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Intercalation-Induced Reactions of Iron Oxychloride

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The preparation and structure of the layered complex formed by the intercalation reaction of FeOCl with propargylamine are reported. The solid isolated from this reaction is a crystalline material with a magnetic susceptibility at room temperature of 0.9×10^{-2} emu g^{-1} and μ_{eff} 18 BM. Reaction of this complex by heating under argon by exposure to moist air, or by washing with water results in new materials with larger susceptibilities, 1.8×10^{-2} emu g^{-1}, and μ_{eff} 72 BM, but with a more disordered structure as determined by X-ray powder diffraction and scanning electron microscopy. The preparation of the butylamine intercalate of FeOCl under identical conditions gave only the literature-reported product. The formation of a fine-particle green rust (I) and not the hydrolysis product γ-FeOOH from the propargylamine complex of FeOCl is suggested based upon magnetic susceptibility. Mössbauer spectroscopy. FTIR, and X-ray powder diffraction evidence. A model to account for the difference in the reactivity and properties of the butylamine and propargylamine complexes of FeOCl is proposed. © 1994 Academic Press, Inc.

INTRODUCTION

The preparation of FeOCl and its intercalation by organic and organometallic molecules have been investigated extensively (1). FeOCl has been used to prepare novel conducting complexes by the intercalation and *in situ* polymerization of monomers such as pyrrole and 2,2′-bithiophene (2) or by the intercalation of various organosulfur donors to prepare conducting charge transfer complexes (3). Topochemical substitution of FeOCl to give amorphous Fe*O*(NHR) and layered Fe*O*(OCH_3) and $FeO(O_2C_2H_4)_{0.5}$ have also been reported (4). Changes in the physical properties of intercalated FeOCl are well documented. FeOCl is itself a poor semiconductor, $1 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$, but upon intercalation of amines the conductivity of the layered $FeOCl(RNH_2)_x$ complex increases to about $1 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$ (1d). The magnetic properties of FeOCl and its intercalates have been investigated (5) and it has been found that both the host and its intercalates are antiferromagnetic materials.

The reaction of aniline in acetonitrile with FeOCl in air for 1 week has been reported to give a crystalline material, $(C_6H_4NH)_{0.2}FeOCl$, called the α-(I) phase (6). The conducting α-(I) phase (d_{001} at 14.46 Å) is stable in an inert atmosphere or under vacuum but is observed to transform in air to a more conducting material called the β-(I) phase. The Mössbauer, FTIR spectrum, and charge transport properties of the β-(I) phase could be used to distinguish it from the α-(I) phase. The powder diffraction of the β-(I) phase was not reported; however, there were no observed differences in the SEM or elemental analyses of the α-(I) and β-(I) phases. In the course of our work on the intercalation of propargylamine into various layered hosts (7), we have also observed pronounced changes in the magnetic properties and structure of an intercalation complex of FeOCl with propargylamine. These changes are observed to depend upon the presence of air or water. We report here the synthesis, reactivity, and magnetic properties of FeOCl intercalated with propargylamine.

EXPERIMENTAL

Molecular weights of 112.8 and 125.6 g $mole^{-1}$ for all of the propargylamine and butylamine reaction products, respectively, with FeOCl were estimated from TGA data and used to determine the molar susceptibilities. The magnetic susceptibility data were recorded on polycrystalline samples over the temperature range 2–300 K using a Quantum Design MPMS-5S SQUID susceptometer. Measurement and calibration techniques have been reported elsewhere (8). χ_g values for all of the compounds studied are given in Table 1. Mössbauer spectra were fitted using six Lorentzian doublets. Powder X-ray diffraction patterns were collected using a Phillips Electronics Instruments diffractometer or a Scintag PAD-V diffractometer (Cu$K\alpha$) scanned at 2° min^{-1}. FTIR spectra were obtained from KBr pellets using a Nicolet 730 FTIR spectrometer, 10 scans at a resolution of 4 cm^{-1}. Thermogravimetric

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TABLE 1
Magnetic Susceptibility Data, χ_g, at 300 K

Sample	Preparation	χ_g (emu g^{-1})
FeOCl	FeOCl (neat)	3.7×10^{-5}
1	FeOCl + $HC{\equiv}CCH_2NH_2$	0.11×10^{-2}
2	FeOCl + $CH_3CH_2CH_2CH_2NH_2$	2.4×10^{-5}
4	**1** + H_2O	1.8×10^{-2}
5	**1** + Heat	1.2×10^{-2}
6	FeOCl + $CH_3(CH_2)_3NH_2$ + 10% H_2O under argon	1.2×10^{-2}
7	FeOCl + $CH_3(CH_2)_3NH_2$ + 10% H_2O in air	11×10^{-5}
8	FeOCl + $HC{\equiv}CCH_2NH_2$ + 10% H_2O under argon	2.8×10^{-2}
9	FeOCl + $HC{\equiv}CCH_2NH_2$ + 10% H_2O in air	5.0×10^{-5}
γ-FeOOH[a]	FeOCl + H_2O (reflux)	4.2×10^{-5}

[a] See Ref. (27).

analyses were run on a DuPont Instruments 951 thermogravimetric analyzer. Differential scanning calorimetry studies were obtained with a Perkin–Elmer 7 Series thermal analysis system using an aluminum pan reference and an N_2 purge. Butylamine and propargylamine were purchased from Aldrich and were found not to contain water as determined by GC analysis on a Carbowax column heated to 60°C.

$FeOCl(HCCCH_2NH_2)_{0.1}$

Preparation of **1**. Under argon, add 0.43 g of red/violet FeOCl crystals to a Schlenk flask. To this add 4 ml of propargylamine (used as received from Aldrich) with stirring. The slurry quickly becomes dark brown. After 1 week the slurry is observed to undergo a color change from brown to black. It is also observed that the solid in this flask is attracted to a handheld magnet. After 2 weeks remove the excess propargylamine from the reaction mixture under vacuum. Suspend the remaining gummy solid in fresh propargylamine and filter, and dry the remaining solid under a flow of argon. Store the freely flowing black powder product under nitrogen in a glove box.

X-ray powder diffraction, d (Å), (I/I_0): 11.6, (100); 6.3, (38); 5.6, (23); 4.6, (30); 3.7, (35); 3.6, (29); 3.2, (29); 3.0, (47). FTIR (in KBr) ν: 3313, 3282, 3254 (≡CH, s); 2980 (CH_2, s); 2129 (C≡C, w); I602 (m); 1485 (NH_3^+, m); 1117 (m); 997 (s); 639 (m) cm^{-1}. TGA (in air, 10°C min^{-1}): 25–1000°C (−29.1%); calc (−29.2%). Magnetic data, 1-kG field at 300 K; μ, 17 BM; gram susceptibility, 1.1×10^{-3} emu g^{-1}.

Preparation of **3**. Expose **1**, previously prepared and stored under an argon atmosphere, to ambient atmosphere, relative humidity 80%, 30°C, for 1 hr.

