

The crystal structure of gianellaite, $[(\text{NHg}_2)_2](\text{SO}_4)(\text{H}_2\text{O})_x$, a framework of (NHg_4) tetrahedra with ordered (SO_4) groups in the interstices

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ABSTRACT

The crystal structure of gianellaite, $[(\text{NHg}_2)_2](\text{SO}_4)(\text{H}_2\text{O})_x$, cubic, $F\bar{4}3m$, $a = 9.521(6) \text{ \AA}$ $V = 863.1(1.6) \text{ \AA}^3$, $Z = 4$, was solved by direct methods and refined to an R_1 index of 2.1% based on 167 unique observed reflections collected on a three-circle rotating-anode ($\text{MoK}\alpha$ X-radiation) diffractometer equipped with multilayer optics and an APEX-II detector. In the structure of gianellaite, nitrogen-centred $(\text{NHg}_4)^{5+}$ tetrahedra share all corners to form a framework of tetrahedra with an ordered arrangement of interstitial $(\text{SO}_4)^{2-}$ tetrahedra that show strong orientational disorder. Infrared spectroscopy in the principal O–H stretching region shows peaks at ~ 3300 and 1600 cm^{-1} , indicating the presence of (H_2O) , the position(s) of which could not be discerned in difference-Fourier maps.

KEYWORDS: gianellaite, crystal structure, infrared spectroscopy.

Introduction

GIANELLAITE is a Hg-nitride-sulfate mineral from the Perry Pit of the Mariposa mine in the Terlingua District, Brewster County, Texas, USA, described by Tunell *et al.* (1977). The chemical composition was reported as $(\text{NHg}_2)_2(\text{SO}_4)$. The approximate atomic arrangement was determined, with (NHg_4) tetrahedra sharing corners to form a framework of the anti-cristobalite (= cuprite) structure, but the location of the sulfate group was not determined. As part of our continuing interest in Hg minerals (Cooper and Hawthorne, 2003, 2009; Cooper *et al.*, 2013; Hawthorne *et al.*, 1994; Roberts *et al.*, 2002, 2003*a,b*, 2005), the crystal structure of gianellaite has been refined in order to resolve the distribution of the interstitial species.

Experimental methods

X-ray data collection

The single-crystal fragment used in this study is from a specimen donated by George Tunell to the Natural History Museum of Los Angeles County, catalogue number 44159, and designated as type material. This fragment was mounted on a Bruker APEX-II ULTRA three-circle diffractometer equipped with a rotating anode generator ($\text{MoK}\alpha$ X-radiation), multilayer optics and an APEX-II 4 K CCD area detector. The crystal chosen was roughly equidimensional and small, so as to minimize differential absorption effects within the raw intensity data. In excess of an Ewald sphere of intensity data were collected to $60^\circ 2\theta$ using a 4 s frame time and 0.3° frame width at a crystal-to-detector distance of 5 cm. Empirical absorption corrections (*SADABS*; Sheldrick, 2008) were applied and equivalent reflections merged, resulting in 167 unique reflections for the space group $F\bar{4}3m$. The extreme data-collection redundancy (i.e. 8408 intensities measured were reduced to

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TABLE 1. Miscellaneous structural information for gianellaite.

| | | | |
|---------------------------|------------|------------------------------|--------------|
| a (Å) | 9.521(6) | Crystal size (µm) | 40 × 50 × 60 |
| V (Å) ³ | 863.1(1.6) | Radiation | MoKα |
| Space group | $F43m$ | No. of reflections | 8408 |
| Z | 4 | No. in Ewald sphere | 2627 |
| D_{calc} | 7.13 | No. unique reflections | 167 |
| μ (mm ⁻¹) | 71.14 | No. with $F_o > 4\sigma F_o$ | 167 |
| | | R_{merge} % | 2.9 |
| | | R_1 % | 2.1 |
| | | wR_2 % | 5.6 |

167 unique reflections) coupled with the small crystal size (to avoid severe attenuation) and roughly equant shape (to simplify absorption modelling) allowed accurate empirical modelling of absorption and subsequent accurate corrected reflection intensities. The unit-cell dimensions were obtained by least-squares refinement of the positions of 4065 reflections with $I > 10\sigma I$, and are given in Table 1, together with information pertaining to data collection and structure refinement. After collection of the intensity-data frames, various 'precession slices' were generated and evaluated for the possible presence of additional super-lattice reflections and general systematic reflection-absence criteria. All observed spots could be indexed on a cubic- F unit cell ($a = 9.521$ Å)

and are consistent with the reflection conditions for the space group $F43m$, although the reflections observed that violate the presence of a d -glide are noticeably weak.

