The discovery of the *N,N*-dimethylthioformamidium ion. A structural study of $\{(CH_3)_2NCHSH\}_2[HfCl_6]$ in solid state and solution†

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The crystal structure of *N,N*-dimethylthioformamidium hexachlorohafnate(IV), $\{(CH_3)_2NCHSH\}_2[HfCl_6]$, obtained by dissolution of anhydrous hafnium(IV) chloride in *N,N*-dimethylthioformamide and storage under ambient atmosphere, has been determined from single crystal X-ray diffraction data. The bond distance distribution within the *N,N*-dimethylthioformamidium ion is similar to that in *N,N*-dimethylthioformamide molecules strongly bound to metal ions, but significantly different from that in pure *N,N*-dimethylthioformamide. The hafnium(IV) ion coordinates six chloride ions in a near-regular octahedral arrangement with a mean Hf–Cl bond distance of 2.447 Å. The packing in the crystal structure shows clearly the presence of hydrogen bonds of the X–(H)···Cl type, X = C and S, which are sufficiently strong and directional to hold the structure together. The structures of the hexachlorohafnate(IV), $[HfCl_6]^{2-}$, and hexachlorozirconate(IV), $[ZrCl_6]^{2-}$, ions in *N,N*-dimethylthioformamide solution have been determined by means of EXAFS, giving mean Hf–Cl and Zr–Cl bond distances of 2.44(1) and 2.45(1) Å, respectively. The infrared spectrum of solid $\{(CH_3)_2NCHSH\}_2[HfCl_6]$ has been analysed and compared with the data for free and strongly coordinated *N,N*-dimethylthioformamide.

Introduction

N,N-Dimethylthioformamide is a sulfur-donor solvent with a large dipole moment, $\mu = 4.44$ D, and high permittivity, $\varepsilon = 47.4$,[1] which means that most salts are highly soluble and dissociated. *N,N*-Dimethylthioformamide is a strong electron-pair donor, $D_S = 52$,[2] which indicates a soft bonding character of the sulfur atom. *N,N*-dimethylthioformamide has a well-ordered bulk structure as the internal hydrogen bonding is surprisingly strong, as seen in the liquid and solid state structures.[3] The solvation of a metal ion is mainly dependent on the bonding character of the solvent and the way in which the solvated ion affects the solvent bulk structure.[4,5] The soft Lewis base character of the sulfur in *N,N*-dimethylthioformamide gives rise to strong solvation of typically soft acceptors such as silver(I) and mercury(II),[6–8] while hard electron-pair acceptors are weakly solvated, as shown by transfer thermodynamic studies.[5] The structures of a number of *N,N*-dimethylthioformamide solvated metal ions have been studied in solution and solid state.[6,8]

The tetravalent d^0 ions hafnium(IV) and zirconium(IV), studied in the present work, are typically hard electron-pair acceptors, strongly preferring solvents and ligands providing mainly electrostatic interactions. It was, therefore, somewhat surprising to find that the anhydrous tetrachlorides of hafnium(IV) and zirconium(IV) have fairly high solubilities in *N,N*-dimethylthioformamide. In order to characterise the species formed at dissolution, X-ray diffraction, infrared spectroscopy and extended X-ray absorption fine structure (EXAFS) measurements have been performed.

Experimental

Sample preparation and characterisation

N,N-Dimethylthioformamide was prepared from *N,N*-dimethylformamide (Merck) and phosphorus pentasulfide (Merck) following the procedure described by Gutmann *et al.*.[9] The solutions were prepared by dissolving the anhydrous hafnium or zirconium tetrachlorides in *N,N*-dimethylthioformamide to saturation (*ca.* 1.0 M) at *ca.* 315 K. The mixtures were heated to *ca.* 340 K and thereafter the solutions were stored in a refrigerator with a parafilm cover. This means that water vapour was in contact with the solutions and a significant uptake of water took place. The water content has been determined to be 0.4% using Karl–Fischer titration (by Mikrokemi, Uppsala).[10] In the case of hafnium, pale yellow single-crystals of di(*N,N*-dimethylthioformamidium) hexachlorohafnate(IV), $\{(CH_3)_2NCHSH\}_2[HfCl_6]$, and a light grey powder were formed with time (some weeks). In the case of zirconium(IV) no individual crystalline product could be isolated, and only a light grey powder was formed with time. The solution phases were characterised by means of EXAFS showing that the metal ions were present as hexachlorohafnate(IV) and -zirconate(IV) complexes, respectively, see below. However, when hafnium(IV) chloride is dissolved in freshly distilled *N,N*-dimethylthioformamide and the obtained solution is stored in a closed vessel in a refrigerator for one month, no precipitation of $\{(CH_3)_2NCHSH\}_2[HfCl_6]$ was observed. This shows that a small and continued access to water is required for the formation of $\{(CH_3)_2NCHSH\}_2[MCl_6]$. Higher concentrations of water cause decomposition of *N,N*-dimethylthioformamide to hydrogen sulfide and *N,N*-dimethylformamide.

