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Improved Syntheses of $[Fe_2S_2Cl_4]^{2-}$ and $[Fe_2OCl_6]^{2-}$ and Oxo/Sulfido Ligand Substitution by Use of Silylsulfide Reagents

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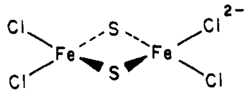
New syntheses of $[Fe_2S_2Cl_4]^{2-}$ (**1**) and $[Fe_2OCl_6]^{2-}$ (**2**) and terminal oxo/sulfido ligand substitution reactions have been devised with use of the reagents $(Me_3Si)_2S$ (**3**), $NaSSiMe_3$ (**4**), and $NaOSiMe_3$ (**5**) in acetonitrile solutions. The preparation of **4** is described. Reactions of $(Et_4N)[FeCl_4]$ with equimolar quantities of **3**, **4**, and **5** in acetonitrile afford the Et_4N^+ salts of **1** (76%, 77%) and **2** (66%), respectively, in good yields. In THF $(Et_4N)_2$(**1**) was isolated in essentially quantitative yield from a reaction using **3**. Equimolar amounts of **2** and **3** give partial conversion to **1** in a bridge oxo/sulfido substitution reaction; a competing reaction is that of product Me_3SiCl with **2** to form $[FeCl_4]^-$. The chelate complex VO(acen) reacts with excess **3** to give a quantitative in situ yield of VS(acen). On a preparative scale a 79% yield was obtained. Similarly, $NbO(S_2CNEt_2)_3$ was converted to yellow $NbS(S_2CNEt_2)_3$ (ν_{NbS} = 493 cm^{-1}) in 52% isolated yield. These syntheses of **1** and **2** in particular offer advantages over previous methods. The results presented suggest that silylsulfide reagents may have extended utility in effecting bridging and terminal oxo/sulfido transformations.

Introduction

The binuclear complex $[Fe_2S_2Cl_4]^{2-}$ (**1**), having a planar $[Fe_2S_2]^{2+}$ core and tetrahedral Fe(III) coordination,[1] has been accessible previously only by means of reaction 1. Its Et_4N^+ salt has been obtained in purified yields of 45–65%.[2] Although originally prepared from $[Fe_2S_2(S_2\text{-}o\text{-xyl})_2]^{2-}$ and benzoyl chloride,[2] **1** can be obtained from other thiolato dimers and acyl chlorides. Reactant dimers have been synthesized by several methods.[3-8] Recently we have been concerned with the possible synthesis of oxo analogues of the biologically significant Fe_2S_2 and Fe_4S_4 clusters[9] and with the general problem of oxo/sulfido ligand substitution. Among oxo complexes with halide ligands the closest approach to **1** is $[Fe_2OCl_6]^{2-}$ (**2**), having tetrahedral Fe(III) stereochemistry and a variable Fe–O–Fe angle (156, 180°) in different compounds.[10,11] The complex has been prepared by partial hydrolysis of $FeCl_3$ in nonaqueous solvents and isolated as the pyridinium[10,12] and $[(Ph_3P)_4C_2Se_2]^{2+}$[11] salts. In the course of investigating the synthesis of polynuclear Fe–O and Fe–S complexes, we have developed new preparations of **1** and **2** using silylsulfide and silyloxy reagents, respectively. Because of their simplicity and novelty and the potential or demonstrated use of **1** and **2** as precursors of other complexes, these syntheses are reported here. Also described is a new method for oxo/sulfido ligand substitution, effected by silylsulfide reagents.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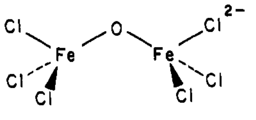
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$$[Fe_2S_2(SR)_4]^{2-} + 4R'COCl \xrightarrow{MeCN} [Fe_2S_2Cl_4]^{2-} + 4R'COSR \quad (1)$$

Experimental Section

Preparation of Compounds. All operations were performed under a pure argon or dinitrogen atmospere. THF was refluxed over and freshly distilled from sodium metal; acetonitrile was freshly distilled from CaH_2. Anhydrous diethyl ether, sodium amide (Fisher Chemical Co.), and hexamethyldisilthiane (Petrarch Systems, Inc.) were used as received. Syntheses of the last compound have been described.[13] $(Et_4N)[FeCl_4]$ was prepared from $FeCl_3$ with use of a method analogous to that for the Fe(II) salt.[14] Analyses were performed by Spang Microanalytical Services, Eagle Harbor, MI.

