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Keywords: tautomerism, polymorphism, hydrogen bonding

L.A.18

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Cation ordering at the nanoscale

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We describe a new mechanism of microstructure formation occurring during cation ordering processes under non-equilibrium conditions: a fully coherent and regular array of nanosized domains develops in columbite crystals through separation into discrete phases which have the same composition but different degree of long-range cation order. Such pattern of microstructure can be created by high temperature annealing of crystals which grew with an initially metastable state of cation disorder. Size and distribution of the domains remain more or less constant over a prolonged period of annealing.

High-resolution and contrast TEM images revealed microstructural features, and synchrotron X-ray powder diffraction allowed the evolution of cation ordering and domain sizes to be observed *in situ* [1]. Progressive ordering takes place within the ordered domains and the disordered matrix without significant changes in microstructure. At some late stage, when the ordering is advanced, the ordered domains again grow until the equilibrium is achieved. Analysis of IR and Raman spectra collected on samples with different compositions and degrees of order together with the real space analysis of the diffraction data using the Pair Distribution Function technique provide new information on the evolution of the local and mesoscopic structure of columbite, as well as an estimation of the spatial extent of the ordered/disordered domains, thus allowing to gain further insights and a better understanding of the factors controlling the ordering process in columbite.

We can speculate that a new family of such microstructures might appear during ordering under metastable conditions of other oxide phases. The new decomposition mechanism observed in columbite might offer another alternative toward self-organizing systems.

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Keywords: ordering, microstructure, oxide

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Experimental and theoretical charge density studies of lidocaine barbiturate.

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The major goal of crystal engineering is the prediction of structure-property relationship. Nowadays, high resolution, low temperature X-ray diffraction experiments enable the extraction and analysis of the charge density distribution in crystals. Electron density and its properties can be considered as a valuable tool for the analysis of chemical bonding, in particular hydrogen bonding. Recently, comparative experimental and theoretical charge density analysis was carried out for two out of the polymorphic forms of urea

barbituric acid co-crystals [1]. Herein we report the charge density analysis results for polar structure of lidocaine barbiturate: space group $P2_1$, $a=11.1322(5)$, $b=11.4604(6)$, $c=14.8607(8)\text{\AA}$, $\beta=92.712(3)^\circ$. The experimental charge density was evaluated using the XD2006 [2], the multipole refinement was carried out using the Hansen-Coppens formalism [3] implemented in XD2006. Periodic single-point quantum calculations were performed using CRYSTAL06 [4] with the DFT method at the B3LYP/6-31G** level. The multipole refinement based on the amplitude of the theoretical static structure factors was carried out with the XD2006. In the structure there are two symmetrically independent barbiturate ions and two lidocaine cations. Molecular recognition and the formation of specific hydrogen patterns in the examined structure will be discussed. In addition an attempt was made to calculate the static polarizability and first hyperpolarizability tensors for the crystalline system [5], [6].

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Keywords: crystal engineering, charge density, non-linear optical materials

L.A.20

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Synthesis of new Cu(III) substituted dithiolate complexes (CH₃P(Ph)₃)[Cu(bdtCl₂)₂]

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Coordination compounds of copper in the oxidation state Cu(III) are quite unusual. The series of several dithiolate complexes of general formula R[M(bdt)₂] with benzene-1,2-dithiol (bdt), M = Ni, Co and Cu as the central atom and various ammonium (phosphonium) derivatives R = Me₄N⁺, Et₄N⁺, Pr₄N⁺, Me₃PhN⁺, MePh₃P⁺, Ph₄P⁺, were prepared [1]. A wide range of technical applications (e.g. superconductors, resins, polarization filters, vulcanization accelerators) of the dithiolate complexes, as well as their biological activity (anticholinesterase activity, pesticides) makes them interesting subjects for the research. Our previous attempt to study the electronic structure of these complexes from diffraction data was not successful due to large anisotropic displacement parameters (ADPs) [2]. In order to reduce the thermal motion in the complex, chloro-substituted ligand, 3,6-dichloro-1,2-benzenedithiol (bdtCl₂) was used for the synthesis.

Preparation of (MePh₃P)[Cu(bdtCl₂)₂]: Solution of Na (0.08 g, 3.3 mmol) in MeOH (10 cm³) was added to 3,6-dichloro-1,2-benzenedithiol (0.34 g, 1.6 mmol). To this mixture, CuCl₂·2H₂O (0.13g, 0.76 mmol) in MeOH (10 cm³) was added. Finally, MePh₃PBr (0.57 g, 1.6 mmol) in MeOH (10 cm³) was added. The resulting solution was stirred for 24 hours. The complex was precipitated by the slow addition of water, with vigorous stirring. The green crystalline powder was filtered off, washed with diethyl ether, and then recrystallized from acetone/methanol solution (40:5) (yield 99%). Crude product was purified by column using eluent mixture toluene/methanol (10:1). Two products were obtained by this method – a complex with methylated and with non-methylated dithiolate ligand. After crystallization a single crystal suitable for X-ray analysis was selected.