The crystals of $\{(CH_3)_2NCHSH\}_2[HfCl_6]$ were characterised with single crystal X-ray diffraction and IR spectroscopy, while the solution and the residual light grey powder were studied by means of EXAFS. An EXAFS study of a freshly prepared

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† Electronic supplementary information (ESI) available: 7 tables and 5 figures of IR, EXAFS and X-ray data as described in the text. See http://www.rsc.org/suppdata/nj/b2/b210969g/

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N,*N*-dimethylthioformamide solution of zirconium(IV) chloride has been performed as well. The infrared spectrum of solid di(*N*,*N*-dimethylthioformamidium) hexachlorohafnate(IV) is given for identification in Fig. S1 [see Electronic supplementary information (ESI)]. The density of the crystals was determined by the flotation technique using a solvent mixture of *n*-heptane, carbon tetrachloride and tetrabromoethene.[11] The densities of the solvent mixtures and the solutions studied by EXAFS were measured with an Anton Paar DMA 35 densitometer.

Crystallography

A pale yellow transparent crystal was mounted in a 0.5 mm glass capillary, which was flame sealed. Data were collected at 295 ± 1 K with a Bruker SMART CCD 1k diffractometer.[12] The structure was solved by standard direct methods and refined by full matrix least-squares, first in isotropic and finally in anisotropic approximation. The positions of the methyl hydrogen atoms were calculated geometrically and included in the final cycles of the refinement in isotropic approximation. The positions of the protons attached to the sulfur and amide carbon atoms were located in difference Fourier syntheses and included into the final cycles of refinement in isotropic approximation. All calculations were performed with the SHELXTL programs in PC version (v. 5.3).[13]

Crystal data for *N*,*N*-dimethylthioformamidium hexachlorohafnate(IV). $C_6H_{16}N_2S_2Cl_6Hf$, $M = 571.542$, monoclinic, space group $P2_1/c$ (No. 14), $a = 8.0963(9)$, $b = 15.2585(17)$, $c = 8.2235(9)$ Å, $\beta = 113.024(2)°$, $V = 934.98(18)$ Å^3, $Z = 2$, μ(Mo-Kα) = 6.642 mm^{-1}, 5283 reflections measured, 2074 unique ($R_{int} = 0.0233$), which were all used in the calculations. The final $wR(F^2)$ values were 0.0430 [$I > 2\sigma(I)$] and 0.0459 (all data). Selected bond distances and angles are summarised in Table 1.

CCDC reference number 201373. See http://www.rsc.org/suppdata/nj/b2/b210969g/ for crystallographic files in CIF or other electronic format.

EXAFS

The EXAFS spectra of *N*,*N*-dimethylthioformamide solutions of $\{(CH_3)_2NCHSH\}_2[MCl_6]$, M = Hf and Zr, a freshly prepared solution of zirconium(IV) chloride, and the grey powder formed together with $\{(CH_3)_2NCHSH\}_2[MCl_6]$, were collected in both transmission and fluorescence mode simultaneously at ambient room temperature at Stanford Synchrotron Radiation Laboratory (SSRL, Stanford, USA). SSRL operates at 3.0 GeV and a maximum current of 100 mA. The measurements were performed at the wiggler beam-line 4–1 using a Si(220) double-crystal monochromator, which was detuned to 50% of maximum intensity at the end of the scans in order to remove higher order harmonics. For internal energy calibration, hafnium or zirconium metal foils were recorded simultaneously. Three scans were collected and averaged for each sample. The ionisation energies of the Hf L_{III} and Zr K electrons in the metals are defined as 9561 and 17998 eV, respectively.[14] The calibration, averaging and EXAFS data treatment were performed with use of the EXAFSPAK program package.[15] The EXAFS oscillations were isolated using standard procedures for pre-edge subtraction, data normalisation and spline removal.[16] In order to obtain quantitative information the k^3-weighted EXAFS oscillations were analysed by a non-linear least-squares fitting procedure of model parameters. The model fitting was performed using theoretical phase and amplitude factors, including single and multiple back-scattering paths, calculated by means of the *ab initio* code FEFF (v. 6.0).[17]

