

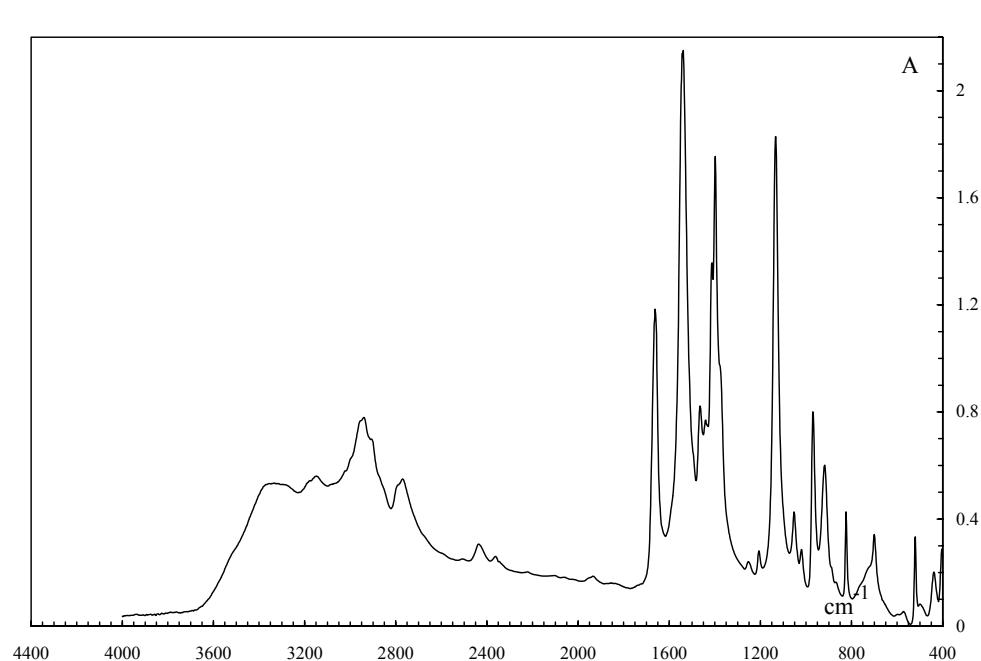
The Discovery of the *N,N*-Dimethylthioformamidium Ion.  
A Structural Study of  $((\text{CH}_3)_2\text{NCHSH})_2[\text{HfCl}_6]$  in Solid State  
and Solution

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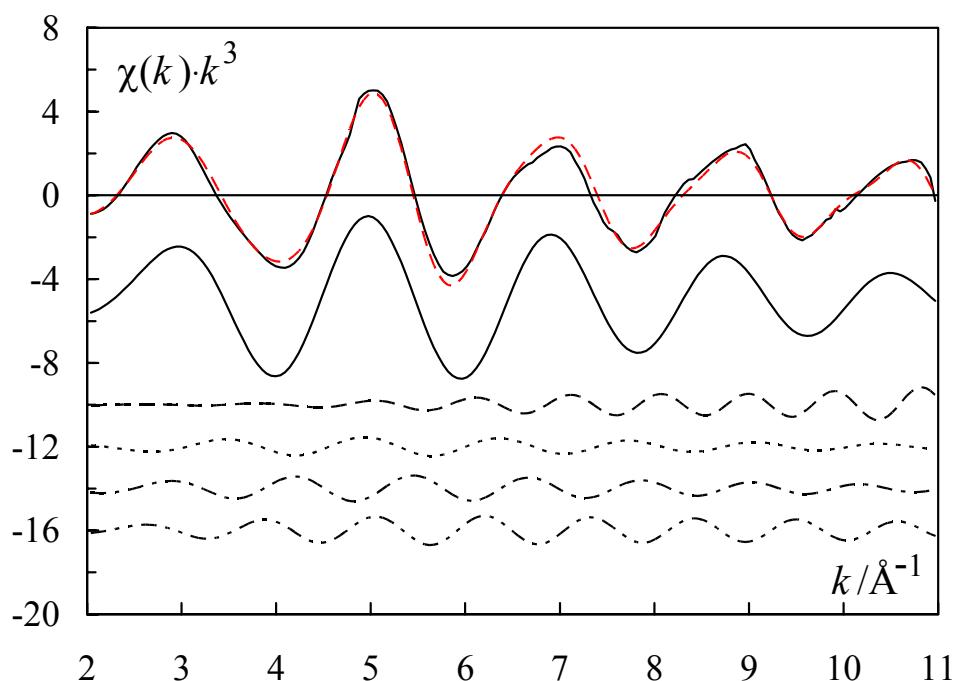
**Supplementary Material**

