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Chemically induced symmetry breaking in the crystal structure of guanidinium uranyl sulfate

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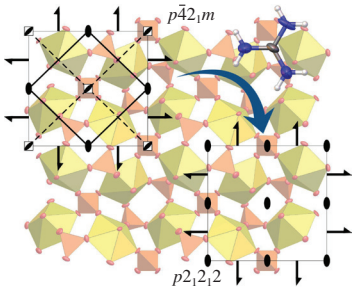
The novel uranyl sulfate templated by protonated guanidinium molecules was obtained from aqueous solution under ambient conditions. Its crystal structure was determined by the single crystal X-ray diffraction analysis and evaluated using a topological approach and information-based complexity calculations. The Se-for-S substitution resulted in a symmetry breaking (from orthorhombic in sulfate to monoclinic in selenate) due to the rearrangement of oxygen atoms, so the resulting symmetry is a consequence of interplay between the template-substructure interactions and size of the tetrahedral cation.



The U^{6+}-bearing compounds demonstrate a fascinating diversity of chemical compositions and structural architectures, in particular, due to the large variety of high-valent tetrahedral TO_4 oxyanions (T = S, Cr, Se, Mo, *etc*.) that link uranyl ions into inorganic polymeric structures.[1–4] Among these compounds of both natural and synthetic origins, sulfates and selenates make the greatest contribution with about 200 compounds known nowadays for each of these two groups. Organically templated uranyl sulfates and selenates represent a special group of particular interest due to the opportunity to combine properties inherent in organic and inorganic substructural units, which explains the large number of works devoted to them.[5–11] Selenium resembles sulfur in both its various pure polymorphs and compounds.[12] However, the comparison of uranyl sulfates with its selenates reveals many differences in their structure-building principles. In particular, our recent studies on crystallization phenomena associated with the selective Se-for-S substitution and related crystal-chemical restrictions have partially explained the existing small number of isotypic uranyl sulfate and selenates.[13,14] The present work continues our ongoing research in this field and reports on the crystals of novel guanidinium uranyl sulfate $[(NH_2)_3C]_2[(UO_2)_2(SO_4)_3]$ (GUS), which have been obtained from aqueous solutions under ambient conditions.†

Crystal structure of GUS‡ contains one crystallographically nonequivalent U atom with two short $U^{6+}\equiv O^{2-}$ bonds forming an approximately linear UO_2^{2+} uranyl ion (Ur), where $\langle U–O_{Ur}\rangle$ distance is 1.752 Å. The Ur cation is coordinated to five oxygen atoms ($\langle Ur–O_{eq}\rangle$ = 2.392 Å) belonging to sulfate tetrahedra that are arranged in the equatorial plane of the UO_7 pentagonal bipyramid. Each of two symmetrically nonequivalent S^{6+} atoms is tetrahedrally coordinated to four O^{2-} atoms. The $S(1)O_4^{2-}$ group

† Guanidine sulfate $[(NH_2)_2CNH]_2{\cdot}H_2SO_4$ (Sigma-Aldrich, 99%), uranyl nitrate hexahydrate $(UO_2)(NO_3)_2{\cdot}6H_2O$ (Vekton, 99%), and H_2SO_4 (Sigma-Aldrich, 98%) were used as received. Single crystals of GUS were prepared by evaporation from an aqueous solution containing uranyl nitrate (0.07 g, 0.14 mmol), H_2SO_4 (0.05 ml, 0.93 mmol), and guanidine sulfate (0.012 g, 0.05 mmol) in deionized water (2 ml). Homogeneous liquid solution was left on a watch glass at room temperature. The pH values of solution were in the range from 1 to 0 with the values closer to 1 for the freshly prepared solutions, while precipitation of crystals increased the acidity. The yellowish-green flattened crystals of GUS were formed in a couple of days.

‡ *Crystal data for GUS.* $C_2H_{12}N_6O_{16}S_3U_2$, M = 948.42, orthorhombic, space group $P2_12_12$, a = 9.907(3), b = 9.597(3) and c = 9.762(3) Å, V = = 928.2(5) Å^3, and Z = 2. Single crystal of GUS has been selected for the data collection under an optical microscope, encased in an oil-based cryoprotectant, and mounted on cryoloop. Data were collected using a Bruker SMART diffractometer equipped with an APEX II CCD area detector operating at monochromated MoKα radiation (λ[MoKα] = = 0.71073 Å) at 50 kV and 40 mA. Diffraction data were recorded at room temperature with frame widths of 0.5° in ω and φ, and exposure of 20 s spent per each frame. Data were integrated and corrected for the background and Lorentz and polarization effects using the Bruker programs APEX2 and XPREP. Absorption correction was applied using the empirical spherical model within the SADABS program.[25] The unit-cell parameters were refined by the least-squares techniques on the basis of 6883 reflections with 2θ in the range of 5.86–55.00°. The structures were solved by direct methods and refined to R_1 = 0.025 (wR_2 = 0.059) for 2066 reflections with $|F_0| \geqslant 4\sigma F$ using the SHELX programs[26] incorporated in the OLEX2 program package.[27] The final model included coordinates and anisotropic displacement parameters for all the non-H atoms. The nitrogen-bound H atoms were placed in calculated positions and were included in the refinement within the 'riding' model approximation, with U_{iso}(H) set to 1.2U_{eq}(N) and N–H of 0.86 Å. The crystal structure of GUS was refined as a two-component inversion twin using the [–1 0 0/0 –1 0/0 0 –1] matrix.

