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A Tetranuclear Planar Hafnium Complex Containing O–Hf–S Moieties

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Dedicated to the memory of Professor Klaus Müller[‡]

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The Hf^{IV}-oxothiocluster, $[Hf_4(\eta^2\text{-}\mu_2\text{-}SAc)_4(\eta^2\text{-}\mu_2\text{-}SAc)_2(\eta^2\text{-}\mu_2\text{-}BuO)_4(\eta^2\text{-}BuO)_2(\mu_3\text{-}O)_2]$, was synthesized by reaction of hafnium butoxide with thioacetic acid. The crystal structure shows the presence of a planar tetranuclear Hf_4 core, in which the metal atoms are μ_3-O bridged and the thioacetate ligands coordinate the Hf ions both through a bridging and a chelating mode. The structural findings are confirmed by multinuclear NMR spectroscopic data.

Introduction

The design and synthesis of polynuclear structures based on bridging S and O ligands are challenging issues in inorganic chemistry.[1] In the last few years, starting from different carboxylate ligands, we have prepared a large variety of diverse organically modified oxoclusters[2] of various metals, such as Ba,[3] Ba–Ti,[3] Zr,[4,5] Hf,[4] Ti–Hf,[5] Zr–Ti–Hf.[5] These compounds are characterized not only by different nuclearities, structures and connectivities, but also by the presence of different functional groups, which may allow, in further synthetic steps, their embedding into a matrix by reaction with suitable precursors.

We are now exploring the extension of this oxocluster chemistry to the homologue oxothiocluster through the formation of similar polynuclear structures by using S,O-based ligands, particularly with Hf and other group IV transition metals. While the Hf–Cl cluster chemistry[6] is relatively well known and Hf–F-based di- and trinuclear complexes have been isolated by Roesky et al.,[7] there are few examples of polynuclear Hf complexes based on other donor ligands.[8] Moreover, different crystalline acetate- $\{[Hf_6O_4(OH)_4(\text{acetate})_{12}]_2\}$,[9] methacrylate- $\{[Hf_4O_2(OMc)_{12}]$, $[Hf_6O_4(OH)_4(OMc)_{12}(BuOH)]$, $[Ti_4Hf_6O_4(OBu)_4(OMc)_{16}]$ and $[Ti_2Zr_5HfO_6(OMc)_{20}]$ (OMc = methacrylate)$\}$[5] or mercaptopropionate-functionalized $\{[Hf_{12}(\mu_3\text{-}O)_8(\mu_3\text{-}OH)_8(MP)_{24}\cdot 5(MPA)]$, MPA = $HS\text{-}(CH_2)_2\text{–}C(O)OH$; MP = $HS\text{–}(CH_2)_2\text{–}C(O)O\}$[4a] hafnium oxoclusters, characterized by the presence of O–Hf–O moieties, have been isolated and structurally characterized. These polynuclear complexes have been obtained by reaction of hafnium butoxide with acetic-, methacrylic- or 3-mercaptopropionic acid, respectively.

However, there are few reports on Hf mono- and polynuclear S complexes. Indeed, in the Cambridge Structural Database only 18 crystal structures, with at least one Hf–S bond, are present. Only one case, a dinuclear Hf compound, (μ_2-1,2,4,5-benzenetetrathiolato)-bis[bis(η^5-trimethylsilyl-cyclopentadienyl)-hafnium], in which two Hf ions are bridged through the μ_2-1,2,4,5-benzenetetrathiolato anion, is reported.[10] Moreover, two heterometallic sulfur-containing complexes, bis(η^5-cyclopentadienyl)-1,3-dimethyl-1,3-diarsena-2-thiapropan-1,3-dithione-hafnium and bis{μ_3-2,2′-thiobis[4-(1,1,3,3-tetramethylbutyl)phenolato]}-hexamethyl-di-aluminium-hafnium dichloromethane solvate,[11] both monometallic, have been reported.

