present.

**Equilibrium Measurements.** The presence of two coordinated water molecules in  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]^+$  allows the equilibria shown in Scheme 1 to set in. UV–vis spectra of aqueous solutions of the complex at different pH values (Figure 2a,b) ( $[\text{Fe}(\text{III})] = 5 \times 10^{-5}$  to  $5 \times 10^{-4}$  M) did not show any evidence for dimer formation. The UV–vis spectrum of this complex at pH 3 indicates an absorbance maximum at 290 nm and a shoulder at 313 nm. A gradual decrease in the acidity of the solution decreases the absorbance at 290 nm, accompanied by an absorbance increase at the shoulder at 313 nm. The equilibrium between the diaqua and aquahydroxo species is characterized by two isosbestic points at 302 and 455 nm, as shown in Figure 2a. The equilibrium between the aquahydroxo and dihydroxo



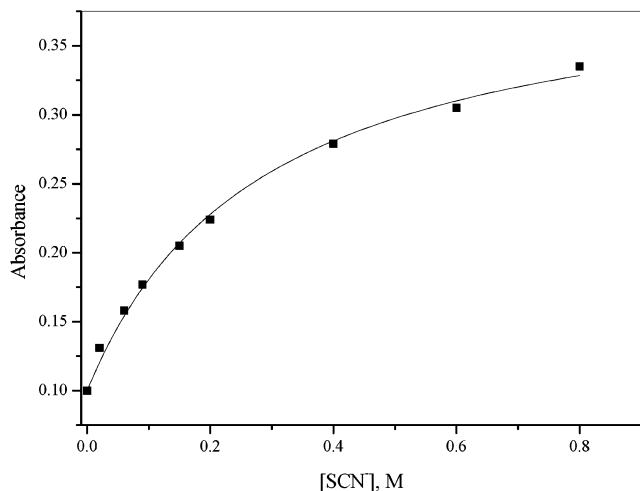
**Figure 2.** UV–vis spectrum of  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]^+$  as a function of pH at 25 °C,  $[\text{Fe}(\text{III})] = 5 \times 10^{-5}$  M,  $\mu = 0.1$  M: (a) at pH 3–9 and (b) at pH 9–12.

species is characterized by isosbestic points at 268 and 379 nm, as shown in Figure 2b. Analysis of the plot of absorbance versus pH at 315 (Figure S1a) and 302 nm, the wavelength at which an isosbestic point for the first deprotonation step appears (Figure S1b, see Supporting Information), results in  $\text{p}K_{a1}$  and  $\text{p}K_{a2}$  values of  $5.78 \pm 0.04$  and  $9.45 \pm 0.06$  at 25 °C, respectively. The same values were obtained at  $I = 0.1$  and 2 M.

It is known from the literature<sup>17,18</sup> that aqueous solutions of the PBP complexes  $[\text{Fe}(\text{B})\text{X}_2]^+$  and  $[\text{Fe}(\text{C})\text{X}_2]^+$ , which have macrocyclic  $\text{N}_5$  pentadentate chelates (B = 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12,3,1]octadeca-1(18),2-,12,14,16-pentaene and C = 2,14-dimethyl-3,6,10,13,19-pentaazabicyclo[13,3,1]nonadeca-1(19),2,13,15,17-pentaene) in an equatorial plane with  $\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{SCN}^-$ , do not reveal any differences in their UV–vis spectra, which are characteristic for  $[\text{Fe}(\text{B})(\text{H}_2\text{O})_2]^{3+}$  and  $[\text{Fe}(\text{C})(\text{H}_2\text{O})_2]^{3+}$  cations. This demonstrates that the equilibria of these complexes are significantly shifted toward the diaqua species. It has qualitatively been shown that the stability constants decrease in the order  $\text{SCN}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$ .<sup>17</sup>

For the presently investigated complex, addition of  $\text{Cl}^-$  and  $\text{Br}^-$  ions to an aqueous solution does not cause any changes in the UV–vis spectrum, whereas a significant excess of  $\text{I}^-$  ions shows only small spectral change. On the other hand, addition of  $\text{SCN}^-$  increases the absorbance in

- (18) Drew, M. G. B.; bin Othman, A. H.; McIlroy, P. D. A.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1975**, 2507.  
 (19) Bonardi, A.; Merlo, C.; Pelizzi, C.; Pelizzi, G.; Trasconi, P.; Cavatorta, F. *J. Chem. Soc., Dalton Trans.* **1991**, 1063.  
 (20) Drew, M. G. B.; Grimshaw, J.; McIlroy, P. D. A.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1976**, 1388.  
 (21) Drew, M. G. B.; bin Othman, A. H.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1976**, 1394.  
 (22) Al-Daher, A. G. M.; Bagnall, K. W. *J. Chem. Soc., Dalton Trans.* **1986**, 843.  
 (23) Scheidt, W. R.; Lee, Y. J.; Geiger, D. K.; Taylor, K.; Hatano, K. *J. Am. Chem. Soc.* **1982**, 104, 3367.



**Figure 3.** Changes in absorbance at 440 nm on addition of  $\text{SCN}^-$  to  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]^+$  (pH 2.5,  $[\text{Fe}(\text{III})] = 5 \times 10^{-5}$  M). The solid line is a fit of the data to eq 1 in the text.

the range 380–480 nm, which suggests that the stronger nucleophile  $\text{SCN}^-$  displaces coordinated water.

Spectrophotometric titrations of  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]\text{ClO}_4$  ( $5 \times 10^{-5}$  M) at pH 2.5 were monitored by following the increase in absorbance at 440 nm, where the largest change in absorbance occurred. The solid line in Figure 3 represents a fit of the experimental data to eq 1. The values of  $A_0$  and

$$A_x = A_0 + (A_\infty - A_0)K[\text{SCN}^-]/1 + K[\text{SCN}^-] \quad (1)$$

$A_\infty$  represent absorbance at 0 and 100% formation of the thiocyanate complex, respectively, and  $A_x$  represents the absorbance at any given thiocyanate concentration. The values of  $K$  and  $A_\infty$  were calculated from a nonlinear least-squares fit of the experimental data to eq 1. A similar titration was carried out at pH 4.5. The  $K$  values obtained at pH 2.5 and 4.5 are identical, viz.  $3.3 \pm 0.2 \text{ M}^{-1}$  at 25 °C. Analysis of these data at pH 2.5 by plotting  $\log(A_x - A_0)/(A_\infty - A_x)$  versus  $\log[\text{SCN}^-]$  gave a good linear plot with a slope of  $0.97 \pm 0.02$ , which indicates the coordination of only one  $\text{SCN}^-$  ligand to the metal center. A similar log–log plot was obtained at pH 4.5. It is interesting to note that at pH 4.5, the log–log plot first gives a slope of  $0.95 \pm 0.01$  and then, starting from a  $\text{SCN}^-$  concentration of 0.9 M, the slope increases to 1.4. This suggests that at a high  $\text{SCN}^-$  concentration, a second thiocyanate ligand coordinates to the metal center. The intercept of these linear plots gives the value of  $\log K$ , which is in good agreement with those obtained from eq 1.

