Crystal structure of bis(*N,N,N*-trimethylethanaminium)bis(tetraselenido- $\kappa^2\text{Se}^1,\text{Se}^4$)mercurate(II), $\text{C}_{10}\text{H}_{28}\text{HgN}_2\text{Se}_8$

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Abstract

$\text{C}_{10}\text{H}_{28}\text{HgN}_2\text{Se}_8$, monoclinic, $P2_1/c$ (no. 14), $a = 12.5103(2)$ Å, $b = 11.2942(2)$ Å, $c = 16.6940(3)$ Å, $\beta = 94.980(1)^\circ$, $V = 2349.9$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0721$, $wR_{\text{ref}}(F^2) = 0.1874$, $T = 173$ K.

Table 1. Data collection and handling.

Crystal:	dark purple blocks, size 0.236×0.281×0.352 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	189.38 cm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{\text{max}}$:	57.02°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	21003, 5907
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3718
$N(\text{param})_{\text{refined}}$:	191
Programs:	SHELX [10], WinGX [11], DIAMOND [12]

Source of material

All synthetic experiments were performed under an atmosphere of dry argon or nitrogen using either a glove box or a Schlenk line. To a 50 mL DMF solution of 0.59 g (1.5 mmol) K_2Se_4 and 0.32 g (1.5 mmol) EtMe_3NI , a 10 mL DMF solution of 0.20 g (0.75 mmol) HgCl_2 was added dropwise over a 20 min period. A 60 mL

ether was slowly layered over the filtrate solution, after removing undissolved precipitates by filtration. Upon standing at room temperature for 3 days, dark purple crystals were yielded. These crystals were isolated and washed with ether several times. More crystals were obtained upon layering an additional 50 mL ether over the solution after isolation of the first crop of crystals. The overall yield was 76%, based on Hg.

Experimental details

H atoms were positioned geometrically and treated as riding, with C–H = 0.97 (CH₂) and 0.96 (CH₃) Å with $U_{\text{iso}}(\text{H}) = 1.2$ (1.5 for methyl) $U_{\text{eq}}(\text{C})$. H atoms of the CH₃ were positioned to be staggered with respect to the shortest other bond to the atom to which the CH₃ is attached. The largest difference electron peak is located near the Hg1 atom.

Discussion

A family of bis(tetrachalcogenido)metallate, $[\text{M}(\text{Q}_4)_2]^{2-}$ (Q = S, Se, Te) is one of the most well known molecular complexes in the metal polychalcogenide chemistry [1, 2]. For the $[\text{Hg}(\text{Se}_4)_2]^{2-}$ anion, there are four structurally characterized complexes, as stabilized by $[\text{Na}(15\text{-crown-5})]^+$, $[\text{K}(18\text{-crown-6})]^+$, $[\text{Ph}_4\text{P}]^+$, and $[\text{Me}_4\text{N}]^+$ [3–7]. The title compound, $(\text{EtMe}_3\text{N})_2[\text{Hg}(\text{Se}_4)_2]$, which has been prepared by the reaction of HgCl_2 , K_2Se_4 and EtMe_3NI in DMF solvent, is composed of $[\text{Hg}(\text{Se}_4)_2]^{2-}$ anions stabilized with EtMe_3N^+ alkylammonium cations containing mixed alkyl (methyl and ethyl) groups. The structure of $[\text{Hg}(\text{Se}_4)_2]^{2-}$ in $(\text{EtMe}_3\text{N})_2[\text{Hg}(\text{Se}_4)_2]$ is essentially the same as that of the $[\text{Na}(15\text{-crown-5})]^+$, $[\text{K}(18\text{-crown-6})]^+$, $[\text{Ph}_4\text{P}]^+$, and $[\text{Me}_4\text{N}]^+$ salts. A Hg atom in the $[\text{Hg}(\text{Se}_4)_2]^{2-}$ anion is tetrahedrally coordinated by two chelating tetraselenide ligands. The average Hg–Se and Se–Se distances are 2.66(3) and 2.333(8) Å, respectively. Both HgSe_4 rings in $[\text{Hg}(\text{Se}_4)_2]^{2-}$ exhibit the envelope conformation. The Hg1, Se1, Se2, and Se4 atoms are in a plane with a mean deviation of 0.12(7) Å, while the Se3 atom lies 1.21 Å below it. Similarly, the Hg1, Se5, Se7, and Se8 atoms are in a plane with a mean deviation of 0.16(9) Å, and the Se6 atom lies 1.16 Å above it. The dihedral angle between the two planes discussed before is found to be 67.6°. The shortest intermolecular Se–Se distance is 3.415(2) Å, appearing to be slightly shorter than that of 3.537(5) Å found in $(\text{Me}_4\text{N})_2[\text{Hg}(\text{Se}_4)_2] \cdot 0.5\text{DMF}$ [7]. Even if the Me_4N^+ cation is smaller than the EtMe_3N^+ , DMF solvent molecules were cocrystallized in the $(\text{Me}_4\text{N})_2[\text{Hg}(\text{Se}_4)_2] \cdot 0.5\text{DMF}$, to separate the $[\text{Hg}(\text{Se}_4)_2]^{2-}$ complexes a little bit more. Based on the intermolecular Se–Se distances, we can estimate how close the $[\text{M}(\text{Se}_4)_2]^{2-}$ complexes are to one another. It has been known that the $[\text{M}(\text{Se}_4)_2]^{2-}$ molecular complexes are unstable and reorganize into higher dimensional structures if they come close to one another excessively [8]. One of our concern was to reveal how close the $[\text{M}(\text{Se}_4)_2]^{2-}$ molecular complexes could get in contact without

