$[M_4(Se_2)_2(PSe_4)_4]^{8-}$: a novel, tetranuclear, cluster anion with a stellane-like core

Konstantinos Chondroudis and Mercouri G. Kanatzidis*

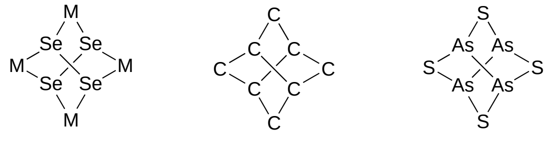
Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, USA

The molecular cluster compounds $[M_4(Se_2)_2(PSe_4)_4]^{8-}$ (M = Cd, Hg) form by the reaction of Cd and Hg with basic polychalcophosphate fluxes.

The polychalcophosphate fluxes are a powerful tool for the synthesis of new ternary and quaternary chalcophosphate compounds.[1−12] In the presence of metal ions, these reactive fluxes give rise to highly anionic $[P_yQ_z]^{n-}$ (Q = S, Se) ligands which bind in an amazing number of ways to the metals, forming new materials.[1] The variation of the flux composition stabilizes different ligands such as $[PQ_4]^{3-}$, $[PSe_5]^{3-}$, $[P_2Q_6]^{4-}$, $[P_2Q_7]^{4-}$, $[P_2Se_9]^{4-}$, *etc.*[1−12] which become the building blocks of various polymeric solid-state structures. Lately, we demonstrated that the same fluxes can be used to provide access to molecular compounds if appropriate conditions are employed.[8] This includes modification (usually increase) of the flux Lewis basicity, which can be achieved by increasing the concentration of the $[P_yQ_z]^{n-}$ ligands in it. Application of this technique to group 12 yielded the tetranuclear, stellane-like $Rb_8[M_4(Se_2)_2(PSe_4)_4]$ (M = Cd, Hg) and herein, we report the synthesis,† structural characterization, optical and thermal properties of this novel complex.

$Rb_8[Cd_4(Se_2)_2(PSe_4)_4]$ and $Rb_8[Hg_4(Se_2)_2(PSe_4)_4]$‡ are isostructural. The single-crystal structure determination was performed on the mercury compound. The discrete $[Hg_4(Se_2)_2(PSe_4)_4]^{8-}$ anion is a tetranuclear complex, of approximate D_{2d} symmetry, containing the relatively rare $[PSe_4]^{3-}$ ligand but also diselenide Se_2^{2-} ligands in a novel cluster arrangement [Fig. 1(*a*)]. The most intriguing feature of the molecule is its stellane-like, $[Hg_4(Se_2)_2]^{4+}$ core, composed of four Hg^{2+} ions and two Se_2^{2-} ligands. In this arrangement every Se_2^{2-} ligand coordinates to all four metals and the two diselenides are perpendicular to each other (Scheme 1, structure **A**). The four metal centres define a perfect 3.612(1)×3.612(1) Å square and the entire molecule resides on a $\bar{4}$ crystallographic site. A similar cage structure, has been observed in the organic molecule tricyclo[3.3.0.0^{3,7}]octane,[13,14] (Scheme 1, structure **B**). Its projection is reminiscent of a four-pointed star and because of that is also known as stellane. β-Tetraarsenic tetrasulfide is known to crystallize in discrete As_4S_4 molecules with a similar cage structure,[15] only in this molecule the sulfur atoms occupy the four corners of the 'star' (Scheme 1, structure **C**).

The stereoview in the Graphical Abstract can be useful in perceiving the cage core structure. This core acting as a gigantic metal centre is being coordinated by four $[PSe_4]^{3-}$ ligands. Each $[PSe_4]^{3-}$ employs two of its four available donor sites to bind to two neighboring metal atoms. In polyhedral terms, each $[PSe_4]^{3-}$ tetrahedron shares two corners with the four-pointed $[M_4(Se_2)_2]^{4+}$ star giving rise to the $[M_4(PSe_4)_4(Se_2)_2]^{8-}$ formula. Even though the $[PSe_4]^{3-}$ ligand is bidentate, its disposition is such that one of its non-coordinating Se atoms interacts with the diselenide ligand [Fig. 1(*b*)], as evidenced by the Se(3)–Se(5) distance of 3.327(3)Å (van der Waals radii sum is 3.8 Å).[16] In support of this observation the diselenide bond of 2.416(4) Å for Se(5)–Se(5″) is relatively long, for this coordination mode, compared, for example, to $[Hg_7Se_{10}]^{4-}$,[17] where a similarly bound Se_2^{2-} ligand has a 2.349(6) Å bond length. This is consistent with partial electron transfer from the terminal Se(3) atoms to the σ* orbital of the Se(5)–Se(5″) ligand.