X-ray powder diffraction, d (Å), (I/I_0): 11.6, (100); 7.7, (100); 4.0, (80); 3.4, (100). FTIR (in KBr) ν: 3247 (≡CH, s); 2137 (C≡C, w); 2024 (NH_3^+, w); 1485 (NH_3^+, s); (1117, m); 1011 (m); 716 (m); 688 (m); 457 (m) cm^{-1}. TGA (in air, 10°C min^{-1}): 25–200°C (−33.3%); 200–700°C (−38.7%); 700–900°C (−5.9%).

Preparation of **4**. Suspend **1** or **3** in excess H_2O and then filter the resulting slurry. Wash filtered solid until the washings are clear. Air dry to obtain a black solid.

X-ray powder diffraction, d (Å), (I/I_0): 2.5, (100). FTIR (in KBr) ν: 3381 (s, br); 2961 (s); 2129 (C≡C, m); 1602 (m); 582 (vs) cm^{-1}. TGA (in air, 10°C min^{-1}): 25–100°C (−5.0%); 100–550°C (−11.5%); 550–900°C (−11.4%). Magnetic data, 1-kG field at 300 K; μ, 69 BM; susceptibility, 17.7×10^{-3} emu g^{-1}.

Preparation of **5**. Heat 17 mg powdered **1** to 200°C under argon at 10°C min^{-1} and keep the sample temperature isothermal for 1 hr. A weight loss of (−37.6%) is observed from rt to 150°C; no weight loss is observed from 150 to 200°C. A fused black insulating material is obtained.

X-ray powder diffraction, d (Å), (I/I_0): amorphous. FTIR (in KBr) ν: 3409 (s); 3135 (s); 3050 (s); 2059 (m); 1609 (s); 1405 (s); 1011 (s); 1201 (s); 1039 (s); 585 (s) cm^{-1}. Magnetic data, 1-kG field at 300 K; μ, 56 BM; susceptibility, 11.8×10^{-3} emu g^{-1}.

$HCCCH_2NH_2 \cdot HCl$

X-ray powder diffraction, d (Å), (I/I_0): 9.5, (84); 5.0, (69); 4.1, (13); 4.0 (14); 3.6, (36); 3.4, (45); 3.2, (41); 3.1, (100); 2.9, (84); 2.8 (14); 2.7, (9). FTIR (in KBr) ν: 3247 (≡CH, s); 2122 (C≡C, m); 2025 (NH_3^+, m); 1485 (NH_3^+, s); 1117 (s); 1011 (s); 716 (s); 688 (s); 540 (s) cm^{-1}. UV–VIS in H_2O: 202 nm.

Preparation of **6**. Mix 0.059 g of FeOCl, 1 ml butylamine, and 0.1 ml distilled H_2O and stir the mixture under argon. The slurry is black and is readily attracted to a handheld magnet after 6 hr. Filter this solid in air, wash with acetone, and store under argon.

X-ray powder diffraction, d (Å), (I/I_0): 7.8, (100) FTIR (in KBr) ν: 3431 (s, br); 2938 (s); 1616 (m); 1503 (m); 1468 (m); 1264 (m); 1011 (m); 801 (w); 737 (w); 584 (m, br); 456 (m, br); 348 cm^{-1}. Magnetic data, 1-kG field at 300 K; μ, 65 BM; susceptibility, 12.3×10^{-3} emu g^{-1}.

Preparation of **7**. Mix 0.057 g FeOCl, 1 ml butylamine, and 0.1 ml H_2O in air and stir. The initial black solid turns red-brown after one day. Filter the solid, wash with acetone, and store in air.

X-ray powder diffraction, d (Å), (I/I_0): amorphous. FTIR (in KBr) ν: 3444 (m); 3360 (m); 2966 (m); 1630 (w); 1110 (m); 1025 (m); 737 (m); 547 (s, sh); 470 (s) cm^{-1}. Magnetic data, 1-kG field at 300 K; μ, 5.8 BM; susceptibility, 11.2×10^{-5} emu g^{-1}.

Preparation of **8**. Mix 0.030 g of FeOCl, 1 ml propargylamine, and 0.1 ml distilled H_2O and stir under argon. The slurry is dark brown and is readily attracted to a handheld magnet after 3 days. Filter this solid in air, wash with acetone, and store under argon.

X-ray powder diffraction, d (Å), (I/I_0): 7.7, (100); 4.3, (100); 2.5, (50). FITR (in KBr) ν: 3431 (br, s); 3280 (sh); 2129 (vw); 1630 (m, br); 1025 (m); 744 (m); 547 (s); 470 (s) cm^{-1}. Magnetic data, 1-kG field at 300 K; μ, 5.8 BM; susceptibility, 27.7 $\times$ 10^{-3} emu g^{-1}.

Preparation of **9**. Mix 0.055 g FeOCl, 1 ml propargylamine, and 0.1 ml H_2O in air and stir. The initial black solid turns red after 3 days. Filter the solid, wash with acetone, and store in air.

X-ray powder diffraction, d (Å), (I/I_0): amorphous. FTIR (in KBr) ν: 3384 (s, br); 2966 (s, sh); 2121 (vw); 1602 (m); 482 (s) cm^{-1}. Magnetic data, 1 kG field at 300 K, μ, (3.7 BM); susceptibility, 5.0 $\times$ 10^{-5} emu g^{-1}.

RESULTS

Intercalation of the FeOCl host with organic amines typically requires contact of the host with the amine for several hours in an inert atmosphere, whereas topochemical substitution reactions of FeOCl require several months of contact (4). FeOCl, d_{001} at 7.9 Å (5a), was prepared and stirred with neat propargylamine ($HC{\equiv}CCH_2NH_2$) under argon. After 2 weeks this reaction gave a black slurry which was observed to be readily attracted to the handheld magnet used to manipulate the Teflon-coated stir bar in the reaction flask. After this slurry was filtered, a gummy black solid was isolated. Washing this material with excess propargylamine and drying gave a free flowing black-brown solid. The stoichiometry of this solid was determined by heating the sample in air for several hours at 1000°C to obtain its bulk weight loss. The pyrolysis reaction resulted in a weight loss of 29.1%, and the red solid residue that formed was identified by powder X-ray diffraction as α-Fe_2O_3. The observed weight loss corresponds to a calculated formula of $FeOCl(HCCCH_2NH_2)_{0.1}$ which we abbreviate as **1**, Eq. [1]. The stoichiometry of the guest in this complex is about half that observed in alkyl amine intercalates of FeOCl, such as the butyl amine intercalate $FeOCl(CH_3CH_2CH_2CH_2NH_2)_{0.25}$, (1d), **2**, in which the guest is present as a bilayer in the interlayer space of the host. Differential scanning calorimetry of **1** revealed a sharp exotherm at 130°C, Fig. 2, which is lower by about 60°C than that observed for the propargylamine intercalates $M(O_3YOH)_2(HC{\equiv}CCH_2NH_2)_a \cdot H_2O$ of (M=Zr, Sn, Ti; Y=As, P) (9). The observed heat of the reaction for this exotherm was -810 J g^{-1}. The thermogravimetric analysis of **1** in dry air showed an initial weight loss of 4.6% from 25 to 150°C, corresponding to the observed exotherm, Fig. 1a. A gradual weight loss of 10.2% occurred from 250 to 600°C:

$$FeOCl + HC{\equiv}CCH_2NH_2 \xrightarrow[\text{Argon}]{\text{14 days}} FeOCl(HC{\equiv}CCH_2NH_2)_{0.1}. \quad [1]$$

