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Bronze, silver and gold: functionalized group 11 organotin sulfide clusters†

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The synthesis, properties and reactivity of group 11 organotin sulfide clusters $[(R^1Sn)_4(SnCl)_2(MPPh_3)_2S_8]$ (M = Cu, Ag), $[(R^3Sn)_{10}Ag_{10}S_{20}]$, and $[(R^{1,3}Sn)_2(AuPPh_3)_2S_4]$ with covalently bound, carbonyl or hydrazine-terminated ligands R^1 = $CMe_2CH_2C(Me)O$ or R^3 = $CMe_2CH_2C(Me)NNH_2$ are reported.
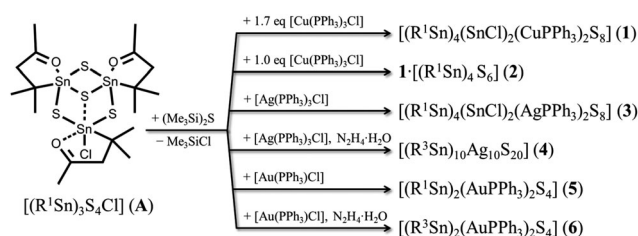
The last few decades have afforded a large variety of ligand-protected chalcogenide clusters of group 11 metals.[1] Ternary complexes and clusters were also reported,[2] which often combined structural and physical properties of the binary components.[3] Additionally, with regard to further reactivity, the introduction of functionalized phosphines was achieved.[4] Consequently, the combination of functional organic ligand shells with finely tunable (ternary or multinary) inorganic cores, providing even more diversity, is thus of interest for diverse purposes, such as for optoelectronics or solar cell development.[5] To address suitable functional materials, the synthesis and directed derivatization of clusters with covalently attached organic groups have currently been investigated in detail for polyoxometalates[6] as well as for group 14/16 compounds,[7] for instance.

The organic groups on the periphery of organogermanium and organotin sulfide complexes of the general type $[(R^fT)_xS_y]$ (R^f = functionalized organic ligand: R^1 = $CMe_2CH_2C(Me)O$, HR^2 = C_2H_4COOH; T = Ge, Sn; x/y = 4/6, 6/10) are reactive towards hydrazine derivatives, which allowed further derivatizations of the organic ligand shell.[8] Hereby, an extension of the ligand shell towards ligands such as R^3 = $CMe_2CH_2C(Me)NNH_2$, R^4 = $\{CMe_2CH_2C(Me)NNH\}_2CO$, or R^5 = $CMe_2CH_2C(Me)NNC(2-py)_2$ was achieved. Reactions with transition metal compounds additionally enabled the extension of the inorganic core to form the organofunctionalized ternary clusters $[(R^3T)_2(CuPR_3)_6S_6]$,[8] $[(R^2Sn)_6(OMe)_6Cu_2S_6]^{4-}$,[8] $[(R^3Ge)_4Pd_6S_{12}]$[9] and $[R^4{}_2\{Sn(\mu\text{-}S)_2\text{-}Cu(PPh_2Me)\}_4]$.[10] Bispyridine-decorated clusters $[(R^5Sn)_4(ZnX)_4S_8]$ (X = Cl, Br, I) were obtained by slow diffusion of zinc halide solutions into solutions of the organotin sulfide cluster $[(R^5T)_6S_{10}]$.[11]

Further structurally characterized ternary group 11 metal/organotin sulfide clusters have so far been surrounded by unreactive organic groups, as in $[(PhSn)_2(CuPPh_2Me)_6S_6]$,[12] $[(PhSn)_{12}Cu_{19}(PEt_2Ph)_3S_{28}]^+$,[13] and the mixed-valence compound $[\{(CH_2)_4Sn^{IV}\}_6(CuPPh_3)_6Sn^{II}Cu_4S_{12}]$.[14] Ternary complexes containing Ag/Sn/S or Au/Sn/S cores have not been characterized yet using X-ray diffraction.‡

