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Crystal Structures and Vibrational Spectra of $M\mathrm{SnF_6 \cdot 6H_2O}$ (M = Fe, Co, Ni)

W. Mikenda[1,*], **F. Pertlik**[2], and **S. Steinböck**[1]

[1] Institut für Organische Chemie, Universität Wien, A-1090 Wien, Austria
[2] Institut für Mineralogie und Kristallographie, Universität Wien, A-1090 Wien, Austria

Summary. Single crystal X-ray structural data (at $T = 300\,\mathrm{K}$) are reported for $\mathrm{CoSnF_6 \cdot 6H_2O}$ (rhombohedral; $\mathrm{R\bar{3}\text{-}C^2_{3i}}$; $a = 9.735(7)\,\mathrm{Å}$, $c = 10.095(7)\,\mathrm{Å}$, $\gamma = 120°$; $Z = 3$; $R = 0.047$) and for $\mathrm{NiSnF_6 \cdot 6H_2O}$ (rhombohedral; $\mathrm{R\bar{3}\text{-}C^2_{3i}}$; $a = 9.697(1)\,\mathrm{Å}$, $c = 10.021(1)\,\mathrm{Å}$, $\gamma = 120°$; $Z = 3$; $R = 0.038$). The two compounds are isostructural to $\mathrm{FeSnF_6 \cdot 6H_2O}$. IR and Raman spectroscopic data (at $T = 300$ and $75\,\mathrm{K}$) are reported for hydrated and for partially deuterated samples of $M\mathrm{SnF_6 \cdot 6H_2O}$ (M = Fe, Co, Ni). Two rather similar $\bar{\nu}$(OD) stretching frequencies and one $\bar{\nu}$(HDO) bending frequency of isotopically dilute HDO molecules are observed for either of the three compounds, which is consistent with one crystallographically distinct water molecule forming two different, but rather similar $\mathrm{O \cdots F}$ hydrogen bonds.

Keywords. Crystal structure; Hexafluorostannate hexahydrate; Hydrogen bonding; IR spectra; Raman spectra; X-ray diffraction.

Kristallstrukturen und Schwingungsspektren von $M\mathrm{SnF_6 \cdot 6H_2O}$ (M = Fe, Co, Ni)

Zusammenfassung. Die Kristallstrukturen von $\mathrm{CoSnF_6 \cdot 6H_2O}$ (rhomboedrisch; $\mathrm{R\bar{3}\text{-}C^2_{3i}}$; $a = 9.735(7)\,\mathrm{Å}$, $c = 10.095(7)\,\mathrm{Å}$, $\gamma = 120°$; $Z = 3$; $R = 0.047$) und von $\mathrm{NiSnF_6 \cdot 6H_2O}$ (rhomboedrisch; $\mathrm{R\bar{3}\text{-}C^2_{3i}}$; $a = 9.697(1)\,\mathrm{Å}$, $c = 10.021(1)\,\mathrm{Å}$, $\gamma = 120°$; $Z = 3$; $R = 0.038$) wurden mittels Röntgen-Einkristalldaten (bei $T = 300\,\mathrm{K}$) bestimmt. Die beiden Verbindungen sind isostrukturell zu $\mathrm{FeSnF_6 \cdot 6H_2O}$. IR- und Raman-Spektren von $M\mathrm{SnF_6 \cdot 6H_2O}$ (M = Fe, Co, Ni) wurden von Proben mit unterschiedlichem Deuterierungsgrad gemessen (bei $T = 300$ und $75\,\mathrm{K}$). Bei allen drei Verbindungen findet man für isotopenverdünnte HDO Moleküle zwei nur geringfügig unterschiedliche $\bar{\nu}$(OD)-Valenzfrequenzen und eine $\bar{\nu}$(HDO)-Deformationsfrequenz, was mit der Existenz von nur einer Art von Wassermolekülen mit zwei verschiedenen, aber doch sehr ähnlichen $\mathrm{O \cdots F}$ Wasserstoffbrückenbindungen übereinstimmt.

Introduction

In the course of a spectroscopic and structural study on $\mathrm{O{-}H \cdots F}$ type hydrogen bonds in crystalline hydrates [1] the hexafluorostannate hexahydrates of iron, cobalt, and nickel have been investigated. At room temperature, $\mathrm{FeSnF_6 \cdot 6H_2O}$ crystallizes in the rhombohedral space group $\mathrm{R\bar{3}\text{-}C^2_{3i}}$ ($a = 9.826\,\mathrm{Å}$, $c = 10.106\,\mathrm{Å}$, $\gamma = 120°$, $Z = 3$) [2]. The crystal structures of $\mathrm{CoSnF_6 \cdot 6H_2O}$ and $\mathrm{NiSnF_6 \cdot 6H_2O}$ have not been determined previously; there were, however, strong evidences, *e.g.*

from vibrational spectroscopic data (see below), that they are isostructural to the iron compound.

