bond lengths are a function of the number of donor atoms. As the coordination number goes up, the bonds to sulfur get longer. It is not surprising, then, that the 15S5 complex (five metal–sulfur bonds) has such long bonds compared to the 16S4 complex (four metal–sulfur bonds). It is interesting, however, that the Cd–S bonds are also much longer in the 15S5 complex than in the bis 9S3 complex (six metal–sulfur bonds). The cadmium–oxygen bond involving the water molecule (Cd–O9 = 2.253 Å) is nearly equal to the sum of their covalent radii (2.21 Å for Cd–O[20]). The cadmium–oxygen bond involving the perchlorate anion, however, is longer (2.653 Å) than the sum of the covalent radii. Although the perchlorate ion occupies a "coordination site", it cannot be considered as being bonded to the cadmium.

Note that the axially bonded ligands have shorter bonds than the corresponding equatorially bonded. Equatorial Cd–S bonds average 2.78 Å, while the axial Cd–S bond is 2.67 Å long. Similarly, the axial Cd–O(water) is 2.25 Å and the equatorial Cd–O(perchlorate) is 2.65 Å. Steric effects clearly are responsible for these differences. In an ideal pentagonal bipyramid the angle between the equatorial ligands is only 72°, while the angle between an axial ligand and its neighbors is 90°. This steric crowding around the perimeter of the structure can be relieved by metal–ligand bond lengthening. Besides occupying an equatorial coordination site, the perchlorate anion is a relatively bulky ligand itself, which probably accounts for the much longer Cd–O bond in that ligand.

There is evidently a great deal of strain imparted to the ligand upon coordinating the cadmium ion in this complex. The "bite" angles for the chelate rings involving only equatorially disposed sulfur atoms average 74°, smaller than the corresponding bite angles observed in $[(9S3)_2Cd](ClO_4)_2$ (83°).[18] In addition, the conformation forced upon the macrocyclic ring causes transannular steric interactions between the hydrogen on C5 with one of the hydrogens on C9 (H···H $\simeq$ 2.1 Å). Note that the sum of the van der Waals radii for hydrogen is 2.4 Å.[21] The strain in the macrocyclic ring may be responsible for some remarkable deviations from normally observed bond lengths, 1.81 Å for C–S and 1.54 Å for C–C.[21]

Acknowledgment. This research was generously supported by grants from the National Institutes of Health (G.J.G. and W.N.S.), the Petroleum Research Fund, administered by the American Chemical Society (G.J.G. and W.N.S.), and the Research Corp. (W.N.S. and G.J.G.).

Supplementary Material Available: Listings of complete bond lengths and bond angles, complete atom positional parameters, and anisotropic thermal parameters (7 pages); a listing of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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α- and β-$FeF_3{\cdot}3H_2O$ Revisited: Crystal Structure and ^{57}Fe Mössbauer Spectra

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Received August 13, 1991

Neilsen[1] prepared the two different crystalline forms of $FeF_3{\cdot}3H_2O$ by evaporation of an HF solution of Fe^{3+} at room temperature (α-form) and above 50 °C (β-form). The crystal data for β-$FeF_3{\cdot}3H_2O$ as reported by Teufer[2] identified the space group as $P4/m$ with a = 7.846 Å and c = 3.877 Å. Maak et al.[3] assigned a *J6* type structure to the α-form with a = 9.49 Å and c = 9.58 Å. ^{57}Fe Mössbauer studies of $FeF_3{\cdot}3H_2O$ have been reported by several investigators.[4-6] Dêzsi et al.[5] found the α- and β-forms could be distinguished by the difference in their quadrupole splitting in the room-temperature Mössbauer spectra. Imbert et al.[6] found an antiferromagnetic transition at T_N = 14.7 K for β-$FeF_3{\cdot}3H_2O$.

