interactions in the structures 1-6 are the weak (CH₂...O and CH₂...Cl) bonds. In addition, in the structure 6 the stacking interactions between the fragments Ph-NO₂ are observed.

The derivatives of glycine and alanine (7 and 8) can be described as “freeze” cation-anion pairs. The Si...Br interatomic distances (2.7095(8) and 2.9704(7) Å, for 7 and 8, respectively) are much larger than those in the compounds of tetracoordinated Si (for instance, in the tris(pentafluorophenylmethyl)silylbromide the corresponding bond length is 2.208 Å). In turn, the Si-O bond in 7 and 8 is considerably shorter than in 1-6. In contrast to 1-6, the coordination polyhedron corresponds to the distorted tetrahedron with weak additional Si-O coordination bond.

To estimate the energy of intermolecular interactions, we have carried out quantum chemical calculations of the isolated molecules 7-8 and their associates. Also, the solid-state MAS Si spectra of 7 and 8 were simulated using plane-wave DFT calculations.

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Keywords: N-organosulfonyl-2-aminoacids, hypervalent silicon, crystal packing

MS61.P10

The influence of crystal packing on the structure of N-organosulfonyl-2-aminoacids complexes containing OSiC₂F coordination unit

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Silylfluorides with pentacoordinated Si atom obtained from N-organosulfonyl-2-aminoacids contain bioactive fragments and have high hydrolytic stability. In this study, we analyzed the influence of crystal packing on the geometry of coordination environment of the silicon atom in sixpentacoordinated silylfluorides containing OSiC₂F coordination polyhedron.

Taking into account similar inductive effect of exocyclic substituents in the complexes a-f, one would expect the coordination site of the silicon atom to have a similar structure. Indeed, in all cases OSiC₂F coordination polyhedron corresponds to a distorted trigonal pyramid. The deviation of the silicon atom from the plane of the equatorial C atoms varies within a fairly narrow range of 0.05 Å. The Si-O bond length increases along with an increase in Si-F one. These bonds vary in the ranges of 2.135(2)-2.384(1) and 1.681(2)-1.646(1) Å, respectively. Observed differences in the lengths of the Si-O bond are mainly related to intermolecular interactions rather than to the nature of R and R’ substituents. The presence of strong N-H...F bonds causes a strengthening of the coordination bond Si-O. In contrast, the formation of a N-H...O bond with the endocyclic O atom leads to weakening of the Si-O coordination bond.

In the solid state, molecules a and e form chains via NH...O and N-H...O bonds, respectively; in the cases of c, d and f complexes, centrosymmetric dimers are formed via N-H...O bonds with carbonyl (d and f) and sulfonyl (e) groups of neighboring molecules. The shortest Si-O bond is observed in the structure of e, where F atom is involved in N-H...F hydrogen bond, which leads to the weakening of Si-F bond. In turn, the longest Si-O bond is found in the structure of b (2.384(1) Å), which is the maximum value for all the earlier described complexes with OSiC₂F coordination polyhedron; the reason for this being is the intramolecular N-H...O hydrogen bond. Quantum chemical calculations of isolated molecules and their dimers were carried out to evaluate the energy of hydrogen bonds.

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Keywords: N-organosulfonyl-2-aminoacids, hypervalent silicon, crystal packing

MS61.P11

Crystal structure of [Cu₂(L)_2(HO₂)_2](SO₄)∙2H₂O (L = pyridoxal thiosemicarbazone)

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Dark red monocrystals of the title complex were prepared by the reaction of methanol solutions of CuSO₄·5H₂O and pyridoxal thiosemicarbazone (L) in mole ratio 1:1. Dinuclear complex cation has centrosymmetric structure. The Cu(II) is situated in a square-pyramidal environment (τ = 0.039). The equatorial plane is formed by chelate oxygen atom by 0.173(12) Å. The Cu...atom ligator bond lengths are in the range 1.917(2)–1.967(2) Å for O(1) N(3) and O(7), while Cu–S(1) and Cu–O(2) are longer (2.2998(9) Å and 2.233(2) Å, respectively. Pyridoxal thiosemicarbazone is coordinated in neutral, zwitterionic form as tetradentate bridging ligand, i.e. via phenol oxygen, hydrazine nitrogen, thioamide sulfur and hydroxymethyl oxygen, which, as the bridging ligator, connects the subunits. Such coordination results in formation of two metalloccycles, five-membered (thiosemicarbazide) and six-membered (pyridoxildiene). The coordinated ligand slightly deviates from planarity, and dihedral angles between pyridine ring, six- and five-membered metalloccycles are 7.54(10)°, 4.80(7)°, respectively. The six-membered metalloccycle is in screw-boat conformation and can be described by the following puckering parameters: Q = 0.20(2) Å, θ = 67.99(1)°, φ = 34.3(9)°, while the other rings are planar. Crystal structure of the complex is stabilized by an extended inter- and intra- molecular 3D hydrogen-bond network. It can be mentioned that all possible hydrogen donors are involved in hydrogen-bonding, and that sulfate anion acts as multiple hydrogen acceptor.