Physical Measurements. Electronic spectra were recorded on a Cary Model 219 spectrophotometer. ^1H NMR spectra (300 MHz) were obtained with a Bruker WM-300 spectrometer. Infrared spectra were measured with a Perkin-Elmer 599B spectrophotometer. All measurements were made under anaerobic conditions with use of dry solvents.

$NaSSi(CH_3)_3$. To a vigorously stirred slurry of 3.0 g (77 mmol) of $NaNH_2$ in 350 mL of ether was added 17.7 mL (15.1 g, 84 mmol) of $(Me_3Si)_2S$ (*Caution*: malodorous!). Within 15 min a flocculent white microcrystalline solid formed. The reaction mixture was stirred under a positive N_2 stream until the evolution of ammonia ceased (6–12 h). The solid was collected, washed with 2 × 30 mL of ether, and dried in vacuo. This material was dissolved in the minimum volume of THF (~200 mL), and the solution was filtered. The light yellow filtrate was reduced to 25% of its original volume. Addition of 200–300 mL of ether caused separation of a solid, which was collected, washed with copious amounts of ether, and dried in vacuo. The product (3.15 g, 32%) was obtained as a white microcrystalline solid. ^1H NMR (CD_3CN): δ 0.04. IR (mull): 1241 (s), 831 (vs), 748 (m), 679 (m), 639 (s), 490 (s) cm^{-1}. Anal. Calcd for C_3H_9NaSSi: C, 28.09; H, 7.09; S, 25.03; Si, 21.90. Found: C, 27.92; H, 7.13; S, 24.76; Si, 21.62.

$(Et_4N)_2[Fe_2S_2Cl_4]$. (a) From $(Me_3Si)_2S$. To a stirred solution of 3.28 g (10 mmol) of $(Et_4N)[FeCl_4]$ in 50 mL of THF was added dropwise 2.10 mL (1.79 g, 10 mmol) of $(Me_3Si)_2S$. Formation of a deep red-purple solution was followed by separation of a black solid, which was collected, washed with THF and ether, and dried in vacuo. The pure product (2.79 g, 96%) was obtained as purple-black crystals. When the procedure was carried out on the same scale in 10–15 mL

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of acetonitrile, a total of 2.18 g (76%) of product was obtained from the solid that separated from the reaction mixture and a second crop produced by addition of ether to the reaction mixture filtrate.

(b) From $NaSSiMe_3$. To a stirred solution of 1.50 g (4.57 mmol) of $(Et_4N)[FeCl_4]$ in 25 mL of acetonitrile was introduced a slurry of 0.5. g (4.6 mmol) of $NaSSiMe_3$ in 15 mL of acetonitrile. The deep purple-red solution that immediately formed was stirred for 1 h under dynamic vacuum. All volatile components were removed in vacuo, and the residue was dissolved in a minimum volume (~25 mL) of acetonitrile. This solution was filtered, and ether was added to the point of incipient crystallization. After 30 min of standing the solution was filtered and the solid was washed and dried as in the preceding preparation, affording 1.02 g (77%) of purple-black crystals. The product may be recrystallized from acetonitrile/ether with nearly quantitative recovery.

(c) From $[Fe_2OCl_6]^{2-}$ and $(Me_3Si)_2S$. To a stirred solution of 0.60 g (1.0 mmol) of $(Et_4N)_2[Fe_2OCl_6]$ (vide infra) in 15 mL of acetonitrile was added 0.21 mL (0.18 g, 1.0 mmol) of $(Me_3Si)_2S$. A color change from yellow-brown to purple-red quickly ensued. The solution was stirred for 40 min, after which time a small quantity of white solid was removed by filtration. The filtrate was treated with THF (30–40 mL) to the point of incipient crystallization. After the solution stood for 10 min at room temperature the solid was collected by filtration, washed thoroughly with THF and ether, and dried in vacuo; 0.12 g (42% based on $(Me_3Si)_2S$ in reaction 7, text) of product was obtained as purple-black microcrystals. This material was treated with excess $(Et_4N)(SPh)$ in $(CD_3)_2SO$ solution. The ^1H NMR spectrum was that of $[Fe_2S_2(SPh)_4]^{2-}$;[4,5] a very slight amount of $[Fe(SPh)_4]^{2-}$ [5] was also detected. The UV/visible spectra of the products of preparations a–c are indistinguishable from that of authentic $(Et_4N)_2[Fe_2S_2Cl_4]$.[2]