Reinvestigation of the two forms of $FeF_3{\cdot}3H_2O$ found a surprising correspondence of the crystal structure of α-$FeF_3{\cdot}3H_2O$ with a reported[7] structure of $FeF_2{\cdot}4H_2O$. Also, a T_N of 19.3 K for β-$FeF_3{\cdot}3H_2O$ was discovered instead of the reported T_N of 14.7 K. Both results are explained by the difficulty of preparing pure samples of the Fe^{2+}–Fe^{3+} fluoride hydrates.

Both the white α-$FeF_3{\cdot}3H_2O$ and the pink β-$FeF_3{\cdot}3H_2O$ were prepared by Neilsen's method—crystallization from an HF solution of Fe^{3+} at room temperature (α) or above 50 °C (β). Powder X-ray diffraction patterns showed that, in most cases, the products were mixtures of the two forms. The solution becomes quite concentrated before precipitation, so filtration of the product is rather slow. Meanwhile, some of the metastable α-form converts[5] to the β-form during attempts to prepare pure α material. The cooling of the hot solution during filtration introduces some α-form into the β-form preparation.

Pure β-$FeF_3{\cdot}3H_2O$ was prepared by evaporation to dryness at 80–100 °C. Precipitation of α-$FeF_3{\cdot}3H_2O$ by mixing a saturated solution with cold ethanol was, at times, successful in preparing pure α-form material, but more often this method also produced mixtures. No reliable method was found for preparing pure α-form samples. As reported by Dêzsi et al.,[5] the solid α-form is unstable and begins conversion to the β-form within a few days. All preparations were characterized by X-ray diffraction.[8] Nine samples of both forms were analyzed. Anal. Calcd: Fe, 33.45; F, 34.17. Found: Fe, 33.80 (42); F, 34.09 (59).

Analysis of a pure α-form sample found 31% F. Attempts to analyze β-form samples for water by Karl Fischer found less than 0.01% H_2O. Evidently, CH_3OH will not displace the water of hydration. There was a weight loss of 29% after 16 h at 90 °C in a hard vacuum, compared with a calculated 32 wt % content for the trihydrate.

^{57}Fe Mössbauer measurements were performed as previously described.[9] The isomer shifts in their ^{57}Fe Mössbauer spectra definitely establish that both α- and β-forms are trivalent iron compounds.

X-ray Diffraction Results

The X-ray diffraction pattern from a polycrystalline sample of α-$FeF_3{\cdot}3H_2O$ was indexed as a hexagonal cell with a = 9.5135 (7) Å, c = 4.7882 (8) Å, and space group $R\bar{3}m$, which are virtually identical with the reported[7] data for "$FeF_2{\cdot}4H_2O$". The indexing included 51 peaks. Details of the structure comparison are given as supplementary material, including a comparison with the isostructural α-$CrF_3{\cdot}3H_2O$.

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(8) The refined pattern was acquired with Cu radiation, and an internal Mo standard was used to correct d values. The symmetry and unit cell parameters were obtained with the Siemens Visser program. Peak positions were confirmed and lattice parameters refined with the Siemens Appleman program. Integrated intensities were obtained with the Alfred ADR program and estimated visually for weak peaks.

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0020-1669/92/1331-1118$03.00/0

Table I. Mössbauer Parameters for α-$FeF_3 \cdot 3H_2O$[a]

sample	T, K	δ, mm/s	ΔE, mm/s	Γ, mm/s
1[b]	298	0.416 (6)	0.339 (9)	0.22
2[c]	298	0.42 (5)	0.55 (2)	0.25
	8.6	0.40 (5)	0.54 (5)	0.30
	4.2	0.50 (5)	0.53 (5)	0.30
d	298	0.40	0.37	0.40

[a] δ = isomer shift relative to α-iron standard, $^{57}Co(Rh)$ source; ΔE = quadrupole shift; Γ = line half-width at half-maximum. [b] Average of three pure samples. [c] Sample estimated to be 95% pure. [d] Dézsi et al.[5]

