1116 *Inorg. Chem.* **1992**, *31*, 1116–1118

Contribution from the Departments of Chemistry,
University of Alabama in Huntsville,
Huntsville, Alabama 35899,
and University of Tennessee at Chattanooga,
Chattanooga, Tennessee 37403, and School of Chemistry,
Georgia Institute of Technology, Atlanta, Georgia 30332

Crystal and Molecular Structure of (1,4,7,10,13-Pentathiacyclopentadecane)cadmium(II) Perchlorate Hydrate: A Seven-Coordinate Cadmium[1]

William N. Setzer,*[,2a] Yaping Tang,[2a] Gregory J. Grant,[2b] and Donald G. VanDerveer[2c]

Received August 15, 1991

Thioether ligands may serve as selective metal extraction agents for "soft" metal ions such as cadmium and mercury.[3] Multidentate ligands such as these may have important utility as antagonists for treatment of heavy-metal poisoning.[4] How well macrocyclic polythioethers may serve in this capacity will doubtless depend upon ring cavity size, chelate ring size, preferred ligand conformation[5] (i.e., ligand "preorganization"[6]), and preferred metal coordination geometry.[7] In order to gain insight into the structures and stabilities of coordination complexes of thioether ligands, we have synthesized[8] and studied[9] a number of sulfur-containing cyclic compounds. In this paper we report the crystal and molecular structure of the cadmium(II) complex of a macrocyclic pentathioether, (1,4,7,10,13-pentathiacyclopentadecane)cadmium(II) perchlorate hydrate, $[(15S5)Cd](ClO_4)_2{\cdot}H_2O$.

Experimental Section

Methods and Materials. All reagents were obtained from Aldrich Chemical Co., Milwaukee, WI. Solvents were dried using standard techniques. Analyses were carried out by Atlantic Microlab, Inc., Norcross, GA.

Safety Note. Although we have not observed any explosive tendencies of this compound, perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

Table I. Crystal Data for $[(15S5)Cd](ClO_4)_2{\cdot}H_2O$

mol formula	$C_{10}H_{22}S_5Cl_2O_9Cd$	λ, Å	0.71073
mol wt	629.88	$2\theta_{max}$, deg	50.0
space group	orthorhombic, $Pna2_1$	$F(000)$	1224.00
cell dimens		d_{calcd}, g cm^{-3}	1.895
a, Å	17.842 (4)	no. of unique data	3868
b, Å	8.7610 (10)	no. of obsd data	2978
c, Å	14.080 (3)	abs coeff, mm^{-1}	1.72
V, Å^3	2200.9	$R(F_o)^a$	0.038
Z	4	$R_w(F_c)^b$	0.037

[a] $R = \sum(F_o - F_c)/\sum(F_o)$. [b] $R_w = [\sum(w(F_o - F_c)^2/\sum(wF_o^2)]^{1/2}$.

