



Physico-Chemical Studies of Tris (adamantan-1-aminium) Hexachlorostannate (IV) Chloride Monohydrate

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Abstract

The structural characteristics of organic ammonium salts of the hexahalogenostannates (IV) with a general formula $(R-NH_3)_3SnX_6$ have not yet been studied extensively. In the course of investigating these types of materials, the title compound, a double salt of adamantan-1-aminium chloride and hexahalogenostannate (IV), with the formula $(C_{10}H_{18}N)_3[SnCl_6]Cl \cdot H_2O$, was crystallized. Its asymmetric unit contains three independent cations of protonated adamantan-1-amine, one chloride anion, one Hexachlorostannate (IV) ion and a hydrate water molecule. The atomic arrangement can be described as inorganic $SnCl_6^{2-}$ units isolated from each other by the organic cations, the chloride anions and the co-crystallized water molecules. The compound exhibits bifurcated and simple hydrogen-bonding interactions between the ammonium groups, the water molecules and the chlorine atoms, with little variation in the hydrogen-bonding interactions. The ^{119}Sn , ^{13}C and ^{15}N CP-MAS NMR spectra are in agreement with the X-ray structure.

Keywords: Tin (IV) compound, X-ray diffraction, IR spectroscopy, CP-MAS NMR.

Introduction

Organic-inorganic hybrid materials with the formula $(R-NH_3)_2SnX_4$, where X = F, Cl, Br or I have been investigated structurally because of their interesting magnetic and

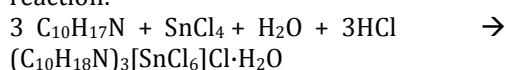
electronic properties [1-4]. In contrast, the structural characteristics of compounds with the formula $(R-NH_3)_3SnX_6$ have not been studied extensively. In the course of investigating compounds with this formula, the title compound, displaying a

combination of anions and cations, was crystallized. Tris (adamantan-1-aminium) Hexachlorostannate (IV) chloride monohydrate is a double salt of adamantan-1-aminium chloride and hexahalogenostannate (IV), with the formula $(C_{10}H_{18}N)_3[SnCl_6]Cl \cdot H_2O$.

Experimental

Chemical preparation

The title compound was prepared according to the following chemical reaction:



by the slow evaporation of an aqueous solution of adamantan-1-amine, tin(IV) chloride dihydrate and hydrochloric acid in 3 : 1 : 3 molar ratio. Colourless prismatic crystals were obtained after one week (yield 65 %). The crystals are stable for months under normal conditions of temperature and humidity. *Anal. Calc:* C, 42.77; H, 6.41; N, 4.99; *Found:* C, 42.56; H, 6.57; N, 5.23 %.

The characterization of this coordination compound was carried out using X-ray diffraction, solid state NMR and IR spectroscopy.

X-ray single crystal structural analysis

The intensity data were measured at 100 K on a Bruker AXS SMART APEX CCD diffractometer using graphite-monochromated MoK α radiation with the omega scan technique. The absorption corrections were carried out using the Apex2 software [5]. The structure was solved by direct methods using SHELXS and refined by full matrix least squares against F^2 with all reflections using SHELXL [6] and SHELXLE [7]. The H-atoms of the water molecules were located from different Fourier maps, while the H-atoms of the ammonium groups were placed in geometrically calculated positions. The drawings were made with Diamond [8]. Crystal data and experimental parameters used for the intensity data collection are summarized in Table 1. The low fraction of observed reflexions is due to the low-quality crystal.

Investigation techniques

Table 1 : Experimental details

CRYSTAL DATA	
CHEMICAL FORMULA	3(C ₁₀ H ₁₈ N)·Cl ₆ Sn·Cl·H ₂ O
MR	841.62
CRYSTAL SYSTEM, SPACE GROUP	TRICLINIC, P-1
TEMPERATURE (K)	100
A, B, C (Å)	13.557 (5), 16.340 (6), 19.300 (7)
A, B, Γ (°)	71.990 (6), 77.372 (6), 67.575 (6)
V (Å ³)	3733 (2)