Table II. Mössbauer Parameters for β-$FeF_3 \cdot 3H_2O$

T, K	δ, mm/s	ΔE, mm/s	H_{eff}, kOe	Γ, mm/s
4.2	0.50	0.50	433	
7.9	0.53	0.43	419	
12.1	0.51	0.62	387	
17.1	0.53	0.55	297	
18.3	0.50	0.51	253	
18.8	0.51	0.54	222	
25	0.54	0.60		0.22
36	0.54	0.60		0.22
298	0.42	0.61		0.22
298[a]	0.44			
298[b]	0.43	0.60		0.42
298[c]	0.33	0.62		0.36
4.2[c]	0.43	0.56	449	0.38

[a] Champion et al.[4] [b] Dézsi et al.[5] [c] Imbert et al.[6] Data collected with a $^{57}Co(Cu)$ source.

It appears that Penfold and Taylor[7] actually determined the crystal structure of α-$FeF_3 \cdot 3H_2O$ rather than that of $FeF_2 \cdot 4H_2O$. They reported finding two different types of white crystals after evaporating an HF–Fe^{2+} solution. Both "oxidized" to yield $FeF_3 \cdot 4^1/_2H_2O$. Later, $FeF_3 \cdot 4^1/_2H_2O$ was identified as β-$FeF_3 \cdot 3H_2O$.[5] Both types had the correct iron content for $FeF_2 \cdot 4H_2O$, as determined by ignition in air to Fe_2O_3. However, the iron content of $FeF_3 \cdot 3H_2O$ differs from the tetrahydrate by only 0.2 wt %; thus, distinguishing between the tri- and tetrahydrates without a fluoride or water analysis is extremely difficult. Penfold and Taylor also could not distinguish an F atom from an O atom by X-ray measurements. Their X-ray structure determination was excellent but was assigned to the wrong compound.

In both α- and β-$FeF_3 \cdot 3H_2O$, the Fe^{3+} ions are at the center of a nearly regular octahedron.[2,7] The difference between their structures is that the discrete octahedra of the α-form are randomly oriented,[7] while the octahedra of the β-form share apices on the *c* axis.[2] The Fe–X (X = F or H_2O) distances for the α-form are 1.955 Å[7] and for the β-form are 1.951 Å (F) and 1.94 Å (H_2O).[2] This correspondence of bond lengths supports the other data that identify "$FeF_2 \cdot 4H_2O$" as α-$FeF_3 \cdot 3H_2O$.

^{57}Fe Mössbauer Results

The Mössbauer spectrum of α-$FeF_3 \cdot 3H_2O$ showed only paramagnetic behavior between room temperature and 4.2 K. The Mössbauer parameters (Table I) agree reasonably well with those of Dézsi et al.[5] and show no appreciable change in the quadrupole splitting or isomer shift at low temperatures.

β-$FeF_3 \cdot 3H_2O$ is paramagnetic over the temperature region 20–300 K and orders magnetically at 19.3 K (Figure 1). The Mössbauer parameters are listed in Table II and agree well with those of Dézsi et al.[5] in the paramagnetic region. Aside from a T_N of 19.3 K instead of 14.7 K, the parameters also agree fairly well with the data of Imbert et al.[6] in the ordered region. The internal magnetic field, H_{eff}, is 433 ± 5 kOe at 4.2 K—slightly lower than the T_N of 449 ± 3 kOe reported by Imbert et al.[6] The increase of H_{eff} with decreasing temperature is illustrated in Figure 2.

It appears that mixtures, as determined by X-ray diffraction, of the α- and β-forms of $FeF_3 \cdot 3H_2O$ are not simple mixtures of two phases, since the Néel points depend on composition. The α-$FeF_3 \cdot 3H_2O$ sample in Table I, estimated to be 95% pure, ordered magnetically at 5.5 K. Other mixtures showed ordering at 9.7, 12.4, and 16 K. The T_N of 14.7 K found by Imbert et al.[6] must have also been measured on a mixture. A possible explanation is that, in these mixtures, the composition of the β-phase is changing, perhaps by inclusion of α-$FeF_3 \cdot 3H_2O$ in its structure.

