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[TeSe₃]²⁻ as a tridentate ligand: syntheses and crystal structures of [PPh₄][(CpM(μ₂-Se₂))₃(μ₃-O)(μ₃-TeSe₃)] (M = Zr, Hf)

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Dedicated with fondness to my good friend Francis Sécheresse on the occasion of his sixtieth birthday (JAI)

Abstract

The isostructural compounds [PPh₄][(CpM(μ₂-Se₂))₃(μ₃-O)(μ₃-TeSe₃)] (M = Zr, Hf) have been synthesized by the reactions of Na₂[TeSe₃] with Cp₂MCl₂ in N,N-dimethylformamide (DMF). The structure of the anion comprises a triangle of MCp groups bridged by μ₂-Se₂ groups and capped by a μ₃-TeSe₃ and a μ₃-O group. These compounds represent the first examples of the μ₃-TeSe₃²⁻ ligand capping a metal system. To cite this article: S.M. Dibrov, J.A. Ibers, C. R. Chimie 8 (2005).

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Résumé

Les composés isostructuraux [PPh₄][(CpM(μ₂-Se₂))₃(μ₃-O)(μ₃-TeSe₃)] (M = Zr, Hf) ont été synthétisés par réaction de Na₂[TeSe₃] avec Cp₂MCl₂ dans le N,N-diméthylformamide (DMF). La structure de l’anion comprend un triangle formé de groupes MCp pontés par des groupes μ₂-Se₂ et coiffés par un groupe μ₃-TeSe₃ et μ₃-O. Ces composés constituent les premiers exemples dans lesquels un ligand μ₃-TeSe₃²⁻ coiffe un système métallique. Pour citer cet article : S.M. Dibrov, J.A. Ibers, C. R. Chimie 8 (2005).

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Keywords: Crystal structure; Hafnium; Heteropolychalcogenides; Trinuclear cluster; Zirconium

Mots clés : Clusters trinucléaires ; Hafnium ; Hétéropolychalcogénures ; Structure cristalline ; Zirconium

1. Introduction

The study of heteropolychalcogenide anions has developed largely during the last decade [1–7]. In particular, the Te/Se system includes the [TeSe₂]²⁻ [4], [TeSe₃]²⁻ [2,4], [Te(Se₂)₂]²⁻ [8], [Te(Se₃)₃]¹⁻ [9], [(Te(Se₂)₂)(μ₂-Te(Se₂))²⁻ [9], and [Te₃Se₆]²⁻ [10] anions. Some of these anions should be able to ligate metal systems. Surprisingly, there are only a few such examples known. These include the species [Hg(TeSe₂)₂]²⁻ [11], [Au(TeSe₂)]²⁻ [12], [Au-
Here we describe the preparation and structural characterization of the new compounds $[\text{PPh}_4][\text{CpM}(\mu_2-\text{Se}_2)]_3(\mu_3-O)(\mu_3-\text{TeSe}_3)$ ($M = \text{Zr}, \text{Hf}$), in which $\text{TeSe}_3^{2-}$ groups act as tridentate ligands to form three $\text{M–Se}$ bonds.

2. Preparation

2.1. General procedures

All experiments were carried out under an $N_2$ atmosphere with the use of Schlenk-line techniques. $\text{Na}_2[\text{TeSe}_3]$ was synthesized by the reaction of stoichiometric quantities of the elements in liquid $\text{NH}_3$. Te powder and Se powder were purchased from Aldrich Chemical Co., Milwaukee, Wisconsin and Cerac, Inc., Milwaukee, Wisconsin, respectively, and used as received. $\text{Cp}_2\text{ZrCl}_2$ and $\text{Cp}_2\text{HfCl}_2$ were purchased from Strem Chemicals, Inc., Newburyport, Maine. Anhydrous $\text{Et}_2\text{O}$ from Fisher Chemicals, Inc., Fair Lawn, NJ was dried over $\text{Na/benzophenone}$; $\text{N,N}$-dimethylformamide (DMF) from Fisher Chemicals, Inc. was dried over molecular sieves.