Infrared spectroscopy

A Fourier-transform infrared spectrum of gianellaite (Fig. 1) was collected on a thin film, prepared by a Diamond Micro Compression Cell, using a Bruker Hyperion 2000 IR microscope equipped with a liquid-nitrogen-cooled MCT detector. Data over the range 4000–650 cm⁻¹ were obtained by averaging 100 scans with a resolution of 4 cm⁻¹. In the principal OH-stretching region (3800–2800 cm⁻¹), the spectrum shows a broad band centred at ~3300 cm⁻¹ due to stretching vibrations of H₂O. The broad weak band at ~1600 cm⁻¹ is associated with H–O–H bending vibrations of H₂O. In the low-frequency region, there is a strong band at 1064 cm⁻¹ (with a shoulder at ~1088 cm⁻¹) and a weak peak at 953 cm⁻¹ that are attributed to S–O stretching vibrations of the SO₄ group. The peak at 688 cm⁻¹ may be assigned to a SO₄ bend.

Crystal-structure refinement

The Hg₂N framework constituents occupy the same crystallographic sites as proposed by Tunell *et al.* (1977), with each Hg linked to two N atoms in a linear N–Hg–N group, and each N tetrahedrally coordinated by four Hg atoms. In the earlier study, an attempt to

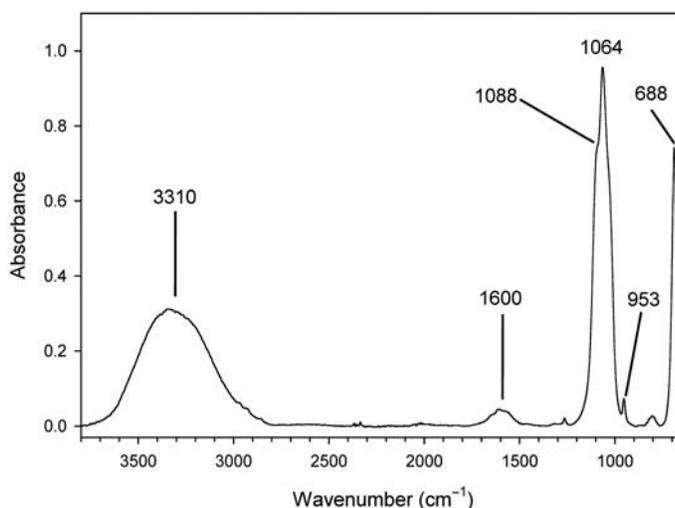


FIG. 1. The Fourier-transform infrared spectrum of gianellaite.

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 TABLE 2. Final atom coordinates and displacement parameters (\AA^2) for gianellaite.

| Atom | Wyckoff site | x | U^{11} | U^{23} | $U_{\text{eq}}/U_{\text{iso}}$ |
|------|--------------|---------------|-----------|--------------|--------------------------------|
| Hg | 16e | 0.37489(5) | 0.0221(3) | -0.00129(10) | 0.0221(3) |
| N(1) | 4c | $\frac{1}{4}$ | | | 0.013(2)* |
| N(2) | 4b | $\frac{1}{2}$ | | | 0.013(2)* |
| S | 4a | 0 | | | 0.0278(17) |
| O(1) | 16e | 0.089(7) | | | 0.51(17) |

*Constrained to be equal during refinement.

locate the four sulfate groups *puc* (per unit cell) in the cavities centred at 0,0,0 and $\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$ (each site potentially contributing up to four per formula unit) was unsuccessful, and they were presumed to be disordered over the cavities (Tunell *et al.*, 1977). In our refinement, there is significant electron density in the difference-Fourier map only at the 0, 0, 0 position. We tried adding S at both potential sites (0,0,0 and $\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$), assigning the S scattering factor to both, with fixed U_{iso} values of 0.02, and then refined the site occupancy independently at both sites. The S-site occupancy at 0,0,0 refined to 1.01(7) and at $\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$ it refined to 0.02(6); this result is consistent with S completely ordered at the 0,0,0 position, the $\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$ position vacant and a total of four S atoms per formula unit. The S position at 0,0,0 was subsequently retained in the model with a fixed full site-occupancy, and S was removed from the $\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$ position (which is assigned the letter V in later figures). The U_{iso} was allowed to refine for the S atom, and then the difference-Fourier map was investigated for evidence of the O atom presumed to be associated with an SO_4 group. During refinement, the S position behaved in a manner consistent with a high degree of positional order [$U_{\text{iso}} = 0.0278(18)$], and the most prominent peak remaining in the difference-Fourier map was in tetrahedral coordination about the S atom (i.e. at the 16e site at x,x,x), at a distance of 2.14 \AA from the S atom. This was unexpected, as a $\langle \text{S}^{6+}\text{-O} \rangle$ distance for an (SO_4) group should be close to the grand mean $\text{S}^{6+}\text{-O}$ distance of 1.473 \AA found in sulfate minerals (Hawthorne *et al.*, 2000). The difference in observed and expected distance raised the possibility that this peak was an artifact and that the S-bearing species that is responsible for electroneutrality in the $(\text{Hg}_2\text{N})_2^{2+}$ framework could be possibly $(\text{SO}_4)^{2-}$ or S^{2-} . However, the infrared spectrum of gianellaite (Fig. 1) indicates the presence of an (SO_4) group. The largest peak from the difference-Fourier map was inserted into the refinement model as a fully occupied O site, with a variable isotropic-displacement