CCDC 1896327 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

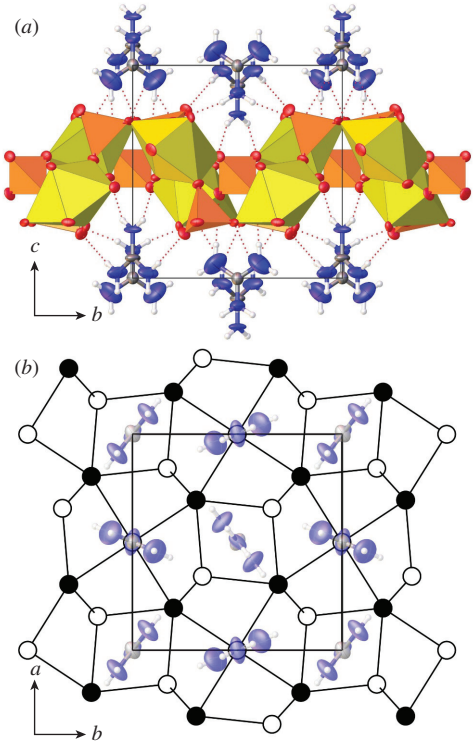


Figure 1 (*a*) The crystal structure of GUS, view along [100] and (*b*) graphical representation of the layered complex with superimposed guanidinium molecules. Ellipsoids are drawn at the 50% probability level. Legend: U polyhedra are yellow, S polyhedra – orange, C and N atoms are grey and blue, respectively, hydrogen atoms are small white circles, H-bonds are drawn as red dashed lines, black nodes are U atoms, and white nodes – S atoms.

is 3-connected sharing three vertices with the three adjacent uranium polyhedra. The non-shared vertices of tetrahedra are oriented either up or down relative to the layer plane. The S(2) O_4^{2-} group is 4-connected containing all the four oxygen atoms common with uranium polyhedra. The S(2) atom occupies a special position on the 2-fold axis. The U and S coordination polyhedra polymerize forming two-dimensional anionic layers of uranyl sulfate $[(UO_2)_2(SO_4)_3]^{2-}$ [Figure 1(*a*)] arranged parallel to (001). Two protonated guanidinium cations $[(NH_2)_3C]^+$ are located between the layers, thus compensating their negative charge and maintaining their linkage into a three-dimensional structure. It should be noted that the guanidinium cations occupy special positions at the 2-fold axis passing through the C atom and one of the amine groups. Analysis of the topology of uranyl sulfate layers in the structure of GUS [Figure 1(*b*)] indicates that 2D units belong to the *cc*2–2:3–14 type.[15] Its topological graph consists only of dense 4-membered cycles. This topology has been previously observed in the structures of several inorganic and organically templated structures, including the family of cesium actinyl compounds $Cs_2[(AnO_2)_2(TO_4)_3]$ (An = U, Np; T = S, Cr, Se, Mo)[14,16–20] containing various tetrahedral oxyanions.