Within our work on O–H···F hydrogen bonds, the room temperature structures of $CoSnF_6 \cdot 6H_2O$ and $NiSnF_6 \cdot 6H_2O$ have been determined by X-ray diffraction and IR and Raman spectra have been measured at room temperature and at liquid nitrogen temperature for hydrated and for partially deuterated samples of the three title compounds. Some of the data, which are relevant for a characterization of hydrogen bonds (hydrogen bond distances and angles; uncoupled $\bar{\nu}$(OD) frequencies of isotopically dilute HDO molecules), have already been in included a recent survey about O–H···F hydrogen bonds [1]. In the present paper, some more details of the structural and spectroscopic work shall briefly be reported.

Results and Discussion

Crystal structures

Atomic coordinates and temperature factors of $CoSnF_6 \cdot 6H_2O$ and $NiSnF_6 \cdot 6H_2O$ are given in Table 2, selected bond distances and angles in Table 3*. For sake of comparison, corresponding data of $FeSnF_6 \cdot 6H_2O$ [2] are also included in Table 3. $CoSnF_6 \cdot 6H_2O$ and $NiSnF_6 \cdot 6H_2O$ are isostructural to $FeSnF_6 \cdot 6H_2O$. The structures consist of almost regular SnF_6 and $Fe(H_2O)_6$ octahedra which are linked by

Table 1. Summary of crystal data and experimental details

	$CoSnF_6 \cdot 6H_2O$	$NiSnF_6 \cdot 6H_2O$
Space group	$R\bar{3}$-C_{3i}^2	$R\bar{3}$-C_{3i}^2
a[Å]	9.735(7)	9.697(1)
c[Å]	10.095(7)	10.021(1)
γ[°]	120	120
Z	3	3
V[Å^3]	825.5	816.1
μ(MoKα) [cm^{-1}]	37	40
Step width [°]	0.03	0.03
$2\theta_{max}$[°]	80	80
Range of h, k, l	$\pm h, \pm k, +l$	$\pm h, \pm k, -l$
Measured reflections	4446	4180
Unique reflections	1152	1138
Reflections with $F_0 > 6\sigma(F_0)$	1067	1056
$R_{int}[\sum \lvert I - \langle I \rangle / \sum I]$	0.015	0.039
Number of variables	31	31
R	0.047	0.038
R_w	0.049	0.039
$(\Delta/\sigma)_{max}$	<0.01	<0.01
$(\Delta\rho)_{max/min}$	−1.7/2.1	−3.2/1.7

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* Structure factor tables are available from the authors upon request

Table 2. Atomic coordinates and temperature factors (with esd's in parentheses) of $\mathrm{CoSnF}_6 \cdot 6\mathrm{H}_2\mathrm{O}$ and $\mathrm{NiSnF}_6 \cdot 6\mathrm{H}_2\mathrm{O}$

				$\mathrm{CoSnF}_6 \cdot 6\mathrm{H}_2\mathrm{O}$					
	x/a	y/b	z/c	U_{11}/U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	0.0000	0.00000	0.50000	0.0571(7)	0.0571(7)	0.0250(4)	0.0285(3)	0.0000	0.0000
Sn	0.0000	0.00000	0.00000	0.0508(4)	0.0508(4)	0.0222(2)	0.0254(2)	0.0000	0.0000
F	0.1371(4)	0.1787(3)	0.1123(3)	0.0807(22)	0.0424(14)	0.0398(13)	0.0023(7)	−0.0042(7)	0.0038(6)
O	0.1765(4)	0.1731(4)	0.3821(3)	0.0398(15)	0.0555(19)	0.0360(14)	0.0071(7)	0.1765(4)	0.0046(7)
H1	0.2723(106)	0.1979(102)	0.4211(78)	0.1206(298)					
H2	0.1619(107)	0.1746(105)	0.2981(87)	0.1174(298)					

				$\mathrm{NiSnF}_6 \cdot 6\mathrm{H}_2\mathrm{O}$					
	x/a	y/b	z/c	U_{11}/U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	0.0000	0.00000	0.50000	0.0478(5)	0.0478(5)	0.0209(3)	0.0239(2)	0.0000	0.0000
Sn	0.0000	0.00000	0.00000	0.0425(3)	0.0425(3)	0.0187(2)	0.0213(1)	0.0000	0.0000
F	0.1320(4)	0.1820(3)	0.1138(2)	0.0800(18)	0.0368(11)	0.0338(10)	0.0014(6)	−0.0045(6)	−0.0038(5)
O	0.1730(3)	0.1752(3)	0.3848(2)	0.0332(11)	0.0458(13)	0.0308(10)	0.0066(5)	0.0006(4)	0.0042(5)
H1	0.2745(64)	0.2120(60)	0.3982(47)	0.0583(145)					
H2	0.1646(81)	0.1940(79)	0.2998(67)	0.1046(231)					

