

been reported. Among examples, can be named the following ones: anilinium nitrate [7], anilinium hydrogenphosphite and anilinium hydrogenoxalate [8]. This structure may be described as formed by alternating sheets of cations and anions which are held together with four five centered N-H...O bonds to form  $C_4^4(10)C_4^4(10)$  infinite chains running through the c direction. Moreover, strong O-H...O hydrogen bonds observed between bisulfate anions generate  $C_2^2(8)$  chains in the a axis direction. The infinite chains resulting from anion-anion and anion-cation interactions can be described as zigzag layers parallel (ac) plans. The crossing of these chains builds up different rings with  $R_3^3(10)$  and  $R_5^4(16)$  graph set motifs [9].

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**Keywords:** graph theory, hybrid compounds, hydrogen bonds.

### MS53.P33

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#### Thiadiazolo[2,3-a](py) as an oxidative cyclization of (py)carbamothioyl by $Cu^{2+}$

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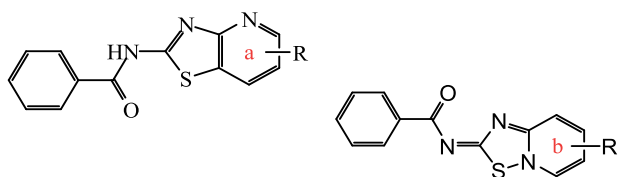
Some compounds are worth from different aspects. The existences of specific functional groups cause unique properties for them. Reaction of benzoyl chloride, potassium thiocyanate with 2-aminopyridine and 2-aminopicoline in one pot produces carbamothioyl benzamide derivatives. These compounds possess various sites to react with numerous reactants.

When 2-aminopyridine was used in above reaction, N-(pyridine-2-ylcarbamothioyl) benzamide was formed. This compound and the other synthesized derivatives were characterized by CHN, IR-,  $^1H$ NMR- and  $^{13}C$ NMR spectroscopies. Also their crystal structures were determined.

The reaction of 2-aminopyridine and 2-aminopicoline with  $Cu(II)$  salts resulted in oxidative cyclization. There are two possibilities of oxidative cyclization and two different structures (**a** & **b**) for these compounds. The products were characterized CHN, IR-,  $^1H$ NMR- and  $^{13}C$ NMR spectroscopies.

The obtained crystals and x-ray single crystal diffraction confirmed the structure **b** is correct. The structure **b** of different derivatives is able to act as anti cancers.

Increasing of the anti cancer property of these products will be researched by changes and replacement of various groups and functions in both of aromatic rings.



**Keywords:** oxidative cyclization, thiadiazolo[2,3-a]pyridine

### MS53.P34

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#### mosquito® Crystal: fast, reliable automation of Protein Crystallization drop set-up

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Automation of protein crystallography screening has contributed significantly to the rapid progress of crystallography based structural biology. Automation allows samples to be screened using smaller volumes of both protein and screen solutions, reducing costs and saving valuable protein. Additional benefits include increased throughput and accuracy.

One of the challenges to automating this process is the necessity to accurately pipette solutions of varying viscosities. Another challenge is that of drop positioning. The low volume drops have to be placed extremely accurately in order that protein and screen drops coalesce and are not distorted by the edge of the crystallization plates' subwell.

The ability of mosquito® Crystal to address these issues and to automate both micro batch and vapour diffusion methods of protein crystallography (sitting drop, hanging drop) without instrument configuration change offers ultimate flexibility for the crystallography laboratory.

**Keywords:** Screening-1, Pipetting-2, Mosquito-3

### MS54.P01

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#### Ion substitution in tourmaline with chromophore elements growing in hydrothermal conditions

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Unique physical properties of tourmaline crystals (pyroelectric, piezoelectric) and possibility of their use in jewelry makes the growing of synthetic tourmalines a topic of the most immediate interest. Our work is devoted to the crystal chemistry of synthetic tourmalines doped by transition metal (3d) elements (Ni, Cr, Co, Fe, Cu) which are identified as coloring agents (table 1).

