Trigonal Planar [HgSe$_3$]$^{4-}$ Unit: A New Kind of Basic Functional Group in IR Nonlinear Optical Materials with Large Susceptibility and Physicochemical Stability

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Ⓢ *Supporting Information*

ABSTRACT: A new mercury selenide BaHgSe$_2$ was synthesized. This air-stable compound displays a large nonlinear optical (NLO) response and melts congruently. The structure contains chains of corner-sharing [HgSe$_3$]$^{4-}$ anions in the form of trigonal planar units, which may serve as a new kind of basic functional group in IR NLO materials to confer large NLO susceptibilities and physicochemical stability. Such trigonal planar units may inspire a path to finding new classes of IR NLO materials of practical utility that are totally different from traditional chalcopyrite materials.

Nonlinear optical (NLO) crystals convert laser frequencies and are widely used in many fields such as industrial processing, noninvasive medical diagnostics, laser guidance, and signal communication.[1] In the UV and visible range, several outstanding NLO crystals have been developed over the last few decades, such as KTiOPO$_4$ (KTP),[2] LiNbO$_3$,[3] β-BaB$_2$O$_4$ (BBO),[4] and LiB$_3$O$_5$ (LBO).[5] In the deep UV range (<200 nm), currently only KBe$_2$BO$_3$F$_2$ (KBBF)[6] is capable of generating coherent light below 200 nm using direct SHG methods; however, its practical application is hindered by difficulties in crystal growth originating from its layered structure and the presence of toxic BeO as a raw material. In the IR range, only a few NLO crystals (e.g., chalcopyrite-type AgGaQ$_2$ (Q = S, Se)[7] and ZnGeP$_2$[8]) are commercially available to date, each suffering from drawbacks that severely limit their wider application. Thus, there is an urgent need to investigate new NLO materials in the deep UV and IR ranges.[9]

The important borate NLO crystals (BBO, LBO, KBBF) owe much of their development to anionic group theory, which states that large NLO effects can be realized when favorable NLO-active structural units occur in high density and in coparallel alignment within the crystal.[10] Among various structural units, the planar π-conjugated [BO$_3$]$^{3-}$ anionic group, which leads to moderate birefrigence and large microscopic second-order susceptibility, makes it suitable for UV and deep-UV NLO materials. Recent studies suggest that other π-conjugated trigonal

planar inorganic anions, in particular the [CO$_3$]$^{3-}$ group, can also impart promising NLO properties in the UV and deep-UV range.[11]

Metal chalcogenides, phosphides, and halides have much wider IR transparent range (above 5 µm) than do oxides and thus have been extensively investigated as IR NLO materials. In many of the new materials recently discovered, the microscopic NLO-active structural units include tetrahedra (GaS$_4$,[12] GeS$_4$,[13] ZnP$_4$[8]), various M-centered polyhedra (MQ$_n$, where M = transition metal such as Ta^{5+} or Zr^{4+} and Q = chalcogen),[14] and anionic groups containing stereochemically active lone pairs ([AsS$_3$]$^{3-}$, [SbS$_3$]$^{3-}$, [GeCl$_3$]$^-$ etc.).[15−17] It is noteworthy that very few IR NLO materials contain planar groups as the basic structural units. Indeed, the only reported example involves thioborate [BS$_3$]$^{3-}$,[18] which is the sulfide analogue of the borate group [BO$_3$]$^{3-}$.[6] In contrast to stable [BO$_3$]$^{3-}$ groups, however, [BS$_3$]$^{3-}$ groups are mostly reactive and impart much lower NLO susceptibility compared to other IR NLO materials, making thioborates unlikely candidates for practical applications.

Nevertheless, planar groups should be among the most desirable structural features for NLO materials, according to anionic group theory.[10] Unfortunately, other than [BS$_3$]$^{3-}$ groups, these planar units are much less commonly encountered in NLO materials that are not oxides. We propose that Hg-containing chalcogenides may be amenable to forming these units. Hg^{2+} is a highly polarizing ion (as a result of both relativistic effects and the decreased shielding ability of 4f electrons) and has a strong tendency to form bonds with covalent character, especially to S-, Se-, N-, and P-containing ligands. As part of a search for new IR NLO materials, we report here the compound BaHgSe$_2$, which contains corner-sharing [HgSe$_3$]$^{4-}$ trigonal planar structural units and exhibits attractive NLO and other physicochemical properties. Through careful experimental and theoretical analyses, we propose [HgSe$_3$]$^{4-}$ as a new kind of trigonal planar NLO-active basic structural units, possessing much larger NLO coefficients and greater chemical stability than the [BS$_3$]$^{3-}$ thioborate group.