Table 3. Selected bond distances [Å] and angles [°] (data for $\mathrm{FeSnF}_6 \cdot 6\mathrm{H}_2\mathrm{O}$ are taken from Ref. [2])

	$\mathrm{FeSnF}_6 \cdot 6\mathrm{H}_2\mathrm{O}$	$\mathrm{CoSnF}_6 \cdot 6\mathrm{H}_2\mathrm{O}$	$\mathrm{NiSnF}_6 \cdot 6\mathrm{H}_2\mathrm{O}$
Sn–F	1.945(2)	1.942(3)	1.948(2)
F–Sn–F	89.2(1)	89.3(1)	89.2(1)
M–O	2.116(2)	2.077(3)	2.045(3)
O–M–O	90.0(1)	89.6(1)	88.7(1)
O–F (via H1)	2.731(3)	2.727(5)	2.730(3)
O–F (via H2)	2.742(3)	2.755(4)	2.750(3)
O–H1	1.12(5)	0.93(6)	0.87(4)
O–H2	1.14(4)	0.86(6)	0.88(7)
H1–O–H2	115(4)	124(6)	105(4)

O–H···F hydrogen bonds (Fig. 1). Sn–F distances and F–Sn–F angles within the SnF_6 octahedra of the three compounds are almost identical. The differences between the M–O distances within the $\mathrm{M(H_2O)_6}$ octahedra comply well with the corresponding ionic radii for six-coordinated cations: $r(\mathrm{Fe}^{++}$, high spin) = 0.77 Å, $r(\mathrm{Co}^{++}$, high spin) = 0.735 Å, $r(\mathrm{Ni}^{++}) = 0.70$ Å [6]. The O–F distances of the two crystallographically non-equivalent O–H···F hydrogen bonds, which link SnF_6 and $\mathrm{M(H_2O)_6}$ octahedra, are also very similar for the three title compounds. Hydrogen positions have been located from the difference Fourier maps for both $\mathrm{CoSnF}_6 \cdot 6\mathrm{H}_2\mathrm{O}$ and $\mathrm{NiSnF}_6 \cdot 6\mathrm{H}_2\mathrm{O}$. In the first case, however, an unrealistic, much too large H–O–H angle of 124(6)° has been obtained, which, besides the inherent inaccuracies of X-ray determined hydrogen positions, additionally limits the relevance of distances and angles involving hydrogen atoms.

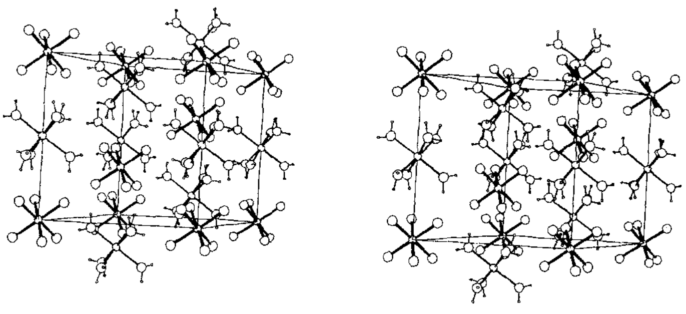

Fig. 1. Stereoview of $NiSnF_6 \cdot 6H_2O$ (view along the y axis)

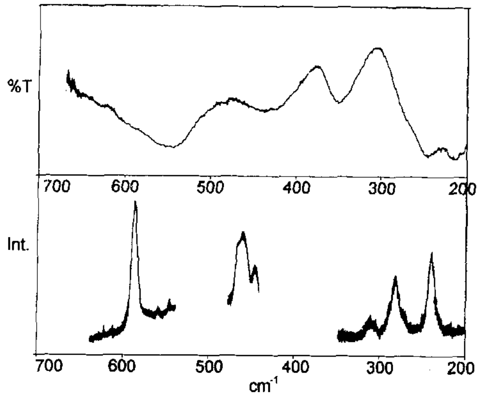

Fig. 2. IR spectra (nujol mull between polyethylene plates) and Raman spectra (polycrystalline material) of $FeSnF_6 \cdot 6H_2O$

Table 4. Selected vibrational frequencies [cm^{-1}]