parameter. The refining fractional coordinate x , and the displacement parameter U_{iso} , were allowed to refine simultaneously with the constraint of full occupancy; as one would expect, there is a significant degree of correlation (0.77) between these two parameters. However, this refinement model converged smoothly to a crystal-chemically reasonable model, i.e. $\text{S-O} = 1.46(11)$ \AA . The U_{iso} value of 0.51(17) for the O atom indicates significant positional disorder. A set of intensity data were collected at 100 K on the same crystal to try and quench any dynamic disorder of the (SO_4) group, but there was no significant difference between the room-temperature and 100 K structure models. The structure converged to a final R_1 index of 2.1%. Refined atom coordinates and anisotropic-displacement parameters are listed in Table 2, selected interatomic distances are given in Table 3, and bond valences, calculated with the parameters of Brese and O'Keeffe (1991) and Cooper *et al.* (2013), are given in Table 4.

Structure

The Hg atoms in gianellaite are each coordinated to two N atoms in a linear N–Hg–N linkage with a Hg–N distance of 2.06 \AA , and each N is tetrahedrally coordinated by four Hg atoms to

 TABLE 3. Interatomic distances (\AA) and angles ($^\circ$) in gianellaite.

| | |
|--------------|---------------------|
| Hg–N(1) | 2.060(2) |
| Hg–N(2) | 2.063(2) |
| Hg–O(1) | 2.77(8) \times 3 |
| N(1)–Hg–N(2) | 180.00(2) |
| O(1)–Hg–O(1) | 103.4(1.9) |
| S–O(1) | 1.46(11) \times 4 |

TABLE 4. Bond valences* (valence units) for gianellaite.

| | Hg | S | Σ |
|----------|---|----------------------|----------|
| N(1) | 0.74 \rightarrow x ⁴ | | 2.96 |
| N(2) | 0.74 \rightarrow x ⁴ | | 2.96 |
| O(1) | 1x ³ 0.10 \rightarrow x ³ | 1x ⁴ 1.56 | 1.86 |
| Σ | 1.78 | 6.24 | |

*Bond-valence curves Hg–O, S–O (Bresle and O’Keeffe, 1991); Hg–N (Cooper *et al.*, 2013).

form a net with six-sided channels along [011] (Fig. 2). This Hg₂N net conforms to a higher symmetry ($Fd\bar{3}m$) and is the basis for the inorganic compounds referred to as ‘Millon’s Base and its Salts’ (i.e. Lipscomb, 1951; Lund *et al.*, 2013). In gianellaite, the (SO₄) tetrahedron is ordered at the 0,0,0 position with each O atom of the tetrahedron forming three longer contacts to neighbouring Hg atoms, and in turn, each Hg atom also forms three contacts to three nearby (SO₄) vertices. The (SO₄) group is centred at the 4*a* position and the O atoms are at the 16*e* position. However, the value for U_{iso} for O is 18 times larger than the value for U_{eq} for S,