BaHgSe$_2$ belongs to the orthorhombic noncentrosymmetric space group $Pmc2_1$ (no. 26) with unit cell parameters $a = 4.3580(9)$ Å, $b = 14.881(3)$ Å, $c = 7.5900(15)$ Å, and $Z = 4$. The crystallographically unique atoms are Ba1 (2a), Ba2 (2a), Hg1 (2b), Hg2 (2b), Se1 (2b), Se2 (2a), Se3 (2b), and Se4 (2b). Both Ba^{2+} cations are surrounded by seven Se atoms. The Ba–Se distances range from 3.274(3) Å to 3.427(3) Å (Figure S2), which are comparable to those of BaSe (3.287(2) Å).[19] Hg1 cations are coordinated to three Se atoms with Hg–Se bond lengths ranging from 2.555(3) Å to 2.642(2) Å and a fourth Se at a much longer distance of 3.133(3) Å (Figure 1a). It is not
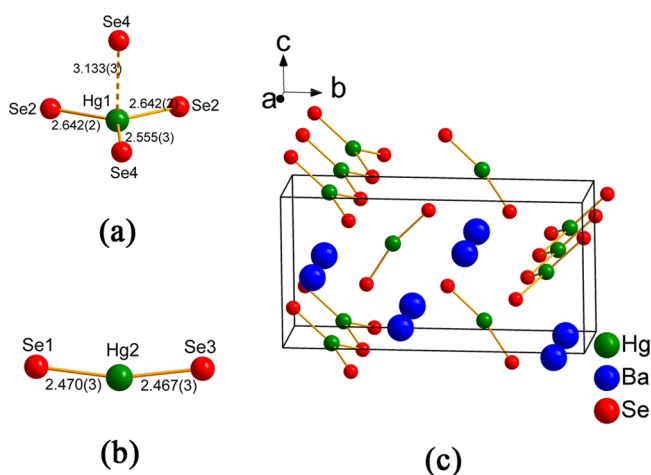

Figure 1. Coordination environment of (a) Hg1 and (b) Hg2 and (c) crystal structure of BaHgSe$_2$.

obvious if the coordination geometry around Hg1 should be considered as trigonal pyramidal, which was also inappropriately described as "tetrahedral" (CN4) in a redetermination of the analogous sulfide BaHgS$_2$.[20] The evidence suggests that a trigonal planar (CN3) geometry is more appropriate, as was already correctly described in the original determination of the sulfide BaHgS$_2$.[21] First, analysis of the crystal orbital Hamilton population (COHP)[22] curves reveals that for the three shorter Hg–Se contacts, the bonding is perfectly optimized with all bonding and no antibonding levels occupied up to the Fermi level, whereas for the longer Hg–Se contact, bonding and antibonding levels cancel out to give essentially nonbonding character overall. The integrated COHP values (ICOHP) are 2.1 eV/bond for the three shorter Hg–Se contacts but 0.3 eV/bond for the longer one (Figure 2). The long Hg–Se contact is well beyond the range of normal Hg–Se bond lengths (2.40–2.75 Å, or an average of 2.57 Å for 261 entries as reported in crystallographic databases).[23] Second, if only the three shorter Hg–Se contacts are considered, the bond valence sum[24] for the Hg1 atom is 2.0, in perfect agreement with the expected valence, but becomes 2.12 if the fourth Hg–Se contact is included. Third, the sum of the bond angles subtended by the three shorter Hg–Se bonds is 359.22(2)°, indicating an essentially flat trigonal plane. The Hg1 atom is displaced only 0.13 Å above this plane, or 4% of the height to fourth Se atom, compared to 25% for the location of a central atom within a tetrahedron (Figure S3). Hg-centered trigonal planar units are frequently seen in metal complexes,[25,26] and a very recent study further proves its stable existence in inorganic hydrates.[27] The Hg2 atom is surrounded by two Se atoms making a bond angle of 166.45(11)° at distances
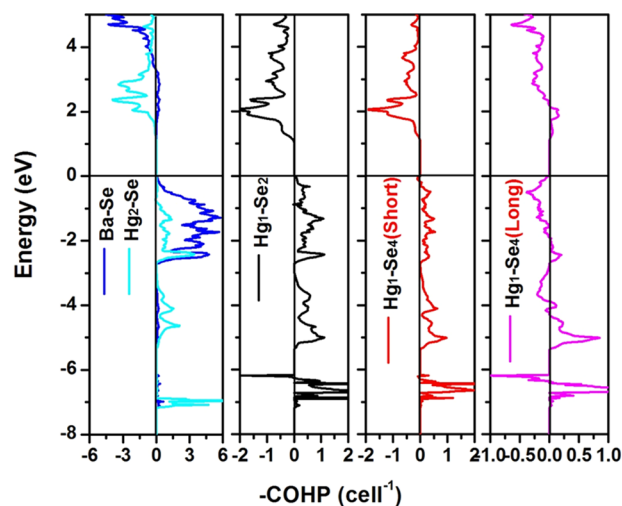