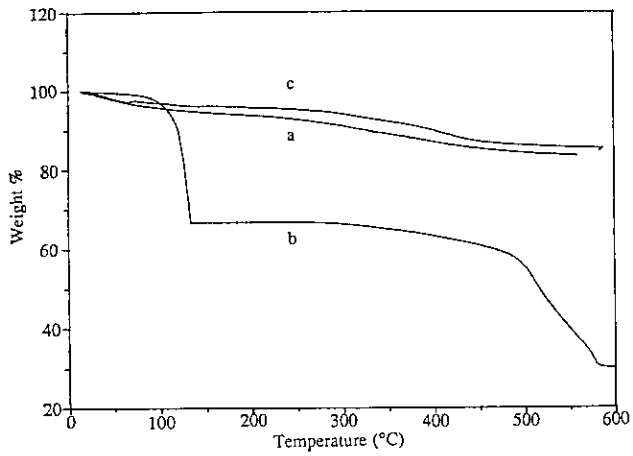

FIG. 1. Thermal gravimetric analysis of (a) **1**; (b) **3**; and (c) **4**.

Powder X-ray diffraction showed **1** to be a crystalline product with an interlayer spacing of 11.6 Å. In one preparation of **1**, a 14.4-Å phase was observed in addition to the 11.6-Å phase, but the 14.4-Å phase disappeared upon further reaction of the complex with propargylamine. The interlayer spacing of the 11.6-Å phase suggests the presence of a monolayer of the propargylamine guest, with a van der Waals radius of about 4 Å, in the interlayer space of the FeOCl host. The formation of two product phases, 14.5 and 10.9 Å, during the preparation of the ester, $FeO(O_2C_2H_4)_{0.5}$, and the disappearance of the 14.5-Å phase upon drying or washing the product with acetone have also been reported (4a).

Scanning electron microscopy of the starting FeOCl showed that it consisted of particles ranging in size from 50 to 1000 μm with the expected blade-like morphology. Upon intercalation of propargylamine, the product **1** consisted of 500-μm aggregates of small plate-like 10- to 50-

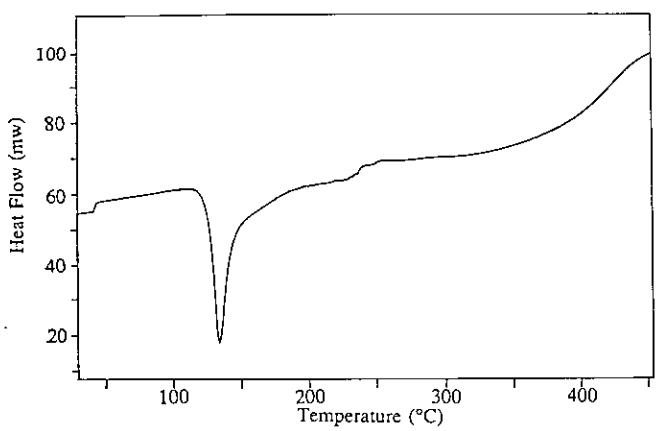

FIG. 2. Differential scanning calorimetry of the propargylamine intercalate of FeOCl.

FIG. 3. Scanning electron micrograph of **1**.

μm particles (Fig. 3). This observation supports the powder X-ray diffraction result that the product complex retained the layered morphology of the starting FeOCl. The FTIR spectrum of **1**, like those of the propargylamine intercalates of the metal phosphates $M(O_3POH)_2 \cdot (CC)_x$, (7) contains a C≡C stretching band at 2129 cm^{-1} superimposed on an NH_3^+ combination band at 2059 cm^{-1} (Fig. 4). **1** has both of these bands and also shows additional medium-intensity NH_3^+ combination bands in the region between 2300 and 2700 cm^{-1}. A single strong stretch due to the acetylenic ≡C—H stretch is observed in propargylamine hydrochloride, $HC{\equiv}CCH_2NH_3Cl$, at 3247 cm^{-1} and in the layered intercalation complex $Zr(O_3PO^-)_2(HC{\equiv}CCH_2NH_2)_2$ at 3289 cm^{-1} (17). In **1** several very intense peaks at 3318, 3282, and 3254 cm^{-1} are present in this region of the spectrum. The strong Fe–O stretch at 480 cm^{-1}, normally observed in FeOCl intercalates (10), is absent or very weak in **1**. In fact, in contrast to **2**, which we have prepared as a reference and which has a single strong band at 480 cm^{-1}, this region of the spectrum for **1** consists of broad bands on which a number of fine line features are superimposed (Fig. 4a).

The Mössbauer spectrum of FeOCl has a doublet resonance with an isomer shift of 0.39 mm sec^{-1} and a nearly temperature-independent quadrupole splitting of 0.92 mm sec^{-1}. Magnetic hyperfine Zeeman splitting is observed in this material at 90 K due to antiferromagnetic ordering of the host lattice. A doublet is also observed in the spectrum upon intercalation of FeOCl with amines but the

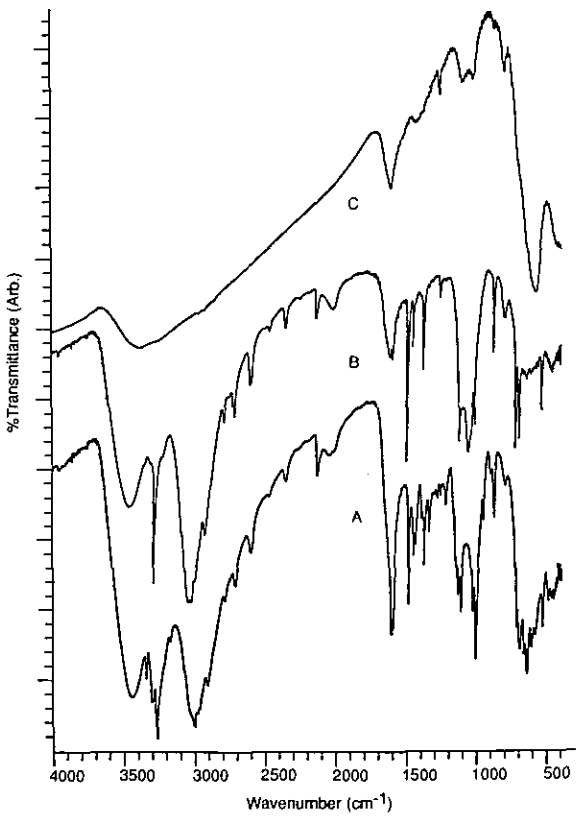

FIG. 4. FTIR spectra of (A) **1**; (B) **3**; and (C) **4**.