The spectral changes that accompany the coordination of the second thiocyanate ion (studied by rapid-scan techniques) are in the same direction as those observed for the binding of the first thiocyanate ion. Thus no isosbestic points could be observed for the formation of the 1:2 complex. The small contribution of the dithiocyanato complex to the overall absorbance spectrum does not allow a clear spectroscopic identification of this complex.

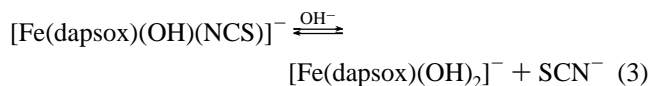
From the pH dependence of the absorbance at 314 nm for a  $5 \times 10^{-5}$  M solution of  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]\text{ClO}_4$  in 1 M

$\text{SCN}^-$  (required for complete formation of the 1:1 complex), a  $\text{p}K_{\text{a}(\text{SCN})}$  value of  $6.30 \pm 0.06$  was obtained, which represents the deprotonation equilibrium in (2). The reduced



positive charge on the monothiocyanato complex, as compared to the starting diaqua complex, causes a reduced acidity of the water molecule trans to coordinated  $\text{SCN}^-$  ( $\text{p}K_{\text{a}(\text{SCN})} = 6.30 \pm 0.06$  as compared to  $\text{p}K_{\text{a}1} = 5.78 \pm 0.04$ ). It follows that this water molecule is of considerably higher acidity than the water molecule in the aquahydroxo complex ( $\text{p}K_{\text{a}2} = 9.45$ ), regardless of the fact that a hydroxide and a thiocyanate group are of the same overall charge. This is because thiocyanate has significantly stronger  $\pi$ -acceptor properties than  $\text{OH}^-$ . The earlier discussed linear coordination of thiocyanate, where the nitrogen donor has predominantly sp character, causes a reduction in the  $\sigma$ -donor and an increase in the  $\pi$ -acceptor properties of thiocyanate, which is in agreement with the established trend in the  $\text{p}K_{\text{a}}$  values.

Following the equilibrium described in eq 2, the subsequent equilibrium (3) is maintained at pH > 8.2:

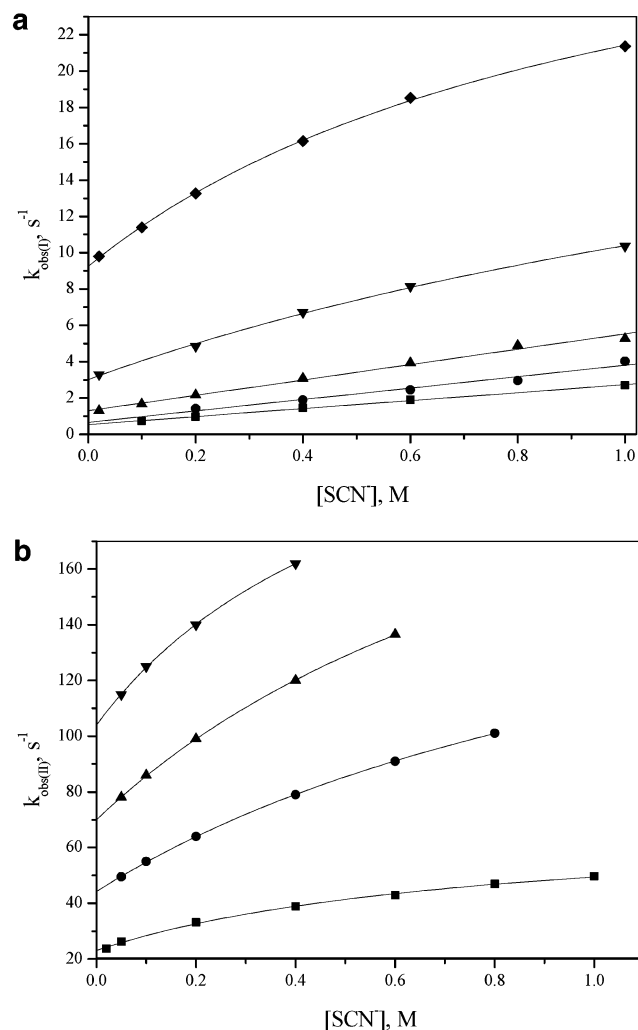


This is demonstrated by identical UV–vis spectra obtained at higher pH values for the  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]\text{ClO}_4$  complex itself, and for the complex in the presence of  $\text{SCN}^-$ .

**Kinetic Measurements.** The kinetics of the reaction of  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]^+$  with thiocyanate was studied on the stopped-flow spectrophotometer at 440 nm. Reaction rates were measured under pseudo-first-order conditions for a complex concentration of  $5 \times 10^{-5}$  M and thiocyanate concentrations ranging from 0.02 to 1.0 M. The effect of pH, thiocyanate concentration, temperature, and pressure was studied to gain detailed insight into the mechanism.

Figure 4 presents the dependence of  $k_{\text{obs}(\text{l})}$  on the thiocyanate concentration in the pH range 2–5.2. This figure shows a linear increase in  $k_{\text{obs}(\text{l})}$  with increasing nucleophile concentration over the whole concentration range for pH 2.0–3.0. However, at pH > 3.0 a slight curvature in the plots was observed, which became more prominent at higher pH. Figure 4 also shows that the reaction rate increases with increasing pH. This increase is not only noted for the forward reaction (slope of plots), but also for the reverse reaction (intercept of plots), indicating that the reactions are base-catalyzed. Furthermore, for pH  $\geq 4.5$  the kinetic traces were best fitted with two exponentials, suggesting that two subsequent reactions take place, of which the first is always faster than the second. At pH  $\geq 5.5$ , only the slower reaction step could be monitored, since under these conditions the first reaction step becomes too fast to be followed by stopped-flow techniques (dead time 4 ms).

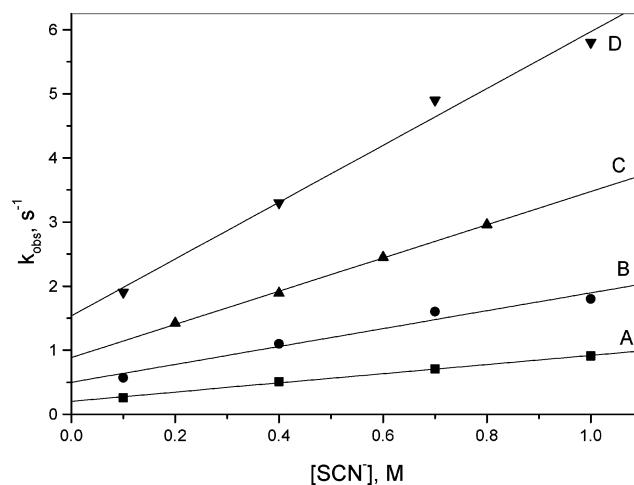
A careful analysis of the two reaction steps separately shows that the first reaction exhibits a prominent pH-dependence, with its rate constantly increasing with increas-



**Figure 4.**  $k_{\text{obs}(I)}$  versus  $[\text{SCN}^-]$  for the first step of the reaction between  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]^+$  and  $\text{SCN}^-$  as a function of pH,  $[\text{Fe}(\text{III})] = 5 \times 10^{-5}$  M, 25 °C, and  $I = 2$  M ( $\text{NaClO}_4$ ): (a) pH 2.0 (■), 2.5 (●), 3.0 (▲), 3.5 (▼), and 4.0 (◆); (b) pH 4.5 (■), 4.7 (●), 5.0 (▲), and 5.2 (▼).

ing pH. On the other hand, the increase in the rate of the second reaction is much smaller in the pH range 4.5–5.5. However, at pH 6.4 this reaction starts to become slower and thermodynamically less significant (data not reported).