$(Et_4N)_2[Fe_2OCl_6]$. $NaOSiMe_3$, prepared by a published method,[15] was further purified by recrystallization from petroleum ether. To a vigorously stirred solution of 3.28 g (10 mmol) of $(Et_4N)[FeCl_4]$ in 15–20 mL of acetonitrile was slowly added a solution of 1.12 g (10 mmol) of $NaOSiMe_3$ in 50–60 mL of acetonitrile. A yellowish brown solution formed. After the reaction mixture was stirred for ~12 h, its volume was reduced by two-thirds under reduced pressure. The solution was filtered through Celite on a medium-porosity frit to remove finely divided NaCl. The filter bed was washed with acetonitrile, and the filtrates were combined, giving a volume of 50–60 mL. The filtrate was cooled in an ice bath, and anhydrous ether was added until a flocculent beige material just began to separate. After 10 min of standing the mixture was filtered through a medium-porosity frit. This procedure was repeated until no more flocculent material appeared. The stirred yellow-brown filtrate was treated with additional ether until cloudiness was evident. Shortly thereafter golden flakes appeared. The mixture was cooled in an ice bath for ~1 h and then was filtered rapidly. The collected solid was washed with 9:1 v/v ether/acetonitrile and with ether and then was dried in vacuo. Addition of ether to the filtrate afforded a second crop of solid. The combined yield was 2.0 g (66%) of product as flaky golden brown crystals. Anal. Calcd for $C_{16}H_{40}Cl_6Fe_2N_2O$: C, 31.98; H, 6.71; Cl, 35.40; Fe, 18.59; N, 4.66. Found: C, 31.98; H, 6.77; Cl, 35.31; Fe, 18.94; N, 4.53. Absorption spectrum (acetonitrile): λ_{max} 370 (sh, ϵ_M 5000), 312 (sh, 17 100), 303 (sh, 17 900), 292 (18 700), 243 (12 200) nm. IR (KBr): 855 (vs, $\nu_{FeOFe}{}^{as}$), 360 (s, $\nu_{FeCl_3}{}^{as}$), 315 (m, $\nu_{FeCl_3}{}^{s}$) cm^{-1}. (Lit. IR: 860, 360, 311 cm^{-1};[10] 832, 378, 321 cm^{-1};[11] 868, 360 cm^{-1}.[12a] Lit. Raman: 870, 357, 311 cm^{-1}.[12a])

Oxo/Sulfido Ligand Substitution. (a) $[Fe_2S_2Cl_4]^{2-}$ from $[Fe_2OCl_6]^{2-}$. The course of the reactions in preparation c above was examined by ^1H NMR at ~23 °C. A solution of 35 μmol of $(Et_4N)_2[Fe_2OCl_6]$ and 35 μmol of $(Me_3Si)_2S$ in 0.40 mL of CD_3CN after 10 min reaction time exhibited signals of unreacted $(Me_3Si)_2S$ (δ 0.32) and of the reaction products Me_3SiCl (δ 0.42) and $(Me_3Si)_2O$ (δ 0.05). At 40 min the sulfide signal was absent and the intensity ratio $I(\delta\ 0.05)/I(\delta\ 0.42) = 2.3$, suggesting partial consumption of Me_3SiCl in a subsequent reaction. In a separate experiment, the NMR spectrum of a solution initially containing 50 μmol of $(Et_4N)_2[Fe_2OCl_6]$ and 100 μmol of Me_3SiCl in 0.40 mL of CD_3CN became constant at 40 min and revealed $(Me_3Si)_2O$ as the Si-containing reaction product. The other product was identified in a preparative experiment. A solution of 0.50 g (0.83 mmol) of $(Et_4N)_2[Fe_2OCl_6]$ in 40 mL of acetonitrile was treated with excess Me_3SiCl (1 mL, 8 mmol). The color changed immediately from yellow-brown to yellow with a greenish tint. The solid residue obtained after 1 h of reaction and removal of volatile components was dissolved in 5 mL of acetonitrile. Addition of ether caused precipitation of a yellowish solid, identified as $(Et_4N)[FeCl_4]$ (0.46 g, 86%) by IR spectral comparison with an authentic sample.

