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Synthesis, Hyperfine Interactions, and Lattice Dynamics of the Intercalation Compound FeOCl(Kryptofix-21)_{1/18}

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The intercalation compound FeOCl(Kryptofix-21)_{1/18} (Kryptofix-21 = 1,7,10-trioxo-4,13-diazacyclopentadecane) has been synthesized and characterized by elemental analysis, powder X-ray diffraction, and ⁵⁷Fe Mössbauer-effect spectroscopy. The *b*-axis expansion of 4.1 Å of the FeOCl matrix, which arises from localization of the guest molecular species in the van der Waals layers of the solid, indicates significant interpenetration of the polyether into the chlorine layers of the host lattice. The available data—including the observed stoichiometry and the relative magnitudes of the ⁵⁷Fe Mössbauer resonance for the majority and minority iron atoms—are consistent with the conclusion that both nitrogen atoms of the ring are involved in chemical bonding to the iron atoms at low (less than ~150 K) temperatures. This behavior is consistent with that observed for the symmetrical Kryptofix-22 intercalate. The magnetic hyperfine field at the iron atoms at 4.2 K is comparable to that observed for the unintercalated matrix, but the sign of the principal axis of the efg tensor appears to be anomalous compared to the case of related intercalation compounds of FeOCl, probably due to the lowered symmetry of the electric field gradient at the metal atom lattice site.

Introduction

In a previous paper,¹ the synthesis and spectroscopic properties of the intercalation compound formed between FeOCl and a cyclic polyether, 1,7,10,16-tetraoxa-4,13-diazacyclopentadecane (Kryptofix-22),² were discussed in considerable detail. As was pointed out in that study, the use of ⁵⁷Fe Mössbauer effect spectroscopy to help in the characterization of such materials permits the comparison of the properties of intercalation compounds in which the chemical nature of the matrix is held constant, and the "guest" molecular species introduced into the layers can be subjected to subtle and specific changes in stereochemistry, basicity, symmetry, and molecular dimensions, inter alia. In the present investigation we report the properties of the intercalation compound formed when 1,7,10-trioxo-4,13-diazacyclopentadecane (hereafter referred to as Kryptofix-21)² is inserted into the FeOCl matrix, and compare these to the results obtained in the earlier study. In addition, ⁵⁷Fe Mössbauer data at temperatures well below the magnetic ordering temperature are reported for the two polyether intercalates and are discussed in the context of the systematics observed for other Lewis base intercalates of FeOCl.

Experimental Section

(a) **Synthesis and Characterization.** Kryptofix-21 was obtained from PCR Chemicals Corp. and purified by literature methods.³ All manipulations with the polyether were carried out in subdued light due to the photosensitivity of such compounds, and the purified product was stored under vacuum in light-protected ampules. Iron(III) oxochloride was prepared as described earlier⁴⁻⁷ and a sieved fraction (~200 mesh) used for the intercalation reaction. The latter was effected by dissolving ~1.0 g of Kryptofix-21 (~4.5 mmol) in ~3 cm³ of dry ethanol to which 0.5 g of FeOCl (~4.5 mmol) had been added. The ampule containing the reaction mixture was thoroughly degassed, sealed under vacuum, and maintained (light excluded) at 73 ± 2 °C for 22 days. At the end of the reaction period, the product was removed from the liquid supernate by filtration under dry N₂, washed with dry EtOH, dried under vacuum, and stored under nitrogen

(light excluded). Anal.⁸ Calcd for FeOCl(C₁₀H₂₂O₃N₂)_{1/18}: Cl, 29.69; C, 5.58; H, 1.03; N, 1.30. Found: Cl, 29.54; C, 5.37; H, 1.18; N, 1.48.

In view of the unexpectedly low ratio of guest to host stoichiometry, which is identical for the Kryptofix-21 and Kryptofix-22 intercalates (vide infra), an experiment was carried out with the latter in which the reaction time was lengthened to 4 weeks at 73 °C. The stoichiometry of the isolated product again corresponded to FeOCl-(Kryptofix-22)_{1/18}, and hence it is concluded that for these guest molecules, the limiting stoichiometry is reached within the reaction period discussed above.