Table II. Final Atomic Parameters for $[(15S5)Cd](ClO_4)_2{\cdot}H_2O$

atom	*x*	*y*	*z*	*B*, Å^{2a}
Cd	−0.14067 (2)	−0.18773 (5)	0.0	3.04 (4)
S1	−0.1981 (1)	−0.2205 (2)	0.1818 (1)	4.3 (1)
C2	−0.2888 (5)	−0.1353 (10)	0.1768 (6)	4.4 (4)
C3	−0.3177 (4)	−0.1018 (10)	0.0779 (6)	4.5 (4)
S4	−0.25346 (9)	0.0127 (2)	0.0022 (4)	4.0 (1)
C5	−0.2954 (5)	0.0098 (11)	−0.1058 (6)	4.7 (4)
C6	−0.2908 (4)	−0.1250 (11)	−0.1614 (6)	5.1 (4)
S7	−0.1989 (1)	−0.2206 (3)	−0.1820 (2)	4.32 (9)
C8	−0.1487 (6)	−0.0675 (12)	−0.2466 (6)	6.9 (6)
C9	−0.1121 (5)	0.0562 (9)	−0.1947 (5)	3.9 (4)
S10	−0.0429 (2)	−0.0229 (3)	−0.1170 (2)	5.1 (1)
C11	−0.0470 (5)	0.1528 (9)	−0.0375 (5)	4.3 (4)
C12	−0.0034 (5)	0.1219 (11)	0.0503 (6)	5.6 (4)
S13	−0.0430 (1)	−0.0282 (3)	0.1170 (2)	4.7 (1)
C14	−0.1119 (5)	0.0408 (10)	0.2010 (6)	5.5 (5)
C15	−0.1450 (4)	−0.0919 (11)	0.2545 (5)	4.4 (4)
Cl1	−0.24368 (8)	−0.5674 (2)	−0.0006 (3)	3.4 (1)
O1	−0.2466 (3)	−0.4043 (5)	−0.0011 (11)	7.2 (5)
O2	−0.2128 (4)	−0.6146 (8)	0.0778 (4)	7.2 (4)
O3	−0.2021 (3)	−0.6244 (7)	−0.0873 (4)	4.8 (3)
O4	−0.3181 (3)	−0.6198 (6)	0.0100 (11)	6.2 (4)
Cl2	−0.4994 (3)	−1.0030 (7)	−0.7501 (4)	4.06 (7)
O5	−0.4362 (4)	−1.0365 (10)	−0.6965 (5)	9.0 (5)
O6	−0.5231 (6)	−0.8621 (9)	−0.7139 (10)	14.2 (8)
O7	−0.5540 (5)	−1.1064 (10)	−0.7297 (8)	12.0 (6)
O8	−0.4776 (6)	−0.9978 (14)	−0.8427 (5)	12.8 (7)
O9	−0.0639 (3)	−0.3914 (5)	0.0053 (9)	5.0 (3)

[a] *B*, the isotropic temperature factor, is the mean of the principal axes of the thermal ellipsoid.

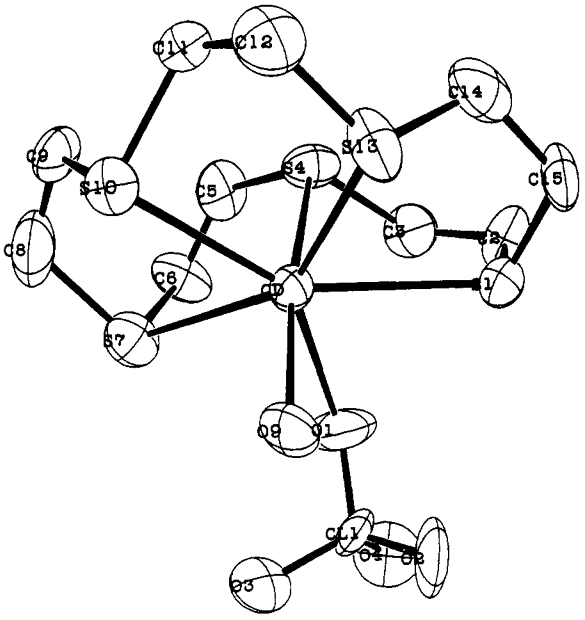

Figure 1. ORTEP perspective view of $[(15S5)Cd](ClO_4)_2{\cdot}H_2O$.

Preparation of (1,4,7,10,13-Pentathiacyclopentadecane)cadmium(II) Perchlorate Hydrate, $[(15S5)Cd](ClO_4)_2{\cdot}H_2O$. A solution of 1,4,7,10,13-pentathiacyclopentadecane (62.9 mg, 0.209 mmol) in 4 mL of anhydrous nitromethane was added to a solution of cadmium perchlorate hexahydrate (91.3 mg, 0.218 mmol) in 4 mL of anhydrous nitromethane. Colorless crystals were grown from the reaction mixture by solvent diffusion with diethyl ether to give 49.8 mg (37.8% yield) of $[(15S5)Cd](ClO_4)_2{\cdot}H_2O$. IR (KBr): 3600–3400, 2910, 1416,

---

(1) Synthesis and Complexation Studies of Mesocyclic and Macrocyclic Polythioethers. 9. Part 8: Grant, G. J.; Sanders, K. A.; Setzer, W. N.; VanDerveer, D. G. *Inorg. Chem.* **1991**, *30*, 4053. This work was presented in part at the Sixteenth International Symposium on Macrocyclic Chemistry, Sheffield, U.K., Sept 1–6, 1991.

