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Short Communication

Synthesis of $[Tl_4Se_{16}]^{4-}$: a novel tetranuclear Tl^{3+} polyselenide

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Abstract

$(Ph_4P)_4[Tl_4Se_{16}]$ was prepared hydrothermally in a sealed pyrex tube by the reaction of TlCl, K_2Se_4 and Ph_4PCl in a 1:1:1 molar ratio at 110 °C for one day. The red crystals were obtained in 50% yield. Crystals of $(Ph_4P)_4[Tl_4Se_{16}]$: triclinic $P\bar{1}$ (No. 2), $Z=1$, $a=12.054(9)$, $b=19.450(10)$, $c=11.799(6)$ Å, $\alpha=104.63(4)$, $\beta=98.86(6)$, $\gamma=101.99(6)°$ and $V=2555(3)$ Å^3 at 23 °C, $2\theta_{max}=40.0°$, $\mu=120.7$ cm^{-1}, $D_{calc}=2.23$. The structure was solved by direct methods. Number of data collected: 5206. Number of unique data having $F_o^2>3\sigma(F_o^2)$: 1723. Final $R=0.075$ and $R_w=0.089$. $[Tl_4Se_{16}]^{4-}$ consists of four, almost already linearly arranged, tetrahedral thallium centers which are coordinated by two chelating Se_4^{2-}, two bridging Se_2^{2-} and four bridging Se^{2-} ligands. $[Tl_4Se_{16}]^{4-}$ sits on an inversion center and possesses a central $\{Tl_2Se_2\}^{2+}$ planar core. The Tl(1)–Tl(1)′ distance in this core is 3.583(6) Å. These two thallium atoms are then each linked to two cyclic $Tl(Se_4)$ fragments via bridging Se_2^{2-} and Se^{2-} ligands forming $Tl_2Se(Se_2)$ five-membered rings.

The coordination chemistry of thallium with polyselenide and polytelluride ligands remains relatively unexplored [1]. To date, only one polyselenide complex $(Et_4N)_3[Tl_3Se_{15}]$ [2] has been reported. As part of our continuing effort to explore the polychalcogenide chemistry of Group 13 elements we have investigated the Tl^+/Se_x^{2-} system in detail. In the case of $(Et_4N)_3[Tl_3Se_{15}]$ a redox reaction between TlCl and K_2Se_5 coupled with metathesis gave rise to Tl^{3+} [2, 3]. Redox chemistry between metal ions and polychalcogenide is limited to a small number of metals such as Mo [4], W [5], V [6], Fe [7] and Au [8], and thus it is worthwhile to study the Tl^+/Se_x^{2-} system further. We have shown that the application of the hydrothermal technique can result in new polychalcogenide complexes not readily obtainable by room temperature procedures [9]. Thus, we applied this technique to thallium and we report here on $(Ph_4P)_4[Tl_4Se_{16}]$, a new compound featuring a novel tetranuclear cluster with three different Se_x^{2-} ligands.

$(Ph_4P)_4[Tl_4Se_{16}]$ was prepared hydrothermally in a sealed pyrex tube filled with 1 ml water (1/10 of tube volume) by the reaction of TlCl, K_2Se_4 and Ph_4PCl in a 1:1:1 molar ratio at 110 °C for one day. **Caution**: TlCl is very toxic. Elemental analysis was performed on a scanning electron microscope equipped with a microprobe energy dispersive system. The elemental ratio of P:Tl:Se was determined, in this fashion, to be P:Tl:Se 1:1:3.9, very close to the expected value. The red crystals were obtained in 50% yield and are soluble in dimethylformamide (DMF). The structure of this material was established from single crystal X-ray diffraction analysis**. The compound crystallizes readily out of hydrothermal conditions. Attempts to repeat the synthesis using a more classical procedure, such as at room temperature in DMF solution, did not produce a well defined product.

The structure of the anion in $(Ph_4P)_4[Tl_4Se_{16}]$ is shown in Fig. 1. The molecule consists of four, almost linearly arranged, tetrahedral thallium centers which are coordinated by two chelating Se_4^{2-}, two bridging Se_2^{2-} and four bridging Se^{2-} ligands. It possesses a central $\{Tl_2Se_2\}^{2+}$ planar core similar to the isoelectronic $\{In_2Se_2\}^{2+}$ core found in $[In_2Se_2(Se_4)_2]^{2-}$ [2]. The