Recently we reported new functional organotin sulfide complexes of the type $[(R^{1,3}Sn)_3S_4Cl]$ that exhibit defect heterocubane scaffolds with carbonyl and hydrazone groups.[15] Herein, we show that these turned out to be suitable precursor complexes as well. $[(R^1Sn)_3S_4Cl]$ (**A**) reacts with the group 11 metal complexes $[Cu(PPh_3)_3Cl]$, $[Ag(PPh_3)_3Cl]$ and $[Au(PPh_3)Cl]$ in CH_2Cl_2 with $(Me_3Si)_2S$, in the case of Ag and Au complexes with subsequent *in situ* derivatization by hydrazine hydrate (Scheme 1), to yield single crystals of the following compounds comprising ternary clusters $[(R^1Sn)_4(SnCl)_2(CuPPh_3)_2S_8]\cdot4CH_2Cl_2$ (**1**·4CH$_2$Cl$_2$), **1**·$[(R^1Sn)_4S_6]$ (hereafter denoted as **2**), $[(R^1Sn)_4(SnCl)_2(CuPPh_3)_2S_8]\cdot[(R^1Sn)_4S_6]$ (**3**·$[(R^1Sn)_4S_6]$), $[(R^3Sn)_{10}Ag_{10}S_{20}]\cdot3.5CH_2Cl_2$ (**4**·3.5CH$_2$Cl$_2$), $[\{R^1Sn(\mu\text{-}S)\}_2\{AuPPh_3(\mu\text{-}S)\}_2]$ (**5**), and $[\{R^3Sn(\mu\text{-}S)\}_2\text{-}\{AuPPh_3(\mu\text{-}S)\}_2]\cdot5CH_2Cl_2$ (**6**·5CH$_2$Cl$_2$). The clusters exhibit

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† Electronic supplementary information (ESI) available: Further details of syntheses, analyses, and crystallographic data/further figures for **1**–**6** and (Me$_3$Si)$_2$S. CCDC 1011096–1011102. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc05666c

Scheme 1 Synthesis of compounds **1**–**6** (R^1 = $CMe_2CH_2C(Me)O$, R^3 = $CMe_2CH_2C(Me)NNH_2$).
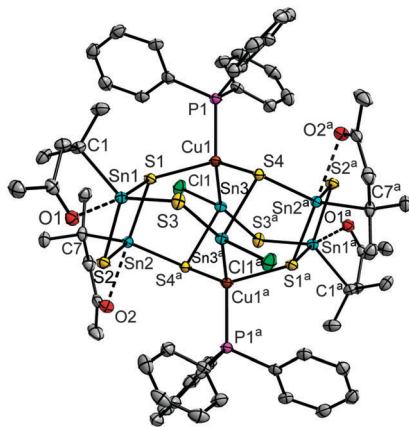
Fig. 1 Molecular structure of **1** without H atoms (ellipsoids drawn at 50% probability); a = 1−x, −y, −z. Selected structural parameter [Å, °]: Sn–S 2.3654(8)–2.5058(8), Sn(1,2)–C 2.183(3)–2.192(3), Sn(1,2)···O(1,2) 2.516(2)–2.537(2), Sn3–Cl1 2.4713(8), Sn3–Cu1 2.6054(4), Cu1–S(1,4) 2.3626(9)–2.3166(8), Cu1–P1 2.2590(8); Sn–S–Sn 86.57(2)–89.70(3), S–Sn–S 91.24(3)–121.81(3), Cu1–Sn3–S3^a 149.75(2), Cu1–Sn3–S4^a 107.60(2), Cl1–Sn3–Cu1 111.23(2), Cl1–Sn3–S3^a 90.20(3), Cl1–Sn3–S4^a 95.70(3), C–Sn–O 72.10(10)–73.71(10).

different topologies and compositions and comprise reactive substituents with either carbonyl or hydrazone groups. In addition, we report the single crystal X-ray diffraction analysis of (Me₃Si)₂S (see ESI†).