A $[M_4(Se_2)_2]^{4+}$ **B** Stellane **C** β-As_4S_4

Scheme 1

In $Rb_8[Hg_4(Se_2)_2(PSe_4)_4]$ the Hg–Se distances average at 2.68(5) Å which compare well with those of $[Hg_7Se_{10}]^{4-}$,[17] and $Hg_2P_2Se_6$.[18] Each cell contains two $[Hg_4(Se_2)_2(PSe_4)_4]^{8-}$ molecules which are separated by the nine-coordinate Rb(1) [range of Rb(1)–Se distances, 3.511(3)–3.800(3) Å; av. 3.661 Å], and by the six-coordinate Rb(2) cation [range of Rb(2)–Se distances, 3.478(3)–3.786(3) Å; av. 3.644 Å]. Selected bond distance and angles are given in the caption of Fig. 1.

$Rb_8[M_4(PSe_4)_4(Se_2)_2]$ (M = Cd, Hg) are insoluble in dmf and acetonitrile but soluble in a solution of crown ether,

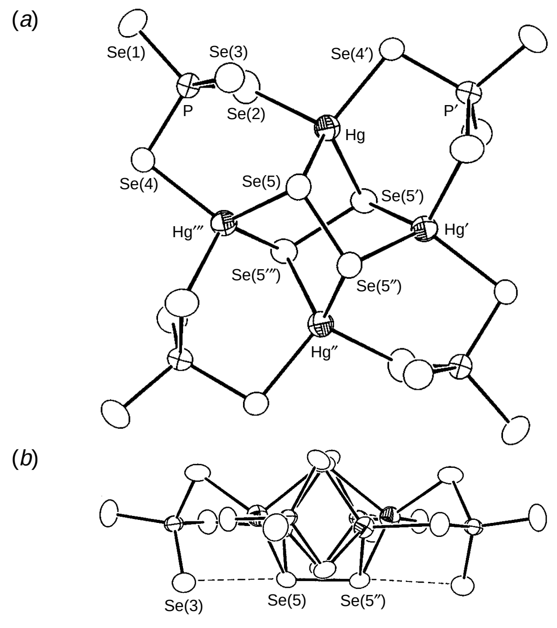


Fig. 1 (*a*) ORTEP representation and labelling of a single $[Hg_4(Se_2)_2(PSe_4)_4]^{8-}$ anion. Selected bond distances (Å) and angles (°): Hg–Se(2) 2.713(2), Hg–Se(4) 2.623(2), Hg–Se(5) 2.669(2), Hg–Se(5′) 2.725(2), P–Se(1) 2.175(5), P–Se(2) 2.221(5), P–Se(3) 2.184(5), P–Se(4) 2.237(5), Se(5)–Se(5″) 2.416(4), Se(3)–Se(5) 3.327(3); Se(2)–Hg–Se(4) 101.44(7), Se(2)–Hg–Se(5) 114.33(6), Se(2)–Hg–Se(5′) 101.98(7), Se(4)–Hg–Se(5) 125.45(7), Se(4)–Hg–Se(5′) 110.70(6), Se(5)–Hg–Se(5′) 100.84(8), Hg–Se(2)–P 96.5(1), Hg–Se(4)–P′ 97.9(1), Hg–Se(5)–Hg‴ 84.07(6), Hg–Se(5′)–Se(5″) 109.43(7), Se(1)–P–Se(2) 108.7(2), Se(1)–P–Se(3) 111.6(2), Se(1)–P–Se(4) 107.9(2), Se(2)–P–Se(3) 110.9(2), Se(2)–P–Se(4) 107.0(2). (*b*) Perpendicular view of the same molecule. Dashed lines indicate Se– Se interactions.

18-crown-6, in dmf. The solution is green–brown and stable, according to UV– VIS, for up to 2–3 days. The dmf–complexant solution gives a different spectrum from the solid material with one medium absorption at *ca.* 585 nm (2.12 eV) and a shoulder at *ca.* 400 nm (3.10 eV), suggesting that the cluster undergoes rearrangement in solution. The solid-state UV–VIS diffuse reflectance spectrum shows sharp optical gaps consistent with semiconducting behaviour (for M = Cd, E_g = 2.57 eV, whereas for M = Hg, E_g = 2.32 eV). The solid-state IR spectrum shows peaks that are characteristic of both the nature and bonding mode of the $[PSe_4]^{3-}$ ligand.§ Differential thermal analysis (DTA), followed by XRD analysis of the residues, shows incongruent melting at 456 and 413° C for M = Cd and Hg, respectively. The decomposition product is a mixture of the starting compound and amorphous $Rb_xP_ySe_z$ flux. Some CdSe or HgSe should also be formed but they are either amorphous or in concentrations and particle sizes undetectable by XRD analysis.

The extremely high charge of this molecular unit would make its synthesis through conventional 'wet' chemistry very difficult, perhaps prohibitive. This accentuates the value of the flux technique in stabilizing highly charged molecular entities. The novelty of the compositional and structural features of the $[M_4(Se_2)_2(PSe_4)_4]^{8-}$ cluster, provides a stimulating example of the new chemistry that becomes accessible and suggests that the molten alkali-metal polychalcogenide approach has not yet been fully exploited.

Financial support from the National Science Foundation DMR-9527347 is gratefully acknowledged. This work made use of the SEM and TEM facilities of the Center for Electron Optics at Michigan State University.