**Figure S1.** The infrared spectrum of solid (*N,N*-dimethylthioformamidium) hexachlorohafniate(IV).



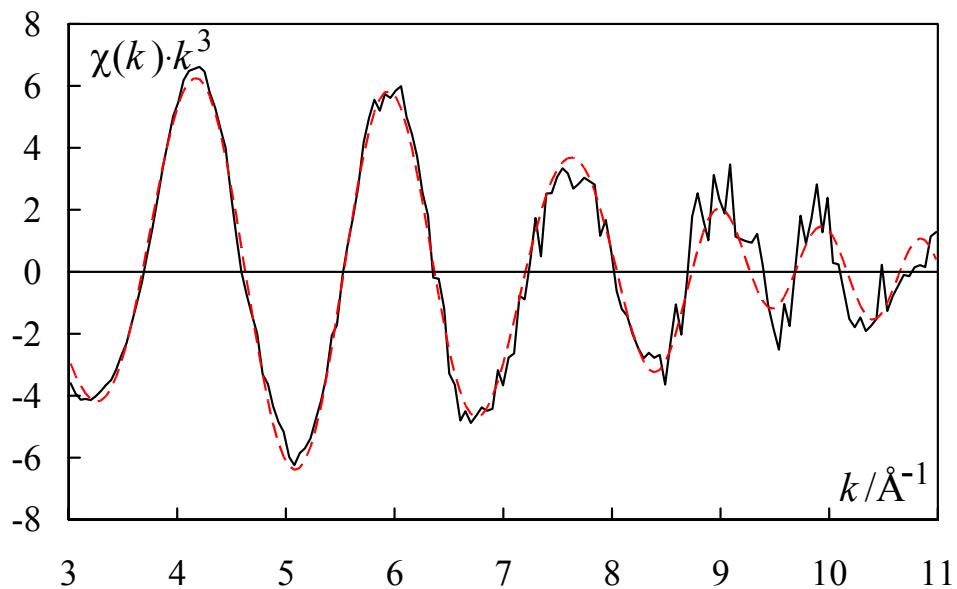
**Figure S2.** The fit and the individual contribution of the different scattering paths of the EXAFS data of the light grey powder formed in the reaction between hafnium(IV) chloride and water in *N,N*-dimethylthioformamide solution, solid line - experimental data, dashed line - calculated model function using the parameters given in Table S5. Individual contributions: solid line (offset -5) - Hf-O single scattering (SS), dashed line (offset -10) - Hf···Hf SS, dotted line (offset -12) - Hf···O (2.75 Å) SS, dash-dotted line (offset -14) - Hf···O (3.10 Å) SS, and dash-dot-dotted line (offset -16) - Hf···O (3.30 Å) SS.

Fig. S2.



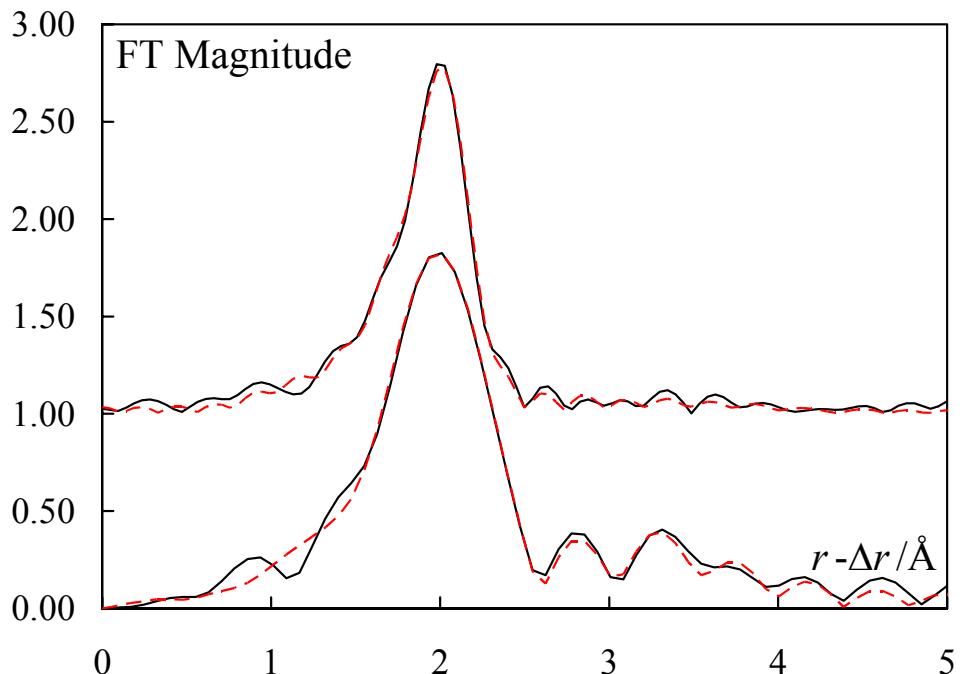
**Figure S3.** The fit of a freshly prepared *N,N*-dimethylthioformamide solution of zirconium(IV) chloride, solid line - experimental data, dashed line - calculated model function using the parameters given in Table S3.