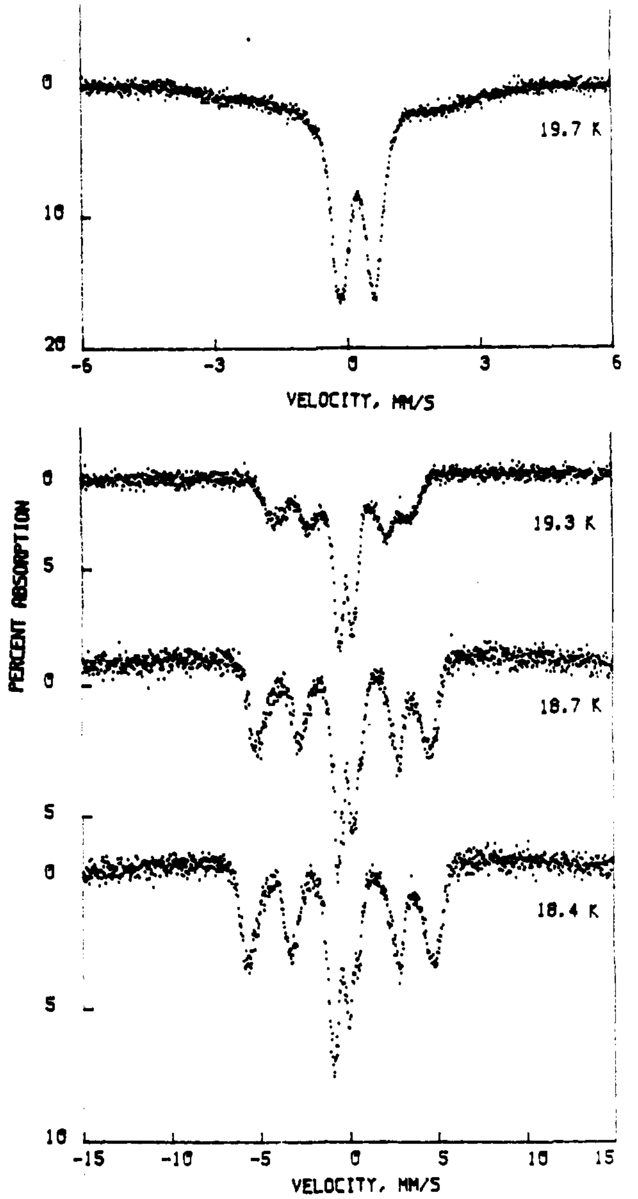

Figure 1. ^{57}Fe Mössbauer spectra of β-$FeF_3 \cdot 3H_2O$ in the region of the Néel temperature.

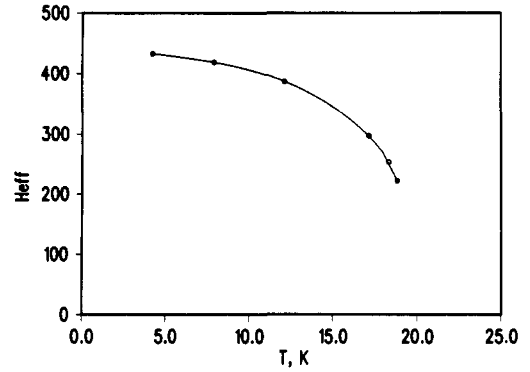

Figure 2. H_{eff} (kOe) of β-$FeF_3 \cdot 3H_2O$ from 4.2 K to the Néel temperature 19.3 K.

Acknowledgment. The information in this paper was developed during the course of work under Contract No. DE-AC09-

89SR189035 with the U.S. Department of Energy.

Supplementary Material Available: A listing of 2θ values, d spacings, line intensities, and hkl indices for α-$FeF_3 \cdot 3H_2O$ and "$FeF_2 \cdot 4H_2O$" (3 pages). Ordering information is given on any current masthead page.