The data were collected on an Oxford Diffraction Gemini S diffractometer using MoKα radiation (λ = 0.71069 Å), and were corrected for Lorentz, polarization and background effects. The structure was solved by direct methods using SIR2004 and refined by full matrix least squares method on F² using SHELXL-97 R=0.036. Crystallographic data: Cu₂H₂CuN₂O₂S₂, Mr = 871.90, monoclinic, space group P2₁/a, a = 7.2529(2) Å, b = 11.1766(4) Å, c = 18.8522(6) Å, β = 93.751(3)°, V = 1524.94(8) Å³, Z = 2, μ(Koα) = 1.756 mm⁻¹, Goof= 1.059.
The structure of complex cation [Cu₂(L₃)(H₂O)]⁺

Keywords: pyridoxal, thiosemicarbazone, copper

MS61.P12


Incorporation of different lithium aluminates to titanium oxide organometallic ligands
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During the last years our research group has investigated the coordination of the organometallic oxides [[Ti₃(C₅H₅)₃(µ-O)]₃(µ-CR)] [R = H(I), Me(2)] to different inorganic fragments of groups 1 and 13 elements. Reactions with group 1 derivatives lead to dehydrogenation processes of the alkylidyne moiety to give [M(µ-O)]₃[Si(η-C₅H₅)₂(µ-CR)] (M = Li, Na, K) complexes [1]. On the other hand, the novel adducts [(E,M)(µ-CR)(µ-O)]₃[Si(η-C₅H₅)₂(µ-CR)] (R = H, Me; M = B, Al, Ga; E = alkyl, haloalkyl, halide) are obtained when group 13 derivatives react with 1 and 2 [2]. These species exhibit coordination of 1 or 2 through one of the three oxygen atoms of the Ti₂O₃ ring to the metal center. Now, we are studying the chemical reactivity of this family of compounds with different alkyl, amide or alkoxyde fragments react with the alkylidyne moiety (see figure).

However, when the same reaction is carried out with p-tolyl lithium and the triphenylgallium adduct, abstraction and redistribution reactions are observed. The lithium atom is then encapsulated by two units of 1 and the new gallate species stabilizes a phenyllithium unit.


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Keywords: aluminates, gallium, titanium

MS61.P13


Discrete role of chlorine substitutions in the conformation and supramolecular architecture of isostructural arylsulfonamides
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Compounds containing sulfonamide groups SO₂NH occur in many biologically active molecules, including antimicrobial, antithyroid, antitumor and antimalarial drugs [1,2,3,4]. In this study, two arylsulfonamide derivatives differing for two chlorine substitutions at one of their two phenyl rings were synthesized and characterized by X-ray diffraction technique in order to establish structural relationships and the chlorine role in the conformation and crystal assembly. The compounds (4-N(phenyl-sulphonyl-amide-acetophenone)) (I) and 4-N [(2, 5-dichlorophenyl)sulfonyl-amide] acetophenone (II) were obtained by the equimolar coupling between benzene sulfonyl chloride and 2,5-dichlorobenzene sulfonl chloride and 4-aminoacetophenone in dichloromethane or acetone as solvent at 343K for until six hours. The precipitate was re-crystallized in suitable solvents to obtain the single crystals. Crystallographic data for compounds (I) and (II) were collected using a Enraf Nonius diffractometer at room temperature. All crystal structures were solved by Direct Methods, and refined by full matrix least square method on F². The non hydrogen atoms were refined anisotropically. All C-H hydrogens were placed geometrically and refined using riding model. The hydrogen H1 bonded to nitrogen was found from the difference Fourier map and its positional parameters were refined freely. The tables, geometrical calculations, molecular packing and drawings were done with the WinGX [5,6], program package, obtaining the following results: (I) Molecular formula: C₁₉H₁₅NO₂S. Unit Cell Parameters: a = 13.0007(5) Å, b = 8.3615(4) Å, c = 12.5179(6) Å, β = 98.118(3)°, monoclinic, space group P2₁/c, Z = 4, V = 1347.13(1) Å³. 5393 measured reflections with 3009 unique and 2214 observed. Final indices R₁ = 0.0483 for 177 refined parameters. (II) Molecular formula: C₁₉H₁₅NO₂S. Structure: a = 13.3622(2) Å, b = 8.1542(2) Å, c = 15.6845(5) Å, β = 120.180(1)°, monoclinic, space group P2₁/c, Z = 4, 1477.24(5) Å³, 5653 measured reflections with 2972 unique and 2463 observed. Final indices R₁ = 0.049 for 195 refined parameters. There are several classical and non-classical hydrogen bonds and π-π stacking interactions contributing to stabilize the crystal packing of the compounds.

Keywords: sulfonamide, arylsulfonamide, crystallographic analysis.