As mentioned above, analysis of the spectrophotometric titration (log–log plot) of the  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]^+ - \text{SCN}^-$  system at pH 4.5 indicated the coordination of the second  $\text{SCN}^-$  ligand at higher nucleophile concentrations. It follows that the first reaction involves the formation of a monothiocyanato complex, whereas the second reaction represents the formation of a dithiocyanato species. However, unclear is why the second reaction step is not observed in the lower pH range. This is presumably due to the fact that the monothiocyanato complex is a neutral species of lower solubility and precipitates under conditions where the subsequent formation of the dithiocyanato complex is slow. At higher pH, the formation of the dithiocyanato complex is much faster and competes effectively with the precipitation of the monothiocyanato complex. Interestingly at pH 3.5 and a higher temperature of 35 °C, it is possible to observe both reaction steps, most probably due to the higher solubility of the monothiocyanato complex under these conditions. Fur-



**Figure 5.** Plot of  $k_{\text{obs}(I)}$  versus  $[\text{SCN}^-]$  for the first step of the reaction between  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]^+$  and  $\text{SCN}^-$  as a function of temperature. Experimental conditions:  $[\text{Fe}(\text{III})] = 5 \times 10^{-5}$  M, pH 2.5,  $I = 2$  M ( $\text{NaClO}_4$ ), and  $T = 10.0$  (A), 18.0 (B), 25.0 (C), and 30.0 °C (D).

**Table 1.** Kinetic Data for the First Step of the Reaction of  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]^+$  with  $\text{SCN}^-$  at Different Temperatures

temp, °C	$k_{f(I)}$ , $\text{M}^{-1} \text{s}^{-1}$	$k_{r(I)}$ , $\text{s}^{-1}$
10	$0.72 \pm 0.03$	$0.20 \pm 0.02$
18	$1.4 \pm 0.2$	$0.5 \pm 0.1$
25	$2.6 \pm 0.1$	$0.89 \pm 0.03$
30	$4.4 \pm 0.3$	$1.5 \pm 0.2$
$\Delta H^\ddagger$ , $\text{kJ mol}^{-1}$	$62 \pm 3$	$69 \pm 3$
$\Delta S^\ddagger$ , $\text{J K}^{-1} \text{mol}^{-1}$	$-30 \pm 10$	$-14 \pm 10$

<sup>a</sup> pH 2.5,  $[\text{Fe}(\text{III})] = 5 \times 10^{-5}$  M,  $\mu = 2$  M ( $\text{NaClO}_4$ ).

thermore, it is possible to observe the second slower substitution reaction directly when the diaqua complex, in the presence of 0.03 M  $\text{SCN}^-$  at pH 4.5, is treated with 0.2 M  $\text{SCN}^-$ . All these observations confirm the nature of the two reaction processes.

Under conditions where only the first reaction is observed at lower pH (2 to 3.0), where there is a linear dependence of  $k_{\text{obs}}$  on  $[\text{SCN}^-]$  with a significant intercept as shown in Figure 4a, the rate law can be expressed by eq 4, where  $k_{f(I)}$

$$k_{\text{obs}(I)} = k_{f(I)}[\text{SCN}^-] + k_{r(I)} \quad (4)$$

and  $k_{r(I)}$  represent the rate constants for the forward and reverse reactions of the first step, respectively. The reaction was studied as a function of temperature at pH 2.5, and the results are shown in Figure 5. The good linear plots with significant intercepts are in agreement with the rate law given in (4). The values of  $k_{f(I)}$  and  $k_{r(I)}$  as function of temperature, along with the corresponding activation parameters, are summarized in Table 1. The pressure dependence of the reaction was investigated under the same experimental conditions, and the results are shown in Figure 6. A plot of  $\ln k_{f(I)}$  versus pressure gave a good linear fit from which  $\Delta V_{f(I)}^\ddagger$  for the forward reaction was found to be  $-2.5 \pm 0.2$   $\text{cm}^3 \text{mol}^{-1}$ .

Starting from pH 3.5, the kinetic data in Figure 4 exhibit significant curvature, which can be interpreted in terms of an interchange mechanism that involves precursor formation as shown in Scheme 2. A similar scheme can be formulated



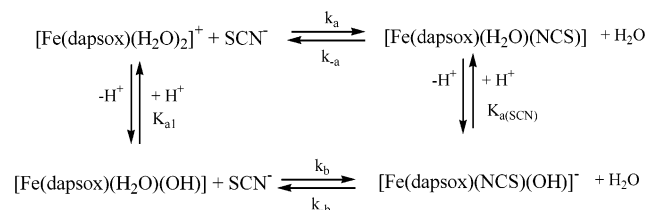
## Substitution Behavior of a 7-Coordinate Fe(III) Complex

**Table 3.** Kinetic and Thermodynamic Data as a Function of pH for the Reaction of  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]^+$  with  $\text{SCN}^-$  at 25 °C According to a Dissociative Mechanism

pH	$k_1k_2/k_{-1},^a \text{ M}^{-1} \text{ s}^{-1}$	$k_{-2},^a \text{ s}^{-1}$	$k_2/k_{-1},^a \text{ M}^{-1}$	$k_1k_2/k_{-1}k_{-2},^a \text{ M}^{-1}$	$k_1k_2/k_{-1},^b \text{ M}^{-1} \text{ s}^{-1}$	$k_{-2},^b \text{ s}^{-1}$	$k_2/k_{-1},^b \text{ M}^{-1}$
3.5	12 ± 1	3.0 ± 0.1	0.5 ± 0.1	4.0 ± 0.5			
4.0	33 ± 2	9.2 ± 0.1	1.0 ± 0.1	3.6 ± 0.3			
4.5	90 ± 10	23.0 ± 0.5	1.3 ± 0.2	3.9 ± 0.5	22 ± 3	5.1 ± 0.2	1.0 ± 0.2
4.7	146 ± 4	44.3 ± 0.3	0.7 ± 0.1	3.3 ± 0.2	34 ± 6	10.0 ± 0.3	1.4 ± 0.3
5.0	235 ± 10	70.0 ± 0.4	0.9 ± 0.1	3.4 ± 0.2	40 ± 6	11.0 ± 0.2	1.7 ± 0.3
5.2	413 ± 35	104 ± 1	1.6 ± 0.2	4.0 ± 0.4	45 ± 5	11.0 ± 0.2	1.7 ± 0.2
5.5					55 ± 21	11.6 ± 0.8	2.1 ± 1.0

<sup>a</sup> Data for the first step of the reaction fitted to eq 6. <sup>b</sup> Data for the second step of the reaction fitted to eq 6.

