The Discovery of the *N,N*-Dimethylthioformamidium Ion. A Structural Study of $((CH_3)_2NCHSH))_2[HfCl_6]$ in Solid State and Solution

Camelia Hagfeldt, Vadim Kessler and Ingmar Persson*

Department of Chemistry, Swedish University of Agricultural Sciences, P.O. Box 7015, SE-750 07 Uppsala, Sweden

Supplementary Material

Table S1. infrared frequencies, cm^{-1}, and assignments for solid (*N,N*-dimethylthioformamidium) hexachlorohafniate(IV), and data for pure *N,N*-dimethylthioformamide, and bis(*N,N*-dimethylthioformamide)mercury(II) are perchlorate given for comparison.

DMTF[a]	$(dmtfH)_2[HfCl_6]$	$[Hg(dmtf)_2](ClO_4)_2$[a]	Assignment[a]
	3160		
3002	3008		$\nu_{as}(CH_3)2$
2961	2989		$\nu_{as}(CH_3)1$
2937	2943	2954,2943	$\nu_s(CH_3)2$
2903			$\nu_s(CH_3)1$
		2872	$\nu_s(CH)$
2853		2850	$\nu(CH)$
	2775		
	2437		$\nu(SH)$
		1616,1592	$\nu(CN)+_{as}(C'_2N)$
1542	1539		$\nu(CN)$
1464			$\delta_{as}(CH_3)$
1443		1441	$\delta_{as}(CH_3)$
1414		1410	$\delta_s(CH_3)$
1399	1403		$\delta(NCH)$
1385		1389	$\delta_s(CH_3)$
1206		1203	$\nu_{as}(C'_2N)$

1134	1132	1146	$\rho(CH_3)$
		1112	$\nu_3(ClO_4^-)$
1100			$\rho(CH_3)$
		1086	$\rho(CH_3)$
1052		1046	$\rho(CH_3)$
970	969		$\nu(CS)$
		941	$\gamma_s(CH)$
		933	$\gamma_{as}(CH)$
916	920	913	$\gamma(CH)$
824	817	817	$\nu_s(C'_2N)$
	698		
		625	$\nu_4(ClO_4^-)$
520	524	515	$\sigma(NC'_2)+ \delta(CS)$
		457	$\nu_2(ClO_4^-)$
405		414	$\sigma(NC'_2)+ \rho(NC'_2)$
		382	
$\nu_s(HgS)+ \sigma_{as}(C'_2N)+\delta_{as}(CS)$			
		371	$\nu_s(HgS)$
363		360	$\gamma(C'N)$
		276	$\sigma(NCS)+ \rho(NC'_2)$
220			$\tau(CH_3)$
191			$\tau(CH_3)$
		184	$\nu_{as}(HgS)+\delta_{as}(NCS)$

[a] C.M.V. Stålhandske, J. Mink, M. Sandström, I. Papai and P. Johansson, *Vibr. Spectroscopy* 1997, **14**, 207.

Table S2. Mean bond distances, *d*/Å, Debye-Waller factors, σ^2, number of distances, *N*, the threshold energy, E_o/eV, and the amplitude reduction factor, S_o^2, of the light grey powder precipitating with time from a reaction between hafnium(IV) chloride, *N,N*-dimethylthioformamide in presence of moisture as determined by EXAFS.

Interaction	*N*	*d*	σ^2	E_o	S_o^2
Hf-O	8	2.131(3)	0.0077(4)	9562.0(4)	0.69(3)
Hf--Hf	1.3(2)	3.544(9)	0.0035		
Hf--O	2	2.75(2)	0.009(3)		
Hf--O	4	3.11(2)	0.009(4)		
Hf--O	4	3.30(2)	0.005(2)		

Table S3. EXAFS model parameters for *N,N*-dimethylthioformamide solvated zirconium(IV) tetrachloride, $ZrCl_4(dmtf)_2$, in a freshly prepared solution.

Interaction	*N*	*d*/Å	σ^2/Å^2	E_o/eV	S_o^2
Zr-Cl	4	2.38(1)	0.0055(12)	18005.9(8)	1.25(5)
Zr-S	2	2.55(1)	0.0045(12)		
Zr…C	2	3.43(2)	0.005(2)		
Zr-S-C	4	3.80(2)	0.005(2)		

Table S4. EXAFS model parameters for the hexachlorohafniate(IV), $HfCl_6^{2-}$, and hexachlorozirconate(IV), $ZrCl_6^{2-}$, ions in *N,N*-dimethylthioformamide solution.

Interaction	*N*	*d*/Å	σ^2/Å^2	E_o/eV	S_o^2
Hf-Cl	6	2.441(2)	0.0044(2)	9570.3(3)	0.63(2)
Hf-Cl-Cl	24	4.27(5)	0.014(7)		
MS [a]	3x6	4.95(3)	0.014(3)		
Zr-Cl	6	2.448(2)	0.0043(2)	18007.9(4)	0.68(2)
MS [a]	3x6	4.99(5)	0.023(7)		

[a] The linear multiple scattering pathways, M-Cl-Cl and two different M-Cl-M-Cl, have been refined with the same value for their corresponding structure parameters (*d*, n and σ^2).