The reaction of **A** with 1.7 eq. [Cu(PPh₃)₃Cl] and (Me₃Si)₂S in CH₂Cl₂, and subsequent layering with *n*-hexane yielded [(R¹Sn)₄(SnCl)₂(CuPPh₃)₂S₈]·4CH₂Cl₂ (**1**·4CH₂Cl₂) as light yellow crystals. In the molecular structure of the cluster, two {R¹Sn(μ-S)-(μ₃-S)}₂ moieties are linked by two {(CuPPh₃)(SnCl)} units (see Fig. 1). The R¹Sn atoms Sn1 and Sn2 show a trigonal bipyramidal coordination environment, with the axial positions being occupied by O1, O2 and S1, whereas S2, S3 and C1 (Sn1) or S2, S4^a and C7 (Sn2) are situated in the equatorial positions. The μ₃-S-bridging atoms S1 and S4, and the μ-bridging atom S3 connect the {R¹Sn(μ-S)(μ₃-S)} moieties to the central part of the cluster. Here, Cu1 is surrounded in a tetrahedral fashion by a PPh₃ ligand, S1, S4 and Sn3. The latter has a formal oxidation state of +II and exhibits a distorted pseudo-trigonal bipyramidal environment, with Cu1 and S3^a in the "axial" positions (Cu1–Sn3–S3^a 149.75(2)°), and Cl1, S4^a and the sterically active lone pair in the "equatorial" positions; further pseudo-trigonal bipyramidal coordination geometries of Sn^{II} atoms have been described by Jurkschat and co-workers.[16] The mixed-valence situation in **1** was confirmed using DFT calculations (see below). As another peculiarity, **1** comprises a rare Cu–Sn bond (Cu1–Sn3 2.6054(4) Å), which was formed *in situ*.[17] It is not possible to monitor the formation process in detail due to the fairly complex reaction mixture and due to the poor solubility of the product. However, we assume that the reduction of RSn^{IV} to Sn^{II} comes along with the oxidation of the released organic ligand as discussed for the mixed valence compounds [(R^{1,3}Sn)₃Se₄][SnCl₃] under similar reaction conditions;[15] the oxidation of PPh₃ or Cu^I, however, was not observed under the reaction conditions, which was clarified using NMR studies and test for Cu^{2+} with NH₃.

The observation of formal Sn^{II} and Sn^{IV} atoms is in agreement with natural charges, obtained by natural population analyses (NPA)[18] of the DFT wave function, which was calculated by simultaneous optimization of the geometric and electronic structure using the program system TURBOMOLE.[19] The formal Sn^{IV} atoms exhibit charges of +1.38 and +1.47, which are larger than the +0.88 charge calculated for the formal Sn^{II} atoms by a factor of 1.6 to 1.7. Details of the DFT calculations are provided in the ESI.†

Neither variation of the stoichiometry of the starting materials nor attempts to replace the Cl⁻ ligand have led to the isolation of further clusters until now. An analogous reaction with 1.0 eq. [Cu(PPh₃)₃Cl], however, yielded **1**·[(R¹Sn)₄S₆] (**2**). The structural parameters of the two large co-crystallizing clusters in **2** are similar to those observed in **1**·4 CH₂Cl₂ (see ESI†) and [(R¹Sn)₄S₆].[20]

Upon reaction with [Ag(PPh₃)₃Cl] and (Me₃Si)₂S at −78 °C in CH₂Cl₂, and subsequent, careful warming-up to room temperature, a colorless precipitate was obtained, which was re-dissolved by addition of excess of CH₂Cl₂. Layering with *n*-hexane afforded [(R¹Sn)₄(SnCl)₂(AgPPh₃)₂S₈]·[(R¹Sn)₄S₆] (**3**·[(R¹Sn)₄S₆]) as light yellow crystals. The ternary cluster is isostructural to that in **2**, hence the structural parameters are similar to those observed in **1** or **2**, except the expected elongation of M–S, M–P and M–Sn bonds (Ag1–Sn3 2.6803(3) Å) for M = Ag in comparison with M = Cu, and a larger Sn–M–P angle (**1**: 115.40(3) for M = Cu, **3**: 131.23(2) for M = Ag). For the selected structural parameters and NPA results see the ESI.†

Addition of hydrazine hydrate to the re-dissolved solution, and subsequent layering with *n*-hexane produced orange crystals of the hydrazone functionalized cluster [(R³Sn)₁₀Ag₁₀S₂₀]·3.5CH₂Cl₂ (**4**·3.5CH₂Cl₂). **4** consists of three {R³Sn(μ-S)(μ₃-S)}₂ units and two {[R³Sn(μ-S)]₂(μ₃-S)(μ₄-S)} moieties that are linked by ten Ag atoms (see Fig. 2). All Sn atoms exhibit trigonal bipyramidal coordination, with N and S atoms in the axial positions. Four Ag atoms (Ag1, Ag5, Ag7, Ag10) are coordinated in a linear manner, while six other Ag atoms exhibit trigonal planar coordination. Closest Ag···Ag distances are in the range of 2.9353(7) Å to 3.3260(7) Å. Eight of the Ag atoms are connected this way, with a central butterfly-like arrangement and to adjacent Ag···Ag units, while one Ag···Ag unit is further apart. The cluster possesses pseudo-C_2-symmetry. The pseudo-C_2-axis runs through the centers of the Ag···Ag four-ring and the separate Ag···Ag dimer. In contrast to known silver sulfide clusters,[1a] the cluster does not additionally contain stabilizing phosphine groups attached to the silver atoms. N→Sn coordination of the bidentate organic ligands seems to provide sufficient kinetic stabilization.