Footnotes

† *Syntheses:* $Rb_8[Cd_4(Se_2)_2(PSe_4)_4]$ was synthesized from a mixture of Cd (0.25 mmol), P_2Se_5 (0.50 mmol), Rb_2Se (1.00 mmol) and Se (2.50 mmol) heated to 550 °C for 4 d followed by cooling to 150 °C at 2 °C h^{-1}. Most of the excess $Rb_xP_ySe_z$ flux was removed with degassed dmf. Following this, the product was washed with *ca.* 2 ml of tributyl phosphine to remove residual Se. Further washing with anhydrous diethyl ether revealed light yellow, needle-like crystals that are air-stable but sensitive in H_2O. (Yield *ca.* 66% based on Cd). Microprobe analysis gave an average composition of $Rb_{8.0}Cd_{4.0}P_{4.4}Se_{19.6}$. *Cell data* at 23 °C: $a = b = 17.564(3)$, $c = 7.275(2)$ Å, $U = 2244.3(8)$ Å^3.

$Rb_8[Hg_4(Se_2)_2(PSe_4)_4]$ was synthesized from a mixture of HgSe (0.50 mmol), P_2Se_5 (0.25 mmol), Rb_2Se (1.00 mmol) and Se (2.50 mmol) heated to 500 °C for 4 d followed by cooling to 150 °C at 2 °C h^{-1}. Isolation as above revealed light yellow, needle-like crystals that are air-stable but sensitive in H_2O. (Yield *ca.* 78% based on Hg). Microprobe analysis gave an average composition of $Rb_{8.0}Hg_{4.4}P_{4.0}Se_{20.0}$.

‡ *Crystal data* at 23 °C: tetragonal, space group $P4_2/n$ (no. 86) $a = b = 17.654(2)$, $c = 7.226$ (2) Å, $U = 2253.6(9)$ Å^3, $Z = 2$, $D_c = 4.699$ g cm^{-3}, μ(Mo-Kα) = 380.81 cm^{-1}, $2\theta_{max} = 50°$, total data collected, 2162; unique data, 1838; data with $F_o^2 > 3\sigma(F_o^2)$, 1254. Number of variables: 82. An empirical absorption correction based on ψ scans was applied to the data during initial stages of refinement. DIFABS correction was applied after full isotropic refinement as recommended in N. Walker, *Acta Crystallogr., Sect. A*, 1983, **39**, 158. Final R, R_w = 0.040, 0.049 (0.46, 0.56 before DIFABS).

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/358.

§ The far-IR spectrum displays three strong absorptions at *ca.* 461, 434 and 417 cm^{-1}. These vibrations can be assigned to PSe_4 stretching modes and are of diagnostic value in distinguishing this selenophosphate ligand from others.[1,6] Weak absorptions below 200 cm^{-1} can be assigned to M–Se vibrations.[1]

References

1 T. J. McCarthy and M. G. Kanatzidis, *Inorg. Chem.*, 1995, **34**, 1257 and references therein.
2 T. J. McCarthy, T. Hogan, C. R. Kannewurf and M. G. Kanatzidis, *Chem. Mater.*, 1994, **6**, 1072.
3 T. J. McCarthy and M. G. Kanatzidis, *J. Alloys Compd.*, 1996, **236**, 70.
4 T. J. McCarthy and M. G. Kanatzidis, *J. Chem. Soc., Chem. Commun.*, 1994, 1089.
5 T. J. McCarthy and M. G. Kanatzidis, *Chem. Mater.*, 1993, **5**, 1061.
6 K. Chondroudis, T. J. McCarthy and M. G. Kanatzidis, *Inorg. Chem.*, 1996, **35**, 840.
7 K. Chondroudis and M. G. Kanatzidis, *Inorg. Chem.*, 1995, **34**, 5401.
8 K. Chondroudis and M. G. Kanatzidis, *Chem. Commun.*, 1996, 1371.
9 K. Chondroudis, T. J. McCarthy and M. G. Kanatzidis, *Inorg. Chem.*, 1996, **35**, 3451.
10 K. Chondroudis, A. J. Hanko and M. G. Kanatzidis, submitted for publication.
11 K. Chondroudis and M. G. Kanatzidis, *C. R. Acad. Sci. Paris, Ser. B*, 1996, **322**, 887.
12 J. H. Chen and P. K. Dorhout, *Inorg. Chem.*, 1995, **34**, 5705; J. H. Chen, P. K. Dorhout and J. E. Ostenson, *Inorg. Chem.*, 1996, **35**, 5627.
13 P. K. Freeman, V. N. M. Rao and G. E. Bigam, *Chem. Commun.* 1965, **21**, 511.
14 J. L. Adcock and H. Zhang, *J. Org. Chem.*, 1996, **61**, 1975.
15 E. J. Porter and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1972, 1347.
16 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.
17 K-W. Kim and M. G. Kanatzidis, *Inorg. Chem.*, 1991, **30**, 1966.
18 M. Z. Jandali, G. Eulenberger and H. Hahn, *Z. Anorg. Allg. Chem.*, 1978, **447**, 105.

Received, 5th November; Com. 6/07549E