### Scheme 4



reported in Table 2 and also increase significantly with increasing pH. The values of  $k_2/k_{-1}$  represent the efficiency of  $\text{SCN}^-$  as compared to water to scavenge the six-coordinate intermediate, which according to the data in Table 3 remains rather constant over the investigated pH range. This means that  $k_1$  increases significantly with increasing pH due to the dissociative behavior of the aquahydroxo complex formed at higher pH.

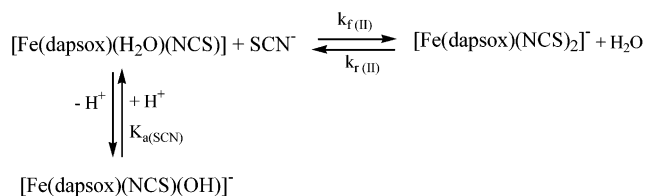
Formation of  $[\text{Fe}(\text{dapsox})(\text{NCS})(\text{H}_2\text{O})]$  involves the participation of both the diaqua and aqua-hydroxo complexes (Scheme 4), such that the pH dependence of  $k_{f(I)}$  and  $k_{r(I)}$  can be expressed with eqs 7 and 8, respectively.

$$k_{f(I)} = \frac{k_a[\text{H}^+] + k_bK_{a1}}{[\text{H}^+] + K_{a1}} \quad (7)$$

$$k_{r(I)} = \frac{k_{-a}[\text{H}^+] + k_{-b}K_{a(\text{SCN})}}{[\text{H}^+] + K_{a(\text{SCN})}} \quad (8)$$

At pH > 5.2 it is difficult to obtain accurate values for  $k_{\text{obs}(I)}$  since the reaction then becomes too fast for stopped-flow measurements. A fit of the available data in Table 2 to eqs 7 and 8 did not result in accurate values for  $K_{a1}$  and  $K_{a(\text{SCN})}$ , when  $k_a$ ,  $k_b$ , and  $K_{a1}$ , or  $k_{-a}$ ,  $k_{-b}$ , and  $K_{a(\text{SCN})}$ , were taken as variables, respectively. The kinetic data were, therefore, fitted to eqs 7 and 8 by using only one unknown parameter, i.e., taking the spectrophotometrically determined values for  $K_{a1}$  and  $K_{a(\text{SCN})}$ , and  $k_{f(I)} = 2.19 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{r(I)} = 0.54 \text{ s}^{-1}$ , values obtained at pH 2 for  $k_a$  and  $k_{-a}$ . The values then obtained for  $k_b$  and  $k_{-b}$  are  $1172 \pm 22 \text{ M}^{-1} \text{ s}^{-1}$  and  $1449 \pm 35 \text{ s}^{-1}$ , respectively. A similar procedure was adopted for the data in Table 3, from which it followed that  $k_b = 1864 \pm 56 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{-b} = 1449 \pm 35 \text{ s}^{-1}$  (since the values of  $k_{r(I)}$  in Table 2 and  $k_{-2}$  in Table 3 are identical). It follows from the values for  $k_a$  and  $k_b$  that the reaction of thiocyanate with the aquahydroxo complex is ca.  $10^3$  times faster than the corresponding reaction with the diaqua complex. Since  $\text{p}K_{a1}$  is 5.78, this ratio of rate constants will imply that at

### Scheme 5



pH > 3.5 the major reaction route will proceed via the more labile aquahydroxo complex. Thus Schemes 2 and 3 given above are valid for the reaction of the aquahydroxo complex under such conditions. Furthermore, the ratio of  $k_a$  and  $k_b$  also accounts for the fact that a significant influence of the aquahydroxo complex is observed in a pH range quite far away from the  $\text{p}K_{a1}$  value.

On the basis of the observed kinetic behavior and especially the value of  $\Delta V_{f(I)}^\ddagger$ , it is suggested that the reaction of  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]^+$  with  $\text{SCN}^-$  follows an  $I_a$  mechanism in the lower pH range where the diaqua complex is the main reactive species. At higher pH, the observed rate law and activation parameters suggest that the substitution process is of a more dissociative character, i.e., there is a systematic changeover in the mechanism from  $I_a$  to  $I_d$  or  $D$  on increasing the pH. This is ascribed to an increasing contribution of the second reaction pathway in Scheme 4, involving the more labile aquahydroxo complex under these conditions.

Kinetic data for the formation of  $[\text{Fe}(\text{dapsox})(\text{NCS})_2]^-$  (Scheme 5) at pH 4.5–5.5 (Figure S2), can be fitted to eqs 5 and 6, for which the results are included in Tables 2 and 3, respectively. The values of  $k_{f(II)}$ ,  $k_{r(II)}$ ,  $K_{(II)}$ , and  $k_2/k_{-1}$  are given in Tables 2 and 3. Since the rate of formation of  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})(\text{NCS})]$  increases significantly with increasing pH, a moderate acceleration of the second reaction step also occurs. However, at higher pH where the inert complex  $[\text{Fe}(\text{dapsox})(\text{NCS})(\text{OH})]^-$  becomes the dominating species in solution, formation of  $[\text{Fe}(\text{dapsox})(\text{NCS})_2]^-$  was observed to become slower again. Furthermore, at this pH the reaction is not thermodynamically favored, which is reflected in small absorbance changes observed during the reaction, coupled to inaccurate kinetic data. The calculated values for  $K_{(II)}$  are similar to those for  $K_{(I)}$ , which suggests that the nature of the weak interactions responsible for the formation of the precursor complex must be the same for both reaction steps. The values of  $k_{f(II)} = k_1k_2/k_{-1}$  in Table 3 are larger than those reported in Table 2, but show the same trend. The values of  $k_2/k_{-1}$  in Table 3 remain constant within the experimental error limits for the formation of the 1:2 complex.



**Table 4.** Kinetic Data for the Second Step of the Reaction of  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})(\text{NCS})]^+$  with  $\text{SCN}^-$  at Different Temperatures

temp, °C	$k_{\text{f(II)}}, \text{M}^{-1} \text{s}^{-1}$
5	$3.5 \pm 0.1$
15	$8.0 \pm 0.2$
25	$21 \pm 1$
35	$46 \pm 1$
$\Delta H^\ddagger, \text{kJ mol}^{-1}$	$60 \pm 2$
$\Delta S^\ddagger, \text{J K}^{-1} \text{mol}^{-1}$	$-19 \pm 6$

<sup>a</sup> pH 5.5,  $[\text{Fe}(\text{III})] = 5 \times 10^{-5} \text{ M}$ ,  $[\text{SCN}^-] = 1 \text{ M}$ ,  $I = 2 \text{ M}$  ( $\text{NaClO}_4$ ).