(b) **X-ray Diffraction.** Powder patterns were obtained on the intercalation compounds with Cu Kα radiation and a Phillips-Norelco diffractometer calibrated with a standard silicon wafer. The increase in the *b*-axis interlayer distance was calculated from the positions of the (010), (020), and (030) reflections.

(c) **⁵⁷Fe Mössbauer Spectroscopy.** Nuclear γ resonance spectroscopy was effected by using a constant acceleration spectrometer as described earlier,¹ and all other aspects of this spectroscopy (i.e., sample temperature control, spectrometer calibration, sample geometry, etc.) were identical with those used in the earlier study. Data reduction was effected by using the SPECTRA program of Vieggers and Trooster⁹ which was modified to run on the Rutgers University IBM 370/168 computer.

Results and Discussion

(a) **Lattice Parameters of FeOCl(Kryptofix-21)_{1/18}.** For unintercalated FeOCl, the lattice parameters of the orthorhombic space group *P*_{mmn} (*D*_{2h}¹³) with two formula units per unit cell are¹⁰ *a* = 3.780, *b* = 7.917, and *c* = 3.302 Å at room temperature. Although the *a* and *c* parameters do not change significantly when a "guest" molecule is intercalated into the iron oxochloride matrix, the *b* parameter—which defines the distance between successive identical chlorine atom layers—increases to 12.02 Å. This increase of 4.1 Å is similar to the 4.3-Å expansion observed¹ on the intercalation of Kryptofix-22 and is comparable to that observed¹¹ for a number of FeOCl-alkylamine intercalates. It is, however, significantly smaller than the molecular dimension (specifically the nitrogen-nitrogen distance) calculated from the crystallographic data of Herceg and Weiss¹² and can be rationalized on the basis of a significant interpenetration of the ring moiety into the layers defined by the chlorine atoms of the matrix. The most probable orientation of the nitrogen-hydrogen bond to-

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Table I. Summary of ^{57}Fe Mössbauer Data

parameter	FeOCl	FeOCl(Kryptofix-22) $_{1/18}$		FeOCl(Kryptofix-21) $_{1/18}$	
		Fe(III)	"Fe(II)"	Fe(III)	"Fe(II)"
IS(78 K), ^a mm s ⁻¹	0.511 ± 0.008 ^b	0.509 ± 0.022	1.216 ± 0.030	0.510 ± 0.010	1.25 ± 0.03
IS(300 K), ^a mm s ⁻¹	0.389 ± 0.006	0.462 ± 0.010		0.463 ± 0.010	
QS(78 K), mm s ⁻¹	0.929 ± 0.010 ^b	1.149 ± 0.024	2.575 ± 0.088	1.212 ± 0.010	2.525 ± 0.040
QS(300 K), mm s ⁻¹	0.917 ± 0.010	0.722 ± 0.010		0.715 ± 0.008	
d ln [A(T)/A(78)] dT, ^c K ⁻¹	-1.901 × 10 ⁻³	-3.53 × 10 ⁻³	-3.77 × 10 ⁻²	-3.46 × 10 ⁻³	-2.79 × 10 ⁻² ^e
M _{eff} , ^d amu	76 ± 2	90 ± 2		117 ± 5	
H _{int} (4.2 K), kOe	432 ± 1	427 ± 1		424 ± 1	

^a With respect to the centroid of NBS-SRM metallic iron at 295 K. ^b Value calculated by extrapolation of the data above the magnetic ordering temperature to 78 K. ^c Based on the data in the "high-temperature limit". ^d Based on the temperature dependence of the IS parameter in the "high-temperature limit". ^e Based on the intensity of the minority resonance peak in the interval 78 < T < 140 K.