The employment of a related gold complex, [Au(PPh₃)Cl], along with (Me₃Si)₂S in the reaction with **A** afforded single-crystals of the complex [{R¹Sn(μ-S)}₂{AuPPh₃(μ-S)}₂] (**5**). Moreover, addition of hydrazine hydrate to the reaction mixture yielded the hydrazone functionalized derivative [{R³Sn(μ-S)}₂-{AuPPh₃(μ-S)}₂]·5CH₂Cl₂ (**6**·5CH₂Cl₂) (see Fig. 3). In the present case, the derivatization of the organic ligand did not affect the molecular structure of the complex. In **5** and **6**, a central {R^{1,3}Sn(μ-S)}₂ unit (*cf.* ref. 21) is terminated by two {Au(PPh₃)(μ-S)} groups. As in **1–4**,
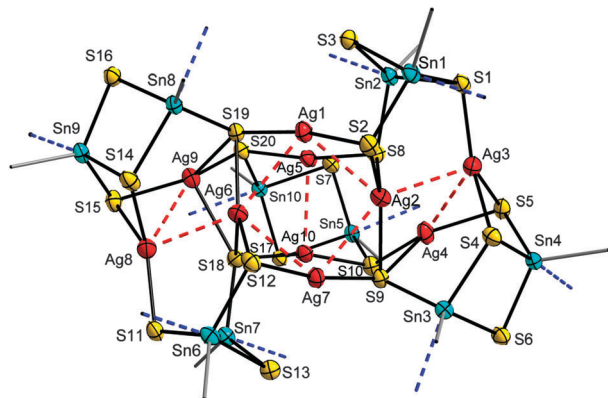
Fig. 2 Molecular structure of the inorganic core of **4** along the pseudo-C_2-axis (ellipsoids drawn at 50% probability, bonds to organic substituents are indicated by dashed lines). Ag···Ag contacts below 3.4 Å are drawn as dashed red lines. Selected structural parameters [Å, °]: Sn–S 2.3865(16)–2.5987(17), Sn–C 2.170(6)–2.187(7), Sn···N 2.362(5)–2.456(5), Ag–S 2.3666(16)–2.9040(16), Ag···Ag 2.9353(7)–3.3260(7); S–Sn–S 89.57(5)–122.29(6), S–Ag–S 83.47(5)–169.97(6), Sn–S–Sn 85.13(5)–89.69(5), Ag–S–Ag 72.65(5)–146.30(6), Ag–S–Sn 80.15(5)–144.91(7), C–Sn–N 71.6(2)–75.8(2).

organo-decorated Sn atoms exhibit a trigonal bipyramidal coordination environment, while all Au atoms show linear coordination. The structural parameters of the central part is similar in both complexes, but the orientation of the attached {Au(PPh$_3$)(μ-S)} units is different. In **5**, they point away from the central Sn$_2$S$_2$ ring, with a C1–Sn1–S2–Au1 *trans* arrangement, whereas in **6**, the corresponding atoms show a *cis* arrangement. While interatomic distances are similar in both complexes, the Sn1–S2–Au1 and S2–Au1–P1 angles show notable differences in both complexes, indicating the influence of the functional group included in the organic ligand.