The interest in this field stems from the importance in basic structural and inorganic chemistry of metal–sulfur compounds as well as from the possible applications of the compounds, characterized by different electronic structures with respect to their oxygen-based homologues, in a number of fields. Moreover, of particular interest is the formation of heteroleptic complexes with S and O atoms chelating the same metal ion, since the S–M–O fragment is expected to be characterized by electronic properties signifi-

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cantly different from those of the O–M–O moiety. At this regard, reports in the literature concern mono- and dinuclear Hf complexes with S,O ligands, such as [Hf(tbop-κ^3O,S,O)$_2$],[12] [Hf$_2$(μ-tbop-κ^3O,S,O)$_2$Cl$_4$][13] {where tbopH$_2$ = 2,2′-thiobis[4-(1,1,3,3-tetramethylbutyl)phenol]}, tetrakis(*N*-methyl-thiotolylhydroxamato)Hf^{IV}[14] and complexes of Hf with *o*-mercaptophenol and 1,2-dihydroxybenzene.[15] Other studies instead focus on S,S ligands used for Hf coordination, such as in bis(pentamethyl)hafnocene 1,8-dithiolatonaphthalene[16] or in the Hf complex with [NEt]$_4$-[M(edt)]$_3$ (edt = ethane-1,2-dithiolate)[17] with secondary phosphane sulfide [Cp$_2$Hf(SPPh)].[18] Further examples of Hf–S complexes are reported in the literature.[19–22]

Results and Discussion

We have synthesized the new Hf^{IV} oxothiocluster Hf$_4$(η^2-μ_2-SAc)$_4$(η^2-μ_2SAc)$_2$(η^2-μ_2-BuO)$_4$(η^2-BuO)$_2$(μ_3-O)$_2$ (Hf4S) and characterized it by X-ray diffraction, and 1D and 2D ^{1}H and ^{13}C NMR spectroscopy. Because of the high sensitivity of Hf4S toward atmospheric water, it was impossible to obtain reasonable results from elemental analyses.

An ORTEP view of the cluster Hf4S is shown in Figure 1, while a list of relevant bond lengths and angles is given in Table S2.

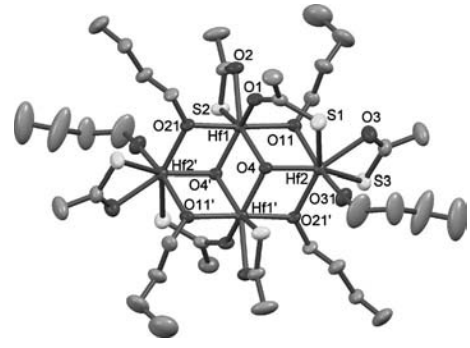

Figure 1. ORTEP view of the structure of Hf4S; ellipsoids are drawn at 50% probability.

The tetranuclear hafnium cluster Hf4S lies on a crystallographic inversion centre so that only half of the molecule is independent. As a consequence of the imposed symmetry, the four hafnium atoms are coplanar. The tetranuclear metal moiety may be described as resulting from two Hf triangles sharing the shortest side, Hf1–Hf1′, with a distance of 3.2996(3) Å. The other two metal–metal separations are 3.3689(3) and 3.3951(3) Å. The two triangular moieties are symmetrically capped by μ_3-O ligands lying on opposite sides of the Hf$_4$ plane as a result of the inversion centre. The O atoms of the μ^3-bridges lie out of the plane of the metal atoms (0.8 Å), while the distances and angles are in the expected range for this type of complex. Even though this 4-metal oxo-bridged core is unprecedented, a comparison may be made with trimetallic "M$_3$-μ^3-oxo" moieties of the Ti group metals, which show similar distances and angles (taking into account the fairly small differences in atomic radii).[23] Moreover, we note that μ^3-oxo bridges are required by (or, if you prefer, consistent with) the Hf^{IV} oxidation state and the complex neutrality.