Fig. S3.



**Figure S4.** The fit of the Fourier transforms of the freshly prepared *N,N*-dimethylthioformamide solution of zirconium(IV) chloride  $\text{ZrCl}_4(\text{dmtf})_2$ , solid line - experimental data, dashed line - calculated model function using the parameters given in Table S7 (no offset), and of an *N,N*-dimethylthioformamide solution of zirconium(IV) chloride stored in presence of water vapour,  $\{(\text{CH}_3)_2\text{NCHSH}\}_2[\text{HfCl}_6]$ , solid line - experimental data, dashed line - calculated model function using the parameters given in Table S6 (offset 1.0).

Fig. S4.



**Figure S5.** The fit and the individual contribution of the different scattering paths of the EXAFS data of a/ *N,N*-dimethylthioformamide solution of (*N,N*-dimethylthioformamidium) hexachlorohafniate(IV), solid line - experimental data, dashed line - calculated model function using the parameters given in Table S4. Individual contributions: solid line (offset -7) - Hf-Cl single scattering (SS), dash-dot-dotted line (offset -14) - Hf-Cl-Cl 3-leg multiple scattering (MS), dashed line (offset -16) - Hf-Cl-Cl linear 3-leg MS, dash-dotted line (offset -18) - Hf-Cl-Hf-Cl 4-leg linear MS, and dotted line (offset -20) Hf-Cl-Hf-Cl 4-leg linear MS, and  
b/ *N,N*-dimethylthioformamide solution of (*N,N*-dimethylthioformamidium) hexachlorozirconate(IV), solid line - experimental data, dashed line - calculated model function using the parameters given in Table S4. Individual contributions: solid line (offset -8) - Hf-Cl single scattering (SS), dashed line (offset -16) - Zr-Cl-Cl linear 3-leg MS, dash-dotted line (offset -18) - Zr-Cl-Zr-Cl 4-leg linear MS, and dotted line (offset -20) Zr-Cl-Zr-Cl 4-leg linear MS.

Fig. S5a.

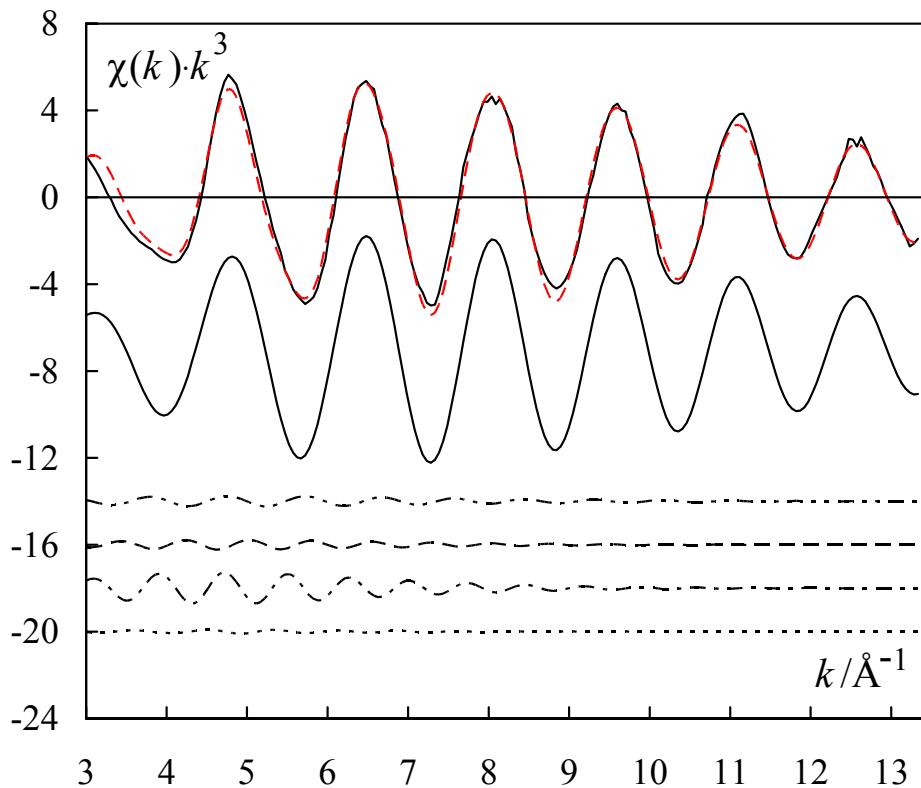


Fig. S5b.

