



Preliminary communication / Communications

$[\text{TeSe}_3]^{2-}$ as a tridentate ligand: syntheses and crystal structures of $[\text{PPh}_4][(\text{CpM}(\mu_2\text{-Se}_2))_3(\mu_3\text{-O})(\mu_3\text{-TeSe}_3)]$ (M = Zr, Hf)

Sergey M. Dibrov, James A. Ibers *

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208-3113, USA

Received 27 May 2004; accepted after revision 8 October 2004

Available online 23 February 2005

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

Abstract

The isostructural compounds $[\text{PPh}_4][(\text{CpM}(\mu_2\text{-Se}_2))_3(\mu_3\text{-O})(\mu_3\text{-TeSe}_3)]$ (M = Zr, Hf) have been synthesized by the reactions of $\text{Na}_2[\text{TeSe}_3]$ with Cp_2MCl_2 in *N,N*-dimethylformamide (DMF). The structure of the anion comprises a triangle of MCp groups bridged by $\mu_2\text{-Se}_2$ groups and capped by a $\mu_3\text{-TeSe}_3$ and a $\mu_3\text{-O}$ group. These compounds represent the first examples of the $\mu_3\text{-TeSe}_3^{2-}$ ligand capping a metal system. **To cite this article :** *S.M. Dibrov, J.A. Ibers, C. R. Chimie 8 (2005).*

© 2005 Académie des sciences. Published by Elsevier SAS. All rights reserved.

Résumé

Les composés isostructuraux $[\text{PPh}_4][(\text{CpM}(\mu_2\text{-Se}_2))_3(\mu_3\text{-O})(\mu_3\text{-TeSe}_3)]$ (M = Zr, Hf) ont été synthétisés par réaction de $\text{Na}_2[\text{TeSe}_3]$ avec Cp_2MCl_2 dans le *N,N*-diméthylformamide (DMF). La structure de l'anion comprend un triangle formé de groupes MCp pontés par des groupes $\mu_2\text{-Se}_2$ et coiffés par un groupe $\mu_3\text{-TeSe}_3$ et $\mu_3\text{-O}$. Ces composés constituent les premiers exemples dans lesquels un ligand $\mu_3\text{-TeSe}_3^{2-}$ coiffe un système métallique. **Pour citer cet article :** *S.M. Dibrov, J.A. Ibers, C. R. Chimie 8 (2005).*

© 2005 Académie des sciences. Published by Elsevier SAS. All rights reserved.

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

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

1. Introduction

The study of heteropolychalcogenide anions has developed largely during the last decade [1–7]. In par-

ticular, the Te/Se system includes the $[\text{TeSe}_2]^{2-}$ [4], $[\text{TeSe}_3]^{2-}$ [2,4], $[\text{Te}(\text{Se}_5)_2]^{2-}$ [8], $[\text{Te}(\text{Se}_5)_3]^{4-}$ [9], $[\{\text{Te}(\text{Se}_2)_2\}_2(\mu_2\text{-Se}_2)]^{2-}$ [9], and $[\text{Te}_3\text{Se}_6]^{2-}$ [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 $[\text{Hg}(\text{Te}_2\text{Se}_2)_2]^{2-}$ [11], $[\text{Au}(\text{TeSe}_2)_2]^{2-}$ [12], $[\text{Au}$

* Corresponding author.

E-mail address: ibers@chem.northwestern.edu (J.A. Ibers).

(TeS₃)₂²⁻ [13], and [(Ag(TeQ₃))₂Te]²⁻ (Q = S, Se) [13]. Here we describe the preparation and structural characterization of the new compounds [PPh₄][(CpM(μ₂-Se₂))₃(μ₃-O)(μ₃-TeSe₃)] (M = Zr, Hf), in which TeSe₃²⁻ groups act as tridentate ligands to form three M–Se bonds.

2. Preparation

2.1. General procedures

All experiments were carried out under an N₂ atmosphere with the use of Schlenk-line techniques. Na₂[TeSe₃] was synthesized by the reaction of stoichiometric quantities of the elements in liquid NH₃. Te powder and Se powder were purchased from Aldrich Chemical Co., Milwaukee, Wisconsin and Cerac, Inc., Milwaukee, Wisconsin, respectively, and used as received. Cp₂ZrCl₂ and Cp₂HfCl₂ were purchased from Strem Chemicals, Inc., Newburyport, Maine. Anhydrous Et₂O from Fisher Chemicals, Inc., Fair Lawn, NJ was dried over Na/benzophenone; *N,N*-dimethylformamide (DMF) from Fisher Chemicals, Inc. was dried over molecular sieves.