Figure 2. COHP curves for Ba–Se and Hg–Se contacts.

of 2.467(3)–2.470(3) Å, which corresponds to strong bonds as confirmed by an ICOHP value of 3.0 eV/bond.

Bonding to Hg atoms, which have a valence electron configuration of $5d^{10}6s^2$, can be rationalized by invoking sp hybridization made possible by the small energy difference between 6s and 6p orbitals. Complexes of Hg atoms bonded to S-, Se-, N-, and P-containing ligands are commonly found in linear (sp), trigonal planar (sp^2), and tetrahedral (sp^3) coordination geometries.[25,26] The strong bond energies to Hg more than compensate for the small promotion energy involved in the hybridization.

In borates, the alignment of [BO$_3$] trigonal planar units within the crystal greatly influences the macroscopic NLO performance.[6] Complete parallel alignment would lead to a large NLO response, but partial tilting or antiparallel arrangement would decrease or cancel the individual dipole contributions of [BO$_3$] groups.[28] Low-coordination groups are attractive for optical properties because of the enhanced polarizability of the central cations.[29] In BaHgSe$_2$, the [HgSe$_3$] trigonal planar units are connected by corner-sharing to form one-dimensional anionic chains [HgSe$_{2/2}$Se$_2$]$^{2-}$ extending along the a-direction. The [HgSe$_{2/2}$Se$_2$]$^{2-}$ chains and the isolated [HgSe$_2$]$^{2-}$ anions are separated by Ba^{2+} cations. The [HgSe$_3$] triangles are aligned parallel to each other within an individual chain, but neighboring chains are tilted with respect to each other. The linear [HgSe$_2$] groups are similarly tilted. Such an arrangement may not be ideal for NLO performance, although the presence of the one-dimensional chain helps to enforce the parallel alignment of the [HgSe$_3$] triangles within one single chain. Nevertheless, the compound still demonstrates a large SHG response, which was experimentally determined to be about 1.5 times that of AgGaS$_2$ with similar particle size under 2.09 μm fundamental light (Figure 3a). This performance is much better than for compounds containing [BS$_3$] thioborate units.[19] More importantly, BaHgSe$_2$ is very stable under air because of its strong covalent Hg–Se bonds, whereas thioborates are highly reactive to moisture, and special attention must be paid to their synthesis. Moreover, BaHgSe$_2$ melts congruently at a rather low temperature of 638 °C (Figure 3b). This congruent-melting behavior is valuable for the growth of bulk single crystals via the Bridgman–Stockbarger technique. It should be emphasized that good crystal growth habit and good chemical stability are important prerequisites for mid-IR NLO crystals to be useful in practice.
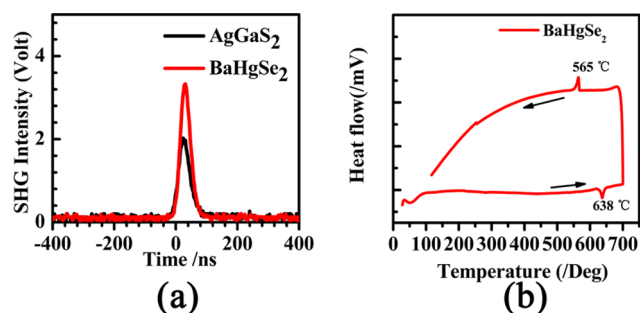
Figure 3. (a) Oscilloscope traces of SHG signals for BaHgSe$_2$ with AgGaS$_2$ as a reference at a particle size of 105 to 150 μm. (b) DSC curve of BaHgSe$_2$.