(2) (a) University of Alabama in Huntsville. (b) University of Tennessee at Chattanooga. (c) Georgia Institute of Technology.

(3) (a) Fekete, D. S. L.; Meider, H. *J. Inorg. Nucl. Chem.* **1980**, *42*, 885. (b) Sevdic, D.; Meider, H. *J. Inorg. Nucl. Chem.* **1981**, *43*, 153. (c) Sekido, E.; Kawahara, H.; Tsuji, K. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1587. (d) Takeshita, H.; Mori, A.; Hirayama, S. *J. Chem. Soc., Chem. Commun.* **1989**, 564.

(4) (a) Jones, M. M.; Banks, A. J.; Brown, C. H. *J. Inorg. Nucl. Chem.* **1975**, *37*, 761. (b) Mitchell, W. G.; Jones, M. M. *J. Inorg. Nucl. Chem.* **1978**, *40*, 1957. (c) Bach, R. D.; Rajan, S. J.; Vardhan, H. B.; Lang, T. J.; Albrecht, N. G. *J. Am. Chem. Soc.* **1981**, *103*, 7727. (d) Bach, R. D.; Vardhan, H. B. *J. Org. Chem.* **1986**, *51*, 1609.

(5) (a) Setzer, W. N.; Ogle, C. A.; Wilson, G. S.; Glass, R. S. *Inorg. Chem.* **1983**, *22*, 266. (b) DeSimone, R. E.; Glick, M. D. *J. Am. Chem. Soc.* **1976**, *98*, 762. (c) Wolf, R. E.; Hartman, J. R.; Storey, J. M. E.; Foxman, B. M.; Cooper, S. R. *J. Am. Chem. Soc.* **1987**, *109*, 4328. (d) Setzer, W. N.; Guo, Q.; Meehan, E. J.; Grant, G. J. *Heteroatom Chem.* **1990**, *1*, 425.

(6) Artz, S. P.; Cram, D. J. *J. Am. Chem. Soc.* **1984**, *106*, 2160.

(7) For reviews on the coordination chemistry of crown thioethers, see: (a) Cooper, S. R. *Acc. Chem. Res.* **1988**, *21*, 141. (b) Schroder, M. *Pure Appl. Chem.* **1988**, *60*, 517. (c) Blake, A. J.; Schroder, M. *Adv. Inorg. Chem.* **1990**, *35*, 1. (d) Cooper, S. R.; Rawle, S. C. *Struct. Bonding* **1990**, *72*, 1.

(8) Setzer, W. N.; Afshar, S.; Burns, N. L.; Ferrante, L. A.; Hester, A. M.; Meehan, E. J.; Grant, G. J.; Isaac, S. M.; Laudeman, C. P.; Lewis, C. M.; VanDerveer, D. G. *Heteroatom Chem.* **1990**, *1*, 375.

(9) (a) Setzer, W. N.; Cacioppo, E. L.; Guo, Q.; Grant, G. J.; Kim, D. D.; Hubbard, J. L.; VanDerveer, D. G. *Inorg. Chem.* **1990**, *29*, 2672. (b) Grant, G. J.; Carpenter, J. P.; Setzer, W. N.; VanDerveer, D. G. *Inorg. Chem.* **1989**, *28*, 4128.