Table 1. Characteristic of growing tourmalines.

| Smp | Color | 3d-elements cont., wt. %               | Unit cell parameters, Å |          | $R_F$ |
|-----|-------|--|-------------------------|----------|-------|
|     |       |  | a                       | c        |       |
| 1   | green | NiO-7.4<br>FeO-5.3                     | 15.897(5)               | 7.145(2) | 0.038 |
| 2   | green | NiO-13.4<br>$Cr_2O_3$ -10.2<br>FeO-0.3 | 15.945(5)               | 7.208(2) | 0.051 |
| 3   | pink  | CoO-14.4                               | 15.753(8)               | 7.053(3) | 0.057 |
| 4   | blue  | CuO-8.4                                | 15.840(4)               | 7.091(1) | 0.041 |

Single crystals of samples 1-3 have been grown from complex boron-containing hydrothermal solutions at range of temperatures of 400-750°C and pressures of up to 150 MPa in the IEM RAS [1]. Cu-bearing tourmaline (sample 4) has been synthesised in the Institute of Mineralogy and Petrography SB RAS [2]. X-ray experiment was carried out on four-circle single-crystal diffractometer Nicolett R3.

The content of 3d-elements in multicolor synthetic tourmalines can rise up to 24 wt. % (in oxide form) and in the case of Ni, Co, Cu-tourmalines it is significantly higher than that found in natural specimens. The total content of 3d-elements and the ratio of its' ionic radii are the reason for the unit cell parameters and octahedral dimensions variations. In all cases chromophore elements occupied Y (mainly) and Z octahedra (table 2).

Table 2. Characteristic of Y and Z octahedral.

| Smp | Y octahedron  |          | Z-octahedron   |          |
|-----|---|----------|--|----------|
|     | Occupation, apfu  | <Y-O>, Å | Occupation, apfu   | <Z-O>, Å |
| 1   | Al <sub>1.69</sub> Ni <sub>0.81</sub> Fe <sub>0.50</sub>  | 1.991    | Al <sub>5.40</sub> Fe <sub>0.60</sub>  | 1.922    |
| 2   | Ni <sub>1.20</sub> Cr <sub>0.96</sub> Al <sub>0.63</sub> ×<br>Fe <sub>0.18</sub> Mg <sub>0.03</sub> | 2.008    | Al <sub>4.26</sub> Ni <sub>1.20</sub> ×<br>Cr <sub>0.48</sub> Ti <sub>0.06</sub> | 1.937    |
| 3   | Al <sub>1.80</sub> Co <sub>1.20</sub>   | 1.949    | Al <sub>5.28</sub> Co <sub>0.66</sub> ×<br>Ti <sub>0.06</sub>                    | 1.907    |
| 4   | Al <sub>1.86</sub> Cu <sub>1.14</sub>   | 1.978    | Al <sub>5.88</sub> Cu <sub>0.12</sub>  | 1.907    |

In the structure of samples 1, 3, 4 the main element in Y and Z sites is aluminium. The samples 3 and 4 (sodium in X site) are analogues of olenite mineral. The sample 1 (X site is mainly vacant) is an analogue of hypothetical oxyfoitite. Incorporation of bivalent 3d-elements (R<sup>2+</sup>) in these tourmalines is described by equation: Al<sup>3+</sup>+O<sup>2-</sup>=R<sup>2+</sup>+OH<sup>-</sup>. There are no close analogues of sample 2 in nature.

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**Keywords: crystallochemistry, silicate, X-ray.**

## MS54.P02

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### First Silicate Mineral with Triple Tetrahedral Layer

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The crystal structure of a new silicate mineral from the Eifel paleovolcanic area, Rhineland-Palatinate, Germany was studied by X-ray single crystal diffraction (diffractometer Xcalibur Oxford Diffraction, CCD-detector). The orthorhombic unit-cell parameters are: *a*=6.528(1) Å, *b*=6.970(1) Å, *c*=37.216(5) Å, *V*=1693.33(4) Å<sup>3</sup>, space group *Pnm*2<sub>1</sub>. The structure was solved by direct methods and refined to *R*=4.9%, 2706 |*F*| > 3σ(*F*). Idealized crystal-chemical formula is: (K,Ca,Ba)<sub>2</sub>(Fe,Ca,Mg,Na)[(Si,Al)<sub>13</sub>O<sub>25</sub>(OH)<sub>4</sub>]·7H<sub>2</sub>O.