The second reaction step was also studied as function of temperature and pressure (pH 5.5, 1 M NaSCN) and the results are summarized in Table 4 and Figure S3, respectively. Figure S3 illustrates a good linear correlation between  $\ln k$  and pressure. The activation parameters  $\Delta H^\ddagger_{\text{f(II)}}$ ,  $\Delta S^\ddagger_{\text{f(II)}}$ , and  $\Delta V^\ddagger_{\text{f(II)}}$  were found to be  $60 \pm 2 \text{ kJ mol}^{-1}$ ,  $-19 \pm 6 \text{ J K}^{-1} \text{mol}^{-1}$ , and  $+8.8 \pm 0.3 \text{ cm}^3 \text{mol}^{-1}$ , respectively. These data along with the observed rate law suggest a dissociative reaction mode, similar to that suggested for the first reaction step in the higher pH range.

**Overall Discussion.** As far as we know, the  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]\text{ClO}_4$  complex is one of only thirteen structurally characterized heptacoordinate Fe(III) complexes.<sup>3,14,16,18,19,26–32</sup> Its structural characteristics,<sup>10</sup> in comparison with X-ray structural data from the literature,<sup>3,14,16,18,26–30,32</sup> indicate a significant delocalization of electron density over the entire pentadentate ligand<sup>16,33,34</sup> and the highest degree of Fe(III)-polydentate  $\pi$ -system conjugation in the  $x$ - $y$  plane. Similar donor-acceptor  $\pi$ - $\pi$  type interactions are also important in the chemistry of iron porphyrins,<sup>35</sup> but it seems that the degree of electron delocalization in the  $x$ - $y$  plane of the present complex is even higher, and also its degree of planarity in the equatorial plane is more prominent.<sup>16,34</sup> Furthermore, it is also known that the electron-withdrawing and electron-donating character of porphyrin ligands affects the properties of a metal and exerts a cis effect on the axial ligands.<sup>35</sup> This is exactly the case for  $\text{dapsox}^{2-}$ , which has an even more prominent electron-withdrawing ability, and results in a shorter Fe–H<sub>2</sub>O bond. The length of the Fe(III)–H<sub>2</sub>O bond is in general between 1.986(7) Å in the case of  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ <sup>36</sup> (or 1.999 Å as determined by EXAFS)<sup>37</sup> and 2.107 Å in the seven-coordinate  $[\text{Fe}(\text{edta})$

$\text{H}_2\text{O}]^-$ , whereas in  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]^+$  its average value is 2.028(3) Å. This value is significantly smaller than the Fe(III)–H<sub>2</sub>O bond length in other heptacoordinate Fe(III) complexes. However, even more significant is that the Fe–H<sub>2</sub>O bond in  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]^+$  is shorter, not only in comparison with the heptacoordinate species, but also when compared to the same bond in the hexacoordinate  $[\text{Fe}(\text{TPP})(\text{H}_2\text{O})_2]^+$  complex, viz. 2.090(2) Å.<sup>38</sup> This means that an increase in coordination number from 6 to 7 does not necessarily always lead to an increase in the lability of the bonds. It is interesting to note that the length of this bond in  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]^+$  is approximately the same as that in  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ .

Such structural characteristics and properties of the  $\text{dapsox}^{2-}$  ligand certainly influence the acidity of the coordinated water molecules. The  $\text{p}K_{\text{a}1}$  value of  $5.78 \pm 0.04$  for the  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]^+$  complex is much lower than that for the edta-type complexes ( $\text{p}K_{\text{a}}$  values are between 6.9 and 8.65 depending on a given ligand)<sup>27,29</sup> and the water-soluble iron(III) porphyrin complexes ( $\text{p}K_{\text{a}}$  ca. 7).<sup>11</sup> This difference must partially be due to the overall charge on the complexes. On the other hand, its acidity is significantly lower than for the more positively charged hexaquaquiron(III) species ( $\text{p}K_{\text{a}} = 2.78$ ).<sup>39</sup> What is important, however, is the fact that its acidity is considerably lower than that of the mentioned  $[\text{Fe}(\text{L}_2)\text{Cl}_2](\text{PF}_6)$  complex with a pentaaza macrocyclic ligand that catalyzes the fast disproportionation of superoxide.<sup>14</sup> As expected, the pentadentate 2- charge on the complex under study is responsible for the increase in the  $\text{p}K_{\text{a}2}$  value, so that at physiological pH, the aquahydroxo  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})(\text{OH})]$  form dominates in solution. This aspect makes the investigated complex a potentially better catalyst than the pentaaza macrocyclic Fe(III) systems mentioned above, since these systems are mainly present in the form of the inert dihydroxo species at pH 7.

Since the solvent molecules occupy two axial positions in  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]^+$ , it is possible to investigate a two-step anation reaction and obtain information on the trans effect of the first coordinated nucleophile on the second substitution step. In the case of a two-step ligation of the water-soluble Fe(III) porphyrins, this is not possible since the thermodynamics favor a bis ligation.<sup>40</sup> With such systems, distinct stages for the first and second ligation reactions are usually not observed in the spectrophotometric titrations, and formation of the 1:1 complex is not always detectable.<sup>11,12,23,40,41</sup> In the present case, however, except for the log–log plot, spectroscopic studies have not offered additional evidence for the formation of the 2:1 complex. An almost identical situation is known from the literature in the case of the reaction of aqueous solutions of  $\text{Fe}^{3+}$  with phosphoric acid,<sup>42</sup> where evidence for the formation of a

(26) Lind, M. D.; Hoard, J. L.; Hamor, M. J.; Hamor, T. A. *Inorg. Chem.* **1964**, *3*, 34.

(27) Sanchiz, J.; Dominguez, S.; Mederos, A.; Brito, F.; Arrieta, J. M. *Inorg. Chem.* **1997**, *36*, 4108.

(28) Hernandez-Padilla, M.; Sanchiz, J.; Dominguez, S.; Mederos, A.; Arrieta, J. M.; Zuniga, F. J. *Acta Crystallogr.* **1996**, C52, 1618.

(29) Seibig, S.; van Eldik, R. *Inorg. Chim. Acta* **1998**, *279*, 37.

(30) Cohen, G. H.; Hoard, J. L. *J. Am. Chem. Soc.* **1966**, *88*, 3228.

(31) Fleischer, E.; Hawkinson, J. *Am. Chem. Soc.* **1967**, *89*, 720.

(32) Palenik, G. J.; Wester, D. W.; Rychlewska, U.; Palenik, R. C. *Inorg. Chem.* **1976**, *15*, 1814.

(33) Ivanovic-Burmazovic, I.; Andjelkovic, K.; Beljanski, V.; Prelesnik, B. V.; Leovac, V. M.; Momirovic, M. *J. Coord. Chem.* **1997**, *42*, 335.

(34) Andjelkovic, K.; Ivanovic-Burmazovic, I.; Gruden, M.; Niketic, S. R. *J. Coord. Chem.* **2001**, *53*, 289.

(35) Caughey, W. S. *Inorganic biochemistry, Vol. 2: Iron Porphyrins—Hemes and Hemins*; Eichhorn, G. L., Ed.; Elsevier Scientific: Amsterdam, The Netherlands, 1973.