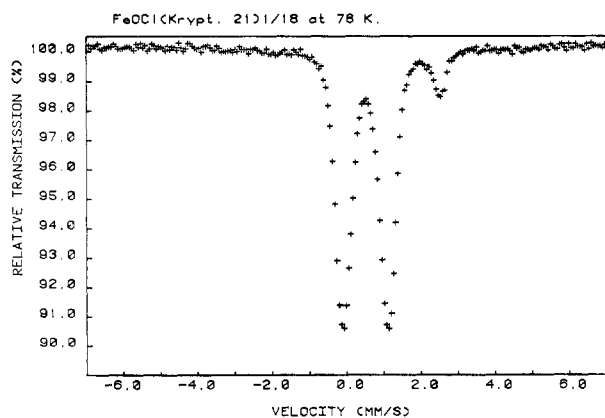


Figure 1. ^{57}Fe Mössbauer spectrum of $\text{FeOCl}(\text{Kryptofix-21})_{1/18}$ at 78 K. The velocity scale is with reference to the centroid of a room-temperature spectrum of NBS-SRM metallic iron, with the same source as employed in this study. The significance of the resonance line at $\sim +2.5$ mm s⁻¹ is discussed in the text.

ward the center of the polyether ring structure has been commented on previously.^{1,13,14}

(b) ^{57}Fe Mössbauer Parameters. The Majority Fe Atoms. As has been observed for a number of Lewis base intercalates of FeOCl , the Mössbauer spectra at liquid-nitrogen temperature consist of three resonance lines, two of which are of nearly (but frequently not exactly) the same intensity, while the third resonance maximum accounts for a small and strongly temperature dependent (vide infra) fraction of the total area under the resonance curve. A typical spectrum at 78 K is shown in Figure 1. The analysis of such spectra into a "majority" iron atom resonance typical of high-spin $\text{Fe}(\text{III})$ and of a "minority" iron atom resonance which can be ascribed to "Fe(II)" formed within the lattice on intercalation, has been detailed earlier,¹ and the present data are very similar to those reported for the Kryptofix-22 intercalate. The numerical values of the ^{57}Fe Mössbauer parameters for the majority iron atoms are summarized in Table I, together with the corresponding data for FeOCl and $\text{FeOCl}(\text{Kryptofix-22})_{1/18}$, and do not merit any further discussion beyond that offered earlier.

As has already been noted, for a number of Lewis base FeOCl intercalates, the most striking temperature dependence of the ^{57}Fe Mössbauer parameters is that of the quadrupole hyperfine interaction. This temperature dependence is very small for unintercalated FeOCl but undergoes a dramatic sigmoid behavior for the expanded lattice. This behavior is illustrated graphically in Figure 2, which summarizes the data (normalized in each case to the liquid-nitrogen temperature data point to facilitate intersample comparison) for uninter-

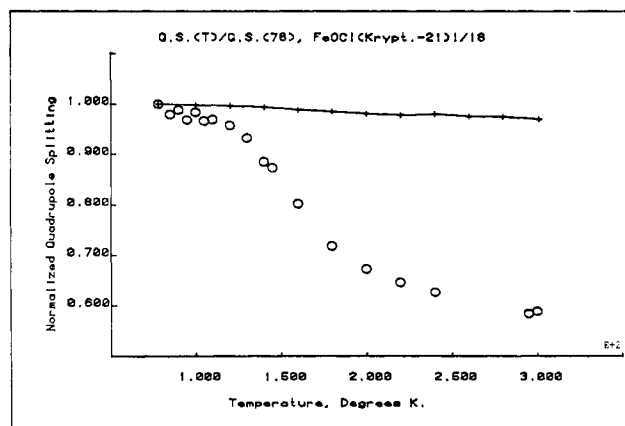


Figure 2. Temperature dependence of the QS parameter for $\text{FeOCl}(\text{Kryptofix-21})_{1/18}$. The data have been normalized to the 78 K data point. The corresponding data for unintercalated FeOCl are indicated by the crossed line. The notation $E + 2$ on the abscissa in this figure and Figures 3–5 indicate the numerical values should be multiplied by 100.