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producing a structural rearrangement. The intermolecular Se–Se distance, 3.415 Å of the (EtMe₃N)₂[Hg(Se₄)₂] is the shortest distance among the reported [M(Se₄)₂]^{2–} compounds and comparable to 3.429 Å found in (EtMe₃N)₂[Cd(Se₄)₂] [9].

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(1A)	4e	0.6798	1.0196	0.8312	0.080
H(1B)	4e	0.6541	0.9630	0.9130	0.080
H(1C)	4e	0.6117	0.9032	0.8317	0.080
H(2A)	4e	0.8193	0.7151	0.9034	0.084
H(2B)	4e	0.6970	0.7169	0.8737	0.084
H(2C)	4e	0.7368	0.7753	0.9561	0.084
H(3A)	4e	0.8525	0.8048	0.7719	0.092
H(3B)	4e	0.7977	0.9255	0.7467	0.092
H(3C)	4e	0.7287	0.8098	0.7479	0.092
H(4A)	4e	0.8680	1.0195	0.8768	0.055

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Hg(1)	4e	0.78944(4)	0.47576(4)	0.75614(4)	0.0347(3)	0.0316(2)	0.0543(4)	0.0044(2)	–0.0001(2)	0.0008(2)
Se(1)	4e	0.7987(1)	0.2440(1)	0.7839(1)	0.0366(6)	0.0272(5)	0.062(1)	–0.0007(4)	0.0004(7)	–0.0006(6)
Se(2)	4e	0.9795(1)	0.22708(9)	0.8303(1)	0.0335(6)	0.0257(5)	0.069(1)	0.0018(4)	0.0041(7)	0.0045(6)
Se(3)	4e	1.0004(1)	0.3882(1)	0.9183(1)	0.0376(7)	0.0417(6)	0.0529(9)	–0.0041(5)	–0.0019(7)	0.0027(6)
Se(4)	4e	0.9716(1)	0.5477(1)	0.8301(1)	0.0344(6)	0.0275(5)	0.067(1)	–0.0007(4)	–0.0015(7)	–0.0009(6)
Se(5)	4e	0.7794(1)	0.5937(1)	0.6182(1)	0.0381(7)	0.0401(6)	0.0512(9)	0.0024(5)	0.0068(7)	0.0036(6)
Se(6)	4e	0.5943(1)	0.5946(1)	0.5880(1)	0.0401(7)	0.0539(7)	0.055(1)	–0.0011(5)	–0.0047(7)	0.0056(7)
Se(7)	4e	0.5323(1)	0.6578(1)	0.7093(1)	0.0298(6)	0.0373(6)	0.068(1)	0.0044(4)	0.0007(7)	0.0042(7)
Se(8)	4e	0.5858(1)	0.5009(1)	0.7934(1)	0.0344(6)	0.0420(6)	0.059(1)	0.0011(5)	0.0081(7)	0.0070(6)
N(1)	4e	0.7693(8)	0.8754(8)	0.8604(8)	0.037(5)	0.030(4)	0.055(8)	–0.004(4)	0.005(6)	0.002(5)