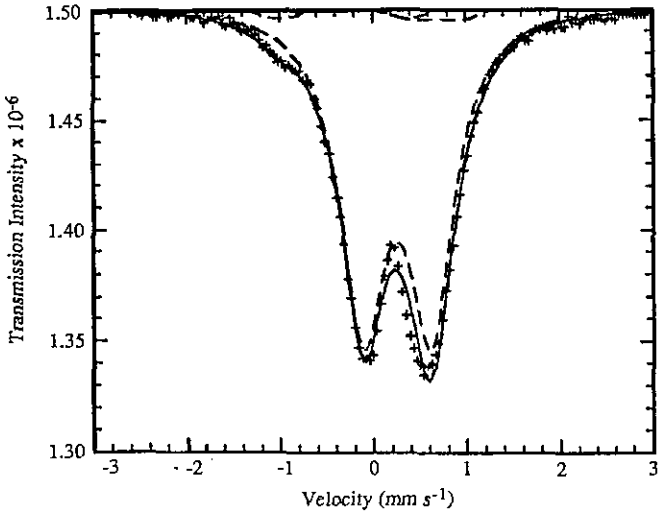

FIG. 5. Mössbauer spectrum of **1**, measured at 77 K.

isomer shift of the complex increases to about 0.46 mm sec^{-1} at 300 K. During intercalation, some Fe^{3+} in FeOCl is reduced by the amine guest to Fe^{2+} and an equivalent amount of the amine hydrochloride salt is formed and remains in the interlayer space to balance the charge (11). This redox intercalation reaction has been previously proposed for other hosts like TaS_2 intercalated with NH_3 or organic amines (11). The observed isomer shift in the intercalated complexes is a time average of the Fe^{2+} and Fe^{3+} isomer shifts due to rapid electron hopping between Fe^{3+} and Fe^{2+} sites. At 78 K, a distinct resonance for the Fe^{2+} site is observed at 2.5 mm sec^{-1}. The quadrupole splitting, 0.7 mm sec^{-1} at 300 K and 1.2 mm sec^{-1} at 77 K, in the amine intercalates is now temperature dependent (11). The Mössbauer spectrum of $FeO(OCH_3)$ was reported at 300 K only and it was found that the valance state of iron this ester of FeOCl was Fe^{3+} (4a).

The Mössbauer spectrum of **1** is shown in Fig. 5. The curve was fit using six Lorentzian lines (three quadrupole doublets). The results of the fit indicate that **1** has three different iron sites: an *A site* (Fe^{3+} *tetrahedral*), a *B site* (Fe^{3+} octahedral), and a C site (Fe^{2+} tetrahedral) (see Table 2). The Mössbauer spectrum consists of a central doublet with an isomer shift at 0.37 mm sec^{-1} and quadrapole splitting 0.73 mm sec^{-1}, which are typical values for octahedrally coordinated Fe^{3+}. The shoulder with isomer shift at 0.89 mm sec^{-1} and quadrupole splitting 1.35 mm sec^{-1} is assigned to Fe^{2+} in a tetrahedral site. Hyperfine splitting was not observed in **1** at 300 K. Reduction of the FeOCl host upon reaction with propargylamine (eq. [2]) is supported by the observation of an Fe^{2+} resonance in the Mössbauer spectrum of **1**. In contrast to the alkyl amine intercalates of FeOCl, which show an Fe^{2+} resonance only at low temperatures (77 K), the Mössbauer spectrum of **1** shows the presence of Fe^{2+} at *room* temperature. Instead of the Fe^{2+} site rapidly exchanging with the Fe^{3+} sites in **1**, some or all of the Fe^{2+} sites in **1** appear to be localized. The observation that all the complexes prepared in this study were insulators also supports the idea that the Fe^{2+} sites are localized and suggests that the FeOCl host itself may be undergoing a chemical reaction:

$$\mathrm{FeOCl} + \mathrm{HC{\equiv}CCH_2NH_2} \xrightarrow{N_2} ((\mathrm{Fe^{2+}})_{0.1}(\mathrm{Fe^{3+}})_{0.9}\mathrm{OCl})(\mathrm{HC{\equiv}CCH_2NH_3^+})_{0.1}. \quad [2]$$

The magnetic susceptibility, χ_m, of FeOCl has been studied and it has been found that χ_m decreases over the temperature range 300–20 K (12). The reported susceptibility of FeOCl was 3×10^{-3} emu $mole^{-1}$ at 300 K, and it decreased by little more than about 10% over the range 300–50 K (5a). The small decrease in χ_m with decreasing temperature has been interpreted to indicate that FeOCl has short-range antiferromagnetic ordering. A more recent study reported that the magnetic susceptibility of FeOCl (3×10^{-3} emu $mole^{-1}$; μ_{eff}, 2.76 BM at 300 K) decreased by little more than about 10% over the range from 300 to 50 K (3). These workers observed a low-temperature paramagnetic tail in their susceptibility plot. Both studies observed increases in χ_m with decreasing temperature below 100 K in the intercalates of FeOCl. For **2** we measured a μ_{eff} of 2.7 BM at 300 K; χ_m also increased with decreasing temperature below 100 K. At room temperature the moment for high-spin Fe^{3+} is the host lattice of **2** should be 5.9 BM. The observed value of 2.7 BM is consistent with antiferromagnetic coupling of the spins within the host lattice of **2**.

The susceptibility over the temperature range 4–300 K for **1** is shown in Fig. 6b. A small anomaly in the susceptibility was observed on cooling below 25 K but was not observed on warming the sample back to 50 K (top set of points in Fig. 6b). Heating the sample to 400 K and cooling it again resulted in an increase in the measured susceptibility (three points above initial plot). At 300 K,

TABLE 2

Mössbauer Isomer Shift and Quadrupole Splitting Values of FeOCl Complexes with Propargylamine and 90% Aqueous Butylamine, Measured at 77 K

	A(Fe^{+3} tetrahedral)		B(Fe^{+3} octahedral)		C(Fe^{+2} tetrahedral)	
Complex	IS	QS	IS	QS	IS	QS
1	0.18	0.62	0.37	0.73	0.89	1.35
6	0.21	1.37	0.41	0.65	0.89	1.35
7	0.23	1.39	0.40	0.62	0.89	1.30