2.2. Synthesis of [PPh₄][(CpM(μ₂-Se₂))₃(μ₃-O)(μ₃-TeSe₃)] (M = Zr, Hf)

Na₂[TeSe₃] (100 mg, 0.26 mmol) was dissolved in 5 ml of DMF. To this brown solution 88 mg (0.30 mmol) of solid Cp₂ZrCl₂ or 115 mg (0.30 mmol) of Cp₂HfCl₂ was added. The resulting solution was stirred under an N₂ atmosphere for 5 h. Then 126 mg (0.30 mmol) of solid [PPh₄]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 N₂. Then the solution was carefully layered with 5 ml of Et₂O and the tube was sealed with a rubber septum and parafilm. In 5 days, several orange crystals of [PPh₄][(CpM(μ₂-Se₂))₃(μ₃-O)(μ₃-TeSe₃)] (M = Zr, 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 α

radiation (λ = 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 ω in four sets of 606 frames at φ 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]. Cell refinement and data reduction were carried out with the use of the program SAINT [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 Na₂[TeSe₃] with Cp₂ZrCl₂ or Cp₂HfCl₂ in DMF followed by slow addition of Et₂O afforded orange plates of [PPh₄][(CpZr(μ₂-Se₂))₃(μ₃-O)(μ₃-TeSe₃)] or [PPh₄][(CpHf(μ₂-Se₂))₃(μ₃-O)(μ₃-TeSe₃)], 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 μ₃ capping atom was assigned to O because of the known oxophilicity of Zr and Hf, the resultant sensible M–O distances, and the reasonable displacement parameters. Thus, we believe there is a μ₃-O cap present in both structures even though the reactions were carried out in the presumed absence of a source of oxygen, other than Et₂O. Attempts have been made to increase the yields of these compounds by introducing an oxygen source, such as O₂, water, hydrogen peroxide, or *m*-chloroperoxybenzoic acid, into the syntheses. These attempts were unsuccessful. Moreover, when Et₂O 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

Table 1

Selected crystallographic data for $[\text{PPh}_4][(\text{CpZr}(\mu_2\text{-Se}_2))_3(\mu_3\text{-O})(\mu_3\text{-TeSe}_3)]$ and $[\text{PPh}_4][(\text{CpHf}(\mu_2\text{-Se}_2))_3(\mu_3\text{-O})(\mu_3\text{-TeSe}_3)]$

	Zr	Hf
Formula	$\text{C}_{39}\text{H}_{35}\text{OPSe}_9\text{TeZr}_3$	$\text{C}_{39}\text{H}_{35}\text{Hf}_3\text{OPSe}_9\text{Te}$
Formula weight	1662.54	1924.35
Crystal system	Monoclinic	Monoclinic
Space group	$\text{P}2_1/n$	$\text{P}2_1/n$
a (Å)	11.1427(9)	11.1457(16)
b (Å)	29.041(2)	29.092(4)
c (Å)	14.5717(12)	14.642(2)
β (°)	111.1600(10)	111.333(2)
V (Å ³)	4397.5(6)	4422.5(11)
T (K)	153	153
Z	4	4
ρ_{calc} (g cm ⁻³)	2.511	2.89
μ (MoK α) (mm ⁻¹)	8.866	15.146
$R_1(F_o)$ ($F_o^2 > 2\sigma(F_o^2)$) ^a	0.0432	0.039
$wR(F_o^2)$ ^b	0.081	0.091

$$^a R_1(F_o) = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR(F_o^2) = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum wF_o^4} \right]^{1/2}; w^{-1} = \sigma^2(F_o^2) + (qF_o^2)^2 \text{ for } F_o^2 > 0; w^{-1} = \sigma^2(F_o^2) \text{ for } F_o^2 \leq 0; q = 0.0246 \text{ for Zr; } 0.0227 \text{ for Hf.}$$

adventitious sources of oxygen produce novel chemical compounds [16–21].