2.2. Synthesis of $[\text{PPh}_4][\text{CpM}(\mu_2-\text{Se}_2)]_3(\mu_3-O)(\mu_3-\text{TeSe}_3)$ ($M = \text{Zr}, \text{Hf}$)

$\text{Na}_2[\text{TeSe}_3]$ (100 mg, 0.26 mmol) was dissolved in 5 ml of DMF. To this brown solution 88 mg (0.30 mmol) of solid $\text{Cp}_2\text{ZrCl}_2$ or 115 mg (0.30 mmol) of $\text{Cp}_2\text{HfCl}_2$ was added. The resulting solution was stirred under an $N_2$ atmosphere for 5 h. Then 126 mg (0.30 mmol) of solid $[\text{PPh}_4]\text{Br}$ was added to the solution. The solution was stirred for an additional hour and then filtered through a cannula. Next 3 ml of this solution was transferred into a glass tube (5 mm diameter) that had been evacuated and filled with $N_2$. Then the solution was carefully layered with 5 ml of $\text{Et}_2\text{O}$ and the tube was sealed with a rubber septum and parafilm. In 5 days, several orange crystals of $[\text{PPh}_4][\text{CpM}(\mu_2-\text{Se}_2)]_3(\mu_3-O)(\mu_3-\text{TeSe}_3)$ ($M = \text{Zr}, \text{Hf}$), suitable for X-ray diffraction studies, were obtained. This synthesis was subsequently repeated several times to afford the same products.

3. X-ray structure determinations

Single-crystal X-ray diffraction data were collected with the use of graphite-monochromatized Mo K $\alpha$ radiation ($\lambda = 0.71073$ Å) at 153 K on a Bruker Smart-1000 CCD diffractometer [14]. The crystal-to-detector distance was 5.023 cm. Crystal decay was monitored by recollecting 50 initial frames at the end of data collection. Data were collected by a scan of 0.3° in $\omega$ in four sets of 606 frames at $\varphi$ settings of 0, 90, 180, and 270°. The exposure times were 15 s per frame. The collection of the intensity data was carried out with the program SMART [14] and face-indexed absorption corrections were performed numerically with the use of the program XPREP [15]. Then the program SADABS [14] was employed to make incident beam and decay corrections.

The structures were solved with the direct methods program SHELXS and refined with the full-matrix least-squares program SHELXL of the SHELXTL suite of programs [15]. Hydrogen atoms were generated in calculated positions and constrained with the use of a riding model. Additional details may be found in Section 5.

4. Results and discussion

Reaction of $\text{Na}_2[\text{TeSe}_3]$ with $\text{Cp}_2\text{ZrCl}_2$ or $\text{Cp}_2\text{HfCl}_2$ in DMF followed by slow addition of $\text{Et}_2\text{O}$ afforded orange plates of $[\text{PPh}_4][\text{CpM}(\mu_2-\text{Se}_2)]_3(\mu_3-O)(\mu_3-\text{TeSe}_3)$ ($M = \text{Zr}, \text{Hf}$), respectively. The yields of these compounds were too low to enable chemical or spectroscopic analyses to be performed. Consequently, their characterization rests entirely on the single-crystal structural analyses. The $\mu_3$ capping atom was assigned to $O$ because of the known oxophilicity of $\text{Zr}$ and $\text{Hf}$, the resultant sensible $\text{M–O}$ distances, and the reasonable displacement parameters. Thus, we believe there is a $\mu_3$-$O$ cap present in both structures even though the reactions were carried out in the presumed absence of a source of oxygen, other than $\text{Et}_2\text{O}$. Attempts have been made to increase the yields of these compounds by introducing an oxygen source, such as $\text{O}_2$, water, hydrogen peroxide, or $m$-chloroperbenzoic acid, into the syntheses. These attempts were unsuccessful. Moreover, when $\text{Et}_2\text{O}$ was added under anaerobic conditions and the reaction flask was sealed with a glass stopper no product was obtained. Thus, we have no explanation for the source of the oxygen. However, it is not unusual to have
adventitious sources of oxygen produce novel chemical compounds [16–21].