(b) VS(acen) from VO(acen). To a solution of 0.87 g (2.9 mmol) of VO(acen)[16] in 100 mL of acetonitrile was added with stirring 3.15 mL (2.68 g, 15 mmol) of $(Me_3Si)_2S$. Within 1 h the color of the reaction mixture changed from intense blue to intense red-brown. After 2 h of further reaction time the volume of the solution was reduced to 5–10 mL under dynamic vacuum, causing separation of red crystals. This material was collected, washed with 2 x 10 mL of *n*-hexane, and dried in vacuo; 0.70 g (79%) of product as a red crystalline solid was obtained. IR (KBr): 554 cm^{-1} (ν_{VS}). (Lit.[17] IR: 556 cm^{-1}.) Absorption spectrum (acetonitrile): λ_{max} 495 (sh, ϵ_M 420), 350 (7180), 318 (10 200), 252 (11 400) nm.

(c) $NbS(S_2CNEt_2)_3$ from $NbO(S_2CNEt_2)_3$. The preparation of the oxo compound has been provided in very brief form;[18] the following description is more explicit. To ~100 mL of a 1 M aqueous tartaric acid solution adjusted to pH 5 by addition of 6 M NaOH was added 1.37 g (1.0 mmol) of $K_7HNb_6O_{19}\cdot 13H_2O$.[19] The pH (~8) of this solution was reduced to ~5 with 1 M HCl. A small amount of white solid was removed by filtration, and 4.05 g (18.0 mmol) of $NaS_2CNEt_2\cdot 3H_2O$ in 15 mL of water was added. A turbid solution developed; its pH was adjusted to ~5 with 1 M HCl. The mixture was stirred for 10 min, and the white solid that formed was collected, washed with water, and air-dried. After recrystallization of this material from dichloromethane/*n*-pentane 2.0 g (60%) of white microcrystalline product was obtained. The IR spectrum (KBr) was essentially identical with that reported,[18] $\nu_{NbO} = 901\ cm^{-1}$. An analogous method using $K_8Ta_6O_{19}\cdot 17H_2O$[19] failed to yield $TaO(S_2CNEt_2)_3$, which has not been previously synthesized. A suspension of 0.55 g (1.0 mmol) of $NbO(S_2CNEt_2)_3$ in ~70 mL of acetonitrile was treated with 2.09 mL (1.78 g, 10 mmol) of $(Me_3Si)_2S$. The stirred reaction mixture was maintained at 50 °C under static vacuum. After 1 h a homogeneous yellow-orange solution formed. At the completion of an additional 2 h of reaction time, the reaction mixture was cooled to room temperature and its volume was reduced until yellow solid separated. After storage at −20 °C and filtration 0.30 g (52%) of yellow product was obtained. This material showed $\nu_{NbS} = 493\ cm^{-1}$ and no ν_{NbO} absorption. An analytical sample was obtained by recrystallization from warm acetonitrile. Anal. Calcd for $C_{15}H_{30}N_3NbS_7$: C, 31.62; H, 5.32; N, 7.38; Nb, 16.30; S, 39.38. Found: C, 31.64; H, 5.16; N, 7.23; Nb, 16.15; S, 39.44. IR (KBr): 1503, 1494 (vs); 1450 (m); 1430 (s); 1372 (m); 1350 (m); 1297 (w); 1270 (vs); 1204 (s); 1066 (s); 1004, 1000 (w); 914 (s); 844 (s); 787 (m); 608 (w); 570 (m); 493 (vs); 359 (vs) cm^{-1}.

Results and Discussion

Synthesis of $[Fe_2S_2Cl_4]^{2-}$ and $[Fe_2OCl_6]^{2-}$. Reactions 2–4

$$2(Et_4N)(FeCl_4) + 2(Me_3Si)_2S \xrightarrow[THF]{MeCN} \underset{76\%,\ 96\%}{(Et_4N)_2[Fe_2S_2Cl_4]} + 4Me_3SiCl \quad (2)$$

$$2(Et_4N)(FeCl_4) + 2NaSSiMe_3 \xrightarrow{MeCN} \underset{77\%}{(Et_4N)_2[Fe_2S_2Cl_4]} + 2Me_3SiCl + 2NaCl \quad (3)$$

