PS08.01.37 SUPERSTRUCTURE OF THE DEFECT PEROVSKITE TYPE COMPOUNDS La1/3NbO3. Y. Tabira, K. Tanabe, K. Suda and N. Ishizawa. Research Laboratory of Engineering Materials, Tokyo Institute of Technology, Nagatsuta, Midori, Yokohama 226, Japan

Superstructure analysis of the title compound (hereafter call LNO) were carried out by the single-crystal X-ray diffraction making use of SR, with the aid of the electron diffraction. The LNO as well as La1/3TiO3 (call LTO) are promising host crystals for the Li+ ion intercalation. Both compounds crystallizes in double layered perovskite structure with perfectly vacant sites of La3+ in the z=1/2 plane and by two third occupied sites of La3+ in the z=0 plane at room temperature. Although reduction of crystal system to which the LNO belongs, from tetragonal space group P4/mnm 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 diffraction intensity data including the superstructure reflections were collected in the independent reciprocal space within sin Θ/λ=0.1 with λ=0.070 nm. The electron diffraction pattern of the h00 plane of the LNO contained weak but sharp superstructure reflections and obeyed an extinction rule for the C-faceted lattice. Of possible five space groups, Cmnm, C2nm, Cm2m and C222, Cm2m seems to be the most probable one since in the refinements it gave the lowest conventional R factor to be 0.048 for all 1150 reflections. The R factor is 0.044 for 636 fundamental, and 0.049 for 514 superstructure reflections whose intensities are much weaker than the fundamental ones. Refined structure has an alternate shift along the b axis of La3+ in the (001) plane and suggests the statistical fluctuation of Nb5+ from the averaged position, which might interact with the local distribution of La3+ ions in the structure.

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

Probable ferricenium polypiodides FeI₃ (n > 1) except for a triiodide FeI₃ [1] are only poorly characterized [2]. During systematic investigations of polypiodide series with suitable cations we proved the compounds of this type with n = 4.33, 5, 7, 8, 9.67 [3] from which the crystal structures of the ferricenium triiodide FeI₃ [4], the bistriflicenium hexafluoriodide (FeO)₂ [5] and a triflicenium nonafluoriodide (FeO)₃ [6] have been solved. Particularly the latter is worth mentioning (FeO)₃, P2₁/m, z = 6, a = 10.631 Å, b = 18.163 Å, c = 20.377 Å, β = 91.51°, R = 0.059, as it is the polypiodide with the largest iodine excess so far [7] containing also hitherto scarcely observed formally three times charged polypiodide ions [8]. Similar reactions of the substituted complexes 1,1′-dihexamethyldiferrrocene and decaamethyldiferrrocne with iodine produce diMeFeI₃ with n = 3 [9], 5, 7 and decamMeFeI₃ 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. Troianov, C. Werner, E. Kermairit, Moscow State University, Chemistry Department, 119899 Moscow, Vorobyevy 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 Me2H₂SO₄ and Me₂H₃SO₄ 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 SO₄ tetrahedron.

All crystal structures contain M⁺ or M²⁺ ions coordinated by O atoms with CN’s from 4 to 10 depending mainly on the metal radius. Counterparts consist of simple HSO₄ tetrahedra or their combination with SO₄³⁻ or H₂SO₄ 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 HSO₄ as compared to those in the H₂SO₄ 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 the H bonding systems for the same N value can vary due to different distribution of acceptor functions between HSO₄ and H₂SO₄ units.

The structures of a NaH₂SO₄ and Li[H(H₂SO₄)](H₂SO₄) 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 Rb₂V₂O₅(As₃O₄)₂(H₂AsO₄)·H₂O: A MIXED-VALENCE VANADIUM(V,V) ARSENATE. Wen-juan Tsai, Sue- Lein Wang*, Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 30043

A new mixed-valence vanadium hydrogen arsenate, Rb₂V₂O₅(As₃O₄)₂(H₂AsO₄)·H₂O 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: H₂AsO₄·Rb₂V₂O₅, monoclinic, P2₁/c, a = 9.7162(1) Å, b = 11.2839(2) Å, c = 13.8463(2) Å, β = 100.843(1)°, V = 1490.95(5) Å³, Z = 4, and R = 0.0445 for 2378 unique reflections. The structure is composed of Rb⁺ cations, water molecules and [(V₂O₅)(H₂AsO₄)₄(H₂AsO₄)]₄ⁿ⁻ cluster anions, in which two of the edge-sharing pairs of VO₆ octahedrons are connected by four HAsO₄ and two H₂AsO₄ groups. Variable-temperature powder magnetic susceptibility data confirm the presence of one V⁴⁺ and one V⁵⁺ ion per formula unit. In this presentation, the hydrothermal synthesis, single-crystal structure, thermal analysis, and magnetic study of Rb₂V₂O₅(As₃O₄)₂(H₂AsO₄)·H₂O will be given. Structural relationship to A₂Mo₂O₇(As₂O₅)₄·H₂O (Å = Cs and CsH₅NH) is also discussed.