0020-1669/92/1331-1116$03.00/0

Table III. Selected Bond Lengths (Å) in $[(15S5)Cd](ClO_4)_2 \cdot H_2O$

Cd–S1	2.771 (2)	S13–C12	1.764 (9)
Cd–S4	2.671 (2)	S13–C14	1.810 (10)
Cd–S7	2.780 (2)	C2–C3	1.514 (12)
Cd–S10	2.801 (2)	C5–C6	1.419 (12)
Cd–S13	2.776 (2)	C8–C9	1.461 (14)
Cd–O9	2.253 (4)	C11–C12	1.485 (12)
Cd–O1	2.653 (5)	C14–C15	1.506 (13)
S1–C2	1.784 (9)	Cl1–O1	1.429 (4)
S1–C15	1.793 (8)	Cl1–O2	1.301 (6)
S4–C3	1.859 (9)	Cl1–O3	1.513 (6)
S4–C5	1.695 (9)	Cl1–O4	1.414 (5)
S7–C6	1.864 (8)	Cl2–O5	1.388 (9)
S7–C8	1.852 (10)	Cl2–O6	1.401 (10)
S10–C9	1.789 (8)	Cl2–O7	1.362 (10)
S10–C11	1.905 (8)	Cl2–O8	1.361 (9)

Table IV. Selected Bond Angles (deg) in $[(15S5)Cd](ClO_4)_2 \cdot H_2O$

O1–Cd–S1	70.9 (3)	C15–S1–C2	103.8 (4)
O1–Cd–S7	70.1 (3)	S1–C2–C3	115.2 (6)
S1–Cd–S13	74.69 (7)	C2–C3–S4	115.0 (6)
S10–Cd–S13	72.45 (7)	C3–S4–C5	103.5 (4)
S7–Cd–S10	75.16 (7)	S4–C5–C6	118.8 (6)
S4–Cd–O9	168.34 (15)	C5–C6–S7	120.7 (6)
S4–Cd–O1	86.77 (12)	C6–S7–C8	100.2 (5)
S4–Cd–S1	77.24 (12)	S7–C8–C9	120.5 (6)
S4–Cd–S7	78.30 (12)	C8–C9–S10	109.1 (6)
S4–Cd–S10	97.88 (10)	C9–S10–C11	91.1 (4)
S4–Cd–S13	97.78 (9)	S10–C11–C12	108.8 (6)
O9–Cd–O1	81.9 (2)	C11–C12–S13	111.7 (6)
O9–Cd–S1	96.5 (3)	C12–S13–C14	111.7 (4)
O9–Cd–S7	100.1 (3)	S13–C14–C15	109.6 (6)
O9–Cd–S10	92.8 (2)	C14–C15–S1	114.0 (5)
O9–Cd–S13	89.8 (2)		

1150–1060 (s, b, ClO_4^-), 690, 624 (s, ClO_4^-) cm^{-1}. Anal. Calcd for $C_{10}H_{22}S_5Cl_2O_9Cd$: C, 19.07; H, 3.52; S, 25.45. Found: C, 19.12; H, 3.49; S, 25.36.

X-ray Crystal Structure of $[(15S5)Cd](ClO_4)_2 \cdot H_2O$. X-ray-quality crystals of $[(15S5)Cd](ClO_4)_2$ were grown by solvent diffusion of diethyl ether into a saturated solution of the complex in nitromethane. A clear colorless rectangular parallelepiped having approximate dimensions of 0.37 × 0.29 × 0.19 mm was mounted on a Syntex $P2_1$ auto diffractometer with graphite-monochromated Mo Kα radiation. The data were collected and the structure solved using techniques described earlier (see Table I).[9]

Results and Discussion

An ORTEP perspective view of the structure of $[(15S5)Cd](ClO_4)_2 \cdot H_2O$ is shown in Figure 1. The crystallographic data and refinement details are summarized in Table I. The final atomic parameters, bond lengths, and bond angles for the complex are compiled in Tables II–IV, respectively.