$$2(Et_4N)(FeCl_4) + 2NaOSiMe_3 \xrightarrow{MeCN} \underset{66\%}{(Et_4N)_2[Fe_2OCl_6]} + (Me_3Si)_2O + 2NaCl \quad (4)$$

afford these complexes in good purified yields from a common,

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simply prepared Fe(III) precursor. Reaction 2 in THF is essentially quantitative. These reactions offer certain advantages over earlier methods. Reaction 1 requires prior preparation of $[Fe_2S_2(SR)_4]^{2-}$. Yields of $[Fe_2OCl_6]^{2-}$ obtained by hydrolysis of $FeCl_3$ in ethanol/pyridine[10,12a] (reaction 5)

$$2FeCl_3 + 3py + H_2O \xrightarrow{EtOH} (pyH)_2[Fe_2OCl_6]{\cdot}py \quad (5)$$

or in dichloromethane[11] were not reported. In the former medium reaction times of 4 days to 1 week were specified. both Me_3SiSR[20] and $(Me_3Si)_2S$[21] have been shown to form M–S–M bridges upon reaction with soluble metal chloride compounds. Reaction 6,[21] affording the cyclic Sn(IV) trimer

$$3Me_2SnCl_2 + 3(Me_3Si)_2S \xrightarrow{C_6H_6} (Me_2Sn)_3(\mu\text{-}S)_3 + 6Me_3SiCl \quad (6)$$

of established structure,[22] is a case in point. Other than the formation of insoluble metal(II) sulfides from MCl_2 and $(Me_3Si)_2S$,[23] reactions 2 and 3 are the first cases of the synthesis of multiple-bridged units from metal halides and silylsulfide reagents. The occurrence of these reactions led to the investigation of the potentially analogous reaction between equimolar amounts of $[FeCl_4]^-$ and $NaOSiMe_3$ in acetonitrile. The only isolable Fe-containing product was $[Fe_2OCl_6]^{2-}$. Evidently the (unknown) $[Fe_2(\mu\text{-}O)_2]^{2+}$ unit does not form under these conditions, it being disfavored by the stabilities of $[Fe_2O]^{4+}$ and the siloxane product. At the mole ratio Fe(III):$NaOSiMe_3$ = 2 a sluggish, ill-defined reaction occurred. At much lower mole ratios the formation of $Fe_2(OSiMe_3)_6$ and $[Fe(OSiMe_3)_4]^-$ has been demonstrated.[24]

Oxo/Sulfido Ligand Substitution Reactions. The reaction of *equi*molar amounts of $[Fe_2OCl_6]^{2-}$ and $(Me_3Si)_2S$ was conducted as a possible means of forming (unknown) $[Fe_2SCl_6]^{2-}$, containing the $[Fe_2S]^{4+}$ unit whose existence we have recently established in $[Fe(salen)]_2S$[25] by X-ray analysis.[26] Instead, $[Fe_2S_2Cl_4]^{2-}$ was isolated as the only Fe–S product from a system comprised of reactions 7 and 8, whose occurrence was established from ^1H NMR and preparative experiments. Reaction 7 is irreversible and affords a 42% isolated yield after <1 h reaction time. Reaction 8 was separately demonstrated, and the product salt was isolated in 86% yield. Reaction 7 is not of preparative value and thus was not optimized, but its occurrence suggested a broader utility of the silylsulfide reagent in O → S ligand substitution reactions. This matter was examined by using two substrate molecules containing terminal oxo groups.

$$(Et_4N)_2[Fe_2OCl_6] + 2(Me_3Si)_2S \xrightarrow{MeCN} (Et_4N)_2[Fe_2S_2Cl_4] + (Me_3Si)_2O + 2Me_3SiCl \quad (7)$$

$$(Et_4N)_2[Fe_2OCl_6] + 2Me_3SiCl \xrightleftharpoons{MeCN} 2(Et_4N)[FeCl_4] + (Me_3Si)_2O \quad (8)$$