Z	4
RADIATION TYPE	Mo KA
μ (MM⁻¹)	1.21
CRYSTAL SIZE (MM)	0.11 × 0.09 × 0.02
DATA COLLECTION	
DIFFRACTOMETER	BRUKER AXS SMART APEX CCD DIFFRACTOMETER
ABSORPTION CORRECTION	MULTI-SCAN APEX2 v2011.2-0 (BRUKER, 2011)
TMIN, TMAX	0.650, 0.746
NO. OF MEASURED, INDEPENDENT AND OBSERVED [$I > 2\sigma(I)$] REFLECTIONS	48882, 18377, 9833
RINT	0.084
(SIN θ/λ)MAX (Å⁻¹)	0.667
REFINEMENT	
R[F2 > 2σ(F2)], wR(F2), S	0.050, 0.093, 0.93
NO. OF REFLECTIONS	18377
NO. OF PARAMETERS	775
$\Delta\rho$MAX, $\Delta\rho$MIN (E Å⁻³)	0.71, -1.14

Physical measurements

The NMR spectra were recorded on a solid-state high-resolution Bruker DSX-300 spectrometer operating at 75.49 MHz for ¹³C and 30.30 MHz for ¹⁵N. The ¹¹⁹Sn NMR spectrum was recorded on a Bruker

DRX500 AVANCE spectrometer operating at 186.5 MHz with a classical 4 mm probehead allowing spinning rates up to 10 kHz. ¹³C, ¹⁵N and ¹¹⁹Sn NMR chemical shifts are given relative to tetramethylsilane, nitromethane and Me₄Sn, respectively (precision 0.5 ppm). The spectra were

recorded by the use of cross-polarization (CP) from protons (contact time 5 ms) and MAS. The delay between two successive scans was optimized to ensure a full relaxation of the proton. The IR spectrum was recorded at r. t with a "Perkin-Elmer FTIR" spectrophotometer 1000.

Results and Discussion

X-ray diffraction study

The asymmetric unit of the title compound (Fig. 1) contains six independent adamantan-1-aminium cations, two chloride anions, two Hexachlorostannate (IV) ions and two water molecules. The Sn atom is six-fold coordinated by chloride ions, forming an octahedral arrangement.

Fig. 2 shows that the atomic arrangement of the title hybrid compound can be described as inorganic SnCl_6^{2-} units isolated from each other by the organic cations, the chloride anions and the co-crystallized water molecules. Multiple hydrogen bonds connect the different entities of the compound to form an infinite three-dimensional network. Fig.2 shows that the structure cohesion is ensured by four types of hydrogen bonds, viz. cation-hexachlorotin anion, cation-chloride anion, cation-water and water-hexachlorotin anion. Atoms H3A3, H1B3 H3A1 and H3B2 of the ammonium groups form bifurcated hydrogen bonds to the acceptor atoms

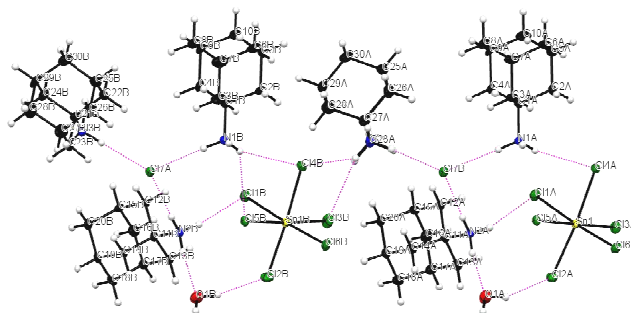


Figure 1: Asymmetric unit of $(\text{C}_{10}\text{H}_{18}\text{N})_3[\text{SnCl}_6]\text{Cl}\cdot\text{H}_2\text{O}$ with the atom numbering scheme and thermal ellipsoids at 50 % probability. The dotted lines indicate hydrogen bonds

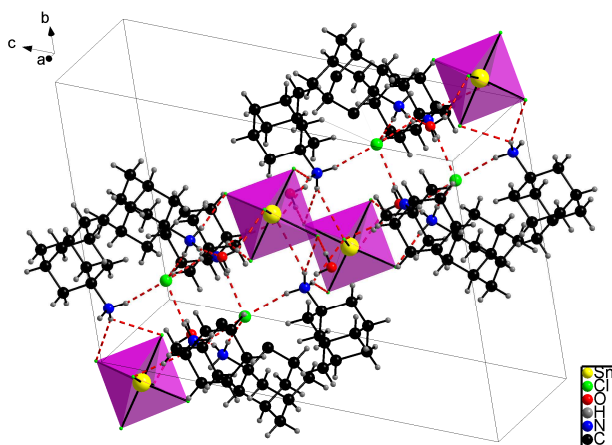


Figure 2: Crystal packing of $(\text{C}_{10}\text{H}_{18}\text{N})_3[\text{SnCl}_6]\text{Cl}\cdot\text{H}_2\text{O}$. The dotted lines indicate hydrogen bonds.