Selected crystallographic data are presented in Table 1. The structure of $[\text{PPh}_4][(\text{CpM}(\mu_2\text{-Se}_2))_3(\mu_3\text{-O})(\mu_3\text{-TeSe}_3)]$ ($M = \text{Zr, Hf}$) comprises well-separated cations and anions. The metrical features of the cation are normal. The $[(\text{CpZr}(\mu_2\text{-Se}_2))_3(\mu_3\text{-O})(\mu_3\text{-TeSe}_3)]^-$

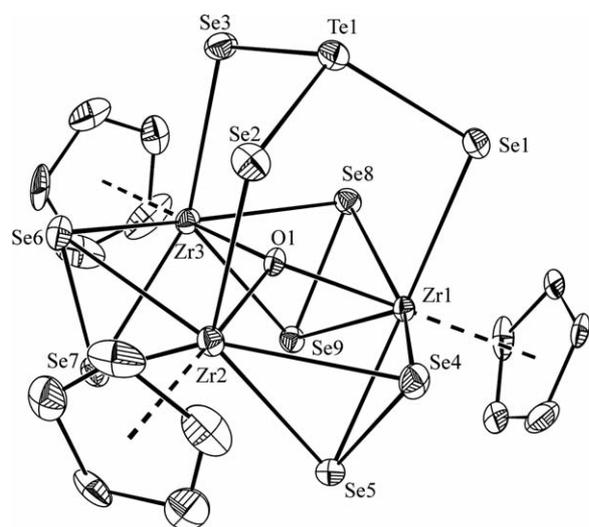


Fig. 1. Structure of the anion of $[\text{PPh}_4][(\text{CpZr}(\mu_2\text{-Se}_2))_3(\mu_3\text{-O})(\mu_3\text{-TeSe}_3)]^-$. The displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

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 $\mu_2\text{-Se}_2^{2-}$ ligands and capped by a $\mu_3\text{-TeSe}_3^{2-}$ and a $\mu_3\text{-O}^{2-}$ ligand. The mean $M\cdots M$ distances of about 3.56 Å are longer than those found

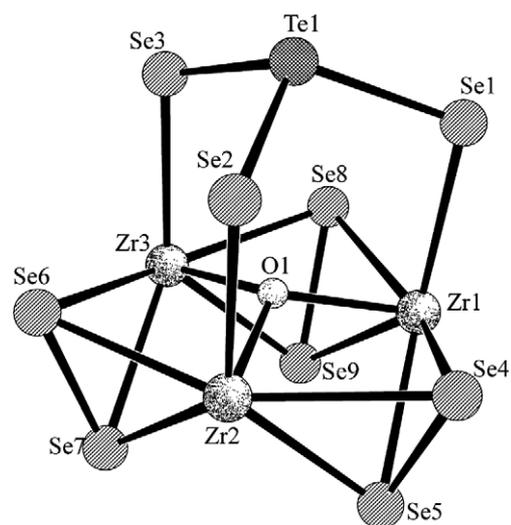


Fig. 2. Sketch of the $[(\text{Zr}(\mu_2\text{-Se}_2))_3(\mu_3\text{-O})(\mu_3\text{-TeSe}_3)]$ core of $[\text{PPh}_4][(\text{CpZr}(\mu_2\text{-Se}_2))_3(\mu_3\text{-O})(\mu_3\text{-TeSe}_3)]^-$.

Table 2

Selected bond distances (Å) and angles (deg) for [PPh₄][(CpZr(μ₂-Se₂))₃(μ₃-O)(μ₃-TeSe₃)] and [PPh₄][(CpHf(μ₂-Se₂))₃(μ₃-O)(μ₃-TeSe₃)]