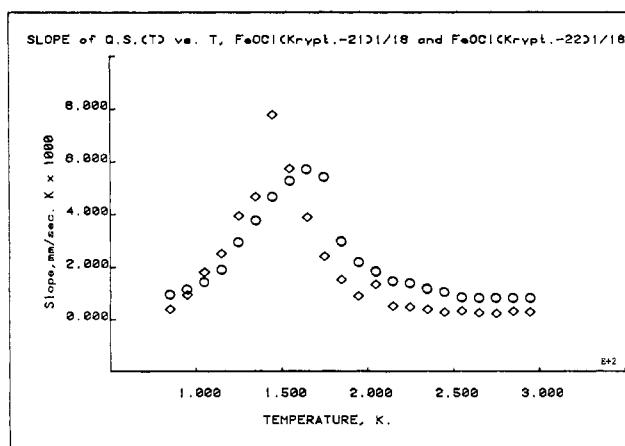


Figure 3. Slope of the temperature dependence of the QS parameter for $\text{FeOCl}(\text{Kryptofix-21})_{1/18}$ (circles) and $\text{FeOCl}(\text{Kryptofix-22})_{1/18}$ (diamonds). The points shown are not experimental points but result from digitization of the smooth curve drawn through data such as that shown in Figure 2.

calated FeOCl and for the majority iron resonance in $\text{FeOCl}(\text{Kryptofix-21})_{1/18}$. The rapid change of the quadrupole hyperfine interaction with temperature for the intercalate is seen more clearly in the data summarized in Figure 3, which is the result of digitization of the smooth curves of the data similar to that of Figure 2 and subsequent calculation of the slope $\Delta\text{QS}/\Delta T$. Comparison of such data for the two cryptate intercalates shows that the maximum slope for $\text{FeOCl}(\text{Kryptofix-21})_{1/18}$ occurs at ~ 156 K and for $\text{FeOCl}(\text{Kryptofix-22})_{1/18}$ it occurs at ~ 148 K, with the former having a

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somewhat larger full width at half-maximum ($\sim 55^\circ$) compared to the latter ($\sim 37^\circ$). These results have been rationalized in the earlier studies^{1,11} in terms of two temperature regimes relative to the interlayer interactions in the intercalation matrix. At low temperatures—i.e., below ~ 120 K—the bonding forces across the van der Waals layer are large compared to the mean thermal excitation energy of the solid, and the matrix behaves as a normal three-dimensional infinite network. At high temperatures—i.e., above ~ 180 K—the bonding forces across the van der Waals layer become small relative to the mean thermal excitation energy, and the solid behaves increasingly like a two-dimensional layer structure with a large anisotropy in the strength of the bonding forces parallel and perpendicular to the crystallographic *b* axis. Since the QS hyperfine interaction is very sensitive to the stereochemistry about the iron atom—specifically the Cl–Fe–Cl bond angle—this parameter provides a sensitive probe of the effect of thermal expansion on the electronic environment of the metal atom in the virgin matrix and in the intercalate structure.

Consistent with the earlier observations¹ for the FeOCl(Kryptofix-22)_{1/18} majority iron atom isomer shift temperature dependence, the isomer shift for FeOCl(Kryptofix-21)_{1/18} shows distinct temperature dependencies in the low- and high-temperature regimes. The two slopes, $d(\text{IS})/dT$, of $-2.42 \times 10^{-4} \text{ mm s}^{-1} \text{ K}^{-1}$ ($78 \leq T \leq 140 \text{ K}$) and $-3.57 \times 10^{-4} \text{ mm s}^{-1} \text{ K}^{-1}$ ($200 \leq T \leq 300 \text{ K}$) reflect not only the tighter binding of the lattice across the van der Waals layer at low temperatures but also the gradual transition to the high-temperature behavior similar to that extracted from the temperature dependence of the QS parameter as discussed above. In this context, it is interesting to note that the effective vibrating mass, M_{eff} , calculated from the equations developed earlier,^{15,16} is significantly larger for the present polyether intercalate than was observed in the earlier study (and, of course still larger than M_{eff} calculated from the high-temperature isomer shift data for the unintercalated lattice⁷). The relationship between M_{eff} , which reflects the average temperature dependence of IS for all of the (different) Fe atoms in the solid, and the strength of the specific chemical interaction between the lattice iron atoms and the guest molecular species, is in need of further systematic study before these relationships are completely understood.