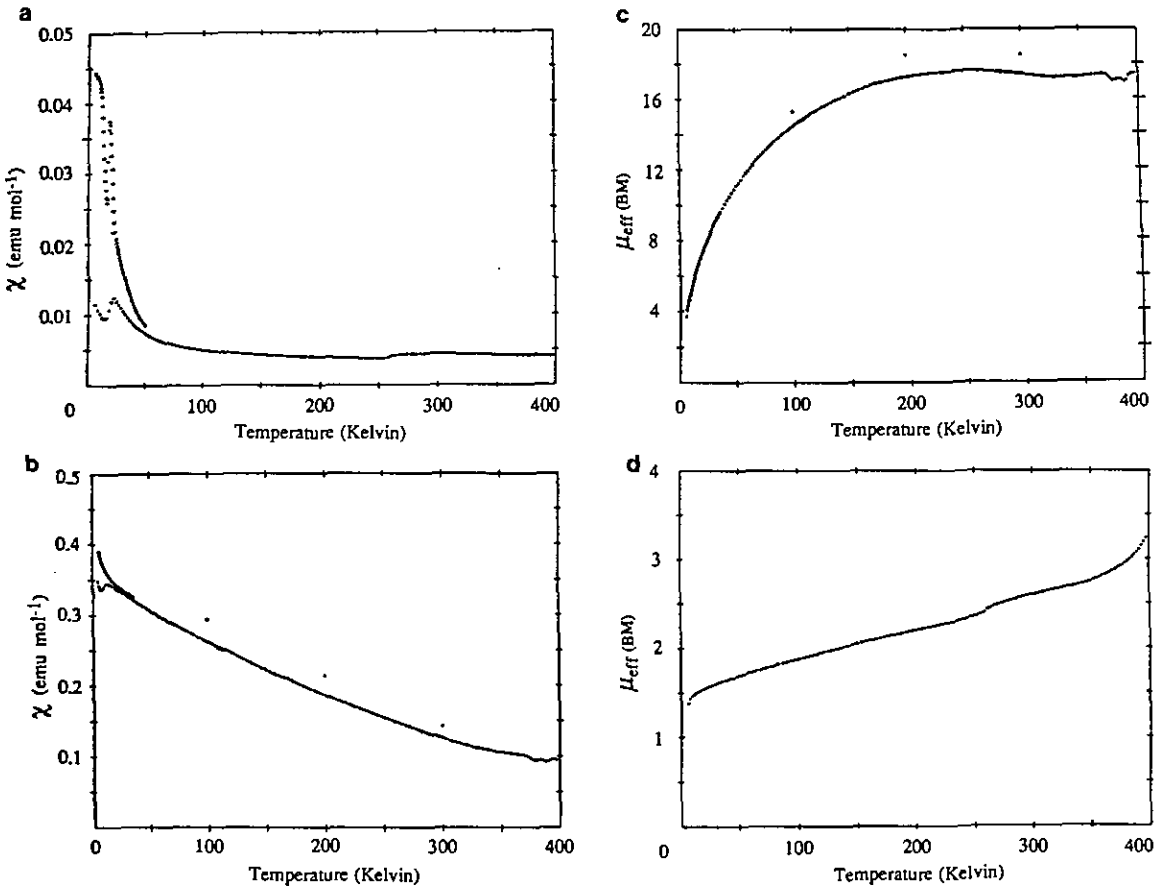

FIG. 6. Magnetic data plots of (a) χ_m vs T for FeOCl; (b) χ, vs T for **1**; and (c) μ_{eff} vs T for **1**; (d) μ_{eff} vs T for **2**.

χ_g for **1** was 1.1×10^{-3} emu g^{-1} and μ_{eff} was 18 BM, which is much larger than expected for the high-spin Fe^{3+} of the host. A plot of μ_{eff} versus temperature was nearly constant from 200 to 400 K. At 200 K the μ_{eff} drops sharply, characteristic of an antiferromagnetic interaction within the material Fig. 6c. For comparison the plot of μ_{eff} versus temperature for **2**, which illustrates its antiferromagnetic behavior, is shown Fig. 6d.

Reactivity of **1**

$FeOCl(HC{\equiv}CCH_2NH_2)_{0.1}$, **1**, was weakly attracted to a stir bar or to a handheld magnet. In the initial susceptibility experiments the susceptibility of **1** increased on heating to 400 K. It was subsequently observed that extended exposure of **1** to air, washing **1** with water, or heating **1** under argon above 100°C resulted in dramatic changes in the powder X-ray diffraction patterns, FTIR, TGA, and magnetic susceptibility relative to **1**. Exposure of the black-colored **1** to moist air for more than 1 hr gave a caramel-colored solid **3**. Suspending **1** or **3** in water and filtering gave a dark brown or black solid, **4**.

The thermal gravimetric analysis of the caramel-colored **3** was significantly different from that of **1** (Fig. 1b). In air, weight losses of 33.3% (rt–150°C), 38.2% (150–600°C), and 6.9% (600–900°C) were observed. The total weight loss for **3** was 78.5%. The rapid initial weight loss between 50 and 150°C suggests that the loss was due to absorbed water in the complex. The remaining weight loss, 45.1%, is greater than 15% over the starting **1**. Thermal gravimetric analysis of **4** in air gave a total weight loss of only 30% on heating to 950°C for an extended period (Fig. 1c, shown only from rt to 600°C). In **4** the major weight loss transition occurred from 275 to 425°C.

Heating **1** under argon from 130 to 200°C gave a black material, **5**, which was readily attracted to a magnet. The scanning electron micrograph of **5** shows that this material is composed of a porous polymeric matrix in which plate-shaped particles are embedded. Like **1**, **5** is an insulator. This black material appears to be water-soluble and has a strong absorption in the UV–VIS spectrum at 300 nm which tails out to 600 nm; neat propargylamine hydrochloride in H_2O has a single UV–VIS absorption at 202 nm. The FTIR of **5** has two strong bands at 585 and 449 cm^{-1}.

On standing in moist air, the 11.6-Å phase for **1** disap-

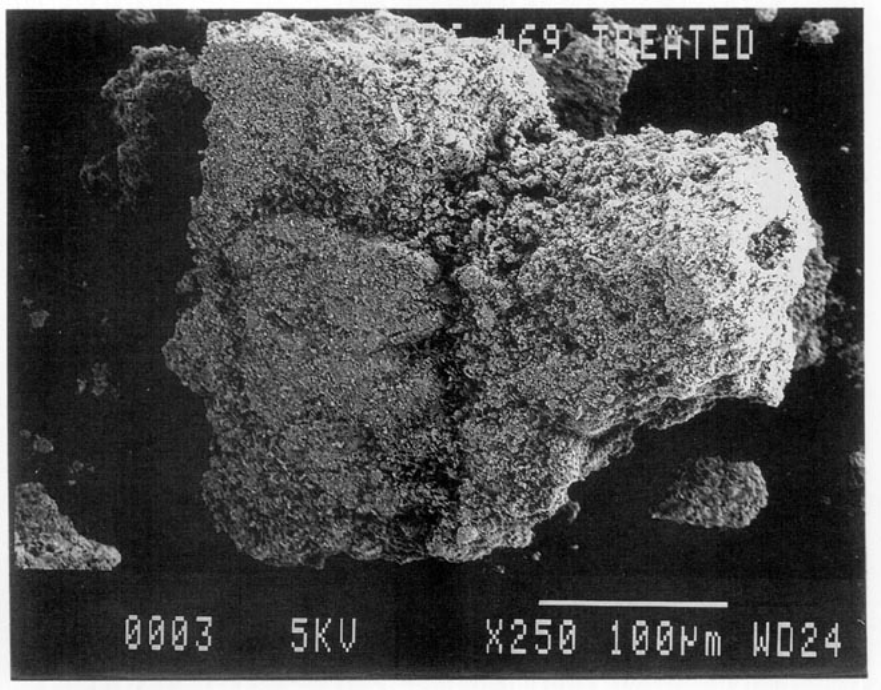

FIG. 7. Scanning electron micrograph of **4**.

peared rapidly (within 1 hr) and the new phase, **3**, formed with a broad peak at 7.7 Å. Washing and filtering **1** with water gave **4**, which had a single very weak diffraction reflection centered at 2.5 Å. The evaporated filtrate from this washing was a crystalline solid whose X-ray diffrac tion pattern had a sharp reflection at d = 9.6 Å. The X-ray diffraction pattern was almost identical with that of $HC{\equiv}CCH_2NH_3Cl$ d = 9.5 Å.