C817

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Keywords: substituted dithiolate, Cu(III), electron density

L.A.21

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The crystal structures of two new synthetic compounds CsNaCu(P₂O₇) and Rb₂Cu(P₂O₇)

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Two new compounds, CsNaCu(P₂O₇) (**1**) and Rb₂Cu(P₂O₇) (**2**), have been obtained by high-temperature solid state reaction of CsNO₃, Cu(NO₃)₂, NaOH and (NH₄)₄P₂O₇. The chemical reagents were mixed in agate mortar in ratios of Cs:Na:Cu:P 1:1:3:4 (**1**) and Rb:Cu:P 1:3:3 (**2**). The mixtures were heated up to 650°C and kept at this temperature for 8 h in air, followed by cooling to 25 °C at a cooling rate of 25 °C/h. The product consisted of blue platy crystals of **1** and **2**.

The structures of synthetic compounds were solved using single crystal X-ray diffraction.

CsNaCu(P₂O₇) (**1**) is orthorhombic, space group *Pmn*2₁, *a* = 5.147(8), *b* = 15.126(2), *c* = 9.717(2) Å, *V* = 756.20 Å³, *R*₁ = 0.0660 for 1221 unique reflections [*I* > 2σ(*I*)]. The structure is based upon 2-D layers of Cu square pyramids and P₂O₇ groups. Rb₂Cu(P₂O₇) (**2**) is orthorhombic as well, space group *Pm*cn, *a* = 5.183(8), *b* = 10.096(1), *c* = 15.146(3) Å, *V* = 793.55 Å³, *R*₁ = 0.0632 for 1326 unique reflections [*I* > 2σ(*I*)]. The structure is based upon the same 2-D layers as in the structure of (**1**), but the adjacent layers are rotated relative to each other by 180° in comparison with their mutual position in (**2**). It is noteworthy that the layers are non-centrosymmetric. The arrangement of layers in the structure of (**1**) is non-centrosymmetric (the sequence of layers is ...AAAA..., whereas it is centrosymmetric in (**2**) (the sequence of layers is ...ABAB... (A and B are two opposite orientations of the same layer).

Keywords: Phosphates-1, X-ray -2, synthesis -3

L.A.22

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Structure and functional characterisation of utrophin and dystrophin N-terminal first spectrin repeats.

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Duchenne and Becker muscular dystrophies (DMD & BMD) are muscle-wasting disorders caused by mutations in the X-linked dystrophin gene. Utrophin is a widely expressed protein with high sequence similarity to dystrophin that has been shown to functionally compensate for dystrophin in cultured muscle cells and in the muscular dystrophy (*mdx*) mice model. Replacement of utrophin for dystrophin in DMD and BMD patients is a potential therapeutic strategy [1].

Dystrophin and utrophin are large cytoskeletal proteins, belonging to the spectrin superfamily, that link intracellular F-actin and the extracellular matrix via a membrane-associated protein complex. Utrophin and dystrophin are characterized by N-terminal

actin binding domains and C-terminal variable domains separated by 22 or 24 spectrin-like repeats respectively. Certain utrophin and dystrophin spectrin repeats can bind F-actin, and were hypothesized to act as a shock absorbers or molecular springs. These multiple spectrin repeat proteins contribute to the stability of the membrane cell. The aim of this research is a structural determination and biochemical comparison of utrophin and dystrophin N-terminal spectrin repeats. The crystal structure of the N-terminal repeats from utrophin and dystrophin have been determined to 1.95 Å and 2.3 Å, and exhibit the characteristic triple-helix structure folded into a left-handed coiled-coil [2]. Studies have shown that spectrin repeats of utrophin are required for a higher affinity interaction of the actin binding domain with F-actin. It is unclear whether the N-terminal repeats have an intrinsic affinity for F-actin and in the current study we are determining the actin-binding properties of these spectrin repeats.

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Keywords: coiled-coil, spectrin repeat, molecular shock absorbers

L.A.24

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Interaction of Saturated Fatty acids with Apoferritin

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Apoferritin has been an attractive model for the study of anesthetic-protein interactions because it binds a wide range of general anesthetics at high affinity (*K_a* ~ 10⁵ M⁻¹) in a single interhelical cavity located at a dimer interface [1,2]. The in vivo function of this interfacial cavity is not clear; apoferritin isolated from tissues such as the horse spleen do not reveal an occupant when crystallized. Because of its tunnel-like “U” shaped geometry, and positively charged “gatekeeper” arginine residues, we hypothesized that ferritin may be an intracellular fatty acid binding protein.

Fatty acids have physiological, behavioral and toxicologic activities. They are known to bind with a variety of small fatty acid-binding proteins as their normal endogenous ligands. A connection to iron metabolism has not been established but would make physiological sense. To evaluate binding interactions between fatty acids and apoferritin, we present the x-ray structural data of apoferritin complexed to caprylic (C8) and myristic (C14) acid, together with the calorimetric data. Using competition assays, we provide evidence that fatty acids share the same binding site as the anesthetic, suggesting that anesthesia could modulate intracellular FA concentrations, and whatever function is subserved by the interaction between FA and ferritin.

Figure 1. Different density map shows C14 Bound to the interface of dimers as U shape

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Key words: ferritin, fatty acid binding protein.