(36) Hair, N. J.; Beattie, J. K. *Inorg. Chem.* **1977**, *16*, 245.

(37) Ozutsumi, K.; Hasegawa, E.; Kurihara, M.; Kawashima, K. *Polyhedron* **1993**, *12*, 2185.

(38) Kastner, M. E.; Scheidt, W. R.; Mashiko, T.; Reed, C. A. *J. Am. Chem. Soc.* **1978**, *100*, 666.

(39) Ishiara, K.; Funahashi, S.; Tanaka, M. *Inorg. Chem.* **1983**, *22*, 194.

(40) Castro, C. E.; Jamin, M.; Yokoyama, W.; Wade, R. *J. Am. Chem. Soc.* **1986**, *108*, 4179.

(41) Walker, F. A.; Lo, M. W.; Ree, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 5552.

(42) Wilhelmy, R. B.; Patel, R. C.; Matijevic, E. *Inorg. Chem.* **1985**, *24*, 3290.

bisphosphato complex was only detected in the analysis of the kinetic data. In that study, the detection of the 2:1 substitution product demonstrated how valuable kinetic techniques are in the characterization of the species in solution.

Furthermore, with respect to the coordination number of 7 and the general labilization induced by chelates on the remaining monodentate ligands in the coordination sphere, it is reasonable to expect a high kinetic lability for the  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]^+$  complex, i.e., an exceptionally rapid substitution reaction and the operation of a limiting dissociative mechanism. Surprisingly, the kinetic measurements have shown that this is not the case. As far as we know, the only kinetic data referring to substitution reactions of heptacoordinate 3d metal complexes have been performed on reactions of  $[\text{Fe}^{\text{III}}(\text{edta})\text{H}_2\text{O}]^-$  with  $\text{HSO}_3^-$ , where the rate constant for the formation of  $[\text{Fe}(\text{edta})(\text{SO}_3)]^{3-}$  was found to be  $4.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C. In light of very high water-exchange rate constants for different polyaminocarboxylate complexes of Fe<sup>III</sup> in the range of  $10^5$  to  $10^8 \text{ s}^{-1}$ ,<sup>3,4</sup> a high lability of the coordinated water molecule is evident, which was accounted for in terms of both a chelate effect and the seven-coordinate nature of these complexes in solution. Yet, the rates at which  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]^+$  reacts with  $\text{SCN}^-$  when it is in the diaqua, aquahydroxo, or aquathiocyanato forms (Tables 2 and 3) are not only far below the rates determined for the heptacoordinate edta complex, but they are even lower than the substitution rates of  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ .<sup>24,25,39,42–46</sup>

Literature data for the second-order rate constants for the reactions of various nucleophiles with  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+}$  range between 73 and  $132 \text{ M}^{-1} \text{ s}^{-1}$  ( $k_a$ ) and  $5 \times 10^3$  and  $4.2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  ( $k_b$ ) at 25 °C, respectively.<sup>24,43,44,47,48</sup> This acceleration is ascribed to the trans effect of coordinated hydroxide. Thus, for  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]^+$ , where  $k_a = 2.19 \pm 0.06 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_b = 1172 \pm 22 \text{ M}^{-1} \text{ s}^{-1}$ , a similar increase in reactivity is observed, but the coordination number of seven is not responsible for the kinetic labilization of the complex as could have been expected based on the above analysis of the structural parameters. Even more so, it seems that the  $\text{dapsox}^{2-}$  pentadentate itself has a stabilizing chelate effect in terms of structure and lability, which results in the more inert nature of this Fe(III) complex.

In comparison to other Fe(III) complexes, kinetic properties of this complex are close to the properties of the  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  ion, not only with respect to the rate of substitution, but also in terms of its mechanistic behavior. Water exchange reactions on  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ ,<sup>49</sup> as well as ligand substitution reactions,<sup>50</sup> in general follow an  $I_a$  and  $I_d$  mechanism, respectively. In terms of the interchange mech-

anism for substitution reactions,  $k_b/k_a$  should be approximately the same as  $k_{\text{ex}}(\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+})/k_{\text{ex}}(\text{Fe}(\text{H}_2\text{O})_6^{3+})$ , with  $k_a$  and  $k_b$  being the second-order rate constant for the reactions of  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  ( $I_a$  mechanism) and  $[\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+}$  ( $I_d$  mechanism), respectively, and  $k_{\text{ex}}$  being rate constants for the water exchange reactions. For  $k_{\text{ex}}(\text{Fe}(\text{H}_2\text{O})_5\text{OH})^{2+}/k_{\text{ex}}(\text{Fe}(\text{H}_2\text{O})_6^{3+}) \approx 750$ ,<sup>45,51</sup>  $k_b/k_a$  values between 300 and 2300 are considered to be acceptable and indicative of the applicability of the interchange mechanism ( $I_d$  versus  $I_a$ ), leaving open the possibility of entering group participation in the transition states.<sup>45</sup> In the present case  $k_b/k_a = 535$ , which falls within this range and suggests the operation of  $I_a$  and  $I_d$  mechanisms for the two reaction paths, respectively (Scheme 4). The rather low value of  $k_b/k_a$  is in agreement with the electron-withdrawing character of the  $\text{dapsox}^{2-}$  pentadentate, which reduces the trans effect of  $\text{OH}^-$ , whereas the electroneutrality of  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})(\text{OH})]$  may also have an effect on its reduced electrophilicity. The  $k_{-b}/k_{-a}$  ratio for the reverse reactions (Scheme 4) is much higher, viz. 2683, because of the very low  $k_{-a}$  value of  $0.54 \text{ s}^{-1}$ . The  $k_{-b}/k_{-a}$  ratio cannot be compared to that for the water exchange reactions, since  $k_{-b}$  and  $k_{-a}$  are related to the aquation of  $[\text{Fe}(\text{dapsox})(\text{OH})(\text{NCS})]^-$  and  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})(\text{NCS})]$ , respectively. The lower value of  $k_{-a}$  can also be understood in terms of the electroneutrality of  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})(\text{NCS})]$  as opposed to the positive charge on  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]^+$ , since the electrophilicity of the metal center will affect the efficiency of an associative interchange mechanism that has been proposed for these two complexes.

For the second substitution step (formation of the bithiocyanato complex), an  $I_d$  mechanism is proposed as in the case of  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})(\text{OH})]$ . The electroneutrality of  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})(\text{NCS})]$  apparently favors a more dissociative reaction with the negatively charged entering nucleophile. The lower rate of the reaction with  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})(\text{NCS})]$  as compared to  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})(\text{OH})]$  is the consequence of a difference in the trans effect of  $\text{SCN}^-$  and  $\text{OH}^-$ . The  $\pi$ -acceptor nature of  $\text{SCN}^-$  decreases the lability of the Fe–OH<sub>2</sub> bond,<sup>52</sup> making the second substitution step slower than the first one.

