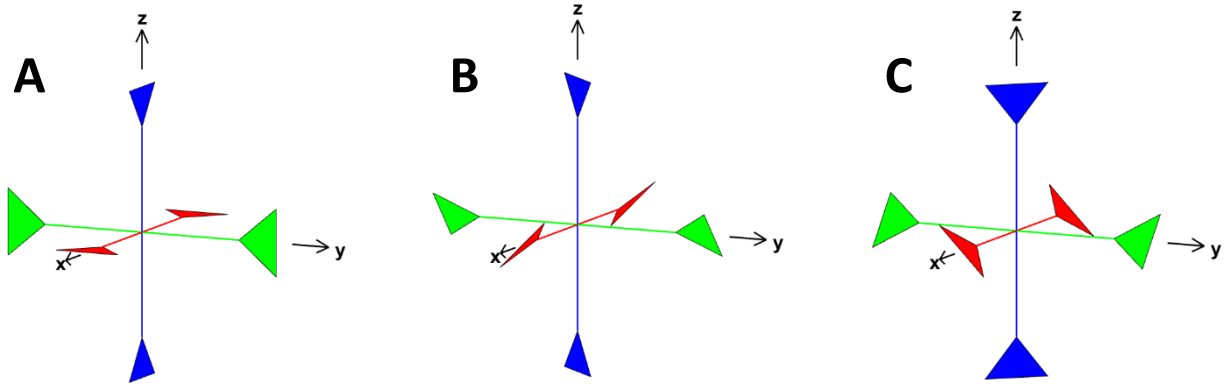
Problem Set 1
Ch153a – Winter 2021
Due: 8 January, 2021

1) Above 13 K, the cesium titanium(III) alum ($CsTi(SO_4)_2 \bullet 12H_2O$) crystallizes in the cubic space group *Pa3* with four crystallographically equivalent $[Ti(OH_2)_6]^{3+}$ cations in the unit cell. The TiO_6 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 TiO_6 units, and assuming O_h symmetry, what is the ground state term symbol for the $[Ti(OH_2)_6]^{3+}$ cation in this alum?
2) The OH_2 ligands of M(III) in $CsM(SO_4)_2 \bullet 12H_2O$ 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 OH_2 plane is 0.3(1)°, and *trans*-OH_2 ligand pairs are nearly coplanar. There are three limiting orientations of the OH_2 planes. In configuration **A**, the OH_2 ligands on the *x*-axis lie in the *xy* plane; the OH_2 ligands on the *y*-axis lie in the *yz* plane; and the OH_2 ligands on the *z*-axis lie in the *xz* plane. In configuration **B**, the OH_2 ligands on the *x*-axis are rotated 45° counterclockwise (positive angle) about the x-axis as viewed from the positive x direction; the OH_2 ligands on the *y*-axis are rotated 45° counterclockwise (positive angle) about the y-axis as viewed from the positive y direction; and the OH_2 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 OH_2 ligands on the *x*-axis are rotated 45° clockwise (negative angle) about the x-axis as viewed from the positive x direction; the OH_2 ligands on the *y*-axis are rotated 45° clockwise (negative angle) about the y-axis as viewed from the positive y direction; and the OH_2 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 $[Ti(OH_2)_6]^{3+}$ 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 $[Ti(OH_2)_6]^{3+}$ as the OH_2 rotation angle increases from $-\pi/4$ to $+\pi/4$ (neglecting spin-orbit coupling).
d) The rotation angle of the OH_2 plane in $CsTi(SO_4)_2 \bullet 12H_2O$ is −20.4(1)°. Identify the point group for this configuration and predict the ground state term symbol for the $[Ti(OH_2)_6]^{3+}$ cation in this alum (neglecting spin-orbit coupling).

e) In the $CsM(SO_4)_2 \bullet 12H_2O$ (M = Co, Rh, Ir) alums, the OH_2 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.