Thus, compounds containing [HgSe$_3$] triangles may form a potential new class of IR-NLO materials of practical utility having totally different structures from traditional chalcopyrite materials. The band gap of BaHgSe$_2$ was deduced to be 1.56 eV from diffuse reflectance measurements[30] (Figure S4). Such a band gap may not be ideal in conjunction with a 1–2 μm pumping source. However, with further development of laser technology, pumping sources of around 2.8 μm[31] will become more sophisticated so that they can be used to pump materials with smaller band gaps.

The electronic band structure of BaHgSe$_2$,[22] plotted along lines of high symmetry within the Brillouin zone, reveals a direct band gap of 1.1 eV at Y (Figure 4a). As expected, Hg- and Se-

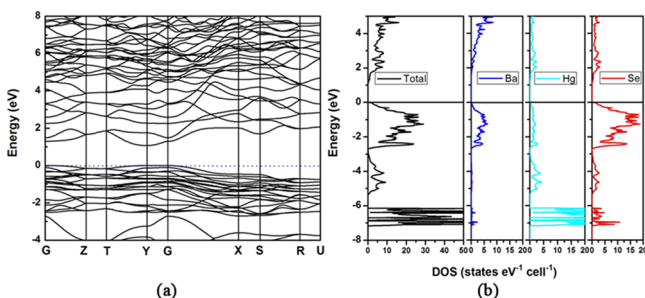**Figure 4.** (a) The calculated electronic band structures along the lines of high symmetry points in the Brillouin zone for BaHgSe$_2$. (b) The partial DOS projected on respective species of atoms in BaHgSe$_2$.

based states constitute most of the valence band (−2.7 to 0 eV), while Ba-based states constitute most of the conduction band (+1.8 eV upward), as seen in the density of states (DOS) curve (Figure 4b). Nevertheless, the presence of some Ba-based states below the Fermi level implies a small but non-negligible contribution of covalent character to Ba−Se bonding. The Hg 5d states account for the sharp spike at −7 to −6 eV and do not contribute significantly to bonding. However, mixing of Hg 6s (hybridized with 6p) and Se 4p states results in strongly bonding Hg−Se bonding levels extending from −5.3 to 0 eV, as confirmed by the COHP curves presented earlier. Because the optical response of a crystal mainly originates from the electronic transitions between the VB and CB states close to the band gap, the Hg−Se groups determine the optical properties.

The nonlinear and linear optical properties were investigated by the scissors-factor-corrected LDA approach (Table S4).[32] The largest SHG tensor is d_{333} = 39.87 pm/V(contribution: Hg1Se$_3$ 79%, Hg2Se$_2$ 14%, Ba 7%) (AgGaS2 d_{36} = 13.6 pm/V) and the averaged powder SHG coefficient (d_{powder}) is 26.52 pm/

V, in good agreement with experimental results. In comparison, the calculated SHG tensor for Ba$_3$(BS$_3$) (SbS$_3$)[18] is d_{21} = 2.73 pm/V. The calculated birefringence of BaHgSe$_2$ is 0.1649 at 1064 nm and 0.1473 at 2090 nm, indicating that it is easy for this compound to achieve the phase-matching condition in the IR spectral region (Figure 5).
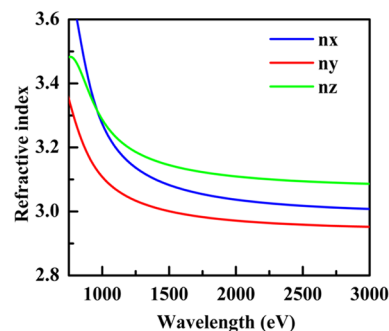

Figure 5. Calculated refractive index for BaHgSe$_2$ crystal at the wavelength range of 800 nm−3200 nm.

In summary, this study of BaHgSe$_2$ demonstrates that [HgSe$_3$] triangles serve as a new kind of basic functional units in IR NLO materials. Compared with thioborate [BS$_3$] triangles, these [HgSe$_3$] triangles exhibit much larger NLO susceptibilities and confer better physicochemical stability, leading to greater promise for practical application. The incorporation of [HgSe$_3$] or other similar triangles may lead to the elucidation of a new class of practically applicable IR NLO materials with structures strikingly different from chalcopyrite materials.

■ ASSOCIATED CONTENT

ⓈSupporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b03107.

Experimental methods and data (PDF)
Crystallographic data for BaHgSe$_2$(CIF)

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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