

acid (hypydcH<sub>2</sub>) and acridine (acr). The compound, (acrH)[Zn(hypydc)<sub>2</sub>].10H<sub>2</sub>O, was characterized by elemental analysis, <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR spectroscopy, single crystal X-ray diffraction method. Zn(II) compound crystallized in monoclinic system with 8 molecules per unit cell. The crystallographic analysis revealed that the complex consist of [Zn(hypydc)<sub>2</sub>]<sup>2-</sup> anion, two acrH<sup>+</sup> cations and ten uncoordinated water molecules. Zn(II) atoms in the complex, is coordinated in a distorted octahedral geometry by two nitrogen and four oxygen atoms of 4-hydroxypyridinedicarboxylate ligand. Acridine is known as proton acceptor ligand. In the crystal structures of the complex extensive O–H...O, N–H...O and C–H...O hydrogen bonds as well as electrostatic forces, C–O...π and π–π stacking play important roles in stabilizing structures.

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### Effects of substituents on the conformational diversity of the new *N*-phosphinylureas

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*N*-phosphoniylureas are some important instances of phosphoramidates that little attention has been given to their biological properties [1] and structural studies [2]. These compounds can cause attractive biological activities due to having urea and peptide moieties. Recently, we evaluated anticancer [3] and antibacterial [4] properties of some of these compounds. Further, in our previous studies, we were synthesized and characterized two novel *N*-phosphinylureas with general formula RC<sub>6</sub>H<sub>4</sub>NHC(O)NHP(O)NHCH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>NH [4]. The crystal structures of compounds containing (R = H (1), NO<sub>2</sub> (2)) are composed of two and one conformers, respectively. These molecules showed *anti* and *syn* conformations with respect to the C=O and P=O bonds for (1) and (2). In order to further investigate, quantum chemical calculations were applied. The results predict a structure with *anti* conformation as the most stable form for 2 due to the packing effect.

In connection with our current work in the field of *N*-phosphinyl ureas chemistry and investigate of effect of substituent, here we synthesized and characterized two novel derivatives with R = CH<sub>3</sub> (3) and F (4). The 3D structures of these molecules have been determined by X-ray crystallography. The title molecules contain four and two conformers in crystalline lattice, respectively. In molecule 3, four types of hydrogen bond are established among these conformers, intramolecular P=O...H-NPh, intermolecular C=O...NHP, C=O...NH and P=O...NH hydrogen bonds. These conformers create two types of chains with different arrangements in the crystal lattice of 3. Linking of these chains by hydrogen bonding leads to form a two-dimensional polymeric chain in the crystal lattice. In molecule 4, intramolecular P=O...H-NPh, intermolecular C=O...NHP, P=O...NH hydrogen bonds cause to form a two-dimensional polymeric chain. It is noteworthy; the new *N*-phosphinylureas crystallize in the triclinic and monoclinic crystal systems with space groups P $\bar{1}$  and P2<sub>1</sub>/c, respectively. The symmetry of the unit cell decreases with increase in the multiplicity of conformers that demonstrate our previous study [5]. The mean P=O

distances fall in the range 1.4803-1.4845Å that are slightly longer than the normal P=O bond length (1.45Å). The phosphoryl oxygen atoms (O(2), O(22), O(23), O(24), O(1) and O(1A)) occupy a pseudoaxial position, and the 4-methyl and 4-fluorophenylureido groups adopt a pseudoequatorial orientation.

In all of the compounds, the P-N<sub>amide</sub> bond length is longer than the P-N<sub>amine</sub> bond lengths. All of these bonds are in the range 1.608 (2) - 1.698(18) Å and thus are significantly shorter than a typical P-N single bond (1.77 Å). The phosphorus atoms have slightly distorted tetrahedral configuration.

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**Keywords:** synthesis, 3D, substituent

## MS56.P13

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### Structural characterization of Mo<sub>3</sub>Fe(NO)S<sub>4</sub> Cubane-type clusters with different electron populations

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Molecule Nitric Oxide plays an important role in biological systems. [1] Many of the important biological functions of NO are iron-mediated, being the synthesis and characterization of new iron nitrosyl complexes a priority target for the understanding of its biological functions. [2] Cubane-type clusters [Mo<sub>3</sub>(FeNO)S<sub>4</sub>(dmpe)<sub>3</sub>Cl<sub>3</sub>]<sup>0/+</sup> (dmpe = 1,2-bis(dimethylphosphine-ethane)) have been isolated (see figure 1). Here we analyze the influence of the different electron population on the molecular structure. A detailed spectroscopic study (NMR, magnetic susceptibility, EPR and IR) is presented to evaluate the effect derived from the non-innocent behaviour of the nitrosyl ligand attached to iron atom on the molecular structure of these clusters.