Reaction 9 was first monitored spectrophotometrically in the visible region with use of ~4 mM solutions of the V(IV) complex VO(acen)[11] and a 5-fold excess of $(Me_3Si)_2S$. Reactions were complete within 8 h at ambient temperature. A 101 ± 2% in situ yield of VS(acen) was found. When the reaction was carried out on a preparative scale with the same mole ratio of reactants, VS(acen) was isolated in 79% yield. This complex was first obtained in 46% yield from the reaction of VO(acen) and B_2S_3 in dichloromethane.[17] The structure of VS(acen), containing a pyramidal $S{=}VO_2N_2$ coordination unit ($d(V{=}S)$ = 2.061 (1) Å) has since been confirmed by X-ray methods.[27] Thiovanadyl(IV) complexes have otherwise been obtained by the oxidative addition of elemental sulfur to V(II) porphyrins[28] and the reaction of H_2S with a dichloro precursor, as in the synthesis of a macrocyclic $S{=}VN_4$ species.[29] The thiovanadate(V) complexes $[VO_{4-n}S_n]^{3-}$ (n = 2–4[30,31]) and $VS(OSiPh_3)_3$[32] have also been prepared.

$$VO(acen) + (Me_3Si)_2S \xrightarrow{MeCN} VS(acen) + (Me_3Si)_2O \quad (9)$$

Reaction 10 was examined in order to explore further O/S ligand substitution and to clarify certain conflicting literature reports of the nature of $MS(S_2CNEt_2)_3$ complexes. The starting complex, $NbO(S_2CNEt_2)_3$,[18] has a pentagonal-bipyramidal structure with the oxo ligand axial, $d(Nb{=}O)$ = 1.74 (1) Å,[30] and ν_{NbO} = 901 cm^{-1}. Reaction with a 10-fold excess of the silylsulfide in warm acetonitrile gave a *yellow* solid (52%) whose total analysis corresponds to the indicated composition, with an intense band at 493 cm^{-1} assigned as ν_{NbS}. From the reaction systems with mole ratios 4–5 NaS_2CNEt_2/MCl_5 in benzene[34] or acetonitrile[35] products formulated as $MS(S_2CNEt_2)_3$ were obtained. Heckley et al.[34] describe the M = Nb and Ta complexes as *green* with ν_{MS} = 502 (Nb) and 483 (Ta) cm^{-1}. Peterson et al.[35] obtained $TaS(S_2CNEt_2)_3$ as *yellow* crystals and established its structure as analogous to that of $NbO(S_2CNEt_2)_3$, with $d(Ta{=}S)$ = 2.18 (1) Å. However, they report ν_{TaS} = 905 cm^{-1}, a value wholly inconsistent with a bond of the M=S type.[31] The material measured may have been a hydrolysis product. We conclude that the pure $MS(S_2CNEt_2)_3$ complexes are yellow with $\nu_{MS} \lesssim 490$ cm^{-1}. $TaS(S_2CNEt_2)_3$ was not obtained in this work because no synthesis of $TaO(S_2CNEt_2)_3$ has yet been devised.

$$NbO(S_2CNEt_2)_3 + (Me_3Si)_2S \xrightarrow{MeCN} NbS(S_2CNEt_2)_3 + (Me_3Si)_2O \quad (10)$$

Recent estimates of silicon–element homolytic bond cleavage energies lead to the order Si–Cl (93 kcal/mol) > Si–O (88 > Si–S (54 kcal/mol).[36] On this basis reactions 2, 3, 6, 7, 9, and 10 have a favorable enthalpic component. It is probable that bridging and terminal oxo/sulfido transformations with silylsulfide reagents can be extended and perhaps generalized, a matter that is under investigation. Of the complexes prepared here $[Fe_2S_2Cl_4]^{2-}$ and $[Fe_2OCl_6]^{2-}$ contain labile chloride ligands and should be useful reactants. Properties of the former complex have been reviewed.[9] The latter is the only

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nonchelate complex with the $[Fe_2O]^{4+}$ core thus far isolated and as such may serve as a precursor to synthetic analogues of met- and oxyhemerythrin active sites, which contain this unit.[37] $[Fe_2OCl_6]^{2-}$ has already been employed as a spectroscopic model of the oxo bridge in hemerythrin.[12a]

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Registry No. $(NEt_4)_2$-**1**, 62682-81-9; $(NEt_4)_2$-**2**, 87495-23-6; $(Et_4N)[FeCl_4]$, 14240-75-6; $[Fe_2S_2(SPh)_4]^{2-}$, 55939-69-0; VS(acen), 74354-70-4; VO(acen), 19195-97-2; $NbS(S_2CNEt_2)_3$, 31388-94-0; $NbO(S_2CNEt_2)_3$, 33774-12-8; $NaSSi(CH_3)_3$, 87495-22-5; $NaNH_2$, 7782-92-5; $(Me_3Si)_2S$, 3385-94-2; $NaOSiMe_3$, 18027-10-6.