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**Single crystal X-ray data were collected on a Rigaku AFC6S diffractomter using Mo radiation. Crystal data for $(Ph_4P)_4[Tl_4Se_{16}]$: triclinic, $P\bar{1}$ (No. 2), $Z=1$, $a=12.054(9)$, $b=19.450(10)$, $c=11.799(6)$ Å, $\alpha=104.63(4)$, $\beta=98.86(6)$, $\gamma=101.99(6)°$ and $V=2555(3)$ Å^3 at 23 °C, $2\theta_{max}=40.0°$, $\mu=120.7$ cm^{-1}, $D_{calc}=2.23$ g/cm^3. The structure was solved by direct methods. No. data collected: 5206. No. unique data having $F_o^2>3\sigma(F_o^2)$: 1723. Final $R=0.075$ and $R_w=0.089$. An empirical absorption correction (based on Ψ scans) was applied to the data, followed by a DIFABS [10a] correction to the isotropically refined structure. A crystal with dimensions of 0.23×0.11×0.41 mm was mounted on a glass fiber with epoxy. The data were collected using a $\omega/2\theta$ scan with 4°/min scan speed. All equivalent reflections were averaged. The structures were solved with SHELXS-86 and was refined with the TEXSAN package [10b] of crystallographic programs. The structure consists of well separated Ph_4P^+ cations and $[Tl_4Se_{16}]^{4-}$ anions. The Ph_4P^+ have the standard tetrahedral structure. The homogeneity of the product was confirmed by comparison of observed X-ray powder diffraction pattern to the one calculated from the single crystal data.

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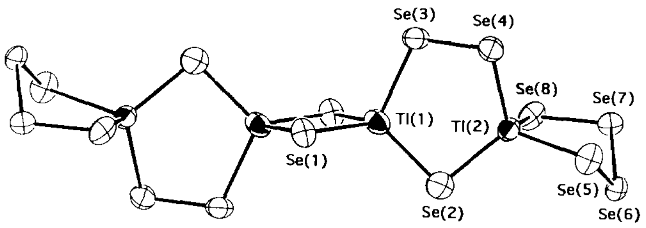

Fig. 1. The structure of the $[Tl_4Se_{16}]^{4-}$ anion. Selected distances (Å) and angles (°) are: Tl(1)–Se(1) 2.609(7); Tl(1)–Se(1) 2.802(8); Tl(1)–Se(2) 2.588(9); Tl(1)–Se(3) 2.738(6); Tl(2)–Se(2) 2.584(7); Tl(2)–Se(4) 2.626(7); Tl(2)–Se(5) 2.661(8); Tl(2)–Se(8) 2.710(7); Se(3)–Se(4) 2.300(10); Se(5)–Se(6) 2.351(9); Se(6)–Se(7) 2.319(8); Se(7)–Se(8) 2.300(10). Se(1)–Tl(1)–Se(1) 97.2(2); Se(1)–Tl(1)–Se(2) 117.9(2); Se(1)–Tl(1)–Se(3) 108.0(2); Se(1)–Tl(1)–Se(3) 108.9(2); Se(2)–Tl(1)–Se(3) 109.4(2); Se(2)–Tl(2)–Se(4) 114.3(3); Se(2)–Tl(2)–Se(5) 118.4(3); Se(2)–Tl(2)–Se(8) 105.9(3); Se(4)–Tl(2)–Se(5) 107.3(3); Se(4)–Tl(2)–Se(8) 109.1(3); Se(5)–Tl(2)–Se(8) 100.7(3); Tl(1)–Se(1)–Tl(1) 82.8(2); Tl(1)–Se(2)–Tl(2) 95.7(3); Tl(1)–Se(3)–Se(4) 109.4(3); Tl(2)–Se(4)–Se(3) 100.8(3); Tl(2)–Se(5)–Se(6) 95.6(3); Tl(2)–Se(8)–Se(7) 98.4(3); Se(5)–Se(6)–Se(7) 100.3(3); Se(6)–Se(7)–Se(8) 101.9(3).

Tl(1)–Tl(1)′ distance in the core is 3.583(6) Å. The two thallium atoms in this core are then each linked to two cyclic $Tl(Se_4)$ fragments via bridging Se_2^{2-} and Se^{2-} ligands forming $Tl_2Se(Se_2)$ five-membered rings. The Tl(1)–Tl(2) distance is 3.834(4) Å. This bridging mode, in which two metal ions are linked exclusively by a monoselenide and a diselenide, is new. However, a similar bridging mode was seen in the polytelluride $[Hg_2Te_5]_n^{2n-}$ [11]. $[Tl_4Se_{16}]^{4-}$ represents a new structure type for a polychalcogenide complex. Each $Tl(Se_4)$ fragment is a five-membered ring possessing an intermediate conformation between envelope and half-chair. The Se(6) lies 1.02 Å above the Tl(2)/Se(5)/Se(8) plane while Se(7) lies 0.42 Å below it. The Tl(1)Se(2)Tl(2)-Se(3)Se(4) five-membered ring is more flat with atoms Se(2)/Tl(1)/Se(3)/Se(4) defining a plane (0.07 Å maximum deviation from the corresponding least-squares plane) and Tl(2) lying 0.9 Å above it. The Se(2)/Tl(1)/Se(3)/Se(4) dihedral angle is 6°. The Tl–Se distances vary considerably from 2.584(7) to 2.802(8) Å with an average of 2.665 Å. The Se–Se bonds in this molecule range from 2.30(1) to 2.351(9) Å with an average of 2.32 Å.