There are three important geometrical arrangements for seven-coordination: (1) pentagonal bipyramid, (2) capped octahedron, and (3) capped trigonal prism.[10] Unless there is a bias due to the requirements of a particular polydentate ligand, these three structures are predicted to be of similar stability. The structure of $[(15S5)Cd](ClO_4)_2 \cdot H_2O$ (Figure 1) indicates the geometry about the cadmium center to be a distorted pentagonal bipyramid with S1, S13, S10, S7, and O1 of one of the perchlorate anions serving as the equatorial ligands and S4 and O9 of the water of hydration occupying the axial positions. The coordination geometry observed in this structure is largely a result of the geometrical constraints imposed by the pentadentate ligand. Since there is no ligand field stabilization effect in Cd^{2+}, the stereochemistry of complexes of this ion is determined by size, electrostatics, and covalent bonding energies.[11] Because of its size, Cd^{2+} commonly has a coordination number of 6 (e.g., $CdCl_2$, $CdCl_2(NH_3)_2$, $CdCl(OH)$, $K_4[CdCl_6]$, CdI_2, $Cd(OH)_2$).[12] A seven-coordinate, distorted pentagonal bipyramidal complex of Cd^{2+} is known, however, $Cd(quin)(H_2O)(NO_3)_2$ (quin = *o*-quinone).[13]

The crystal structure of the free 15S5 ligand shows this compound to adopt an irregular (C_1 symmetry) conformation with all of the sulfur atoms exodentate.[14] Thus, it is necessary for the ligand to undergo a conformational change in order to complex a metal ion in polydentate coordination.

X-ray crystal structures of both the copper(II) perchlorate and copper(I) perchlorate complexes of 15S5 have been previously determined.[15] In the Cu(II) complex, the coordination geometry about the metal center is approximately square pyramidal with four of the sulfur atoms occupying equatorial positions and the fifth sulfur occupying the apical position. The Cu(I) complex of 15S5, on the other hand, shows a distorted tetrahedral arrangement of four sulfur atoms about the metal center with the fifth sulfur atom of the macrocycle uncoordinated. It may be that the larger ionic radius of cadmium(II) (0.97 Å) compared to copper(II) (0.69 Å) is such that it allows the coordination sphere of Cd(II) to expand to seven, accommodating both a perchlorate ion and a water molecule in addition to the five sulfur atoms of the macrocyclic pentathioether. Interestingly, however, the ionic radius of copper(I) (0.96 Å) is nearly the same as that of cadmium(II), but tetracoordination is seen in Cu(I) rather than heptacoordination.

We have carried out molecular mechanics calculations, using the MM2 technique,[16] on the conformations adopted by the free ligand (an exodentate conformation) from the X-ray crystal structure[14] and the conformations adopted by the ligand in complexing Cd^{2+} and Cu^{2+} (both pentadentate and necessarily endodentate).[15] Of these three conformations, the exodentate is the lowest energy. The endodentate conformation in the cadmium complex is 4.46 kcal/mol higher in energy, while the endodentate conformation in the copper(II) complex is 8.34 kcal/mol higher in energy than the exodentate. Thus, in order to adopt an endodentate conformation, suitable for metal ion complexation, it is necessary for the ligand to overcome significant energy differences. It is interesting that the energy difference between the two endodentate conformations is as large as it is (3.88 kcal/mol); it is necessary for the pentathioether ligand to overcome a larger energy difference in order to complex Cu^{2+} as opposed to Cd^{2+}. The complexation geometry of copper(II), coordination number and ionic radius, must be responsible for the higher energy endodentate conformation adopted by 15S5 in this complex.

The sum of the O1–Cd–S1, S1–Cd–S13, S10–Cd–S13, S7–Cd–S10, and O1–Cd–S7 bond angles is 363.4°, indicating these atoms to be nearly planar. The S4 atom is distorted from the perpendicular to the plane of the equatorial atoms. The S4–Cd–S1 and S4–Cd–S7 angles are somewhat acute (77.2 and 78.3°, respectively), while the S4–Cd–S10 and S4–Cd–S13 angles are somewhat obtuse (97.9 and 97.8°, respectively). This distortion is attributable to the geometrical constraints of the ligand; the ethylene bridges between the sulfur atoms do not allow S4 to pull far enough away from S1 and S7 to become perpendicular. The S4–Cd–O1 angle (168.3°) is correspondingly less than the ideal 180°.