Table 1 Interatomic bond lengths (Å^2) and angles (°) in *N*,*N*-dimethylthioformamidium hexachlorohafnate(IV) structure

Hf–Cl(1)	2.4404(10)	Cl(1)–Hf–Cl(1)	180
Hf–Cl(2)	2.4532(9)	Cl(1)–Hf–Cl(2)	89.15(3)
Hf–Cl(3)	2.4486(9)	Cl(1)–Hf–Cl(3)	89.46(4)
		Cl(2)–Hf–Cl(2)	180
		Cl(2)–Hf–Cl(3)	89.27(3)
		Cl(3)–Hf–Cl(3)	180
S–C(4)	1.707(4)	S–C(4)–N(3)	124.4(3)
N–C(4)	1.274(5)	C(4)–N(3)–C(5)	122.6(3)
N–C(5)	1.447(4)	C(4)–N(3)–C(6)	121.1(3)
N–C(6)	1.472(4)	C(5)–N(3)–C(6)	116.3(3)
S–H(1)	1.33(5)	C(4)–S(11)–H(1)	90.0(19)
C(6E)–H(6AE)[a]	0.96(1)		
H(6AE)[a]···Cl(3B)	2.79(1)		
C(6E)[–H(6AE)[a]···]Cl(3B)	3.71(1)	C(6E)–H(6AE)[a]···Cl(3B)	162(2)
S(11S)–H(1S)	1.33(4)		
H(6AE)···Cl(2B)	2.43(4)		
S(11S)[–H(6AE)···]Cl(2B)	3.70(1)	S(11S)–H(1S)···Cl(2B)	158(2)

[a] The hydrogen position is calculated.

Vibrational spectroscopy

The mid-infrared absorption spectrum of solid $\{(CH_3)_2NCHSH\}_2[HfCl_6]$ was measured as a KBr pellet by means of a Perkin–Elmer 1720X spectrometer in the range 400–4000 cm^{-1} at 295 ± 1 K. One hundred scans were collected and averaged at a resolution of 4 cm^{-1}. The spectrum is given in Fig. S1 and the assignments in Table S1 (see ESI).

Results and Discussion

The chemistry

After the dissolution of anhydrous hafnium tetrachloride in *N*,*N*-dimethylthioformamide in ambient atmosphere, solid $\{(CH_3)_2NCHSH\}_2[HfCl_6]$ is formed with time; the *N*,*N*-dimethylthioformamidium ion has not been described before. An EXAFS study of the light grey powder formed together with the title compound shows the presence of tetrameric hafnyl(IV) complexes, seen by the characteristic Hf···Hf distance of 3.55 Å in tetrameric hafnyl(IV) complexes;[18–21] a mean Hf–O bond distance of 2.13 Å indicates the presence of a seven-coordinated hafnium(IV) compound as well, *e.g.* orthorhombic hafnia (HfO_2).[22,23] No Hf–S or Hf–Cl bonds are present in the light grey powder (Table S2 and Fig. S2 in the ESI). This shows that a number of hydrolysis products of hafnium(IV), most probably a mixture of $[Hf_4(OH)_8]^{8+}$ ions and $HfO_2(s) + 2\ H^+$ is formed together with the title compound. It can be assumed that the grey powder formed with zirconium(IV) chloride has a corresponding composition.

The EXAFS study of a freshly prepared *N*,*N*-dimethylthioformamide solution of zirconium(IV) tetrachloride shows that it is dissolved as monomeric solvated molecules, $ZrCl_4(dmtf)_2$ (Table S3, Figs. S3 and S4 in the ESI). The long Zr–S bond distances in comparison with the Zr–Cl ones indicate a weak solvation of zirconium(IV) chloride in *N*,*N*-dimethylthioformamide (Table S7 in the ESI). The Zr···C single scattering and the 3-leg Zr–S–C multiple scattering paths are clearly seen in the Fourier transform, while in the the solutions stored in contact with water vapour the *N*,*N*-dimethylthioformamides are exchanged for chloride ions (Table S4 and Figs. S4 and S5 in the ESI†). This shows that the $ZrCl_4(dmtf)_2$ complex with time and in contact with moisture reacts with water according to reaction (1); stoichiometrically $1/4\cdot[M_4(OH)_8]^{8+}$ is equivalent to $MO_2(s) + 2\cdot H^+$. The EXAFS study indicates that the composition of hafnium in the light grey powder is *ca.* 65% $[Hf_4(OH)_8]^{8+}$ ions and *ca.* 35% HfO_2 (see Fig. S2 and Table S2 of the ESI). The relatively high solubility of MCl_4 in *N*,*N*-dimethylthioformamide is explained by the formation of a neutral solvated hafnium(IV) or zirconium complex as a first step, while the reaction with water is a second much slower step:

$$3\cdot\mathrm{MCl_4}+2\cdot\mathrm{H_2O}+2\cdot(\mathrm{CH_3})_2\mathrm{NCHS}$$
$$\rightarrow 2\cdot[\mathrm{MCl_6}]^{2-}+2\cdot(\mathrm{CH_3})_2\mathrm{NCHSH^+}+1/4\cdot[\mathrm{M_4(OH)_8}]^{8+}$$

The *N,N*-dimethylthioformamidium ion, as well as *N,N*-dimethylthioformamide, decompose in water, forming hydrogen sulfide as one easily recognised product.

Structure of *N,N*-dimethylthioformamidium hexachlorohafnate(IV), $\{(\mathrm{CH_3})_2\mathrm{NCHSH})_2\}[\mathrm{HfCl_6}]$

The centrosymmetric structure of $\{(\mathrm{CH_3})_2\mathrm{NCHSH}\}_2[\mathrm{HfCl_6}]$ is build up of discrete planar *N,N*-dimethylthioformamidium cations, $(\mathrm{CH_3})_2\mathrm{NCHSH^+}$, and octahedral hexachlorohafnate(IV) anions, $[\mathrm{HfCl_6}]^{2-}$, see Fig. 1. It was possible to localise the protons on the sulfur and the amide carbon in the difference Fourier syntheses, while methyl protons were calculated in idealised positions riding on the carbon atom. The fractional atomic coordinates and the equivalent isotropic displacement coefficients are given in Tables S5 and S6 (see ESI), and a summary of the bond distances and angles is given in Table S7 (in the ESI).

The planarity of the molecule and the S–C and N–C bond distances of 1.707(4) and 1.274(5) Å, respectively, show clearly the presence of a delocalised electron system in the *N,N*-dimethylthioformamidium ion.[3] The protonation has caused a significant change in the electron distribution, seen as marked changes in the S–C and N–C bond distances (Tables 2 and S7 in the ESI). The bond distance distribution in the *N,N*-dimethylthioformamidium ion is very similar to the bond distances in *N,N*-dimethylthioformamide molecules strongly bound to soft metal ions as in bis(*N,N*-dimethylthioformamide)mercury(II) perchlorate for example, while coordination to other metal ions with larger coordination numbers causes smaller changes, (Tables 2 and S7). This shows that the S–H bond is indeed strong.

The S–H bond length found in *N,N*-dimethylthioformamidium ion is 1.33(5) Å and the C–S–H bond angle is 90.0(19)° (Table 1). This result is in very good agreement with the structure of trithiocarbonic acid with a mean S–H bond distance of 1.30(3) Å,[24] a powder neutron diffraction study of deuterated hydrogen sulfide, $\mathrm{D_2S}$, with a mean S–D bond distance of 1.33 Å,[25] and a single crystal neutron diffraction study on *N*-acetyl-L-cystein reported by Takusagawa *et al.*[26] for which the S–H bond length is 1.338(2) Å and the C–S–H bond angle is 76.9(2)°; the mean S–H bond distance determined crystallographically is 1.35 Å.[27] The presence of a *ν*(S–H) band at 2437 $\mathrm{cm^{-1}}$ shows that the S–H bond in solid (*N,N*-dimethylthioformamidium) hexachlorohafnate(IV) is strong (Fig. S1 and Table S1 of the ESI).[28]