Within the concept of an interchange mechanism, the reaction is preceded by formation of the outer-sphere precursor complex with the formation constants  $K_{(I)}$  and  $K_{(II)}$  for the first and second reaction steps, respectively. This constant usually depends on the charge on the reactants. In the present case, however, it is approximately the same ( $\approx 1 \text{ M}^{-1}$ ) for both the first and the second reaction step, and does not vary significantly with pH (Table 2). The similarity of the  $K_{(I)}$  and  $K_{(II)}$  values indicates that the precursor formation constant does not depend on the charge of the reactant complex, and questions the nature of the interactions responsible for the precursor formation. From the structure of  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]\text{ClO}_4$ , it is noted that hydrogen bonds between the complex cation and the counterion (see Figure 1) are very important within the hydrogen-bonding network. The crystal organization of  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]\text{ClO}_4$  is

(43) Perlmutter-Hayman, B.; Tapuhi, E. *J. Coord. Chem.* **1976**, 6, 31.

(44) Grant, M.; Jordan, R. B. *Inorg. Chem.* **1981**, 20, 55.

(45) Brink, C. P.; Crumbliss, A. L. *Inorg. Chem.* **1984**, 23, 4708.

(46) Hynes, M. J.; Kelly, D. F. *Inorg. Chim. Acta* **1991**, 187, 159.

(47) Funahashi, S.; Ishiara, K.; Tanaka, M. *Inorg. Chem.* **1983**, 22, 2070.

(48) Grace, M. R.; Swaddle, T. W. *Inorg. Chem.* **1992**, 31, 4674.

(49) Swaddle, T. W.; Merbach, A. E. *Inorg. Chem.* **1981**, 20, 4212.

(50) Ishiara, K.; Funahashi, S.; Tanaka, M. *Inorg. Chem.* **1983**, 22, 3589.

(51) Dodgen, H. W.; Liu, G.; Hunt, J. P. *Inorg. Chem.* **1981**, 20, 1002.

(52) Banerjee, D.; Chakravarti, B. *Inorg. Chim. Acta* **1995**, 240, 117.

characterized by a remarkable feature of ion-pair association provided by the form of the complex ion and the orientation of its C(O)–NH<sub>2</sub> terminal groups. The complex appears as a “tweezer” that can with the hydrogen bonds over the amide-NH<sub>2</sub> groups of both side chains “squeeze” the potential hydrogen acceptors. On the other hand, the nucleophilicity of SCN<sup>−</sup> is weakened by the hydrogen bonds most probably responsible for precursor formation, and that may be a reason the complex is less reactive than expected. Furthermore, the inability to form hydrogen bonds with chloride, bromide, iodide and thiourea may be the reason [Fe(dapsox)(H<sub>2</sub>O)<sub>2</sub>]<sup>+</sup> does not react effectively with these ligands in aqueous solution. It should be noted that the influence of hydrogen-bonding interactions on the value of the precursor formation constant is mentioned in the literature,<sup>44</sup> together with a comment that these interactions may be one of the reasons for the preference of the interchange mechanism in the case of substitution reactions of Fe<sup>3+</sup> ions.<sup>45</sup> Furthermore, the activation parameters obtained for the first and second steps of the reaction clearly support the operation of I<sub>a</sub> and I<sub>d</sub> mechanisms, respectively.

The  $\Delta H_{\text{f(1)}}^{\ddagger}$  value for the first reaction step at pH 2.5 corresponds to the activation enthalpy for this reaction when it proceeds along pathway 1 (Scheme 4). Its value of  $62 \pm 3 \text{ kJ mol}^{-1}$  is between that reported for water exchange on [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> ( $64 \pm 3 \text{ kJ mol}^{-1}$ )<sup>44</sup> and water exchange on the seven-coordinate Fe(III) polyaminocarboxylate complexes (where  $\Delta H^{\ddagger}$  is in the range from  $22 \pm 1$  to  $48 \pm 2 \text{ kJ mol}^{-1}$ , depending on the chelate ligand),<sup>4</sup> which is in line with the earlier discussed length of the Fe–H<sub>2</sub>O bond in [Fe(dapsox)(H<sub>2</sub>O)<sub>2</sub>]<sup>+</sup>. This value is also in general agreement with the  $\Delta H^{\ddagger}$  values found for substitution reactions of [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>, which follow an I<sub>a</sub> mechanism.<sup>47</sup> In the reverse reaction, the  $\Delta H_{\text{b(1)}}^{\ddagger}$  value of  $69 \pm 3 \text{ kJ mol}^{-1}$  is somewhat higher (Table 1), since this reaction involves the breakage of the stronger Fe–NCS bond and the formation of the weaker Fe–H<sub>2</sub>O bond. The activation enthalpy of the second substitution step ( $\Delta H_{\text{f(II)}}^{\ddagger} = 60 \pm 2 \text{ kJ mol}^{-1}$ ) is almost the same as for the first step ( $\Delta H_{\text{f(I)}}^{\ddagger} = +62 \pm 3 \text{ kJ mol}^{-1}$ ). If the second step would follow a limiting D mechanism, we would expect a significantly higher  $\Delta H^{\ddagger}$  value than for the first step.  $\Delta H^{\ddagger}$  values independent of the group in the position trans to the leaving water molecule support the operation of an interchange mechanism.

Negative  $\Delta S^{\ddagger}$  values were found for the forward and reverse reactions of the first substitution step, as well as for the second step (Tables 1 and 4). This is consistent with an interchange mechanism in which the entering group participates in the transition state. Their values correspond to the degree of hydrogen bonding and dipole interactions present in the second coordination sphere of the precursor complexes. Hydrogen-bonding interactions are known to affect the value of the activation entropy much more than they affect the volume of activation.<sup>3</sup> The value of  $\Delta S^{\ddagger}$  ( $-19 \pm 6 \text{ J mol}^{-1}\text{K}^{-1}$ ) is higher when the negatively charged SCN<sup>−</sup> is the entering group and neutral [Fe(dapsox)(H<sub>2</sub>O)(NCS)] is the reactant. Taking also into consideration the second-order rate constants for the back reaction, we can compare the  $\Delta S^{\ddagger}$

values for the forward ( $-30 \pm 10 \text{ J mol}^{-1}\text{K}^{-1}$ ) and reverse ( $-43 \pm 10 \text{ J mol}^{-1}\text{K}^{-1}$ ) reactions of the first step. These values are somewhat more negative than the value for the second step, which is in agreement with the proposed I<sub>a</sub> and I<sub>d</sub> mechanism, respectively.