In summary, a series of ternary group 11 organotin sulfide clusters have been synthesized and structurally characterized. The choice of the very group 11 metal M – although added as similar complexes [M(PPh$_3$)$_x$Cl] (M/x = Cu/3, Ag/3, Au/1) – causes specific coordination environments that affect the molecular structures.
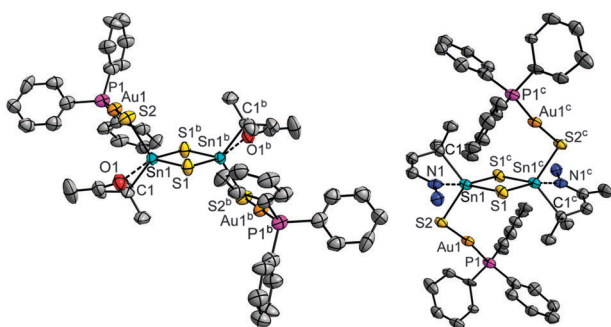

Fig. 3 Molecular structures of **5** (left) and **6** (right) without H atoms (ellipsoids drawn at 50% probability). b = −x, 2−y, 1−z; c = 2−x, 1−y, −z. Selected structural parameters [Å, °]: **5**: Sn–S 2.380(2)–2.463(2), Sn1–C1 2.189(8), Sn1···O1 2.714(6), Au1–S2 2.291(2), Au1–P1 2.260(2); Sn1–S1–Sn1^b 86.30(7), S1–Sn1–S1^b 93.70(7), Sn1–S2–Au1 96.63(9), S2–Au1–P1 178.29(9); **6**: Sn–S 2.389(3)–2.525(3), Sn1–C1 2.186(14), Sn1···N1 2.479(11), Au1–S2 2.298(3), Au1–P1 2.250(3); Sn1–S1–Sn1^c 89.06(11), S1–Sn1–S1^c 90.94(11), Sn1–S2–Au1 103.86(13), S2–Au1–P1 172.84(12).

Accordingly, the products exhibit different compositions and topologies. Unexpectedly, the reaction with the Cu and Ag precursor induced *in situ* reduction of one third of the Sn atoms under Sn–Cu and Sn–Ag bond formation. It was shown for the first time that a functionalized ternary M–Sn–S complex could undergo further derivatization.

Notes and references

‡ X-ray crystallographic data: Data collection on a STOE IPDS2 diffractometer using graphite-monochromatized Mo K$_\alpha$ radiation (λ = 0.71073 Å) at 100 K. Structure solution and refinement by direct methods and full matrix least-squares on F^2, respectively; SHELXTL software.[22]