The Hf–Hf′ distances are too long for a significant metal–metal interaction. The C atoms of the terminal butoxy groups show very large ADPs even at low *T*, which reflects conformational disorder that could not be modeled satisfactorily.

The two independent Hf atoms are both seven-coordinate; however, each metal has a different coordination sphere (see Figure 1). The immediate coordination sphere of Hf1 consists of the oxygen atoms of two μ_2-butoxy ligands (*trans* to each other), μ_3-O, μ_2-SAc [SAc = CH$_3$C(O)S] and a chelating thiocetate ligand; the other independent Hf atom (Hf2) is coordinated to five oxygen atoms (i.e. those from the μ_3-O ligand, the two bridging and one terminal butoxy groups and the chelating SAc ligands) and two S atoms of the SAc ligands (μ_2-SAc and η^2-SAc, respectively). The other distances are in the expected range and similar to those found in clusters with similar topologies.[5]

As can be seen in Figure S1, the tetranuclear cores are surrounded by aliphatic chains, and, consequently, the clusters are held together only by van der Waals interactions. The packing generates two narrow channels (section ca. 3×2 and 1.5×2 Å^2) running parallel to the crystallographic *c* axis (Figure S1).

As for the parent oxoclusters,[2] the Hf4S solutions used for NMR investigations are very sensitive to moisture, which results in hydrolysis of the thioacetates with the formation of butyl acetate, as previously found for the corresponding Zr derivatives.[24] Nevertheless, in addition to the signals assigned to butyl acetate, the ^{1}H and ^{13}C spectra consist of broad resonances typical for the *n*-butoxy moieties (see Experimental Section), which may arise from the butoxy groups that are bonded to the Hf core and are involved in relatively slow chemical exchange processes. Moreover, some weaker and very broad ^{1}H signals appear in the range δ = 2.4–2.6 ppm, which exhibit (i) a set of one-bond H–C heteronuclear correlations with a number of broad ^{13}C resonances centred at δ = 35.9 ppm and (ii) two sets of multiple-bond correlations with very broad ^{13}C signals around δ = 240 and δ = 260 ppm. These signals may be assigned to the ^{13}C nuclei of methyl and thiocarbonyl subunits, respectively, of the thioacetate groups in different coordinative situations around the metal core undergoing a slow chemical exchange. Very similar and unprecedented chemical shift values for the thiocarbonyl subunits have been observed in comparable Zr-oxothioclusters[23] and are attributed to the thiocarbonyl moieties by using the principal component analysis (PCA)[25] as developed by Rittner et al.[26]

Conclusions

We report here the synthesis and characterization of a tetranuclear planar Hf complex comprising O–Hf–S bonds. The crystalline compound, obtained by the reaction of hafnium butoxide with thioacetic acid, was isolated and structurally characterized. NMR analysis reveals the presence of butoxy and thioacetate groups in different coordinative situations around the inorganic core. A reaction pathway similar to that observed in analogous oxoclusters[2d] can be proposed on the basis of: (i) the structural motifs analogous to those observed in the oxoclusters, (ii) the coordination modes (bridging, chelating) of the thiocarboxylate ligands similar to those of the carboxylate ligands in the homologue oxygen-based clusters, (iii) the distances that are in the expected range and similar to those found in clusters with similar topologies.

Experimental Section

All reactions and manipulations were carried out under an argon atmosphere by using standard Schlenk or septum/cannula techniques. $Hf(OnBu)_4$ (95% in *n*-butanol, purchased by ACR GmbH, Karlsruhe, Germany) and *n*-butanol (anhydrous 99+%, purchased by Aldrich, Milan, Italy) were stored under an argon atmosphere and not purified further. Thioacetic acid (96%, purchased by Aldrich, Milan, Italy) was used as received.

