PS08.01.37 SUPERSTRUCTURE OF THE DEFECT PEROVSKITE TYPE COMPOUNDS La$_{1-x}$TiO$_3$(call LTO) were carried out by the single-crystal X-ray diffraction making use of SR, with the aid of the electron diffraction. The LTO as well as La$_{1-x}$TiO$_3$(call LTO) are promising host crystals for the Li$^+$ ion intercalation. Both compounds crystallizes in double-layered perovskite structure with perfectly vacant sites of La$^{3+}$ in the z=1/2 plane and by two third occupied sites of La$^{3+}$ in the z=0 plane at room temperature. Although reduction of crystal system to which the LNO belongs, from tetragonal space group P4/mmm to orthorhombic and a superstructure doubling the a and b dimensions of the fundamental tetragonal unit cell, have been previously reported, no structure refinements have been performed to our knowledge. X-ray diffraction experiment were made using the horizontal-type four-circle diffractometer, utilizing SR from a vertical wiggler at the beam line 14A of the PF(KEK) in Tsukuba, Japan. The geometry of the reciprocal lattice of the LNO insists on being orthorhombic unlike the LTO is tetragonal, and the refined cell parameters are a=0.7817(1), b=0.7836(1), c=0.7910(1) nm. Three dimensional diffused intensity data including the superstructure reflections were collected in the independent reciprocal space within sin $\theta$=0.10 with $\lambda$=0.7079nm. The electron diffusion pattern of the h00 plane of the LNO contained weak but sharp superstructure reflections and obeyed an extinction rule for the C-faced lattice. Of five possible space groups, Cmmm, C2mm, Cm2m, Cmm2 and C222, Cm2m seems to be the most probable one since in the refinements it gave the space group of the crystal system to which the La$_3^+$ ions are accommodated. The dimensions of the fundamental cell, have been previously determined or extended in one, two, or three directions. The connectivity patterns of the H bonding systems for the same N value can vary due to the different distribution of acceptor functions between HSO$_4^-$ and H$_2$SO$_4$ units. The structures of Oa-NSO$_4^-$ and Li[H(HSO$_4$)$_2$](H$_2$SO$_4$)$_3$ contain disordered hydrogen bonds characterized by strong O...O interactions at the distances of 2.51 Å and 2.44 Å, respectively.

PS08.01.38 NOVEL FERRICENIUM POLYIODIDES. Karl-Friedrich Tebbe, Rita Buchem, Institut für Anorganische Chemie der Universität zu Köln, D-50939 Köln, Groenstraße 6, Germany

Probable ferricenium polyiodides FeC$_9$(n > 1) except for a triiodide FeC$_9$ [1] are only poorly characterized [2]. During systematic investigations of polyiodide series with suitable cations we proved the compounds of this type with n = 4, 5, 7, 9, 6.97 [3] from which the crystal structures of the ferricenium heptaiodide FeC$_9$ [4], the bisferricenium hexaiodide (FeO)$_6$ [5] and a trimicronium nonaiodide (FeO)$_9$ [6] have been solved. Particularly the latter is worth mentioning (FeO)$_9$, P2$_1$/n, Z=2, a=10.631 Å, b=18.165 Å, c=20.377 Å, $\alpha=91.51^{\circ}$, R=0.059), as it is the polyiodide with the largest iodine excess so far [7] containing also hitherto scarcely observed formally three times charged polyiodide ions [8]. Similar reactions of the substituted complexes 1,1'-dimethylferrocene and decamethylferrocene with iodine produce diMeFeC$_9$ with n = 3 [9], 5, 7 and decMeFeC$_9$ with n = 3, 5, 6.5 [10]. These frequently in the anionic iodine part highly connected crystal structures will be presented, described, compared and explained.