Cl6B, Cl3B, Cl4B, Cl3B, Cl4B, Cl5B, Cl6A and Cl5A (Table 2). The H...Cl distances of these hydrogen bonds, varying between 2.57 and 2.92 Å are longer than the ones of simple hydrogen bonds, ranging from 2.27 and 2.56 Å.

Previous studies have shown that, in the [SnCl₆]²⁻ anion, the Sn-Cl bond lengths and Cl-Sn-Cl bond angles are not equal, but vary with the environment around the Cl atom [9]. In this complex, the Sn-Cl bond lengths vary between 2.3791(14) and 2.4694(14) Å and the Cl-Sn-Cl bond angles range from

88.08(5) to 93.65(5)°, with an average value of 89.97° (Table 3). Owing to these differences in the geometric parameters, the [SnCl₆]²⁻ anion has a slightly distorted octahedral stereochemistry [10].

The examination of the geometric features of the organic entity shows that the organic molecule exhibits a regular spatial configuration with C-C and C-N distances and C-C-C and C-C-N angles quite similar to those found in other adamantan-1-aminium compounds [11].

Table 2: Hydrogen-bond geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
O1A—H1A...Cl2A	0.83 (2)	2.46 (4)	3.199 (4)	149 (6)
O1A—H1B...Cl6A ⁱ	0.83 (2)	2.47 (3)	3.243 (5)	156 (6)
N1A—H1A1...Cl7B	0.91	2.40	3.257 (4)	156
N1A—H1A2...Cl7A ⁱⁱ	0.91	2.27	3.178 (4)	173
N1A—H1A3...Cl4A	0.91	2.56	3.385 (4)	151
N2A—H2A1...O1A	0.91	1.94	2.828 (6)	166
N2A—H2A2...Cl7B	0.91	2.29	3.190 (4)	171
N2A—H2A2...Cl7B	0.91	2.29	3.190 (4)	171
N3A—H3A1...Cl6B ⁱⁱ	0.91	2.67	3.556 (4)	163
N3A—H3A1...Cl4B ⁱⁱ	0.91	2.86	3.399 (4)	119
N3A—H3A2...Cl7B	0.91	2.35	3.245 (4)	168
N3A—H3A3...Cl4B	0.91	2.61	3.270 (4)	130
N3A—H3A3...Cl3B	0.91	2.93	3.766 (5)	153
O1B—H1C...Cl2B	0.84 (2)	2.50 (4)	3.248 (4)	150 (6)
O1B—H1D...Cl6B ⁱⁱⁱ	0.83 (2)	2.66 (4)	3.356 (5)	142 (5)
N1B—H1B1...Cl7A	0.91	2.37	3.238 (4)	160
N1B—H1B2...Cl7B ⁱⁱ	0.91	2.27	3.174 (4)	172
N1B—H1B3...Cl4B	0.91	2.57	3.368 (4)	147
N1B—H1B3...Cl5B	0.91	2.92	3.363 (4)	111
N2B—H2BE...O1B	0.91	1.97	2.865 (6)	166
N2B—H2BC...Cl7A	0.91	2.32	3.218 (4)	168
N2B—H2BD...Cl1B	0.91	2.41	3.308 (4)	170
N3B—H3B2...Cl6A ⁱⁱ	0.91	2.59	3.418 (4)	152
N3B—H3B2...Cl5A ⁱⁱ	0.91	2.76	3.360 (4)	124

N3B—H3B1...Cl4A^{iv}	0.91	2.41	3.305 (4)	168
N3B—H3B3...Cl7A	0.91	2.34	3.236 (4)	169

Symmetry codes: (i) $-x+1, -y, -z+2$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x, -y+1, -z+1$; (iv) $x-1, y+1, z-1$.

Table 3: Geometric parameters (Å, °) of SnCl₆.