The mineral is representative of a new structure type. The most important specific feature of its structure is a block [Si<sub>13</sub>O<sub>29</sub>] consisting of three connected single layers formed by four- and eight-membered rings of tetrahedra (*T*) centered by Si and Al. Two outer layers [Si<sub>4</sub>O<sub>10</sub>]

are topologically identical to that in some single-layer phyllosilicates (mountainite, shlykovite, cryptophyllite) and in double-layer silicates rhodesite, delhayelite, hydrodelhayelite, macdonaldite, monteregianite-(Y) and fivegite. The third (inner) layer [Si<sub>5</sub>O<sub>11</sub>] is unique and contains an additional tetrahedron.

The triple tetrahedral blocks [Si<sub>13</sub>O<sub>29</sub>] are connected to each other via the discrete polyhedra (Fe,Ca)O<sub>7</sub> to form 3D framework with channels filled by large cations (mainly K, as well as subordinate Ba, Ca) and H<sub>2</sub>O molecules. Thus the new mineral is an intermediate between phyllosilicates and zeolites. One can outline polysomatic structures from single-layer via double-layer to triple-layer ones.

**Keywords: X-ray analysis, mineral, silicate**

## MS54.P03

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### New members in sodium cadmium bisulfate: structure, property and thermal studies

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Bimetallic sulfates form an important constituent of the earth's crust and are recognized to provide essential link to mineral evolution. Depending on the level of hydration they form different class of minerals. The omnipresent water plays a decisive role in the formation of hydrates of complex inorganic materials generating complicated structural frameworks. These compounds exhibit properties like ionic conductivity, phase transitions in the context of electric, magnetic and elastic properties [1, 2] and believed to have played an important role in the formation of earth's atmosphere oxygen [3]. We have synthesized polymorphs of sodium cadmium bisulfate which differ in the extent of hydration and have studied their thermal properties and phase transition. Na<sub>2</sub>Cd<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·3H<sub>2</sub>O, Na<sub>2</sub>Cd(SO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O, Na<sub>2</sub>Cd(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O, were crystallized by slow evaporation method from water. Na<sub>2</sub>Cd<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·3H<sub>2</sub>O crystallizes in a trigonal system with the space group *P3c*. It loses water completely after 250 °C and transforms to a dehydrated phase whose structure has been established using *abinitio* powder diffraction. The dehydrated form crystallizes in the space group *I*  $\bar{4}3d$ . The phase transitions have been investigated using DSC, TGA and ionic conductivity studies. β-Na<sub>2</sub>Cd(SO<sub>4</sub>)<sub>2</sub>, a polymorphic form of α-Na<sub>2</sub>Cd(SO<sub>4</sub>)<sub>2</sub>, has been isolated by quenching the parent compound α-Na<sub>2</sub>Cd(SO<sub>4</sub>)<sub>2</sub> and characterised to belong to a monoclinic system, space group *P2*<sub>1</sub>/*c*. β-Na<sub>2</sub>Cd(SO<sub>4</sub>)<sub>2</sub> takes up water from the atmosphere and gets converted to a Kröhnkite type mineral Na<sub>2</sub>Cd(SO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O. Upon heating, mineral loses water and gets converted to α-Na<sub>2</sub>Cd(SO<sub>4</sub>)<sub>2</sub>. The phase transition analysis provides inputs for exploring the origin of Kröhnkite mineral. Na<sub>2</sub>Cd(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O crystallizes in a monoclinic system with a space group *P2*<sub>1</sub>/*c*. It is isostructural with the mineral Astrakhanite which is also known as Blöditte [4]. This work describes a structure based analysis of phase transitions involved in these complexes, thus providing insights into their evolutionary aspects.

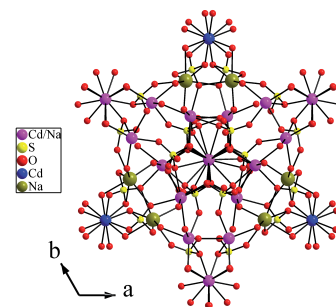


Figure 1. Repetitive unit of Na<sub>2</sub>Cd<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·3H<sub>2</sub>O