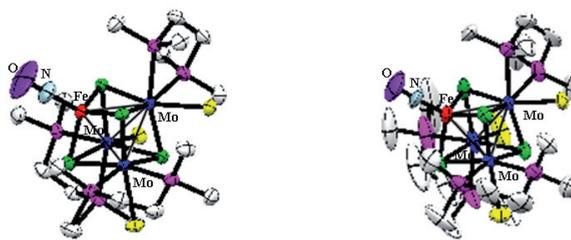


Figure 1: Molecular structure of the molybdenum iron nitrosyl cubane-type clusters [Mo<sub>3</sub>(FeNO)S<sub>4</sub>(dmpe)<sub>3</sub>Cl<sub>3</sub>] (left) and [Mo<sub>3</sub>(FeNO)S<sub>4</sub>(dmpe)<sub>3</sub>Cl<sub>3</sub>]<sup>+</sup> (right)

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**Keywords:** cluster, iron, spectroscopy

## MS56.P14

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### Effects in the atomic structure of BaFe<sub>2</sub>As<sub>2</sub> by pressure and chemical substitution

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The effects of K and Co substitutions and quasi-hydrostatic applied pressure ( $P < 9$  GPa) in the local atomic structure of BaFe<sub>2</sub>As<sub>2</sub>, Ba(Fe<sub>0.937</sub>Co<sub>0.063</sub>)<sub>2</sub>As<sub>2</sub> and Ba<sub>0.85</sub>K<sub>0.15</sub>Fe<sub>2</sub>As<sub>2</sub> superconductors were investigated by extended X-ray absorption fine structure (EXAFS) measurements in the As *K* absorption edge. The As-Fe bond length is found to be slightly reduced (d 0.01 Å) by both Co and K substitutions, without any observable increment in the corresponding Debye-Waller factor. Also, this bond is shown to be compressible ( $\kappa = 3.3(3) \% 10^{-3}$  GPa<sup>-1</sup>). The observed contractions of As-Fe bond under pressure and chemical substitutions are likely related with a reduction of the local Fe magnetic moments, and should be an important tuning parameter in the phase diagrams of the Fe-based superconductors.

**Keywords:** pnictides, superconductivity, EXAFS

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### Anisotropy in Anomalous Scattering in TiO<sub>2</sub> and the influence of point defects

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Diffraction intensities near an absorption edge of one of the crystal's atoms show a considerable dependency on the polarization of the incident and scattered X-rays and also on the corresponding wave vectors called Anisotropy in Anomalous Scattering (AAS). The polarization is usually varied by rotating the crystal around the momentum transfer vector by an angle  $\psi$ . Based on the tensorial treatment of this dependency like described by Kirfel et. al. [1], we studied the forbidden reflection 001 and the allowed reflection 111 of rutile at the titanium K absorption edge. Furthermore we investigated the influence of diluted point defects, in particular oxygen vacancies, on the scattered intensity profiles. Point defects as one possible origin for polarization anisotropy were discussed by Dmitrienko et. al. [2] which formed the basis of our considerations. Variations of the AAS profiles with energy have been observed and theoretically been account for. For the allowed 111 reflection a clear change of these patterns with increasing number of oxygen vacancies has been measured at different beamlines of the light source DORIS at DESY.

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**Keywords:** DAFS, rutile, AAS

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### The Structure and X-ray Absorption Spectrum Studies of Mn and N Co-doped ZnO

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To grow ferromagnetic *P*-type Zn(Mn)O, nitrogen and manganese co-doped ZnO film with wurtzite structure were made by ion implantation method. The Mn *K*-edge and *L*<sub>3,2</sub>-edge peaks of samples have same binding energy with peak of MnO. So the X-ray absorption spectrum show the valence of doped Mn ion is 2+. The ions substitution of Zn by Mn was proved. The X-ray diffraction show a extra peak about 1.3 degree lower than the ZnO(200) peak at 66.39 degree. The lattice length became longer after doping. The Curie temperature, coercive, and saturation moment were measured by SQUID. All of them were tuned by the controlling of nitrogen concentration. The effective magnetic moment and pinning force were enhanced but the Curie temperature was decrease upon the doped nitrogen concentration. The nitrogen substitution for oxygen can change not only carrier concentration but also the magnetic coupling strength between neighboring Mn ions.

**Keywords:** ZnO, X-ray absorption spectrum

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### XRD and dual elemental XAFS analyses of inorganic solids

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Two inorganic solid solutions,  $\gamma$ -Fe<sub>2-x</sub>Cr<sub>x</sub>O<sub>3</sub> and LaFeNiTiO<sub>3</sub>, were studied by X-ray absorption fine structure (XAFS) of K-absorption edge of two elements and by synchrotron radiation X-ray diffraction (XRD). Measurements were performed at the Stanford Synchrotron Radiation Lightsource at room temperature.

High-resolution XRD patterns were processed by means of the Rietveld method, using Fullprof [1]. In Rietveld refinements, the ordered/disordered degree of the considered solutions is indiscernible in cases of atoms being neighbors in the Periodic Table. Crystallographic interpretation of magnetic and ferroelectric phenomena is shortened by this limitation.

Double-element XAFS analysis was applied to clarify, via short-range structure characterization, the nature of investigated systems. In