Sn1—Cl3A	2.3791 (14)	Sn1B—Cl2B	2.3956 (15)
Sn1—Cl2A	2.4097 (15)	Sn1B—Cl3B	2.4043 (14)
Sn1—Cl6A	2.4374 (16)	Sn1B—Cl5B	2.4379 (14)
Sn1—Cl5A	2.4475 (14)	Sn1B—Cl6B	2.4422 (16)
Sn1—Cl1A	2.4527 (16)	Sn1B—Cl4B	2.4476 (14)
Sn1—Cl4A	2.4694 (14)	Sn1B—Cl1B	2.4630 (16)
Cl3A—Sn1—Cl2A	92.54 (5)	Cl2B—Sn1B—Cl3B	93.55 (6)
Cl3A—Sn1—Cl6A	90.86 (5)	Cl2B—Sn1B—Cl5B	89.79 (5)
Cl2A—Sn1—Cl6A	93.65 (5)	Cl3B—Sn1B—Cl5B	176.65 (5)
Cl3A—Sn1—Cl5A	178.54 (5)	Cl2B—Sn1B—Cl6B	92.29 (5)
Cl2A—Sn1—Cl5A	88.35 (5)	Cl3B—Sn1B—Cl6B	90.93 (5)
Cl6A—Sn1—Cl5A	87.93 (5)	Cl5B—Sn1B—Cl6B	88.66 (5)
Cl3A—Sn1—Cl1A	92.60 (5)	Cl2B—Sn1B—Cl4B	176.09 (5)
Cl2A—Sn1—Cl1A	91.39 (5)	Cl3B—Sn1B—Cl4B	90.22 (6)
Cl6A—Sn1—Cl1A	173.76 (4)	Cl5B—Sn1B—Cl4B	86.44 (5)
Cl5A—Sn1—Cl1A	88.53 (5)	Cl6B—Sn1B—Cl4B	88.69 (5)
Cl3A—Sn1—Cl4A	92.56 (5)	Cl2B—Sn1B—Cl1B	91.86 (5)
Cl2A—Sn1—Cl4A	174.59 (4)	Cl3B—Sn1B—Cl1B	91.13 (5)
Cl6A—Sn1—Cl4A	88.08 (5)	Cl5B—Sn1B—Cl1B	89.03 (5)
Cl5A—Sn1—Cl4A	86.58 (5)	Cl6B—Sn1B—Cl1B	175.25 (5)
Cl1A—Sn1—Cl4A	86.57 (5)	Cl4B—Sn1B—Cl1B	87.02 (5)

NMR spectroscopy

The ¹¹⁹Sn CP-MAS NMR spectrum of crystalline is shown in Fig. 3. It exhibits a single resonance peak at -724 ppm relatively large due to the coupling of the

tin (IV) cation with the chlorine atoms. This chemical shift value agrees with those corresponding to the hexachlorostannate (IV) compounds [12]. The single observed peak is in agreement with the presence of only one tin site.

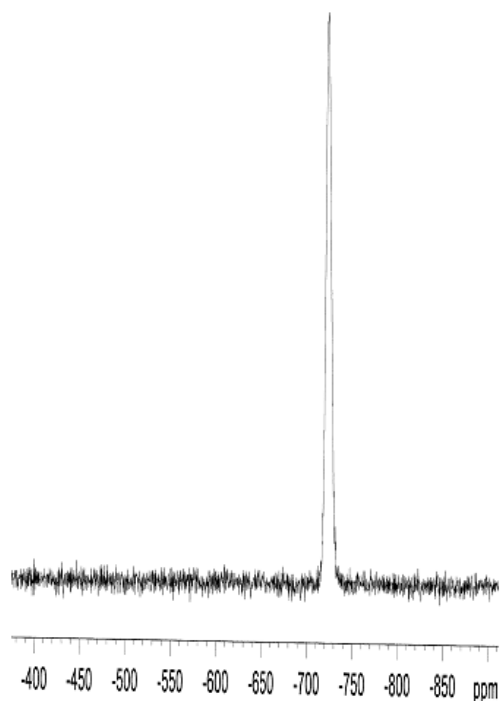


Figure 3: ^{119}Sn CP-MAS NMR spectrum of $(\text{C}_{10}\text{H}_{18}\text{N})_3[\text{SnCl}_6]\text{Cl}\cdot\text{H}_2\text{O}$.

The ^{13}C CP-MAS NMR spectrum of the title compound is shown on Fig. 4. A key point of this spectrum is the presence of three resonances, at 54.1, 55.1 and 55.9 ppm, for the most deshielded signal, corresponding to the carbon atom directly bonded to the

ammonium group. These chemical shift values agree with those of literature [13]. These three resonances also confirm the presence of three organic moieties in the asymmetric unit of the compound, in agreement with the X-ray diffraction data.