indicating that there is strong orientational disorder of the (SO₄) group about the centre of the cavity that it occupies. As indicated above, we also refined the structure at 100 K in an attempt to quench any possible dynamic disorder. However, the results of the two refinements are almost identical, indicating either (1) the displacement is static, or (2) dynamic disorder persists below 100 K. The results of the earlier study by Tunell *et al.* (1977) suggested possible disorder of the (SO₄) group over the 0,0,0 and $\frac{3}{4},\frac{3}{4},\frac{3}{4}$ sites; the $\frac{3}{4},\frac{3}{4},\frac{3}{4}$ site, which is vacant in our structure refinement, is shown in Fig. 2. It is this ordering of the (SO₄) group at 0,0,0 in gianellaite which gives rise to the weak observed *d*-glide violations (i.e. for $Fd\bar{3}m$), and results in the space group $F\bar{4}3m$ (Table 5); the special position 4*a* in $F\bar{4}3m$ has no equivalent counterpart in the space group $Fd\bar{3}m$. We note that several of these *d*-glide violations in Table 5 are statistically significant, but they are also relatively weak reflections that could be easily overlooked in a powder X-ray diffraction pattern, i.e. a simulated powder X-ray diffraction profile shows the strongest *d*-glide-violating reflection (002) as a minor blip above background (Fig. 3). No *d*-glide violations were reported in the original description of gianellaite (Tunell *et al.*, 1977), and we attribute our observance of these reflections mainly to the greater X-ray flux from the

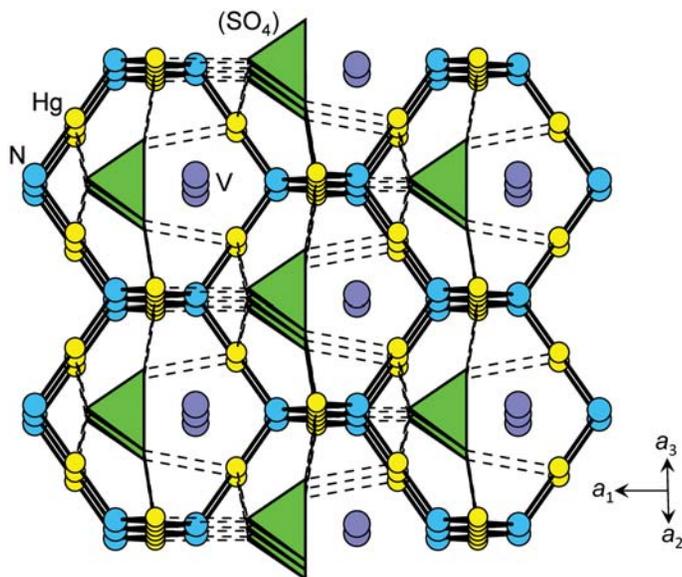


FIG. 2. The crystal structure of gianellaite projected down an axis slightly rotated from [011]. Yellow circles: Hg atoms; blue circles: N atoms; green shaded: (SO₄) group; V: vacant $\frac{3}{4},\frac{3}{4},\frac{3}{4}$ site; black lines: strong –Hg–N– bonding; dashed lines: weaker Hg–O contacts.

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 TABLE 5. Observed reflections incompatible with the *d*-glide plane in gianellaite.

| <i>h</i> | <i>k</i> | <i>l</i> | $ F_o $ | σ | $ F_o /\sigma$ |
|----------|----------|----------|---------|----------|----------------|
| 0 | 0 | 2 | 54.6 | 0.7 | 78 |
| 0 | 2 | 4 | 11.98 | 0.16 | 5 |
| 0 | 0 | 6 | 10.2 | 0.3 | 34 |
| 0 | 4 | 6 | 4.46 | 0.16 | 28 |
| 0 | 2 | 8 | 5.05 | 0.18 | 28 |
| 0 | 6 | 8 | 2.76 | 0.18 | 15 |
| 0 | 0 | 10 | 2.4 | 0.4 | 6 |
| 0 | 4 | 10 | 3.2 | 0.2 | 16 |
| 0 | 8 | 10 | 1.3 | 0.3 | 4 |
| 0 | 2 | 12 | 1.3 | 0.3 | 4 |
| 0 | 6 | 12 | 1.5 | 0.3 | 5 |

combined rotating-anode source and incident-beam multi-layer optics of our instrument. The absence of (H₂O) was inferred from the earlier infrared study (Tunell *et al.*, 1977). However, the absorptions at ~ 3300 and ~ 1600 cm⁻¹ in the infrared spectrum (Fig. 1) indicate the presence of (H₂O). We could find no definitive evidence of electron scattering from an (H₂O) group occupying the channel within our refinement difference-Fourier map, and surmise that the amount of (H₂O) may be small and highly disordered. Airoldi and Magnano (1967) solved the structure of (Hg₂N)₂(SO₄) (H₂O). The structure has the connectivity of gianellaite although the atoms are assigned to different Wyckoff positions in the structure. The presence of (H₂O) was assumed and the amount

was assigned by difference of the chemical analysis from 100 wt.%, but the (H₂O) was not located in the structure. In this regard, the results are similar to ours for gianellaite: the presence of (H₂O) was confirmed by infrared spectroscopy but we were unable to locate the (H₂O) in the structure.