Scanning electron micrographs of **3** show that it has a morphology which appears unchanged from that of **1**. The scanning electron micrographs of **4** showed substantial changes in particle size and morphology compared to **1** or **3**. The particles in **4** are aggregates whose size ranged from 10 to 100 μm (Fig. 7). The aggregates themselves consisted of much smaller (less than 1 μm) particles. The small particle size and or amorphous nature of this material is one reason for our inability to adequately characterize **4** by powder X-ray diffraction.

Several changes in the FTIR spectrum of **1** were observed upon its conversion to **3** (Fig. 4b). In particular, the intensity of the band at 1485 cm^{-1} in **1** increased substantially on its conversion to **3**. A similar band at 1485 cm^{-1} is also found in $HC{\equiv}CCH_2NH_3Cl$ but not in the free propargylamine. This band may be an NH_3^+ deformation or bending mode similar to those observed in amino acid salts and other primary amine hydrochloride salts (13). The NH_3^+ combination bands between 2300 and 2700 cm^{-1} in **1** were still present in **3**. In **3** several new broad bands appeared at 1047, 625, and 457 cm^{-1} which were not present in **1**. In **3** only the single peak at 3247 cm^{-1} in the $\equiv$C–H stretching region was still present compared to the three bands observed initially in **1**. The observation of the 1485 and 3247 cm^{-1} bands in **3** suggests that during the collection of the FTIR spectrum of **1** and **3** may have formed.

The FTIR spectrum of **4** contained weak methylene stretches near 2960 cm^{-1} and a weak C$\equiv$C stretch band at 2129 cm^{-1}. The series of strong NH_3^+ combination bands found in **1** and **3** between 2300 and 2700 cm^{-1} as well as the 1485 cm^{-1} deformation band were very weak in 4. These results indicate incomplete loss of guest on formation of **4**. Strong bands at 582 and 450 cm^{-1} in **4** have replaced the complicated bands previously observed in this region in **1** and **3**. The solid recovered by evaporating the filtrate collected from **4** had an FTIR and ^1H NMR identical with that of $HC{\equiv}CCH_2NH_3Cl$ and supports the X-ray powder diffraction identification of this solid filtrate residue. The formation of $HC{\equiv}CCH_2NH_3Cl$ from **1** shows that some loss of Cl^- from the host surface is occurring.

The FTIR spectra of **1**, **3**, and **4** all show methylene C–H and C$\equiv$C stretches. The FTIR and XRD data indicate that interlayer guest is present in **1**; however, in **3** and **4**, the guest could reside on either the interior or the exterior of the microcrystals. Below 1200 cm^{-1} the FTIR of **4** has bands at 1032 and 800 and strong bands at 582 and 442 cm^{-1} that are characteristic of Fe_3O_4 and ferrites (14). Except for **2**, the 480 cm^{-1} band characteristic of FeOCl

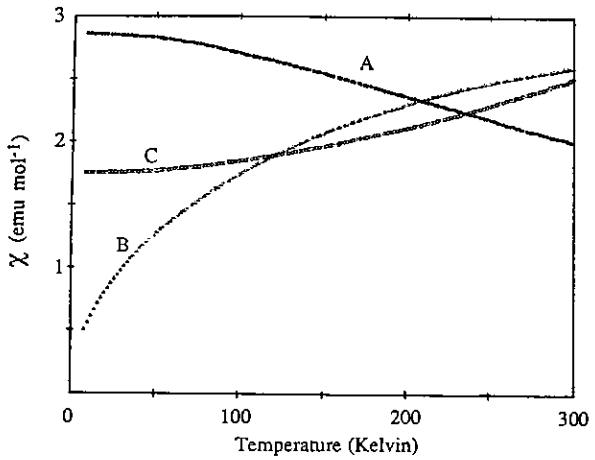

FIG. 8. Magnetic susceptibility plots: (a) χ_m of **4**; (b) μ_{eff} of **4**; and (c) $1/\chi_m$ of **4**.

intercalates is absent in all the compounds prepared in this study.

The magnetic susceptibility data for **4** in the temperature range 4–400 K are shown in Fig. 8a. At 300 K the susceptibility of **4** is almost 20 times that of **1**. The plot of μ_{eff} versus temperature (Fig. 8b) is linear in the region above 200 K but shows a rapid decrease in the moment characteristic of an antiferromagnetic coupling within the material. The temperature dependence of μ_{eff} is similar to that for **1** except that the room temperature moment of 69 BM is nearly four times that found in **1**. For comparison these results are summarized in Table 1.

Reaction of FeOCl with Aqueous Amines

The changes in the structure and properties of **1** on exposure to air or water after its preparation and isolation led to an investigation of the effect that water or air in the presence of an amine would have on the reaction product of the amine with FeOCl. Neat solutions of 90% butylamine with 10% water or 90% propargylamine with 10% water were prepared. The aqueous amine solution was mixed with FeOCl and the slurry stirred either under argon or in air. The reaction of FeOCl with butylamine (10% H_2O) under argon gave a black material, **6**, that was readily attracted to a handheld magnet, in about 6 hr (d = 7.7 Å, FTIR 2931 (s), 1101 (w), 584 (m), 456 (m) cm^{-1}). In air, butylamine (10% in H_2O) gave a red solid, **7**, that was not attracted to a handheld magnet, after 2 days (d-amorphous, FTIR 2931(s), 1021 (m), 547 (m, sh), 456 (vs) cm^{-1}). For FeOCl contacted with propargylamine (10% in H_2O) under argon a black magnetic material, **8**, formed (d 7.7 Å, FTIR 2931 (s), 1021 (m), 547 (s), 470 (s) cm^{-1}). In the presence of air propargylamine (10% in H_2O) with FeOCl gave a red-brown nonmagnetic solid, **9**, after 4 days (d-amorphous, FTIR 2931 (s), 1019 (w), 482 (vs) cm^{-1}). In each of these complexes the presence of methylene stretches near 2931 cm^{-1} suggests that the amine is present.

A fit to the Mössbauer data obtained for **6** and **7** (Fig. 9) suggests that, like **1**, each of these complexes also has three different iron sites (see Table 2). The relative intensities of the peak areas and their ratios show that **1** has the greatest relative proportion of Fe^{3+} (see Table 3). Mössbauer data for the two samples that were observed to be magnetic, **6**, and **1**, have very similar A to C ratios. Also the A to B and C to B ratios for **6** are very similar to each other (0.24 and 0.2) as are the A to B and C to B ratios for **1** (0.054 and 0.049). In contrast, the A to B ratio for **7** is about one-half its C to B ratio.