Whereas  $\Delta S^{\ddagger}$  values are in general intrinsically subjected to large errors due to the inherent extrapolation involved in their determination,<sup>53</sup> the  $\Delta V^{\ddagger}$  values can give a more precise indication of the intimate nature of the reaction mechanism. The small negative  $\Delta V^{\ddagger}$  value of  $-2.5 \pm 0.2 \text{ cm}^3 \text{ mol}^{-1}$  found for the first reaction step at low pH (pathway 1 in Scheme 4) confirms an I<sub>a</sub> mechanism for the reaction of the diaqua complex with thiocyanate. In fact, under the selected conditions (pH 2.5), based on the values of p*K*<sub>a1</sub>, *k*<sub>a</sub>, and *k*<sub>b</sub>, the aquahydroxo complex will contribute ca. 25% to the overall reaction, and since this complex clearly reacts dissociatively, the actual volume of activation for the reaction with the diaqua complex can be significantly more negative than the observed value. For this reaction  $\Delta V^{\ddagger} = \Delta V_{\text{os}}^{\circ} + \Delta V_{\text{solv}}^{\ddagger} + \Delta V_{\text{intr}}^{\ddagger}$ , where  $\Delta V_{\text{os}}^{\circ}$  represents the volume contribution due to outer-sphere precursor formation, and  $\Delta V_{\text{solv}}^{\ddagger}$  and  $\Delta V_{\text{intr}}^{\ddagger}$  represent solvational and intrinsic volume changes that occur in the rate-determining ligand substitution process, respectively. During outer-sphere complex formation the free thiocyanate becomes weakly bound in the precursor complex, which could result in small intrinsic volume collapse. However, partial charge neutralization between [Fe(dapsox)(H<sub>2</sub>O)<sub>2</sub>]<sup>+</sup> and the entering SCN<sup>−</sup> ion is expected to occur, which will result in a decrease in electrostriction of the solvent molecules accompanied by a volume increase. In case of the reaction of [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> with SCN<sup>−</sup>, the value of  $\Delta V_{\text{os}}^{\circ}$  was reported to be  $+2.0 \text{ cm}^3 \text{ mol}^{-1}$ .<sup>47</sup> Furthermore, the preequilibrium hydrogen-bonding interactions between SCN<sup>−</sup> and the amide-NH<sub>2</sub> groups of the coordinate chelate ligand also lead to the release of solvent molecules which were previously hydrogen bonded to the side chains of the pentadentate chelate. This will also make a small positive contribution to  $\Delta V_{\text{os}}^{\circ}$ .<sup>45</sup> For the rate-determining ligand interchange process,  $\Delta V_{\text{solv}}^{\ddagger}$  is expected to be close to zero since there is no net change in charge during the interchange process. It follows that  $\Delta V_{\text{intr}}^{\ddagger}$ , which is the mechanistic decisive parameter since it represents changes in bond lengths and angles that occur during the interchange process, must be more negative than the experimental value, which further supports the associative character of the interchange process. The volume of activation found for this reaction is indeed very close to the corresponding value for the reaction of [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> with SCN<sup>−</sup> reported in the literature,<sup>48</sup> which was also interpreted in terms of an I<sub>a</sub> mechanism.

The  $\Delta V_{\text{f(II)}}^{\ddagger}$  value of  $+8.8 \pm 0.3 \text{ cm}^3 \text{ mol}^{-1}$  found for the second step of the reaction is almost identical with those reported in the literature for the reaction of [Fe(H<sub>2</sub>O)<sub>5</sub>OH]<sup>2+</sup> with SCN<sup>−</sup>, viz.  $+8.5 \pm 1.2 \text{ cm}^3 \text{ mol}^{-1}$ <sup>47</sup> and  $+9.0 \pm 0.4 \text{ cm}^3 \text{ mol}^{-1}$ ,<sup>48</sup> which was suggested to proceed according to an I<sub>d</sub> mechanism. This suggests that an I<sub>d</sub> mechanism is also operative in the formation of both [Fe(dapsox)(NCS)<sub>2</sub>]

(53) van Eldik, R.; Merbach, A. E. *Comments Inorg. Chem.* **1992**, *12*, 341.

(Scheme 5) and the monothiocyanato complex when starting from the  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})(\text{OH})]$  complex (path 2 in Scheme 4). It is quite reasonable that in this case  $\Delta V_{\text{intr}}^\ddagger$  can be slightly smaller than  $\Delta V_{\text{f(II)}}^\ddagger$  for the reasons outlined above, although the difference is expected to be less since the reacting complex is a neutral species and charge neutralization will not play such a prominent role. The changeover in mechanism is clearly controlled by the labilizing effects of coordinated hydroxide and thiocyanate, which will favor a more dissociative substitution mechanism.

## Conclusions

An important observation is that the coordination of the pentadentate  $\text{dapsox}^{2-}$  chelate to form the heptacoordinate Fe(III) complex apparently has no influence on the mechanism according to which the diaqua and aquahydroxo forms of the complex undergo anation reactions when compared to the fully aquated system. Even more, the  $\text{dapsox}^{2-}$  ligand and its particular electronic properties make these reactions slower than the corresponding reactions of  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ . The unexpected  $I_a$  substitution mechanism maintained in the seven-coordinate  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]^+$  complex is made possible by the ideal planarity of the  $\text{dapsox}^{2-}$  ligand as revealed by the X-ray structure,<sup>10</sup> since there is no steric hindrance in the space above and below the equatorial plane of the complex. This favorable steric situation combined with the positive charge on the diaqua complex enable formation of the Fe–NCS bond accompanied by the breakage of the Fe–H<sub>2</sub>O bond in the transition state. Although it is not appropriate to refer to the formation of an intermediate in the case of an interchange mechanism, it is worth noting that Fe(III) complexes with a coordination

number of 8 have been characterized.<sup>54–56</sup> Thus a transition state with a semi-eight-coordinate character does not seem to be unreasonable. A changeover in mechanism from  $I_a$  to  $I_d$  or D for the substitution reactions of  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})(\text{OH})]$  and  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})(\text{NCS})]$  is caused by the electroneutrality of these complexes coupled to a decrease in the electrophilicity of the metal center, as well as by the higher lability of the coordinated water molecule in the trans position relative to  $\text{OH}^-$  and  $\text{SCN}^-$ , respectively.

The results presented in this paper will direct further investigations to elucidate the substitution behavior of other heptacoordinate 3d metal complexes, also in other solvents, to make it possible to follow these reactions for a variety of different chelates and entering nucleophiles.

**Acknowledgment.** The authors gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft (RvE) and the Alexander von Humboldt Foundation (fellowships to I.I.B. and M.S.A.H.).

**Supporting Information Available:** Three figures presenting plots of absorbance versus pH, from which the  $\text{p}K_{a1}$  (Figure S1a) and  $\text{p}K_{a2}$  (Figure S1b) values were obtained,  $k_{\text{obs(II)}}$  versus  $[\text{SCN}^-]$  for the second step of the reaction in the pH range 4.5–5.5 (Figure S2), and high-pressure kinetic data for the second step of the reaction (Figure S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC0200803

- (54) Logan, N.; King, T. J.; Morris, A.; Wallwork, S. C. *J. Chem. Soc. D* **1971**, *11*, 554.  
(55) Kachanova, Zh. P.; Purmalis, A.; Skurlatov, Yu. I. *Zh. Fiz. Khim.* **1973**, *47*, 1680.  
(56) Koch, W. O.; Barbieri, A.; Grodzicki, M.; Schurnemann, V.; Trautwein, A. X.; Krueger, H. J. *Angew. Chem.* **1996**, *35*, 422.