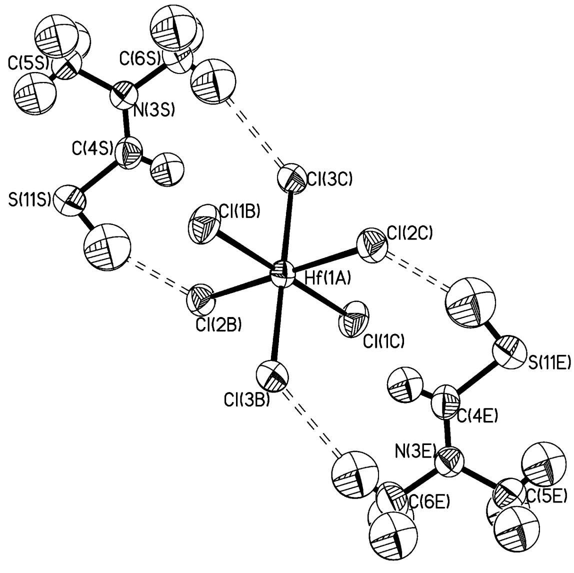

Fig. 1 Molecular structure of di(*N,N*-dimethylthioformamidium) hexachlorohafnate(IV). The displacement ellipsoids are shown at the 30 % probability level for non-H atoms. The hydrogen bonding is shown by dashed bonds. The symmetrically independent unit comprises only one *N,N*-dimethylthioformamidium ion and a half of the $[\mathrm{HfCl_6}]^{2-}$ anion, defined by the atoms Cl(1), Cl(2) and Cl(3).

Table 2 Comparison between the interatomic bond lengths (Å) and angles in solid *N,N*-dimethylthioformamide, $\mathrm{SCHN(CH_3)_2}$, solid bis(*N,N*-dimethylthioformamide)mercury(II) perchlorate, $[\mathrm{Hg(SCHN(CH_3)_2)_2}](\mathrm{ClO_4})_2$, and in *N,N*-dimethylthioformamidium hexachlorohafnate(IV), $\{(\mathrm{CH_3})\mathrm{NCHSH}\}_2[\mathrm{HfCl_6}]$

Bond parameter	$\mathrm{SCHN(CH_3)_2}$[a]	$[\mathrm{Hg(dmtf)_2}](\mathrm{ClO_4})_2$[b]	$(\mathrm{CH_3})\mathrm{NCHSH^+}$
S–C(1)	1.6665(6)	1.703(6)	1.707(4)
S–H			1.33(4)
N–C(1)	1.3212(2)	1.287(7)	1.274(5)
N–C(2)	1.4555(8)	1.475(8)	1.447(4)
N–C(3)	1.4624(8)	1.461(7)	1.472(4)
S–C(1)–N	127.68(4)	122.9(5)	124.4(3)
C(1)–N–C(2)	123.19(5)	121.5(5)	122.6(3)
C(1)–N–C(3)	120.77(6)	123.0(5)	121.1(3)
C(2)–N–C(3)	116.02(5)	115.5(5)	116.3(3)
M–S–C(1)		101.4(2)	90.0(19)

[a] Ref. 3. [b] Ref. 7.

The hafnium(IV) ion binds six chloride ions in a near-regular octahedron in the hexachlorohafnate(IV) complex (Fig. 1). The Hf–Cl bond distances are in the range 2.440–2.453 Å, which is in very good agreement with earlier studies on hexachlorohafnate(IV) complexes.[29–31]

The halide ions, except fluoride, are weak hydrogen bond acceptors. In this study it is shown that hydrogen bonds are formed by chloride ions with the weak hydrogen bond donors in the C–H and S–H bonds. The acidity of the C–H bond must be sufficiently high if a hydrogen bond to the weak hydrogen bond acceptor chloride shall be formed. The (C–)H···Cl and (S–)H···Cl hydrogen bond distances are reported to be in the ranges 2.57–2.94 Å and 2.50–2.92 Å, respectively, and with X–H···Cl bond angles in the ranges 131–158° and 99–164°, respectively.[32] The (S–)H···Cl hydrogen bond distance, 2.43(4) Å, observed in the *N,N*-dimethylthioformamidium ion, is among the shortest observed so far, and the S–H···Cl angle is large at 158(2)° (Table 1). The (C–)H···Cl hydrogen bond distance, 2.79 Å, is close to the mean value for such hydrogen bonds, while the C–H···Cl angle is unusually large at 162(2) °. These hydrogen bonds, even though they are weak, are sufficiently strong and directional to hold the crystal structure together.

The structures of the $\mathrm{HfCl_6}^{2-}$ and $\mathrm{ZrCl_6}^{2-}$ ions in *N,N*-dimethylthioformamide solution

The EXAFS study of the hexachlorohafnate(IV) and zirconate(IV) ions in *N,N*-dimethylthioformamide shows that the hafnium(IV) and zirconium(IV) ions are surrounded by six chlorides in octahedral configuration with Hf–Cl and Zr–Cl bond distances of 2.44(1) and 2.45(1) Å, respectively. This is in very good agreement with the bond distances observed in the solid state. A summary of the scattering path distances is given in Table S4 (ESI). The fit of the experimental data and the individual contributions of the single and multiple scattering paths within the MCl_6 core and the fitted Fourier transforms are shown Figs. S4 and S5 (in the ESI), respectively.

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