Magnetic susceptibility plots for **8** and **9** (Fig. 10) are shown; the same plots for **6** and **7** are similar. While all the compounds have similar shaped susceptibility curves, the susceptibilities for the two dark-colored complexes, **6** and **8**, prepared under argon are at least two orders of

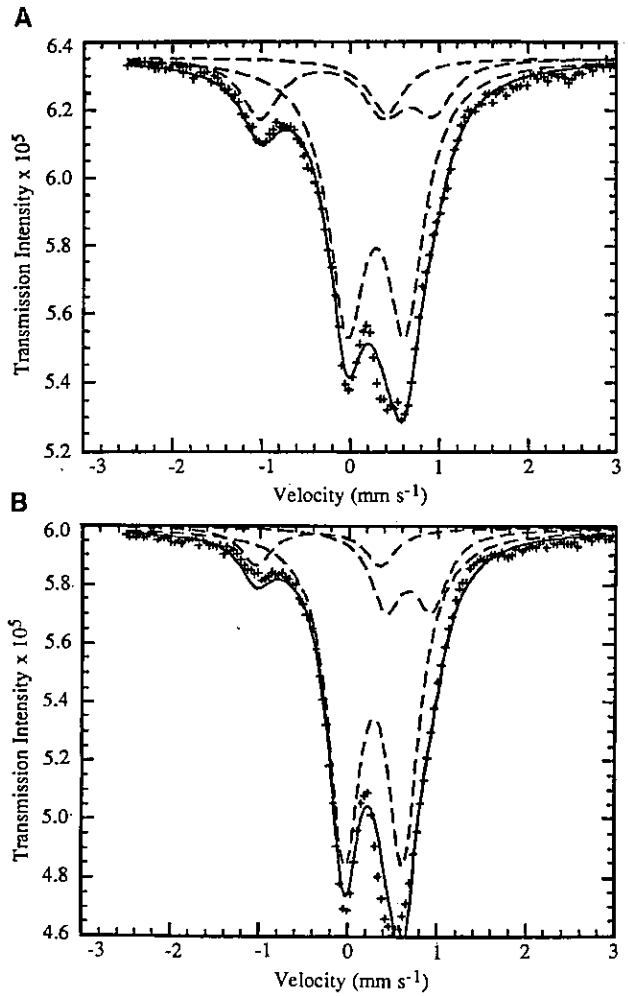

FIG. 9. Mössbauer spectrum of (a) **6**; (b) **7**, measured at 77 K.

TABLE 3

Peak Areas and Peak Area Ratios from Mössbauer Spectra of FeOCl Complexes with Propargylamine and 90% Aqueous Butylamine, Measured at 77 K

	Areas			Ratios		
Complex	A	B	C	A/B	C/B	A/C
1	1.1	20.5	1.0	0.054	0.049	1.1
6	1.2	5.0	1.0	0.24	0.2	1.2
7	1.0	8.0	1.9	0.12	0.24	0.53

magnitude greater than those for the red-colored complexes, **7** and **9**, prepared in air (see Table 1). The low-temperature behavior (less than 100 K) of **6** and **8** is not the same as that observed for **1** and **4**. These results show that while the presence of water, amine, and an inert atmosphere can lead to changes in the magnetic properties of FeOCl, **6** and **8** are not the same materials as **1** or **4**.

DISCUSSION

In the present study the initial reaction of propargylamine with FeOCl gives a material whose stoichiometry and interlayer spacing are consistent with the intercalation of a monolayer of propargylamine into the interlayer space of the FeOCl to give **1**. Acetylenes are known to undergo oxidative coupling reactions to form diacetylenes (15). The oxidative coupling of propargylamine on reaction with FeOCl may occur and lead to the formation of 1,6-diamino-2,4-hexadiyne. It has been found that 1,6-diamino-2,4-hexadiyne gives a less than fully intercalated complex when reacted with the layered host $Zr(O_3POH)_2 \cdot H_2O$ due to polymerization of the guest on the host surface (16). A similar process could occur in FeOCl with 1,6-diamino-2,4-hexadiyne polymerizing on the surface of FeOCl. This surface polymerization reaction may inhibit further intercalation of propargylamine into FeOCl and give a less than close-packed structure of propargylamine in FeOCl in accord with the observed stoichiometry. The presence of localized Fe^{2+} sites at room temperature in the Mössbauer spectrum **1** indicates that changes in host lattice have also occurred. Thermal gravimetric analysis suggests that **1** absorbs water from the air. FTIR spectroscopy shows an increase in the NH_3^+ deformation and combination bands that may be due to $HC{\equiv}CCH_2NH_3^+$ or $HC{\equiv}CCH_2NH_3Cl$ as **3** is formed. X-ray powder diffraction of **3** is consistent with the formation of a green rust (II) formed by the diffusion of water into **1** and hydrolysis of some surface chloride ions *vide infra*. When **1** or **3** is washed with water, TGA, FTIR, and XRD suggest that some $HC{\equiv}CCH_2NH_3Cl$ is lost from **1** or **3** as **4** is formed. As shown by XRD and FTIR, **4** has characteristics which are similar to ferrites which are known to be formed from green rusts *vide infra*. Significant changes in the magnetic properties and structure of FeOCl are observed as it reacts to form **1**. Further changes in structure and magnetic properties are observed as **1** reacts to form **3** or **4**.

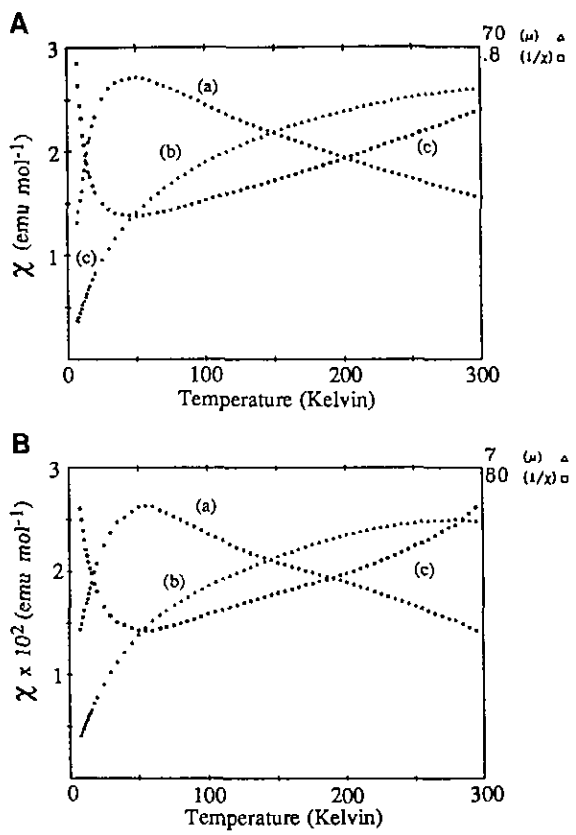

FIG. 10. Magnetic data plots (a) χ_m vs T; (b) μ_{eff} vs T; and (c) $1/\chi_m$ vs T for (A) **8**; (B) **9**.

The changes in the structure and magnetic properties of FeOCl are observed to occur when it is intercalated with propargylamine but not when it is intercalated with butylamine (in an inert atmosphere). This observation suggests that it is the guest, and not the host, that is responsible for the difference in magnetic properties between **1** and **2**. The presence of 10% water in guest amine solutions was found to lead to magnetic or nonmagnetic materials depending upon the presence or absence of oxygen. The magnetic materials prepared by these reactions were similar but not identical to the initially prepared **1** as shown by FTIR and magnetic susceptibility measurements.