	Zr		Hf
Zr(1)···Zr(2)	3.5604(10)	Hf(1)... Hf(2)	3.5610(6)
Zr(1)···Zr(3)	3.5760(10)	Hf(1)... Hf(3)	3.5452(6)
Zr(2)···Zr(3)	3.5677(10)	Hf(2)...Hf(3)	3.5499(6)
Zr(1)–O(1)	2.099(5)	Hf(1)–O(1)	2.093(5)
Zr(2)–O(1)	2.112(4)	Hf(2)–O(1)	2.098(5)
Zr(3)–O(1)	2.109(4)	Hf(3)–O(1)	2.090(5)
Te(1)–Se(1)	2.4868(9)	Te(1)–Se(1)	2.4915(10)
Te(1)–Se(2)	2.4867(9)	Te(1)–Se(2)	2.4799(11)
Te(1)–vSe(3)	2.4809(9)	Te(1)–Se(3)	2.4912(10)
Se(1)–Zr(1)	2.8089(10)	Se(1)–Hf(1)	2.7871(9)
Se(2)–Zr(2)	2.8059(10)	Se(2)–Hf(2)	2.7744(9)
Se(3)–Zr(3)	2.7953(11)	Se(3)–Hf(3)	2.7850(9)
Se(4)–Zr(1)	2.7833(10)	Se(4)–Hf(1)	2.7472(10)
Se(4)–Zr(2)	2.7778(10)	Se(4)–Hf(2)	2.7582(10)
Se(5)–Zr(1)	2.7706(11)	Se(5)–Hf(1)	2.7569(9)
Se(5)–Zr(2)	2.7563(10)	Se(5)–Hf(2)	2.7662(9)
Se(6)–Zr(2)	2.7900(10)	Se(6)–Hf(2)	2.7609(9)
Se(6)–Zr(3)	2.7737(10)	Se(6)–Hf(3)	2.7770(9)
Se(7)–Zr(2)	2.7641(10)	Se(7)–Hf(2)	2.7493(9)
Se(7)–Zr(3)	2.7584(10)	Se(7)–Hf(3)	2.7507(9)
Se(8)–Zr(1)	2.7611(10)	Se(8)–Hf(1)	2.7672(10)
Se(8)–Zr(3)	2.7702(11)	Se(8)–Hf(3)	2.7670(9)
Se(9)–Zr(1)	2.7728(10)	Se(9)–Hf(1)	2.7606(9)
Se(9)–Zr(3)	2.7751(10)	Se(9)–Hf(3)	2.7467(9)
Se(4)–Se(5)	2.3464(11)	Se(4)–Se(5)	2.3637(12)
Se(6)–Se(7)	2.3601(10)	Se(6)–Se(7)	2.3704(11)
Se(8)–Se(9)	2.3507(11)	Se(8)–Se(9)	2.3544(12)
Se(2)–Te(1)–Se(1)	107.40(3)	Se(2)–Te(1)–Se(1)	107.12(4)
Se(3)–Te(1)–Se(1)	107.29(3)	Se(3)–Te(1)–Se(1)	107.11(4)
Se(2)–Te(1)–Se(3)	108.35(3)	Se(2)–Te(1)–Se(3)	107.96(4)

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_(Te) distances to the TeSe₃ capping groups are longer than are the M–(μ₂-Se₂) distances.

These compounds represent the first examples of the μ₃-TeSe₃²⁻ ligand. As would be expected, the Te–Se distances within the TeSe₃ cap are slightly longer than

those reported for the [TeSe₃]²⁻ anion in [K{2,2,2-crypt}][TeSe₃] (2.454(4)–2.465(4) Å) [4]. We anticipate that the [TeSe₃]²⁻ 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(μ₃-O)(μ₃-TeSe₃)] (CCDC 238937) and [PPh₄][(CpHf(μ₂-Se₂))₃(μ₃-O)(μ₃-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.

Acknowledgments

This work was supported in part by the US National Science Foundation under Grant CHE-9819385. This work made use of Central Facilities supported by the MRSEC program of the National Science Foundation (DMR00-76097) at the Materials Research Center of Northwestern University.