Selected crystallographic data are presented in Table 1. The structure of \([\text{PPh}_4][(\text{Cp} \text{Zr}(\mu_2-\text{Se}_2))_3(\mu_3-\text{O})(\mu_3-\text{TeSe}_3)]\) comprises well-separated cations and anions. The metrical features of the cation are normal. The \([(\text{Cp} \text{Zr}(\mu_2-\text{Se}_2))_3(\mu_3-\text{O})(\mu_3-\text{TeSe}_3)]–\) anion is depicted in Fig. 1 and the structure of its \([(\text{Zr}(\mu_2-\text{Se}_2))_3(\mu_3-\text{O})(\mu_3-\text{TeSe}_3)]–\) core is shown in Fig. 2. Selected bond distances and angles for both compounds are summarized in Table 2. The structure of the anion comprises a triangle of what are formally MCp$_3^+$ groups bridged by three $\mu_2$-Se$_2^2–$ ligands and capped by a $\mu_3$-O$_2^–$ ligand. The mean M···M distances of about 3.56 Å are longer than those found

![Fig. 1. Structure of the anion of \([\text{PPh}_4][(\text{Cp} \text{Zr}(\mu_2-\text{Se}_2))_3(\mu_3-\text{O})(\mu_3-\text{TeSe}_3)]\). The displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.](image)

![Fig. 2. Sketch of the \([(\text{Zr}(\mu_2-\text{Se}_2))_3(\mu_3-\text{O})(\mu_3-\text{TeSe}_3)]–\) core of \([\text{PPh}_4][(\text{Cp} \text{Zr}(\mu_2-\text{Se}_2))_3(\mu_3-\text{O})(\mu_3-\text{TeSe}_3)]\).](image)
in other M₃ or M₆ clusters (range 3.22–3.52 Å) where M–M bonds have been assigned [22,23]. The capping O atom lies above the M₃ plane by 0.441 Å (M = Zr) or 0.422 Å (M = Hf). The (µ₃-O)M₃ unit is a common one [24–34]. In these compounds the range of Zr–O distances in the (µ₃-O)Zr₃ core is 2.004–2.336 Å and the range of Hf–O distances in the (µ₃-O)Hf₃ core is 2.018–2.086 Å; thus, the M–O distances in Table 2 are typical. Also typical are the M–Se distances involving the µ₂-Se₂ ligands and the Se–Se distances in those ligands. As can be seen from Table 2, in general the M–Se distances to the TeSe₃ capping groups are longer than are the M–(µ₂-Se₂) distances.

These compounds represent the first examples of the µ₃-TeSe₃⁻ ligand. As would be expected, the Te–Se distances within the TeSe₃ cap are slightly longer than those reported for the [TeSe₃]⁻ anion in [K{2,2,2-crypt}][TeSe₃] (2.454(4) – 2.465(4) Å) [4]. We anticipate that the [TeSe₃]⁻ anion will be a useful capping ligand for trinuclear metal clusters in addition to those of Zr and Hf.

### 5. Supplementary material available

Crystallographic data in CIF format for [PPh₄][((CpZr(µ₂-Se₂))₃(µ₁-O)(µ₁-TeSe₃))] (CCDC 238937) and [PPh₄][((CpHf(µ₂-Se₂))₃(µ₁-O)(µ₁-TeSe₃))] (CCDC 238938). This material is available free of charge from Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge, CB2 1EZ, UK. Tel.: +44-1223-336408; fax: +44-1223-336033. E-mail: data_request@ccdc.cam.ac.uk.

### Table 2

Selected bond distances (Å) and angles (deg) for [PPh₄][((CpZr(µ₂-Se₂))₃(µ₁-O)(µ₁-TeSe₃))] and [PPh₄][((CpHf(µ₂-Se₂))₃(µ₁-O)(µ₁-TeSe₃))]

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Acknowledgments

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