Table S5. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for $((CH_3)_2NCHSH)_2[HfCl_6]$. *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

		x	y	z	*U*(eq)
Hf1	Hf	0.0000	0.0000	0.5000	0.04041(9)
Cl1	Cl	0.29883(13)	0.06194(6)	0.57578(14)	0.0589(3)
Cl2	Cl	-0.06763(14)	0.11006(6)	0.68261(12)	0.0563(3)
Cl3	Cl	-0.12241(15)	0.09885(6)	0.24618(13)	0.0601(3)
S11	S	0.56770(15)	0.24137(7)	0.91263(15)	0.0643(3)
N3	N	0.3469(4)	0.35599(18)	0.6928(4)	0.0444(7)
C4	C	0.4977(6)	0.3417(2)	0.8190(5)	0.0495(9)
C5	C	0.2130(5)	0.2883(2)	0.6202(6)	0.0622(11)
H5A	H	0.2582	0.2338	0.6791	0.093
H5B	H	0.1858	0.2820	0.4962	0.093
H5C	H	0.1060	0.3041	0.6370	0.093
C6	C	0.2980(6)	0.4441(3)	0.6163(5)	0.0694(12)
H6A	H	0.3955	0.4838	0.6739	0.104
H6B	H	0.1931	0.4640	0.6327	0.104
H6C	H	0.2735	0.4421	0.4923	0.104
H1	H	0.723(6)	0.276(3)	1.021(6)	0.113(16)
H4A	H	0.574(5)	0.384(3)	0.863(5)	0.078(14)

Table S6. Anisotropic displacement parameters for $((CH_3)_2NCHSH)_2[HfCl_6]$. The anisotropic displacement factor exponent takes the form: $-2p^2$ ($h^2 \cdot a^* \, 2U_{11} + \ldots + 2h \cdot k \cdot a^* \cdot b^* \cdot U_{12}$).

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hf1	0.04235(13)	0.03115(11)	0.04081(13)	0.00185(11)	0.00878(8)	0.00116(11)
Cl1	0.0461(5)	0.0439(5)	0.0794(7)	-0.0022(5)	0.0167(5)	-0.0050(4)
Cl2	0.0630(6)	0.0481(5)	0.0501(5)	-0.0073(4)	0.0139(5)	0.0080(4)
Cl3	0.0698(7)	0.0525(5)	0.0537(6)	0.0182(5)	0.0194(5)	0.0143(5)
S11	0.0598(7)	0.0549(6)	0.0654(7)	0.0097(5)	0.0108(6)	0.0007(5)
N3	0.0449(18)	0.0415(16)	0.0429(17)	-0.0005(14)	0.0130(15)	-0.0028(13)
C4	0.055(3)	0.044(2)	0.050(2)	0.0007(18)	0.021(2)	-0.0080(19)
C5	0.052(2)	0.050(2)	0.069(3)	-0.004(2)	0.006(2)	-0.0031(19)
C6	0.079(3)	0.047(2)	0.067(3)	0.007(2)	0.012(2)	-0.001(2)

Table S7. Comparison between the interatomic bond distances (Å) in the *N,N*-dimethylthioformamide molecules in the solid state of the solvent it self, $SCHN(CH_3)_2$, and in the coordination compounds $[Hg(SCHN(CH_3)_2)_2(ClO_4)_2]$, $((CH_3)_2NCHSH)_2[HfCl_6]$, $[Zn(SCHN(CH_3)_2)_4](ClO_4)_2$, $[Cd(SCHN(CH_3)_2)_4](CF_3SO_3)_2]$, $[Cu(SCHN(CH_3)_2)_4]ClO_4$ and $[Ag_2(SCHN(CH_3)_2)_6](ClO_4)_2$.

	S - C(1)	N - C(1)	N - C(2)	N - C(3)
$SCHN(CH_3)_2$	1.6665(6)	1.3212(2)	1.4555(8)	1.4624(8)
$((CH_3)_2NCHSH)_2[HfCl_6]$	1.707(4)	1.274(5)	1.447(4)	1.472(4)
$[Hg(SCHN(CH_3)_2)_2(ClO_4)_2]$	1.703(6)	1.287(7)	1.475(8)	1.461(7)
$[Zn(SCHN(CH_3)_2)_4](CF_3SO_3)_2$	1.663(4)	1.297(5)	1.456(6)	1.444(7)
$[Cd((SCHN(CH_3)_2)_2)_4(CF_3SO_3)_2]$	1.673(3)	1.304(3)	1.463(4)	1.456(3)
$[Cu(SCHN(CH_3)_2)_4]ClO_4$	1.661(5)	1.300(6)	1.445(8)	1.453(9)
$[Ag_2(SCHN(CH_3)_2)_6](ClO_4)_2$	1.661(3)	1.310(4)	1.458(4)	1.444(7)