In structures with anions such as O²⁻ and N³⁻ that are not associated with oxysalt units, the bonds to these anions must be fairly isodesmic and the resulting anion-coordination polyhedra link to form polymerized structures in much the same way as structures of cation-coordination polyhedra. This particular structural feature is common in Cu²⁺, Pb²⁺ and Hg minerals, and Filatov *et al.* (1992), Krivovichev (2004, 2008), Krivovichev and Filatov (1999a,b), Krivovichev *et al.* (1998a,b, 2013), Magarill *et al.* (2000), Siidra *et al.* (2008) and Hawthorne (2014) have described structural hierarchies for both minerals and synthetic compounds based on the polymerization of (OM₄) tetrahedra (M = cation); in particular, Magarill *et al.* (2000) and Borisov *et al.* (2005) focused on Hg minerals. Gianellaite is an example of this type of structure as it also may be regarded as a completely connected framework of N-centred (NHg₄) tetrahedra (Fig. 4a). As in mosesite, all tetrahedra share each of their vertices with one other tetrahedron to form a cristobalite-like framework (Krivovichev *et al.*, 2013; Hawthorne, 2014), and the (SO₄)²⁻ and (H₂O) groups occur in the interstices of the framework (Fig. 4b). Thus, gianellaite shows affinities with other completely connected (OM₄) framework structures such as mosesite [(Hg₂²⁺N](Cl,(SO₄),(CO₃),(H₂O); Switzer *et al.*, 1953), klenite [(Hg₂²⁺N](SO₄)_{0.25}Cl_{0.5}) (H₂O)_{0.5}; Giester

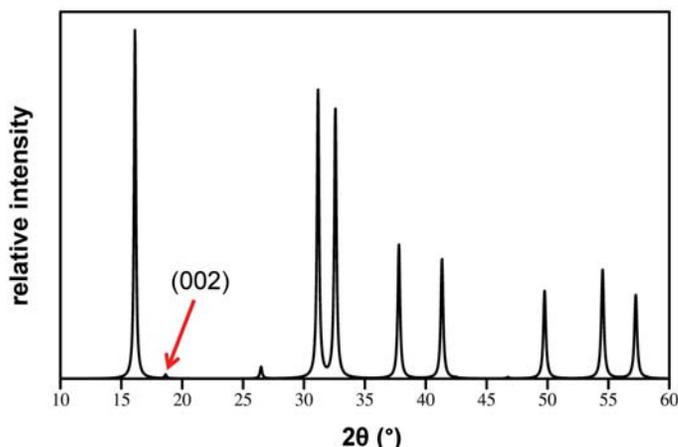


FIG. 3. Simulated powder X-ray diffraction pattern for gianellaite.

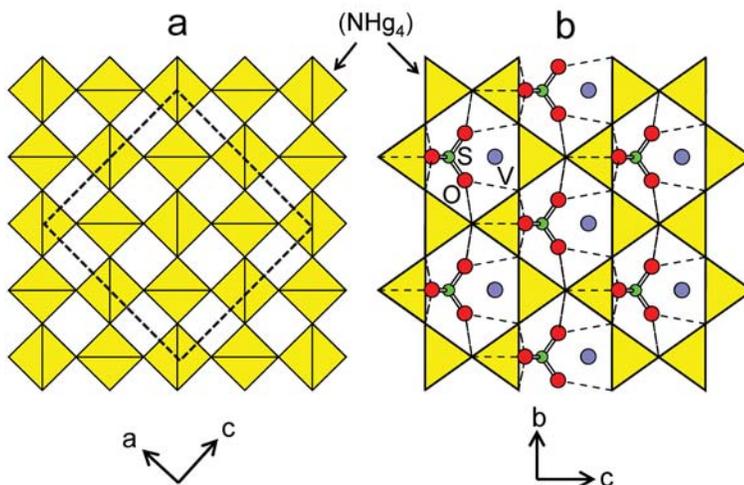


FIG. 4. The crystal structure of gianellaite; (a) the framework of (NHg_4) tetrahedra projected down $[100]$ and (b) the complete structure projected down $[011]$. Yellow polyhedra: (NHg_4) tetrahedra; green circles: S; red circles: O; blue circles: vacant $\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$ site; thick broken lines in (a): outline of unit cell; thin broken lines in (b) closest O–Hg contacts.

et al., 1996), melanothallite (Cu_2OCl_2 ; Krivovichev *et al.*, 2002) and cuprite (Cu_2O).

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