References

- [1] I.G. Zaitseva, T.N. Greiver, É.P. Sal'dau, *J. Appl. Chem. (Leningrad)* 44 (1971) 1502–1506.
- [2] R. Zagler, B. Eisenmann, *Z. Kristallogr.* 183 (1988) 193–200.
- [3] M. Björgvinsson, G.J. Schrobilgen, *Inorg. Chem.* 30 (1991) 2540–2547.
- [4] M. Björgvinsson, J.F. Sawyer, G.J. Schrobilgen, *Inorg. Chem.* 30 (1991) 4238–4245.
- [5] S.-P. Huang, S. Dhingra, M.G. Kanatzidis, *Polyhedron* 11 (1992) 1869–1875.
- [6] W. Bubenheim, G. Frenzen, U. Müller, *Z. Anorg. Allg. Chem.* 620 (1994) 1046–1050.
- [7] U. Müller, W. Bubenheim, *Z. Anorg. Allg. Chem.* 625 (1999) 1522–1526.
- [8] R. Zagler, B. Eisenmann, *Z. Naturforsch. B: Chem. Sci.* 46 (1991) 593–601.
- [9] M. Wachhold, W.S. Sheldrick, *J. Solid-State Chem.* 134 (1997) 364–375.
- [10] P. Sekar, J.A. Ibers, *Inorg. Chem.* 43 (2004) 5346–5441.
- [11] J.C. Bollinger, J.A. Ibers, *Inorg. Chem.* 34 (1995) 1859–1867.
- [12] S.M. Dibrov, J.A. Ibers, *Chem. Commun.* (2003) 2158–2159.
- [13] D.-Y. Chung, S.-P. Huang, K.-W. Kim, M.G. Kanatzidis, *Inorg. Chem.* 34 (1995) 4292–4293.
- [14] Bruker, SMART Version 5.054 Data Collection and SAINT-Plus Version 6.45 Data Processing Software for the SMART System, Bruker Analytical X-Ray Instruments, Inc., Madison, WI, USA, 2003.
- [15] G.M. Sheldrick, SHELXTL DOS/Windows/NT Version 6.14, Bruker Analytical X-Ray Instruments, Inc., Madison, WI, USA, 2003.
- [16] C.G. Pernin, J.A. Ibers, *Inorg. Chem.* 36 (1997) 3802–3803.
- [17] W.J. Evans, T.A. Ulibarri, L.R. Chamberlain, J.W. Ziller, D. Alvarez Jr., *Organometallics* 9 (1990) 2124–2130.
- [18] H. Schumann, G. Kociok-Köhn, J. Loebel, *Z. Anorg. Allg. Chem.* 581 (1990) 69–81.
- [19] D. Fenske, A. Grissinger, M. Loos, J. Magull, *Z. Anorg. Allg. Chem.* 598/599 (1991) 121–128.
- [20] H.C. Aspinall, M.R. Tillotson, *Inorg. Chem.* 35 (1996) 2163–2164.
- [21] L.R. Avens, D.M. Barnhart, C.J. Burns, S.D. McKee, *Inorg. Chem.* 35 (1996) 537–539.
- [22] S.I. Troyanov, *Russ. Chem. Bull.* 43 (1994) 130–135 (*Transl. Izv. Acad. Nauk. SSSR. Ser. Khim.*).
- [23] L. Chen, F.A. Cotton, W.T. Klooster, T.F. Koetzle, *J. Am. Chem. Soc.* 119 (1997) 12175–12183.
- [24] W. Braunwarth, U. Thewalt, *Z. Naturforsch. B: Chem. Sci.* 52b (1997) 1011–1018.
- [25] M. Grün, F. Weller, K. Dehnicke, *Z. Anorg. Allg. Chem.* 623 (1997) 224–230.
- [26] D. Walther, B. Ritter, H. Görls, G. Zahn, *Z. Anorg. Allg. Chem.* 623 (1997) 1125–1130.
- [27] G. Hidalgo, M.A. Pellinghelli, P. Royo, R. Serrano, A. Tiripicchio, *J. Chem. Soc., Chem. Commun.* (1990) 1118–1120.
- [28] W.J. Evans, M.A. Ansari, J.W. Ziller, *Polyhedron* 17 (1998) 869–877.
- [29] L.M. Babcock, V.W. Day, W.G. Klemperer, *Inorg. Chem.* 28 (1989) 806–810.
- [30] Z.A. Starikova, E.P. Turevskaya, N.I. Kozlova, N.Y. Turoa, D.V. Berdyev, A.I. Yanovsky, *Polyhedron* 18 (1999) 941–947.
- [31] G. Kickelbick, U. Schubert, *J. Chem. Soc., Dalton Trans* (1999) 1301–1305.
- [32] L.M. Babcock, V.W. Day, W.G. Klemperer, *J. Chem. Soc., Chem. Commun.* (1988) 519–520.
- [33] F. Boutonnet, M. Zablocka, A. Igau, J. Jaud, J.-P. Majoral, J. Schamberger, G. Erker, S. Werner, C. Krüger, *J. Chem. Soc., Chem. Commun.* (1995) 823–824.
- [34] J. Utiko, S. Pryzbylak, L.B. Jerzykiewicz, S. Szafert, P. Sobota, *Chem. Eur. J.* 9 (2003) 181–190.