As has been observed for a number of Lewis bases intercalated into FeOCl, including $(\text{C}_2\text{H}_5)_3\text{P}$,¹⁵ $(\text{CH}_3\text{O})_3\text{P}$,¹⁵ a number of alkylamines,¹¹ pyridines, and related compounds,^{17,18} as well as the Kryptofix-22 intercalate,¹ the Mössbauer–Debye–Waller factor for these solids, in the temperature range above the magnetic ordering temperature (vide infra), although significantly larger than that observed for the virgin lattice, does not show any change of slope above and below the broad transition temperature discussed above. This observation implies clearly that the phonon spectrum—and in particular the motions which involve the metal atoms in the *ac* plane—is dominated by the *intralayer* bonding forces and is not sensitive to changes in the strength of the bonding across the van der Waals layers. Thus it has not been possible to establish any direct correlation between the temperature dependence of the recoil-free fraction [extracted from $\ln A(T)$ data] and either the magnitude of the *b*-axis expansion or the stoichiometry of the intercalation compound formed with a particular Lewis base. So far, no evidence for the three-dimensional to two-dimensional lattice structure transition can be inferred from

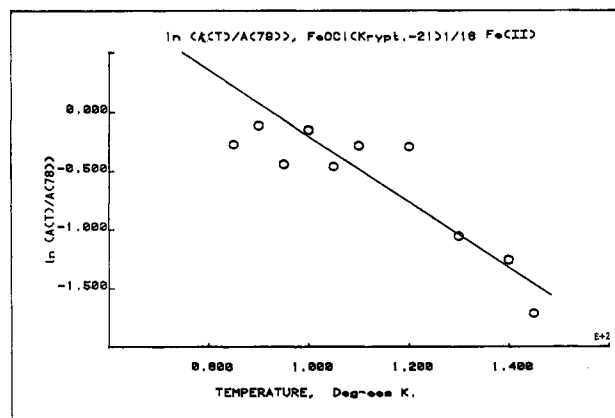


Figure 4. Temperature dependence of the area under the resonance ascribed to "Fe(II)" (see text). The straight line is a least-squares fit through the data.

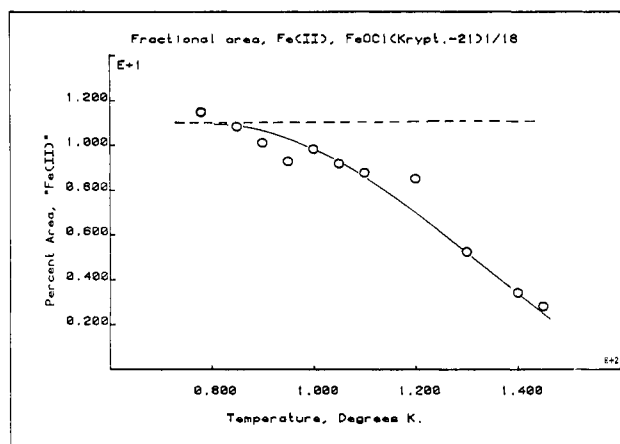


Figure 5. Temperature dependence of the fractional area ascribed to "Fe(II)" (see text). The dashed line represents the expected fraction under the assumptions (a) that both nitrogen atoms of the polyether bond to the metal atoms and (b) that the recoil-free fractions of iron atoms in the solid are (nearly) equal.

the available data related to recoil-free fraction measurements.