The obtained oxothiocluster was characterized by X-ray diffraction and ^{1}H and ^{13}C NMR analysis.

Synthesis of $Hf_4(\eta^2\text{-}\mu_2\text{-}SAc)_4(\eta^2\text{-}\mu_2SAc)_2(\eta^2\text{-}\mu_2\text{-}BuO)_4(\eta^2\text{-}\mu_2BuO)_2\text{-}(\mu_3\text{-}O)_2$ (Hf4S): To $Hf(OnBu)_4$ (1.61 g, 3.4 mmol, 95% in a *n*BuOH solution) was added thioacetic acid (0.98 mL, 13.7 mmol) at room temperature to obtain an alkoxide/thiocarboxylic acid in a molar ratio of 1:4. The reaction mixture was then allowed to stand at 278 K for 9 d, which results in the separation of pale-brown, needle-shaped crystals suitable for X-ray single crystal analysis. The crystals are soluble in acetone, benzene and DMSO. Elemental analysis gave irreproducible data because of the reaction of Hf4S with atmospheric water.

Crystallographic Data for Hf4S: $C_{18}H_{36}Hf_2O_7S_3$, $M = 817.63$, monoclinic, $P2_1/c$ ($Z = 4$), $a = 14.6784(9)$ Å, $b = 22.423(1)$ Å, $c = 8.5935(5)$ Å, $\beta = 104.604(3)°$, $V = 2737.0(3)$ Å^3, $T = 150(2)$ K, 33823 data collected on a Bruker CCD diffractometer of which 7031 were unique ($R_{int} = 0.0244$), full matrix least-squares refinement (based on F^2) by using ADPs for all atoms, except the hydrogen atoms (in calculated positions), which were treated as riding atoms, final $R_1 = 0.0251$ [$I \geq 2\sigma(I)$] and 271 refined parameters.

NMR Analysis for HfSAc4: ν_o (^{1}H) 400.13 MHz; ν_o (^{13}C) 100.61 MHz; solvent [D$_6$]acetone; $T = 298$ K; δ from internal Me_4Si. Core-bonded *n*-butoxy groups (all resonances broadened): ^{1}H, δ = 0.95, 1.28, 1.51, 4.3 ppm; ^{13}C: δ = 14.7, ca. 20, 32.7, 65.9 ppm. Thioacetate groups (all resonances very broad): ^{1}H, 2.4–2.6 ppm; ^{13}C, 35.9 (CH_3), and 220–240 (thiocarbonyl) ppm.

Supporting Information (see also the footnote on the first page of this article): Crystallographic data and details of the NMR analysis are presented.

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[1] a) I. Dance, K. Fisher in *Inorganic Chemistry* (Ed.: K. D. Karlin), J. Wiley & Sons Inc., Interscience Pub., New York, **1994**; b) J. Niu, H. Zheng, H. Hou, X. Xin, *Coord. Chem. Rev.* **2004**, *248*, 169–183; c) F. Devillanova (Ed.), *Handbook of Chalcogen Chemistry: New Perspectives in Sulfur, Selenium and Tellurium*, Royal Society of Chemistry, London, **2006**.

[2] a) U. Schubert, *J. Mater. Chem.* **2005**, *15*, 3701–3715; b) U. Schubert, *J. Sol-Gel Sci. Technol.* **2004**, *31*, 19–24; c) U. Schubert, *Macromol. Symp.* **2008**, *267*, 1–8 and references cited therein; d) G. Kickelbick, M. P. Feth, H. Bertagnolli, M. Puchberger, D. Holzinger, S. Gross, *J. Chem. Soc., Dalton Trans.* **2002**, 3892–3898.

[3] A. Albinati, F. Faccini, S. Gross, G. Kickelbick, S. Rizzato, E. Tondello, A. Venzo, *Inorg. Chem.* **2007**, *46*, 3459–3466.