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Pair Excitations in Vivianite, $Fe_3(PO_4)_2 \cdot 8H_2O$

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Polarized absorption spectra of the mineral vivianite, $Fe_3(PO_4)_2 \cdot 8H_2O$, were measured in the region of spin-forbidden excitations at temperatures between 6 and 100 K. The spectral range from 18 000 to 28 000 cm^{-1} is dominated by hot bands, which show a very steep rise between 6 and 50 K. They are attributed to transitions of ferromagnetically coupled iron(II) pairs arising through an exchange intensity mechanism. It is concluded that S is a good quantum number and spin-orbit coupling plays a minor role. From the observed temperature dependencies the exchange parameter of the iron(II) pairs is estimated: $2J = 5$ cm^{-1}.

Introduction

The mineral vivianite occurs naturally in various parts of the world in the form of light green-blue transparent crystals with interesting pleochroic properties.[1,2] The laboratory synthesis of $Fe_3(PO_4)_2 \cdot 8H_2O$ is complicated by the large number of iron(II) phosphate phases and the tendency of solutions and finely powdered products to oxidize in air.[3] It has so far only been prepared in polycrystalline form. The mineral vivianite has some interesting physical and chemical properties, which have been studied by several techniques.

The crystal structure determination revealed the presence of two types of iron(II) centers:[4] On site I the coordination is *trans*-$FeO_4(H_2O)_2$, point symmetry C_{2h}; the four equatorial ligands are phosphate oxygens. Two site II iron(II) ions are joined to a dimer of the edge-sharing type. This coordination is shown schematically in Figure 1. C_2 is the point symmetry of both the single ion of site II and the composite pair of site II ions. There is abundant hydrogen bonding in the anion/water structure linking the magnetic centers to a three-dimensional network.

Table I. Positions (Centers of Band Systems) and Predominant Polarizations in the 50 K Absorption Spectrum Measured Perpendicular to the *ac* Cleavage Plane of Vivianite

position, $cm^{-1} \times 10^{-3}$	dominant polarizn $\vec{}$ (E vector)	position, $cm^{-1} \times 10^{-3}$	dominant polarizn $\vec{}$ (E vector)
26.5	$\parallel c$	22.0	$\perp c$
25.5	$\parallel c$, $\perp c$	20.8	$\perp c$
23.5	$\parallel c$	19.5	$\perp c$

Magnetic susceptibility[5] and heat capacity measurements[6] showed a number of magnetic anomalies between 2 and 20 K, some of which appear to be sample dependent. A transition to long-range magnetic order at 8.8 K was established by neutron diffraction.[7] The magnetic structure is antiferromagnetic, with the spins of the two iron(II) sites forming a sublattice each and a canting angle between the sublattices of 42°. The two iron(II) spins at the site II constituting the dimer are parallel, indicating ferromagnetic intradimer coupling. This magnetic structure was confirmed by Mössbauer experiments.[7]

Optical absorption spectra of vivianite have been measured at room temperature.[1,2,89] The dominant feature in the near-infrared region is the $^5T_{2g} \rightarrow {}^5E_g$ (O_h notation) ligand field transition. It consists of two main components separated by 3500 cm^{-1}. This large splitting was attributed both to low-symmetry crystal field components[8] and to a dynamic Jahn-Teller coupling in the excited ^5E_g state.[1] In the visible part of the spectrum there is a broad and featureless absorption centered at approximately 15 200 cm^{-1}. This transition is polarized completely parallel to the b axis of the monoclinic unit cell. It is responsible for the light blue color and the pleochroism observed in vivianite. The intensity of this absorption depends on the degree of surface oxidation, and its origin is a $Fe^{2+} \rightarrow Fe^{3+}$ intervalence electron-transfer transition in the iron(II) dimers of site II.[2] A great number of iron-containing minerals exhibit absorptions of the mixed-valence type. Between 18 000 and 28 000 cm^{-1}, i.e. most of the visible region, vivianite is quite transparent. A number of very weak ($\epsilon \sim 0.1$) and rather sharp absorption bands have been reported.[1,9] In this paper we shall report and discuss low-tem-

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