The cadmium–sulfur bonds in $[(15S5)Cd](ClO_4)_2 \cdot H_2O$ (Cd–S_{av} = 2.76 Å) are longer than those observed in $[(16S4)Cd](ClO_4)_2$ (Cd–S_{av} = 2.62 Å)[17] and longer than those found in $[(9S3)_2Cd](ClO_4)_2$ (Cd–S_{av} = 2.65 Å).[18] It has already been observed in mercury(II) thioether complexes[19] that metal–sulfur

---

(10) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; p 15.

(11) Reference 10, p 598.

(12) Wells, A. F. *Structural Inorganic Chemistry*, 3rd ed.; Oxford Press: Oxford, England, 1962.

(13) Reference 10, p 599.

(14) Wolf, R. E.; Hartman, J. R.; Storey, J. M. E.; Foxman, B. M.; Cooper, S. R. *J. Am. Chem. Soc.* **1987**, *109*, 4328.

(15) Corfield, P. W. R.; Ceccarelli, C.; Glick, M. D.; Moy, I. W.; Ochrymowycz, L. A.; Rorabacher, D. B. *J. Am. Chem. Soc.* **1985**, *107*, 2399.

(16) We used the programs ALCHEMY II (Tripos Associates, Inc.), CHEM-CAD (C_Graph Software, Inc.), and MM2 (N. L. Allinger, University of Georgia).

(17) Setzer, W. N.; Tang, Y.; Grant, G. J.; VanDerveer, D. G. *Inorg. Chem.* **1991**, *30*, 3652.

(18) Glass, R. S.; Steffen, L. K.; Swanson, D. D.; Wilson, G. S.; de Gelder, R.; de Graaf, R. A. G.; Reedijk, J. *Inorg. Chim. Acta*, in press.

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.

---

(19) Setzer, W. N.; Guo, Q.; Grant, G. J.; Hubbard, J. L.; Glass, R. S.; VanDerveer, D. G. *Heteroatom Chem.* **1990**, *1*, 317.

(20) *Lange's Handbook of Chemistry*, 10th ed.; Lange, N. A., Ed.; McGraw-Hill: New York, 1967; pp 122–123.

(21) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

Contribution from the Savannah River Site,
Westinghouse Savannah River Company,
Aiken, South Carolina 29808

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

D. G. Karraker* and P. K. Smith

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-$CrF_3 \cdot 3H_2O$.

---

(1) Neilsen, A. H. *Z. Anorg. Chem.* **1940**, *244*, 85.

(2) Teufer, G. *Acta Crystallogr.* **1964**, *17*, 1480.

(3) Maak, I.; Ecklin, D.; Rabenau, A. *Naturwissenschaften* **1961**, *48*, 218.

(4) Champion, A. R.; Vaughn, R. W.; Drickamer, H. B. *J. Chem. Phys.* **1967**, *47*, 2583.

(5) Dêzsi, I.; Ouseph, P. J.; Thomas, P. M. *J. Inorg. Nucl. Chem.* **1974**, *36*, 833.

(6) Imbert, P.; Machetau, Y.; Varret, F. *J. Phys.* (*Paris*) **1973**, *34*, 49.

(7) Penfold, B. R.; Taylor, M. R. *Acta Crystallogr.* **1960**, *13*, 953. A different diffraction pattern for $FeF_2 \cdot 4H_2O$ has been reported: Osteovskaya, T. V.; Amirova, S. A. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1969**, *14*, 755.

(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.

(9) Karraker, D. G. *Inorg. Chem.* **1987**, *26*, 3814.