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Crystal Structures and Thermal Behavior of Bis[dibenzylidimethylammonium]CuBr₄ and Bis[di-benzylidimethylammonium]CuCl₄ crystallized from acetonitrile and dilute HX solutions

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The A₂MX₄ structures have been of interest for a long time because of their structural properties, phase transitions and thermochromic behavior in the solid state. The thermochromic behavior of copper(II) chloride complexes have been divided at least into two classes [1]. In one class the compounds show a phase transition involving a change in the coordination geometry around the copper ion. In the other class, the thermochromism is associated only with the temperature dependence of the line widths of the electronic absorption bands. It has also been observed that the *trans* Cl-Cu-Cl angle is less than 132° when there is no possibility of hydrogen bonding between the cation and the CuCl₄²⁻ anion. When N-H...Cl⁻ hydrogen bonding exists, the *trans* Cl-Cu-Cl angle is greater than 132° [1]. In some cases the anion can even have a planar configuration (Cl-Cu-Cl angle of 180°).

The new R₂R'₂N⁺X⁻ type quaternary ammonium halides [2-3] have enabled us to crystallize and characterise a new kind of (R₂R'₂N)₂MX₄ compounds and examine their thermal behavior in the solid state. Bis[dibenzylidimethylammonium] CuX₄ (X = Br or Cl) were crystallized from acetonitrile and dilute HX solutions. When the acetonitrile solution was used, the acetonitrile molecule co-crystallized into the crystal structure. As a result, the isomorphous structures of Bis[di-benzylidimethylammonium]CuX₄·0.5CH₃CN (X = Br or Cl) in the monoclinic space group P2₁/n were obtained. Interestingly, while a dilute HX solution was used, the Bis[dibenzylidimethylammonium]CuX₄ (X = Br or Cl) crystallized without solvent molecules and the formed crystals were not isomorphous with each other. The tetrabromocuprate structure crystallized in the triclinic space group P-1 and the tetrachlorocuprate structure in the monoclinic space group P2₁/c. In all cases the CuX₄ anion appeared in a distorted tetrahedral geometry as the average of the two large X-Cu-X angles was about 123-133° depending on the structure.

The powder diffraction measurements showed that every compound has the same structure both at room temperature and at the temperature of -100°C. Thermal behavior of these compounds was examined by TG/DTA and DSC measurements. In all cases the primary decomposition of the compounds occurred in two stages. Based on the DSC measurements these compounds had a melting peak or a melting-crystallization-melting peak clearly before or just before the decomposition started. In general, these crystals showed to be exceptionally stable compounds having no phase transitions between -100°C and the melting point. Thus, no marks of any thermochromic behavior were seen in contrast to the general behavior of similar A₂MX₄ compounds. In addition, these crystals are very stable in the air at ambient temperature as they can be stored in the air for several weeks without any marks of the decomposition.

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Structural Characterization of a New Nickel (II) Hybrid Vanadate: Ni₈(4-4 Bpy)₁₆V₂₄O₆₈

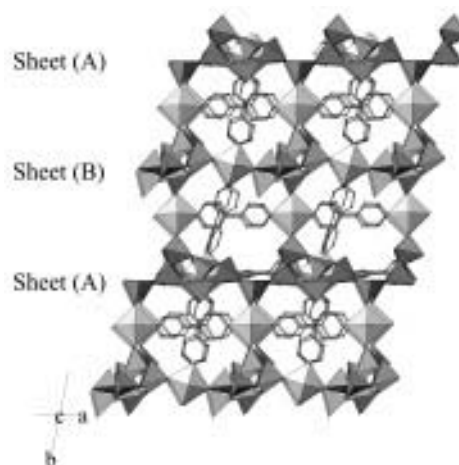
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Due to the diversity of coordination environment and oxidation states of vanadium, the vanadates are a very attractive line of investigation which may provide different porous structures. The introduction of 3d transition metals into the structures gives rise to interesting spectroscopic and magnetic properties. The Ni₈(4-4 Bpy)₁₆V₂₄O₆₈ compound was prepared under mild hydrothermal conditions. The reaction of Ni(NO₃)₂·6H₂O, Na₂HAsO₄·7H₂O, NaVO₃ and 4-4 Bpy in 30ml of water at 170°C during 5 days give green emerald prismatic crystals.

Ni₈(4-4 Bpy)₁₆V₂₄O₆₈ crystallizes in the space group P1, Z=1 with a=11.003(6) Å, b=22.625(1) Å, c=22.622(1) Å, α=105.194(5)°, β=95.786(4)°, γ=99.981(5)°, V=5434 Å³, and d_{obs.}=1.67(2) gr/cm³.

The complex structure of this compound consists of chains formed by five member rings of vanadium tetrahedra, corner linked through single vanadium tetrahedra. These chains are pillared along the "b" direction giving rise to two kind of sheets. Sheets (A) formed by chains parallel to the "a" direction, and sheets (B) parallel to the "c" direction. The chains belonging to the same or different sheet are corner linked through nickel octahedra. Furthermore, the nickel (II) cations are linked through bipyridines in three directions of the space, filling the porous of the structure.



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