As in $(Et_4N)_3[Tl_3Se_{15}]$, $[Tl_4Se_{16}]^{4-}$ is also a Tl^{3+} complex confirming that redox chemistry between Tl^+ and Se_x^{2-} is a favorable process. So far, we have not encountered any Tl^+ polyselenide complexes. However, investigations in the corresponding polysulfide system show that such complexes exist [3, 12]. Although this redox behavior is not currently understood, it resembles that of the Tl^+/I_3^- system in which Tl^+ reacts with excess I_3^- to give a tetrahedral Tl^{3+} complex, $[TlI_4]^-$ [13]. The Te/Se_x^{2-} system also bears considerable resemblance to the Au/Se system which displays Au^+/Au^{3+} behavior with Se_x^{2-}, but not with S_x^{2-}. It was found that only short Se_x^{2-} chains (e.g. $x \leqslant 3$) stabilize Au^+ complexes [8]. Similar behavior is being explored with thallium as well.

The trend in Tl/Se_x^{2-} chemistry appears to be redox reactions, with stabilization of the Tl^{3+} oxidation state. However, as in the Au/Se_x^{2-} system, use of short Se_x^{2-} ($x \leqslant 3$) ligands under proper conditions may yield stable Tl^+ complexes. The novel structure of $[Tl_4Se_{16}]^{4-}$ and its isolation by a hydrothermal synthesis technique underscores two major themes in this chemistry: the great bonding flexibility and adaptability of Se_x^{2-} ligands as building blocks, and the recently recognized usefulness of hydrothermal procedures as tools to produce new polychalcogenide compounds.

Supplementary material

Tables of atomic coordinates of all atoms and anisotropic and isotropic thermal parameters of all hydrogen atoms, and a listing of interatomic distances and angles and calculated and observed structure facts are available from the authors on request.

Acknowledgements

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References

1 (a) M.G. Kanatzidis, *Comments Inorg. Chem., 10* (1990) 161–195; (b) M.A. Ansari and J.A. Ibers, *Coord. Chem. Rev., 100* (1990) 223–266; (c) J.W. Kolis, *Coord. Chem. Rev., 105* (1990) 195–219.

2 S. Dhingra and M.G. Kanatzidis, *Inorg. Chem., 32* (1993) 1350–1362.

3 S. Dhingra, *Ph.D. Dissertation*, Michigan State University, 1992.

4 R.W.M. Wardle, C.-N. Chau and J.A. Ibers, *J. Am. Chem. Soc., 109* (1987) 1859–1860.

5 R.W.M. Wardle, S. Bhaduri, C.-N. Chau and J.A. Ibers, *Inorg. Chem., 27* (1988) 1747–1755.

6 C.-N. Chau, R.W.M. Wardle and J.A. Ibers, *Inorg. Chem., 26* (1987) 2740–2741.

7 H. Strasdeit, B. Krebs and G. Henkel, *Inorg. Chim. Acta, 89* (1984) L1–L13.

8 (a) M.G. Kanatzidis and S.-P. Huang, *Inorg. Chem., 28* (1989) 4667–4669; (b) S.-P. Huang and M.G. Kanatzidis, *Inorg. Chem., 30* (1991) 3572–3575.

9 (a) J.-H. Liao and M.G. Kanatzidis, *J. Am. Chem. Soc., 112* (1990) 7400–7402; (b) *Inorg. Chem., 31* (1992) 431–439; (c) Y. Park, J.-H. Liao, K.-W. Kim and M.G. Kanatzidis, in J.F. Harrod and R.M. Laine (eds.), *Inorganic and Organometallic Polymers and Oligomers*; Kluwer, Dordrecht, 1991, pp. 263–276;

(d) K.-W. Kim and M.G. Kanatzidis, *J. Am. Chem. Soc., 114* (1992) 4878–4883.

(a) N. Walker and D. Stuart, *Acta Crystallogr., Sect. A, 39* (1983) 158–166; (b) *TEXSAN: Single Crystal Structure Analysis Software*, Version 5.0, Molecular Structure Corporation, The Woodlands, TX.

11 R.C. Haushalter, *Angew. Chem., Int. Ed. Eng., 24* (1985) 432–433.

12 S. Dhingra and M.G. Kanatzidis, *Inorg. Chem., 32* (1993) 2298–2307.

13 N.N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon, Oxford, 1984, pp. 269–270.