(c) ⁵⁷Fe Mössbauer Parameters. **The Minority Fe Atoms.** The additional resonance absorption, which is observed in the Mössbauer spectra of FeOCl, intercalates at temperatures below ~ 150 K at a Doppler velocity of $\sim +2.5 \text{ mm s}^{-1}$ with respect to metallic iron (see Figure 1) has been assigned as half of a quadrupole split doublet. The other component of this resonance line pair is hidden under the majority iron atom resonance maximum at $\sim -0.2 \text{ mm s}^{-1}$. The isomer shift and quadrupole splitting parameters which follow from this assignment (Table I) are characteristic of Fe(II) and have been identified with those high-spin Fe(III) atoms of the FeOCl matrix which have a nearest-neighbor interaction with the lone pair of the Lewis base guest molecular species.

The temperature dependence of the area under the "Fe(II)" resonance maximum is summarized graphically in Figure 4. Although the experimental points show a good deal of scatter, and the temperature range over which these parameters can be extracted from the spectroscopic data is severely limited, it is clear that the *apparent* temperature dependence of $\ln [A(T)/A(78)]$ is much greater for the minority Fe atoms than for the majority Fe atom resonance. Rather than indicating a major difference in the recoil-free fraction between the two iron atoms, it is likely that the minority iron atoms become indistinguishable from the remaining metal atoms at temperatures where the transition from a three-dimensional solid (low temperatures) to a *quasi*-two-dimensional solid (high temperatures) has become complete. This interpretation is

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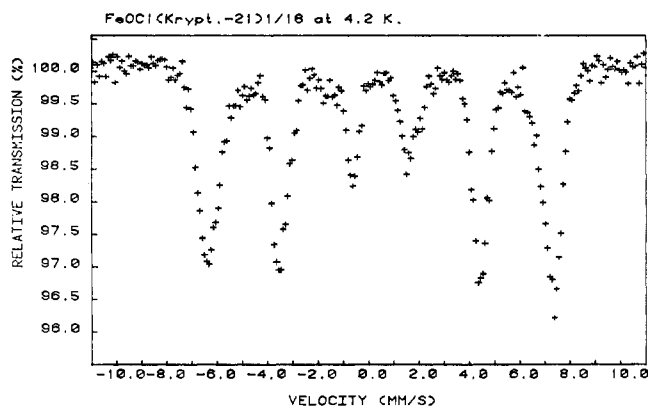


Figure 6. ^{57}Fe Mössbauer spectrum of $\text{FeOCl}(\text{Kryptofix-21})_{1/18}$ at 4.2 K. The presence of two (or more) distinct iron atoms in the solid is clearly indicated by the line widths and asymmetries of the resonance lines.

supported by the data summarized in Figure 5 in which the fraction of the total area under the resonance curve represented by the "Fe(II)" resonance has been plotted as a function of temperature. With the assumption that for Kryptofix-21 (as in the case of the more symmetrical Kryptofix-22) both nitrogen atoms of the ring are equally good electron pair donors and given the stoichiometry ratio of guest to host of 1:18 lead to 11% of the iron atoms of the FeOCl matrix having nearest-neighbor lone pairs. With the further assumption that the recoil-free fraction of the two kinds of iron atoms in the intercalate are essentially identical leads to the condition that the fractional area under the resonance curve of the "Fe(II)" atoms should be $\sim 11\%$. From Figure 5, in which this value is indicated by the horizontal dashed line, it is seen that this value is indeed approached at the lowest temperatures at which the onset of magnetic ordering has not yet become a complicating factor. The model which arises from these assumption envisions two kinds of iron atoms in the structure at low temperatures but that these become indistinguishable at high temperatures where the interaction between the host matrix and the guest intercalant moieties becomes small compared to the mean thermal excitation of the lattice.