It is worth noting that the crystal structure of GUS is also similar to that of recently studied guanidinium uranyl selenate, $[(NH_2)_3C]_2[(UO_2)_2(SeO_4)_3]$ (GUSe).[21] However, these two compounds are not isotypic. The replacement of selenate groups by smaller sulfate oxyanions results in the decreased unit-cell parameters associated with slight rotations of the U and T coordination polyhedra. The geometrical changes in the U-bearing layers are clearly seen from the analysis of the U–O_{br}–T angles incident at the O_{br} atoms bridging between the U and T polyhedra: the average U–O–T(1) angles are 135.7 and 139.3°, while ∠U–O–T(2) are 140.1 and 145.3° for GUSe and GUS, respectively. The observed straightening of the U–O_{br}–T links results in the rearrangement of O_{br} sites, which leads to the symmetry breaking from orthorhombic ($P2_12_12$ for GUS) to monoclinic ($P2$ in GUSe).[21] It is remarkable that in the structure of GUS, the symmetries of array of the U and S atoms, uranyl sulfate layer, and guanidinium molecules correspond to the $p2_12_12$ layer group, while in the structure of GUSe, such a symmetry was only detected for the array of U and Se atoms and the organic substructure (symmetry of the uranyl selenate layer in its structure is described by $p2$ group). The symmetry reduction of uranyl selenate layers as compared to that of uranyl sulfate can be explained by the shifts of O_{br} atoms from their ideal locations towards the protonated amine groups of guanidine molecules due to the formation of hydrogen bonds. The maximal symmetry of *cc*2–2:3–14 type of the actinyl layers is described by the tetragonal $p\text{-}42_1m$ layer group,[21] which was also observed for the crystal structures of cesium actinyl compounds $Cs_2[(AnO_2)_2(TO_4)_3]$ (An = U, Np; T = S, Cr, Se).[14,16–20] The substitution of Cs^+ cations by guanidinium molecules makes the presence of 4-fold screw axis impossible, thus leaving 2-fold axis instead only.

The information-based complexity parameters[22,23] for GUS are given in Table 1. First of all, the structural complexity of uranyl sulfate layer has been analyzed taking into account the real symmetry group of its layer [LG, Figure 2(*a*)]. Secondly, the topological complexity of layer (according to the maximal LG) has been calculated [Figure 2(*b*)]. The complexity parameters for the whole structure have been calculated using ToposPro software package[24] and are presented in comparison with the data for some isotypic uranyl compounds (see Table 1). Complexity calculations revealed that the crystal structure of GUS should be described as an intermediate in complexity possessing 4.480 bits per atom and 367.319 bits per cell. A reduction of the maximal tetragonal symmetry of layer to orthorhombic (GUS) and then to monoclinic (GUSe)[21] results in the gradually increased structural complexity. It should be noted that organic molecules make the most significant contribution to the overall complexity parameters

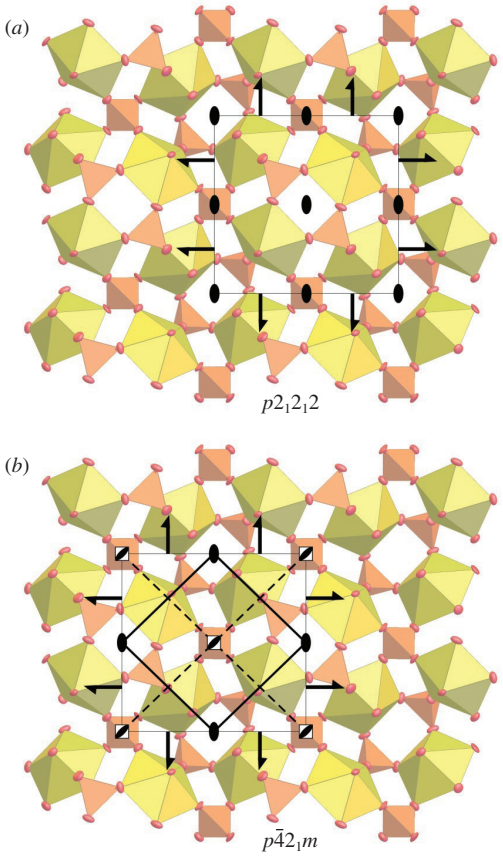


Figure 2 (*a*) Real and (*b*) maximal layer symmetry groups of the uranyl sulfate for 2D complexes observed in GUS.

Table 1 Information-based topological and structural complexity parameters for GUS and some isotypic uranyl compounds.

Complexity	v	I_G (bits per atom)	$I_{G,\,total}$ (bits per cell)	Contribution of $I_{G,\,total}$ (%)
GUS compound				
Topological complexity of the US layer ($p\bar{4}2_1m$)	42	3.059	128.477	35.0
Structural complexity of the US layer ($p2_12_12$)	42	3.440	144.477	39.3
Complexity of GUS	82	4.480	367.319	100
GUSe compound[21]				
Structural complexity of the USe layer ($p112$)	42	4.392	184.477	41.1
Complexity of GUSe	82	5.480	449.319	100
$Cs_2[(UO_2)_2(TO_4)_3]$ (T = S, Se) compound[14]				
Structural complexity of the UT layer ($p\bar{4}2_1m$)	42	3.059	128.477	84.5
Complexity of the structure	46	3.306	152.084	100

due to the large amount of atoms (orbits) forming guanidinium cations: the U : (C + H + N) ratio is 1 : 10. For instance, the contribution of the UT layer to the complexity of the whole structure of pure inorganic $Cs_2[(UO_2)_2(TO_4)_3]$ (T = S, Se)[14] compounds is significantly higher (84.5 *vs*. 39.3% in GUS).

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