Problem Set 1
Ch153a – Winter 2021
Due: 8 January, 2021

1) Above 13 K, the cesium titanium(III) alum (CsTi(SO₄)₂•12H₂O) crystallizes in the cubic space group Pa₃ with four crystallographically equivalent [Ti(OH₂)₆]³⁺ cations in the unit cell. The TiO₆ unit adopts a nearly perfect octahedral structure with Ti-O distances of 2.037(1) Å and O-Ti-O angles of 90.37(2)°. Considering just the TiO₆ units, and assuming Oh symmetry, what is the ground state term symbol for the [Ti(OH₂)₆]³⁺ cation in this alum?

2) The OH₂ ligands of M(III) in CsM(SO₄)₂•12H₂O alums (M = Ti, V, Cr, Mn, Fe, Mo, Ru) have a trigonal planar geometry in which the angle between the Ti-O vector and the OH₂ plane is 0.3(1)°, and trans-OH₂ ligand pairs are nearly coplanar. There are three limiting orientations of the OH₂ planes. In configuration A, the OH₂ ligands on the x-axis lie in the xy plane; the OH₂ ligands on the y-axis lie in the yz plane; and the OH₂ ligands on the z-axis lie in the xz plane. In configuration B, the OH₂ ligands on the x-axis are rotated 45° counterclockwise (positive angle) about the x-axis as viewed from the positive x direction; the OH₂ ligands on the y-axis are rotated 45° counterclockwise (positive angle) about the y-axis as viewed from the positive y direction; and the OH₂ ligands on the z-axis are rotated 45° counterclockwise (positive angle) about the z-axis as viewed from the positive z direction. In configuration C, the OH₂ ligands on the x-axis are rotated 45° clockwise (negative angle) about the x-axis as viewed from the positive x direction; the OH₂ ligands on the y-axis are rotated 45° clockwise (negative angle) about the y-axis as viewed from the positive y direction; and the OH₂ ligands on the z-axis are rotated 45° clockwise (negative angle) about the z-axis as viewed from the positive z direction. MATLAB *.fig files of the three configurations are posted on the course website (https://www.bilrc.caltech.edu/Ch153a_2021/Ch153.html). You might find it easier to visualize the structures if you view these files in MATLAB.

a) What are the point groups of configurations A, B, and C?
b) Give the ground state term for a [Ti(OH₂)₆]³⁺ cation in each configuration (neglecting spin-orbit coupling). Explain each answer on the basis of a simple ligand-field orbital diagram.
c) Draw a qualitative correlation diagram showing the energies of the lowest states in [Ti(OH₂)₆]³⁺ as the OH₂ rotation angle increases from −π/4 to +π/4 (neglecting spin-orbit coupling).
d) The rotation angle of the OH₂ plane in CsTi(SO₄)₂•12H₂O is −20.4(1)°. Identify the point group for this configuration and predict the ground state term symbol for the [Ti(OH₂)₆]³⁺ cation in this alum (neglecting spin-orbit coupling).
e) In the CsM(SO₄)₂•12H₂O (M = Co, Rh, Ir) alums, the OH₂ ligands adopt a pyramidal geometry rather than trigonal planar. Suggest an explanation for the difference on the basis of the electronic structures of the M(III)-aquo ions.