(d) ^{57}Fe Mössbauer Parameters below T_c . Unintercalated FeOCl is known^{7,19} to order antiferromagnetically at a temperature of 90 ± 2 K. When guest molecules are intercalated into this matrix, the onset of magnetic ordering drops well below liquid-nitrogen temperature and shows a temperature behavior which is characteristic of a complex magnetic behavior, possibly similar in origin to that recently described²⁰ by Palvadeau et al. At liquid-helium temperature however, the ^{57}Fe Mössbauer spectra show a well-resolved six-line hyperfine pattern, as shown in Figure 6. Although at first glance such spectra appear to be simple magnetic perturbation spectra of iron atoms having a quadrupole hyperfine interaction, detailed analysis of line intensities and line widths leads to the conclusion that there are several distinct iron atoms present in the solid. If there were only two such distinguishable iron atoms in the structure (as implied by the earlier discussion, section c above), the spectra could be uniquely analyzed in terms of two unique magnetic hyperfine fields, isomer shifts, and quadrupole interactions. The present data suggest, however, that there is a distribution of internal magnetic hyperfine fields, arising from small (but significant) differences in the detailed stereochemistry around each iron atom in the layer

structure of the intercalated matrix. This conclusion is not surprising in view of the fact that the spin-spin correlation in the solid is effected by a superexchange mechanism involving the oxygen atoms linking the metal atoms and is completely confined to the crystallographic *ac* plane, giving rise to what is, in effect, a two-dimensional antiferromagnet.

Making use of the line positions of the (broadened) four outermost lines of the 4.2 K spectrum (without taking into account the distribution of internal fields referred to above) permits the calculation of the internal magnetic field at the iron atom nucleus, H_{int} , and the sign of the principal component of the electric field gradient tensor, V_{zz} . The magnitude of H_{int} so calculated is 424 ± 1 and 427 ± 1 kOe at 4.2 K for $\text{FeOCl}(\text{Kryptofix-21})_{1/18}$ and $\text{FeOCl}(\text{Kryptofix-22})_{1/18}$, respectively. These values are only $\sim 2\%$ smaller than the magnitude of H_{int} reported⁷ for the unintercalated matrix and reflect the insensitivity of this parameter to the interlayer spacing in the solid. The ratio of the energy of separation of the two outermost resonance maxima on each side of the spectrum centroid leads to the conclusion that V_{zz} is negative, but only barely so; in contrast to the earlier observation¹¹ that in both virgin FeOCl (in which V_{zz} is negative) and in the $\text{FeOCl}(\text{py})_{1/3}$ and $\text{FeOCl}(\text{NH}_3)_{3/4}$ intercalates (in which V_{zz} is positive), this ratio shows a large departure from unity. From the available Mössbauer data on FeOCl intercalates, examined well below T_c , it was concluded that the sign of V_{zz} appeared to correlate well with the descriptor n in the representation $\text{FeOCl}(\text{G})_n$ (where G stands for the molecular guest moiety). For compounds for which n is less than $1/3$ (including zero), V_{zz} was observed to be negative, while for compounds in which $n \geq 1/3$, V_{zz} was observed to be positive. No theoretical rationalization for these observations have been offered, but it is clear that the present results do not support the earlier systematics. It is probable that the results observed for the polyether intercalates relate to a lowered symmetry of the electric field gradient at the metal atom lattice site. Better resolution of all of the components of the magnetic hyperfine spectra such as that shown in Figure 6 (and Figure 6 of ref 11) will be required before a detailed theoretical model dealing with the sign of V_{zz} for each distinguishable component iron atom in these compounds can be achieved.

Summary and Conclusions

In the present study, the preparation and lattice dynamical, magnetic, and electronic properties of the iron atoms in the crown ether intercalate $\text{FeOCl}(\text{Kryptofix-21})_{1/18}$ have been reported in detail and compared to the properties of the intercalation compound obtained with the larger (symmetrical) crown ether containing an additional $-\text{CH}_2-\text{CH}_2-\text{O}-$ group in the ring structure. These intercalates show qualitatively the same behavior observed previously with a variety of large Lewis base intercalates of FeOCl, which has been interpreted in terms of a model in which the matrix undergoes a broad transition from a three-dimensional solid to a quasi-two-dimensional solid as the temperature is increased. The lowering of the onset of the antiferromagnetic ordering temperature and the magnitude of the magnetic hyperfine field at the iron atoms at 4.2 K have been examined.

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