1 (a) O. Fuhr, S. Dehnen and D. Fenske, *Chem. Soc. Rev.*, 2013, **42**, 1871; (b) D. Fenske, T. Langetepe, M. M. Kappes, O. Hampe and P. Weis, *Angew. Chem., Int. Ed.*, 2000, **39**, 1857.
2 (a) C. B. Khadka, A. Eichhöfer, F. Weigend and J. F. Corrigan, *Inorg. Chem.*, 2012, **51**, 2747; (b) C. Xu, J.-J. Zhang, Q. Chen, T. Duan, W.-H. Leung and Q.-F. Zhang, *Inorg. Chem. Commun.*, 2012, **21**, 1; (c) A. Eichhöfer, J. Olkowska-Oetzel, D. Fenske, K. Fink, V. Mereacre, A. K. Powell and G. Buth, *Inorg. Chem.*, 2009, **48**, 8977.
3 (a) D. Aldakov, A. Lefrançois and P. Reiss, *J. Mater. Chem. C*, 2013, **1**, 3756; (b) S. Dehnen and M. Melullis, *Coord. Chem. Rev.*, 2007, **251**, 1259.
4 (a) C. B. Khadka, B. K. Najafabadi, M. Hesari, M. S. Workentin and J. F. Corrigan, *Inorg. Chem.*, 2013, **52**, 6798; (b) W. Yu, O. Fuhr and D. Fenske, *J. Cluster Sci.*, 2012, **23**, 753; (c) R. Langer, B. Breitung, L. Wünsche, D. Fenske and O. Fuhr, *Z. Anorg. Allg. Chem.*, 2011, **637**, 995.
5 S. V. Kershaw, A. S. Susha and A. L. Rogach, *Chem. Soc. Rev.*, 2013, **42**, 3033.
6 A. Proust, B. Matt, R. Villanneau, G. Guillemot, P. Gouzerh and G. Izzet, *Chem. Soc. Rev.*, 2012, **41**, 7605.
7 (a) M. Wagner, T. Zoller, W. Hiller, M. H. Prosenc and K. Jurkschat, *Chem. Commun.*, 2013, **49**, 8925; (b) M. Bouška, L. Střižík, L. Dostál, A. Růžička, A. Lyčka, L. Beneš, M. Vlček, J. Přikryl, P. Knotek, T. Wágner and R. Jambor, *Chem. – Eur. J.*, 2013, **19**, 1877; (c) B. E. K. Barth, B. A. Tkachenko, J. P. Eußner, P. R. Schreiner and S. Dehnen, *Organometallics*, 2014, **33**, 1678.
8 Z. Hassanzadeh Fard, L. Xiong, C. Müller, M. Holynska and S. Dehnen, *Chem. – Eur. J.*, 2009, **15**, 6595.
9 M. R. Halvagar, Z. Hassanzadeh Fard, L. Xiong and S. Dehnen, *Inorg. Chem.*, 2009, **48**, 7373.
10 M. R. Halvagar, Z. H. Fard and S. Dehnen, *Chem. Commun.*, 2010, **46**, 4716.
11 B. E. K. Barth, E. Leusmann, K. Harms and S. Dehnen, *Chem. Commun.*, 2013, **49**, 6590.
12 R. Hauser and K. Merzweiler, *Z. Anorg. Allg. Chem.*, 2002, **628**, 905.
13 A. Eichhöfer, J. Jiang, S. Lebedkin, D. Fenske, D. G. McDonald, J. F. Corrigan and C. Y. Su, *Dalton Trans.*, 2012, **41**, 3321.
14 H. P. Nayek, W. Massa and S. Dehnen, *Inorg. Chem.*, 2008, **47**, 9146.
15 J. P. Eußner, B. E. Barth, E. Leusmann, Z. You, N. Rinn and S. Dehnen, *Chem. – Eur. J.*, 2013, **19**, 13792.
16 (a) M. Wagner, C. Dietz, S. Krabbe, S. G. Koller, C. Strohmann and K. Jurkschat, *Inorg. Chem.*, 2012, **51**, 6851; (b) *Tin Chemistry: Fundamentals, Frontiers, and Applications*, ed. A. G. Davies, M. Gielen, K. Pannell and E. Tiekink, Wiley, Hoboken, 2008.
17 Another example for the generation of formal Sn^{II} during cluster formation from a Sn^{IV} precursor was reported in ref. 14 for the compound [{(CH$_2$)$_4$Sn^{IV}}$_6$(CuPPh$_3$)$_6$Sn^{II}Cu$_4$S$_{12}$]. [[C$_4$H$_7$N$_2$S)$_6$SnCu$_4$] also exhibits Sn^{II}–Cu bonds, see R. E. Allan, A. Bashall, J. S. Palmer, M. McPartlin, M. E. G. Mosquera, J. M. Rawson, A. E. H. Wheatleya and D. S. Wright, *Chem. Commun.*, 1997, 1975.
18 A. E. Reed, R. B. Weinstock and F. Weinhold, *J. Phys. Chem.*, 1985, **83**, 735.
19 (a) TURBOMOLE Version 6.2, © TURBOMOLE GmbH 2011. TURBOMOLE is a development of University of Karlsruhe and Forschungszentrum Karlsruhe 1989–2007; Ridft program: (b) K. Eichkorn,

O. Treutler, H. Öhm, M. Häser and R. Ahlrichs, *Chem. Phys. Lett.*, 1995, **242**, 652; (*c*) K. Eichkorn, F. Weigend, O. Treutler and R. Ahlrichs, *Theor. Chem. Acc.*, 1997, **97**, 119; BP86 functional: (*d*) A. D. Becke, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1988, **38**, 3098; (*e*) S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.*, 1980, **58**, 1200; (*f*) J. P. Perdew, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, **33**, 8822; TZVP basis sets: (*g*) F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, 7, 3297; (*h*) F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057; ECPs: (*i*) B. Metz, H. Stoll and M. Dolg, *J. Chem. Phys.*, 2000, **113**, 2563.

20 Z. Hassanzadeh Fard, C. Müller, T. Harmening, R. Pöttgen and S. Dehnen, *Angew. Chem., Int. Ed.*, 2009, **48**, 4441.

21 K. Jurkschat, S. van Dreumel, G. Dyson, D. Dakternieks, T. J. Bastow, M. E. Smith and M. Dräger, *Polyhedron*, 1992, **11**, 2747.

22 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112.