[4] a) F. Faccini, H. Fric, U. Schubert, E. Wendel, O. Tsetsgee, M. Klaus, H. Bertagnolli, A. Venzo, S. Gross, *J. Mater. Chem.* **2007**, *17*, 3297–3307; b) G. Trimmel, S. Gross, G. Kickelbick, U. Schubert, *Appl. Organomet. Chem.* **2001**, *15*, 406.

[5] S. Gross, G. Kickelbick, M. Puchberger, U. Schubert, *Monatsh. Chem.* **2003**, *134*, 1053–1063.

[6] R. Y. Qi, J. D. Corbett, *Inorg. Chem.* **1994**, *33*, 5727–5732.

[7] A. Herzog, H. W. Roesky, F. Jaeger, A. Steiner, M. Noltemeyer, *Organometallics* **1996**, *15*, 909–917.

[8] a) S. J. Dalgarno, J. L. Atwood, C. L. Raston, *Inorg. Chim. Acta* **2007**, *360*, 1344–1348; b) A. Otero, J. Fernandez-Baeza, A. Antinolo, J. Tejeda, A. Lara-Sanchez, L. Sanchez-Barba, M. Fernandez-Lopez, I. López-Solera, *Inorg. Chem.* **2004**, *43*, 1350–1358.

[9] M. Puchberger, F. R. Kogler, M. Jupa, S. Gross, H. Fric, G. Kickelbick, U. Schubert, *Eur. J. Inorg. Chem.* **2006**, *16*, 3283–3293.

[10] H. Balz, H. Kopf, J. Pickardt, *J. Organomet. Chem.* **1991**, *417*, 397–406.

[11] O. M. Kekia, A. L. Rheingold, *Organometallics* **1997**, *16*, 5142–5147.

[12] D. Wisniewska, Z. Janas, P. Sobota, L. B. Jerzykiewicz, *Organometallics* **2006**, *25*, 6166–6169.

[13] Z. Janas, D. Godbole, T. Nerkowsi, K. Szczegot, *Dalton Trans.* **2009**, 8846–8853.

[14] K. Abu-Dari, K. N. Raymond, *Inorg. Chem.* **1982**, *21*, 1679–1680.

[15] J. Martin, J. Takats, *Can. J. Chem.* **1975**, *53*, 572–576.

[16] S. D. Robertson, A. M. Z. Slawin, J. D. Woollins, *Polyhedron* **2006**, *25*, 823–826.

[17] J. Martin, J. Takats, *Can. J. Chem.* **1989**, *67*, 1914–1923.

[18] L. Gelmini, D. W. Stephan, *Organometallics* **1987**, *6*, 1515–1522.

[19] R. Hart, W. Levason, B. Patel, G. Reid, *J. Chem. Soc., Dalton Trans.* **2002**, 3153–3159.

[20] C. Capacchione, A. Proto, H. Ebeling, R. Mülhaupt, K. Möller, T. P. Spaniol, J. Okuda, *J. Am. Chem. Soc.* **2003**, *125*, 4964–4965.

[21] V. W. W. Yam, G. Z. Qi, K. K. Cheung, *Organometallics* **1998**, *17*, 5448–5453.

[22] T. D. Tilley, *Organometallics* **1985**, *4*, 1452–1457.

[23] B. Cordero, V. Gomez, A. E. Platero-Platz, M. Reves, J. Echevarria, E. Cremados, F. Barragan, S. Alvarez, *Dalton Trans.* **2008**, 2832.

[24] F. Maratini, L. Pandolfo, M. Bendova, U. Schubert, M. Bauer, M. Rocchia, A. Venzo, E. Tondello, S. Gross, *Inorg. Chem.* **2011**, *50*, 489–502.

[25] J. A. Jackson in *User's Guide to Principal Components Analysis*, Wiley, New York, **1991**.

[26] L. Tasic, R. Rittner, *J. Mol. Struct.* **2009**, *933*, 15–19.

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