PS08.01.39 STRUCTURAL CHEMISTRY OF METAL HYDROGEN SULFATES. S. Troyanov, C. Werner*, E. Kármán*, Moscow State University, Chemistry Department, 119899 Moscow, Vorobyjev Gory, Russia, Humboldt Universität Berlin, Institut für Anorganische Chemie, Hessische Str. 1-2, 10115 Berlin, Germany

A series of new hydrogen sulfates of general formula M$_2$H$_2$SO$_4$ and M$_3$H$_2$SO$_4$ have been synthesized and structurally characterized in the last few years. The general structural aspects are discussed using the value N which defines the average number of hydrogen donor functions (OH groups) per SO$_4$ tetrahedron.

All crystal structures contain M$^{1+}$ or M$^{3+}$ ions coordinated by O atoms with CN's from 4 to 10 depending mainly on the metal radii. Counterparts consist of simple HSO$_4^-$ tetrahedra or their combination with SO$_4^{2-}$ or H$_2$SO$_4$ tetrahedra.

The S-O distances correlate with additional structural functions of O atoms such as coordination by M atom(s), H-acceptor, or H-donor functions. The S-OH distances are generally 0.1 Å longer than the S-O distances. Both S-O and S-OH distances are slightly longer (by 0.02-0.03 Å) in HSO$_4^-$ as compared to those in the H$_2$SO$_4$ unit.

Every H atom forms a hydrogen bond O-H...O. The N value in the formula defines the main features of the hydrogen bonding systems: isolated or extended in one, two, or three directions. The connectivity patterns of H bonding systems for the same N value can vary due to different distribution of acceptor functions between HSO$_4^-$ and H$_2$SO$_4$ units.

The structures of Na$_2$HSO$_4$ and Li[H(HSO$_4$)$_2$](H$_2$SO$_4$)$_3$ contain disordered hydrogen bonds characterized by strong O...O interactions at the distances of 2.51 Å and 2.44 Å, respectively.

PS08.01.40 Rb$_2$Y$_2$O$_3$(HSO$_4$)$_2$(H$_2$SO$_4$)$_3$: A MIXED-VALENCE VANADIUM(V,IV) ARSENATE. Wen-Jiuan Tsai, Sue-Lein Wang*, Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 30043

A new mixed-valence vanadium hydrogen arsenate, Rb$_2$Y$_2$O$_3$(HSO$_4$)$_2$(H$_2$SO$_4$)$_3$: Mixed-Valence Vanadium(V,IV) Arsenate has been synthesized under hydro-thermal conditions and its structure was determined from single-crystal X-ray diffraction data. Intensity measurements were performed on a CCD area detector system. Crystal data: H$_2$AsO$_4$ Rb$_2$Y$_2$O$_3$, monoclinic, P2$_1$/n, a=9.7162(1) Å, b=11.2389(2) Å, c=13.8463(2) Å, $\beta=100.843(1)^{\circ}$. V = 1490.95(5) Å$^3$, Z=4, and $R$=0.0445 for 2378 unique reflections. The structure is composed of Rb$^+$ cations, water molecules and [(V$_2$O$_7$)$_2$(H$_2$AsO$_4$)$_3$(H$_2$SO$_4$)$_3$]$^{2+}$ cluster anions, in which two of the edge-sharing pairs of VO$_6$ octahedra are connected by four HAsO$_4$ and two H$_2$SO$_4$ groups. Variable-temperature powder magnetic susceptibility data confirm the presence of one V$^{4+}$ and one V$^{5+}$ ion per formula unit. In this presentation, the hydrothermal synthesis, single-crystal structure, thermal analysis, and magnetic study of Rb$_2$Y$_2$O$_3$(HSO$_4$)$_2$(H$_2$SO$_4$)$_3$: Mixed-Valence Vanadium(V,IV) Arsenate will be given. Structural relationship to A$_2$Mo$_5$O$_{12}$(HAsO$_4$)$_2$(H$_2$SO$_4$)$_3$: Mixed-Valence Vanadium(V,IV) Arsenate will be discussed.