N(2)	4e	0.6905(8)	0.1796(9)	0.5424(8)	0.035(5)	0.037(5)	0.059(8)	–0.008(4)	0.009(6)	–0.008(5)
C(1)	4e	0.670(1)	0.947(1)	0.859(1)	0.051(8)	0.044(7)	0.07(1)	0.004(6)	0.019(9)	0.002(7)
C(2)	4e	0.754(1)	0.760(1)	0.902(1)	0.049(8)	0.030(6)	0.09(1)	–0.009(5)	0.029(9)	0.003(7)
C(3)	4e	0.789(1)	0.852(1)	0.774(1)	0.06(1)	0.07(1)	0.05(1)	–0.019(7)	–0.008(9)	–0.012(8)
C(4)	4e	0.861(1)	0.944(1)	0.904(1)	0.048(7)	0.025(5)	0.07(1)	–0.002(5)	0.009(8)	0.002(6)
C(5)	4e	0.969(1)	0.883(1)	0.909(1)	0.048(8)	0.041(7)	0.11(2)	–0.005(6)	–0.00(1)	0.009(8)
C(6)	4e	0.611(1)	0.213(1)	0.602(1)	0.051(8)	0.054(7)	0.06(1)	–0.004(6)	0.018(9)	–0.014(8)
C(7)	4e	0.779(2)	0.269(1)	0.548(1)	0.08(1)	0.049(8)	0.07(1)	–0.020(7)	0.01(1)	0.000(8)
C(8)	4e	0.638(1)	0.180(2)	0.459(1)	0.050(9)	0.09(1)	0.05(1)	0.002(8)	–0.011(9)	0.002(9)
C(9)	4e	0.742(1)	0.063(1)	0.563(1)	0.048(8)	0.047(7)	0.08(1)	0.014(6)	0.010(9)	0.009(8)
C(10)	4e	0.668(2)	–0.042(1)	0.562(1)	0.09(1)	0.039(7)	0.09(2)	–0.003(7)	0.03(1)	–0.011(8)

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Table 2. continued.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(4B)	4e	0.8432	0.9610	0.9581	0.055
H(5A)	4e	1.0219	0.9329	0.9364	0.097
H(5B)	4e	0.9881	0.8665	0.8557	0.097
H(5C)	4e	0.9642	0.8098	0.9380	0.097
H(6A)	4e	0.6466	0.2122	0.6552	0.082
H(6B)	4e	0.5534	0.1569	0.5984	0.082
H(6C)	4e	0.5836	0.2907	0.5895	0.082
H(7A)	4e	0.8132	0.2695	0.6013	0.097
H(7B)	4e	0.7492	0.3458	0.5350	0.097
H(7C)	4e	0.8298	0.2488	0.5104	0.097
H(8A)	4e	0.5802	0.1229	0.4546	0.095
H(8B)	4e	0.6893	0.1588	0.4217	0.095
H(8C)	4e	0.6095	0.2570	0.4457	0.095
H(9A)	4e	0.7794	0.0682	0.6158	0.068
H(9B)	4e	0.7949	0.0474	0.5250	0.068
H(10A)	4e	0.7085	–0.1123	0.5751	0.107
H(10B)	4e	0.6310	–0.0503	0.5091	0.107
H(10C)	4e	0.6162	–0.0301	0.6004	0.107

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