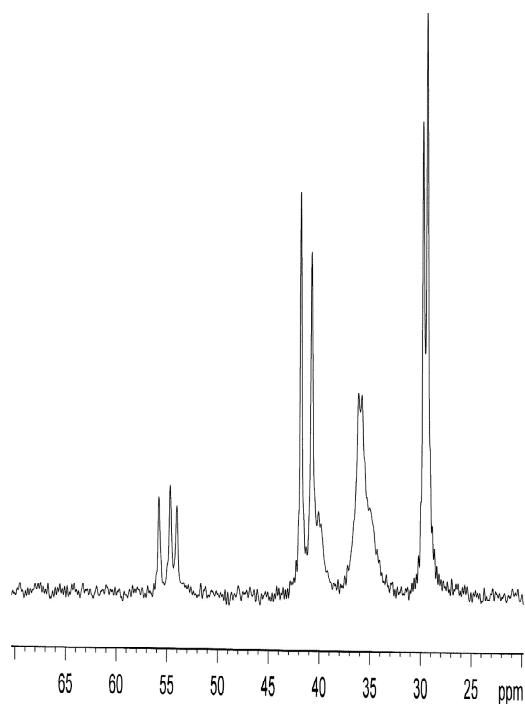


Figure 4: ^{13}C CP-MAS NMR spectrum of $(\text{C}_{10}\text{H}_{18}\text{N})_3[\text{SnCl}_6]\text{Cl}\cdot\text{H}_2\text{O}$.

Fig. 5 shows the ^{15}N CP-MAS NMR spectrum of the title compound. This spectrum exhibits two resonance peaks at -338.6 and -334.6 ppm, with 1: 2 relative intensities. The X-ray structure shows that there are three inequivalent nitrogen

atoms in the unit cell which is in agreement with the NMR results if one assumes that two inequivalent nitrogen atoms resonate at quite the same value. These chemical shift values agree with those of the nitrogen atom of R-NH_3^+ groups in organic compounds [14].

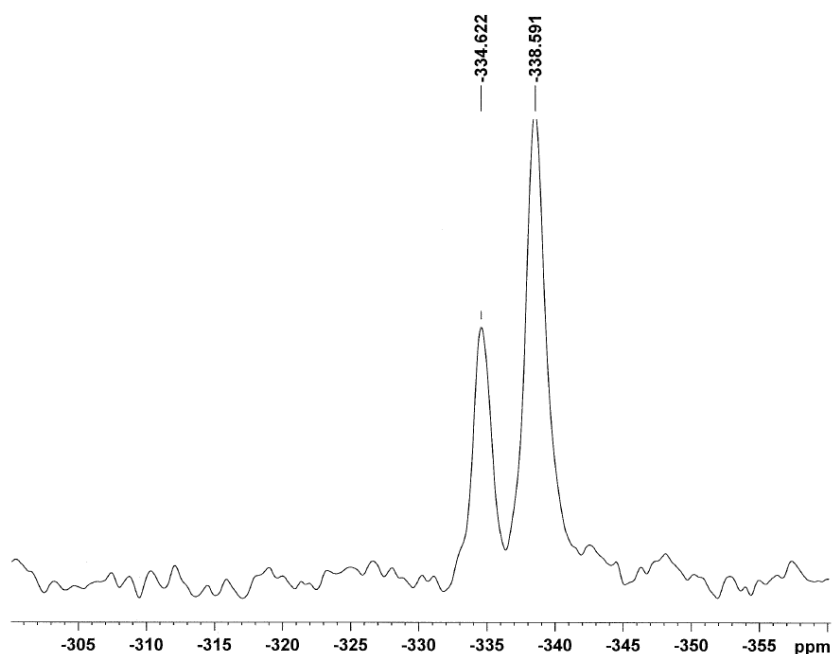


Figure 5: ^{15}N CP-MAS NMR spectrum of $(\text{C}_{10}\text{H}_{18}\text{N})_3[\text{SnCl}_6]\text{Cl}\cdot\text{H}_2\text{O}$

IR spectroscopy

The IR spectrum of crystalline $(\text{C}_{10}\text{H}_{18}\text{N})_3[\text{SnCl}_6]\text{Cl}\cdot\text{H}_2\text{O}$ is shown in Fig. 6. The vibrational modes of this compound were elicited by the comparison of the IR spectra of similar complexes [15, 16]. The broad bands between 3600 and 2500 cm^{-1} correspond to the stretching vibrations of $\nu(\text{C-H})$, $\nu(\text{N-H})$ and $\nu(\text{O-H})$ groups [17].