	$FeSnF_6 \cdot 6H_2O$	$CoSnF_6 \cdot 6H_2O$	$NiSnF_6 \cdot 6H_2O$	Assignments
IR	$3500+3435^1$	$3500+3435^1$	$3500+3435^1$	$\nu(OH)_{H_2O}$
IR	$2611+2532^2$	$2608+2527^2$	$2605+2524^2$	$\nu(OD)_{D_2O}$
IR	$2572+2561^2$	$2569+2555^2$	$2568+2552^2$	$\nu(OD)_{HDO}$
IR	1650	1648	1650	$\delta(H_2O)$
IR	1456^2	1456^2	1455^2	$\delta(HDO)$
IR	1218	1218	1218	$\delta(D_2O)$
Ra	589	591	589	$\nu_1(A_{1g})_{SnF_6}$
IR	546	552	553	$\nu_3(F_{1u})_{SnF_6}$
Ra	462	466	465	
IR	434	434	434	
IR	349	340	365	
Ra	284	282	283	
IR	250	249	255	
Ra	240	240	241	

[1] broad band with two shallow submaxima; [2] from partially deuteriated samples

Spectra

Survey IR and Raman spectra of $FeSnF_6 \cdot 6H_2O$ are shown in Fig. 2 for $\bar{\nu} < 700\,cm^{-1}$. Selected vibrational frequencies and assignments are summarized in Table 4. For reasons given in the experimental section, room temperature IR data are listed along with low temperature Raman data. Assignments are given only for frequencies above $500\,\mathrm{cm^{-1}}$, which are beyond doubt. For frequencies below $500\,\mathrm{cm^{-1}}$, it was not possible (not even by considering H–D isotope effects) to reliably distinguish between water vibrations, internal SnF_6 vibrations and internal $M(H_2O)_6$ vibrations. Assignments of IR bands and Raman lines observed in the spectra below $500\,\mathrm{cm^{-1}}$ would, therefore, be largely arbitrary. More detailed and sophisticated spectroscopic work, which is beyond the scope of this study, would be necessary to obtain reliable assignments. As far as the main intentions of the present study are concerned (*i.e.* O–H···F hydrogen bonding), the basic spectroscopic data excellently agree with the corresponding crystallographic data: two rather similar ν(OD) stretching frequencies and one δ(HDO) bending frequency of isotopically dilute HDO molecules compare with only one kind of water molecules forming two different, but also rather similar O–H···F hydrogen bonds.

Experimental

Compounds. $FeSnF_6 \cdot 6H_2O$, $CoSnF_6 \cdot 6H_2O$, and $NiSnF_6 \cdot 6H_2O$ have been prepared from SnF_2 and the corresponding metal fluorides, MF_2, in dilute HF solution. Partially deuteriated samples (5%–20% and 80% D_2O) were obtained from appropriate H_2O/D_2O mixtures. The samples used for spectroscopic work have been checked by powder X-ray diffraction, comparing the experimental patterns with theoretical patterns calculated from single crystal X-ray data.

X-ray diffraction. Lattice constants, Laue symmetries and extinction rules of $CoSnF_6 \cdot 6H_2O$ and of $NiSnF_6 \cdot 6H_2O$ have been determined by oscillation and Weissenberg film methods. Three dimensional single crystal data were collected with a Stoe four circle diffractometer, AED2, and corrected for Lorenz and polarization effects by standard methods. The structures were solved and refined with SHELX76 [3]. The positions of the non-hydrogen atoms were determined by direct method strategies; the hydrogen atoms were located from difference Fourier maps. The atomic coordinates and the displacement factors (isotropic as well as anisotropic for non-hydrogen atoms) were refined by least squares techniques; the complex scattering factors were taken from standard tables [4]. A summary of crystal data and of experimental details is given in Table 1.

Spectra. IR-spectra of nujol and fluorolube mulls sandwiched between BaF_2 or polyethylene plates were measured with a Perkin-Elmer 1740 FTIR-spectrometer or a Perkin-Elmer 580B IR-spectrometer. It should be mentioned that the use of NaCl or KBr plates resulted in partial decomposition or alteration of the sample material, as it was also observed with many other hydrates of fluorine compounds. Raman spectra of polycrystalline samples were obtained with a PC-controlled Jarrell-Ash 25-300 Raman-spectrometer equipped with a Kr ion laser ($\bar{\nu}_{exc} = 15454\,\mathrm{cm^{-1}}$). For low temperature measurements an Oxford Instruments CF100 cryogenic unit was used. Raman spectra were measured at both room temperature and liquid nitrogen temperature (for $NiSnF_6 \cdot 6H_2O$ only low temperature spectra could be obtained, since at room temperature the samples rapidly decomposed on laser irradiation), while, for technical reasons, IR spectra were measured at room temperature only, except for the 2400–2700 $\mathrm{cm^{-1}}$ range of $\bar{\nu}$(OD) frequencies. No unusual differences have been observed between room and low temperature spectra of the three title compounds, which gives confidence that there are no phase transitions within the temperature range considered ($FeSnF_6 \cdot 6H_2O$ is known to undergo a phase transition at 65 K [5]).

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