FeOCl is known to undergo reactions, in addition to intercalation, to give paramagnetic γ-FeOOH, which like FeOCl contains only octahedrally coordinated Fe^{3+} iron. γ-FeOOH can undergo further reactions to give ferromagnetic and ferrimagnetic materials like γ-Fe_2O_3 (maghemite) and ferrites $M^{2+}Fe_2O_4$ (M^{2+} = Fe^{2+}, Zn^{2+}). For

example, FeOCl can be hydrolyzed to γ-FeOOH by refluxing FeOCl in water (17), by reacting FeOCl with 1% pyridine in water (18), or by treating FeOCl with an aqueous solution that is 20% (NaOH or NH_3) (Eq. [3]) (19). The conversion of γ-FeOOH into ferromagnetic γ-Fe_2O_3 can be brought about by dehydration of γ-FeOOH for 1 hr at 250°C (20). Treating γ-FeOOH with organic bases like pyridine and hexylamine at temperatures of 120 to 140°C has also been reported to result in the formation of γ-Fe_2O_3 Eq. 4 (21):

$$\text{FeOCl} + \text{NaOH} \xrightarrow{H_2O} \gamma\text{-FeOOH} \quad [3]$$

$$2(\gamma\text{-FeOOH}) + R\text{NH}_2 \xrightarrow{120\text{–}140^\circ\text{C}} \gamma\text{-Fe}_2\text{O}_3 + \text{H}_2\text{O} + R\text{NH}_2. \quad [4]$$

Tamaura and co-workers have reported the transformation of γ-FeOOH to ferrites, such as Fe_3O_4 or $M^{2+}Fe_2O_4$, in the presence of Fe^{2+} or Zn^{2+} ions at pH 5–9 and 25°C in aqueous solution [Eq. [5] (22)]. In subsequent work they showed that γ-FeOOH could be transformed into a green rust (II), $(Fe^{3+})_1(Fe^{2+})_2(SO_4^{-2})(OH^-)_{5-2n}(O^{-2})_n$, in the presence of Fe^{2+} and SO_4^{-2} (eq. [6]). Without Fe^{2+} present the γ-FeOOH did not react (23). Green rust (II), $(Fe^{3+})_1(Fe^{2+})_2(SO_4^{-2})(OH^-)_{5-n}(O^{-2})_n$, can be further reacted to give ferrites in the presence of Fe^{2+} ions and temperatures of 50–75°C under a nitrogen atmosphere (Eq. [7]] (24)). Green rust (I), which is similar to green rust (II) except that SO_4^{-2} is replaced by the halogen X^- (Cl^-, Br^-, or F^-) to give $(Fe^{3+})_1(Fe^{2+})_2(X^-)_2(OH^-)_{5-2n}(O^{-2})_n$, can also be prepared by these reactions (25):

$$2(\gamma\text{-FeOOH}) + M^{+2} + OH^- \xrightarrow{\text{pH } 5\text{–}9} M^{2+}Fe_2O_4 + H_2O;\ M = Fe^{2+}, Zn^{2+}, Ni^{2+} \quad [5]$$

$$\gamma\text{-FeOOH} + Fe^{2+} + Cl^- \longrightarrow (Fe^{3+})_1(Fe^{2+})_2(Cl^-)(OH^-)_{5-2n}(O^{-2}) \quad [6]$$

$$(Fe^{3+})_1(Fe^{2+})_2(SO_4^{-2})(OH^-)_{5-2n}(O^{-2}) \xrightarrow[N_2]{50\text{–}75^\circ\text{C}} M^{2+}Fe_2O_4. \quad [7]$$

In this study the transformation of FeOCl to γ-FeOOH (d_{001} at 6.3 Å) during the reaction of FeOCl with propargylamine is not supported by powder XRD or Mössbauer spectroscopy. The absence of the strong bands in the FTIR at 1020 and 470 cm^{-1} characteristic of γ-FeOOH also supports this conclusion. Hyperfine magnetic splitting of the Mössbauer spectrum at room temperature, which would indicate the presence of γ-Fe_2O_3 or Fe_3O_4, is not observed in **1**. Hyperfine coupling is observed in **6**, and although powder XRD and magnetic susceptibility data do not support the presence of Fe_3O_4 or γ-Fe_2O_3 in **6** at room temperature, the formation of these materials (see Eqs. [5]–[7]) cannot be ruled out.

The Mössbauer spectrum observed for a green rust (I) showed that the material contained Fe^{2+} and Fe^{3+} sites that were both octahedrally coordinated (26). The single green rust (I) whose powder XRD pattern has been reported had reflections at 8.0 and 4.0 Å (25). The formation of a phase with broad peaks at 7.7 and 4.0 Å in **3**, the diffraction reflection at 7.7 Å in **6** and **8**, and the observation of octahedral Fe^{2+} and Fe^{3+} sites in the Mössbauer spectrum of all these materials suggest that they are similar to green rust (I). Instead of the complete hydrolysis of FeOCl (Eq. [5]) in the presence of an excess of water, partial hydrolysis of FeOCl in an excess of the amine may lead to the substitution of some surface Cl's for OH to give a green rust (I):

$$((Fe^{2+})_{0.1}(Fe^{3+})_{0.9}(O^{-2})(Cl^-)(HC{\equiv}CCH_2NH_3^+)_{0.1}) + H_2O \rightarrow ((Fe^{2+})_{0.1}(Fe^{3+})_{0.9}(O^{-2})(Cl^-)_{1-x}(OH^-)_x(HC{\equiv}CCH_2NH_3^+)_{0.1} \quad [8]$$

Washing **3** with water results in a dramatic increase in the magnetic susceptibility of the product material to give **4**. The lack of a powder X-ray diffraction pattern and the observation of particles smaller than 1 μm by SEM in **4** further support the idea that the breakup of the original FeOCl host lattice has occurred during the treatment of **1** with water. The isolation of $HC{\equiv}CCH_2NH_3Cl$ from the filtrate of **4** also supports the notion that green rust (I) formation may have already occurred to some extent in **3**. The formation of magnetic materials from this green rust (I) via reactions similar to those in Eq. [7] could occur.

CONCLUSIONS

Extensive changes in the magnetic properties of the layered host FeOCl are observed to occur when it is reacted with propargylamine. Further changes in the structure, thermal, and magnetic properties of the product from this reaction, **1**, are observed to occur when this layered material is exposed to air, moisture, or heated in an inert atmosphere. It is hypothesized that **1** reacts in air or water to form a green rust (I) which accounts for the breakup of the FeOCl host as observed by X-ray powder diffraction and SEM. The reaction of FeOCl with butylamine gives a layered complex that retains its layered structure and magnetic properties even when exposed to moist air and water. This lack of reactivity of **2** is presumably due to the close-packed structure of the butylamine guest in the interlayer space.

New magnetic materials can also be prepared by reacting FeOCl with organic amines containing 10% H_2O. In the presence of the 90% amine solution, reduction of the

FeOCl host occurs as in a normal intercalation reaction; however, a green rust(I) forms rather than an intercalation complex, and ammonium ions are retained to balance the charge of the complex. Reduction of FeOCl by treatment with aqueous amine occurs in both the presence and the absence of air. However, the magnetic properties of the isolated reaction product in each case depend upon these conditions. These results differ from those previously reported when FeOCl is treated with 10% organic amines in an excess of H_2O to give the paramagnetic material γ-FeOOH (19–21). It appears that in the presence of an excess of an organic amine, green rust(I) formation is more rapid than γ-FeOOH formation.

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