The bands in the 1650 - 1100 cm^{-1} region can be attributed to the bending vibrations of the $\delta(\text{N-H})$ and $\delta(\text{O-H})$ groups and to the stretching and bonding modes $\nu(\text{C-C})$, $\nu(\text{C-N})$ and $\nu(\text{C-H})$ [18, 19]. The bands between 1000 and 600 cm^{-1} are assigned to the out of plane bending modes $\gamma(\text{C-H})$, $\gamma(\text{C-C})$ and $\gamma(\text{N-H})$ [20].

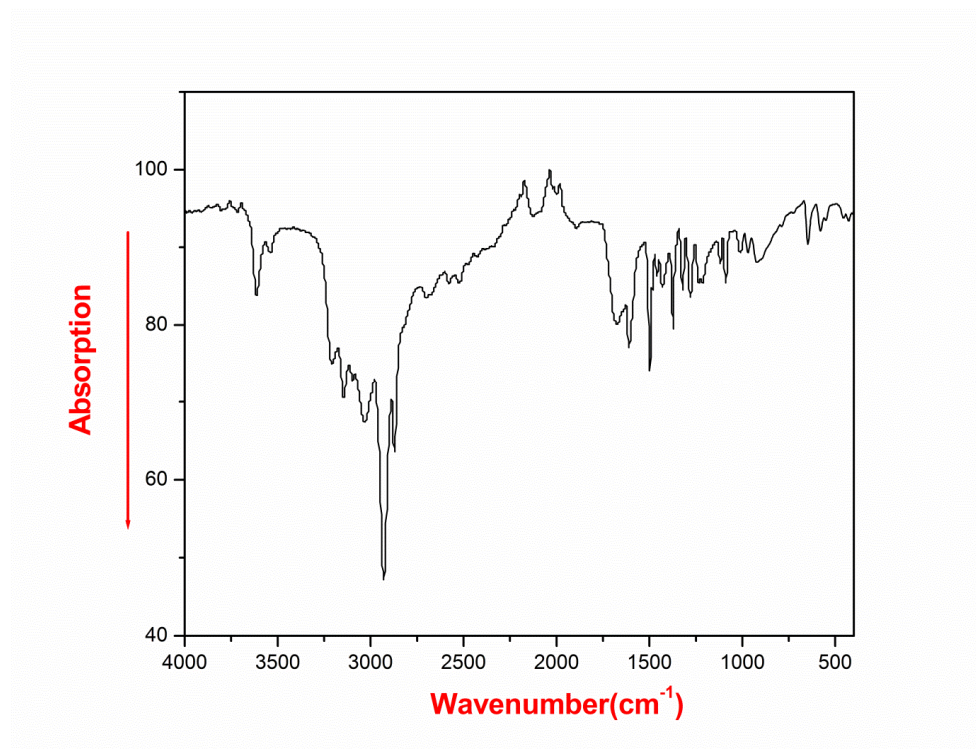


Figure 6: IR absorption spectrum of $(\text{C}_{10}\text{H}_{18}\text{N})_3[\text{SnCl}_6]\text{Cl}\cdot\text{H}_2\text{O}$.

Conclusion

A new Sn(IV) complex, $(\text{C}_{10}\text{H}_{18}\text{N})_3[\text{SnCl}_6]\text{Cl}\cdot\text{H}_2\text{O}$, was synthesized in an aqueous medium and characterized by various physico-chemical methods. On the structural level, the metal centers have 6-coordinated octahedral geometry. Crystal packing is stabilized by intermolecular N-H...Cl, N-H...O and O-H...Cl hydrogen bonds that connect the different entities into a three dimensional lattice. ^{119}Sn , ^{13}C and ^{15}N CP-MAS NMR spectra are in agreement with the X-ray structure.

Supplementary Data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 983168. These data can be obtained

free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK: fax: (+44) 01223-336-033; e-mail: deposit@ccdc.cam.ac.

Acknowledgments

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