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Structural Diversity in Bis(pentamethylcyclopentadienyl)yttrium Chloride Complexes: Cocrystallization of $[(C_5Me_5)_2Y(\mu\text{-}Cl)_2Li(THF)_2]$ and $[(C_5Me_5)_2YCl(\mu\text{-}Cl)Li(THF)_3]$

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Received October 30, 1991

Introduction

The organometallic chemistry of trivalent lanthanide and yttrium complexes is dominated by complexes containing two C_5Me_5 rings and a third anionic ligand.[1] Due to the large size and electrophilic nature of these metals, complexes of the formula $(C_5Me_5)_2LnZ$ (Ln = lanthanide or yttrium; Z = monodentate monoanionic ligand) generally bind an additional ligand and exist as base adducts of formula $(C_5Me_5)_2Ln(Z)(L)$ (L = electron pair donor). In the ionic metathesis reactions commonly used to prepare these complexes, e.g., eqs 1 and 2 (M = alkali metal),

$$LnCl_3 + 2MC_5Me_5 \rightarrow (C_5Me_5)_2LnCl(L) + 2MCl \qquad (1)$$

$$(C_5Me_5)_2LnCl(L) + LiZ \rightarrow (C_5Me_5)_2Ln(Z)(L) + LiCl \qquad (2)$$

the alkali metal halide byproducts can provide the additional ligand, L, and adducts such as $(C_5Me_5)_2LnCl_2M(ether)_x$ or $(C_5Me_5)_2LnZClLi(ether)_x$ are commonly observed. Indeed, the first (pentamethylcyclopentadienyl)lanthanide complexes to be isolated were of this type.[2-4]

Table I. Experimental Data for the X-ray Diffraction Study

formula	$C_{60}H_{100}Li_2O_5Cl_4Y_2$
fw	1234.9
temp	173 K
crystal system	monoclinic
space group	$P2_1/c$ (C_{2h}^5; No. 14)
a	14.622 (2) Å
b	29.314 (5) Å
c	15.157 (2) Å
β	90.055 (13)°
V	6497 (2) Å^3
Z	4
D_{calcd}	1.263 Mg/m^3
diffractometer	Siemens P3 (R3m/V system)
radiation	Mo Kα ($\bar{\lambda}$ = 0.710730 Å)
monochromator	highly oriented graphite
data collected	$+h,+k,\pm l$
scan type	ω
scan width	1.1°
scan speed	3.0° min^{-1} (in ω)
2θ range	4.0–45.0°
μ(Mo Kα)	1.995 mm^{-1}
abs cor	semiempirical (ψ-scan method)
no. of reflns collected	9164
no. of unique reflns with $\lvert F_o \rvert > 0$	7370
no. of reflns with $\lvert F_o \rvert > 3.0\sigma(\lvert F_o \rvert)$	5649
no. of variables	659
R_F; R_{wF}	7.1%; 7.2%
goodness of fit	1.21

Numerous examples of alkali metal adducts of general formula $(C_5Me_5)_2LnZ_2M(ether)_x$ have been reported.[2-35] In general, these compounds are considered to have two ether molecules of solvation and two doubly-bridging Z ligands, i.e., $(C_5Me_5)_2Ln(\mu\text{-}Z)_2M(ether)_2$, which is consistent with the initial crystallographic data obtained on these complexes.[6,7,9,13,15,16,19,20,24,28-30] However, variations in the amount of ether present in these complexes have been observed, both in elemental analytical data and in recent X-ray crystallographic studies. For example, a monosolvated complex, $[(C_5Me_5)_2Ce(\mu_3\text{-}Cl)_2K(THF)]_n$, has been reported,[25] in which the alkali metal achieves five-coordination by interacting with chloride ligands of three different monomer units. The monosolvate $(C_5Me_5)_2Y(\mu\text{-}C{\equiv}CCMe_3)_2Li(THF)$, is not similarly oligomerized.[30] In this case, the steric bulk of two bridging

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