Session VII, June 1, Thursday

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METÓDY ŠTRUKTÚRNEJ ANALÝZY NA KACH PF UPJŠ VYUžÍVANÉ PRI šTÚDIU ŠTRUKTÚRY ZLÚČENÍN S MAGNETOAKTÍVNYMI ČASTICAMI

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V súčasnom období Prírodovedecká fakulta UPJŠ v Košiciach oslavuje 60. výročie založenia a už od akademického roku 1963/1964 sa datuje Katedra chémie, ktorá sa v roku 1965/1966 člení na viaceré disciplíny, v rámci ktorých figuruje aj Anorganická chémia. Problematika štruktúrnej analýzy je v rámci anorganickej chémie súčas ou poskytovaných prednášok už od jej počiatkov a vedením bol poverený doc. Ing. Mikuláš Matherny, CSc., neskôr tento predmet zabezpečovali externí vyučujúci prof. Ing. J. Garaj, CSc., doc. Ing. M. Dunaj-Jurčo, CSc. Tento zoznam od ak. roku 1983/1984 dopĺňa prof. RNDr. Juraj Černák, DrSc., ktorý sa prednáškam venoval do roku 2010, kedy tento predmet preberá doc. RNDr. Ivan Potočňák, PhD. Až do 80. rokov je tento predmet zabezpečovaný v teoretickej rovine, no postupne dochádza k rozšíreniu prístrojovej techniky a na Katedre anorganickej chémie sa buduje laboratórium štruktúrnej analýzy, kde v počiatkoch nachádzame dve zariadenia československej výroby Mikrometa, firmy Chirana Modřany, jedno doplnené o weissenbergovu komoru. Tieto zariadenia na štúdium zlúčenín využívané v prevažnej miere difrakciou na práškových vzorkách, ale aj v obmedzenej miere na monokryštáloch, boli súčas ou laboratória do začiatku 21. storočia. Po ich vyradení z prevádzky došlo k útlmu využívania prístrojovej techniky na pracovisku. V tomto období bolo štúdium štruktúry zlúčenín, ktoré obsahujú magnetoaktívne častice, realizované prevažne v spolupráci so zahraničnými pracoviskami. Oblas výskumu bola zameraná na prípravu a charakterizáciu nízkorozmerných zlúčenín so zaujímavými magnetickými vlastnos ami. Avšak pre potreby rozvoja bolo nevyhnutné obnovi pracovisko rtg štruktúrnej analýzy aj na domovskej fakulte. Neblahý trend sa podarilo zvráti v roku 2008, kedy v rámci spolupráce s Fyzikálnym ústavom AV ČR v Prahe bol v laboratóriu rtg štruktúrnej analýzy inštalovaný monokryštálový difraktometer XCalibur (Oxford Instruments) s polohovo citlivým detektorom (CCD area detector Sapphire 2) a grafitovým monochromátorom. Existujúci základný prístroj bol postupne dovybavený chladičom kryštálov Desktop Cooler a generátorom Spellman DF60N3 z prostriedkov projektov ŠF „Extrem – Centrum pokročilých fyzikálnych štúdií materiálov v extrémnych podmienkach“ (ITMS 26220120005) a „Extrem – Dobudovanie Centra pokročilých fyzikálnych štúdií materiálov v extrémnych podmienkach“ (ITMS 26220120047). Výsledky meraní do roku 2016, kedy došlo k požiaru v budove, v ktorej sa laboratórium nachádza, priniesli viac ako 40 vedeckých publikácií v karentovaných časopisoch, napomohli k rozvoju záverečných prác viac ako 15 študentov. Po návrate do budovy intenzívne štúdium štruktúry zlúčenín obsahujúcich magnetoaktívne častice pokračovalo a do dnešného dňa v rámci projektov grantových agentúr APVV a VEGA vznikli ďalšie vedecké publikácie. Súčasný výskum je zameraný nielen na štúdium štruktúry zlúčenín z oblasti jednomolekulových magnetov, ale aj z oblasti zlúčenín s potenciálnym biologickým účinkom. Laboratórium štruktúrnej analýzy je lokalizované v priestoroch Katedry anorganickej chémie Ústavu chemických vied na Moyzesovej 11 na prvom poschodí. Bývalé nevyhovujúce priestory boli zrekonštruované a prestavané vrátane vybavenia klimatizáciou najmä za podpory projektov APVV a VEGA.

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EXPERIMENTAL ELECTRONIC STRUCTURE OF TRANSITION METAL COMPLEXES

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The properties of molecules correlate with their electronic structure. The valence electron density distribution can be obtained experimentally from accurate single crystal diffraction data. Applying the results of the so-called multipole refinement to the properties of molecules in solution, on surfaces or in a living cell is not easy. In a crystal, interactions with neighboring molecules, so-called "non-bonding interactions", influence the electron density distribution in a certain way. In a different environment of the molecule, the resulting valence electron distribution may be altered and a direct correlation is not possible. The mediator for studying the correlation between valence electron distribution and compound properties is theoretical calculations.

Despite the fact that in transition metal complexes the ratio of the core to valence electrons is not favorable for the study of the experimental electronic structure, when the crystals are of good quality and the experiment is carried out with high redundancy, important results can be obtained. The distribution of valence electrons is a robust property, so the main features are easily recognized. The classical coordination bond was found in Cu-Cu and Cr-Cr dinuclear acetate complexes. Metal-metal interactions are discussed [1]. The titanium(IV) coordination compound with peroxo anion is a possible model structure of the reaction center for the theoretical study of hemoglobin. We have shown that the O—O bonding electron density is significantly shifted towards the central titanium atom. The O-O bond in the peroxide complex is weakened and, therefore, could be susceptible to a nucleophilic addition reaction [2]. The study of Ni(II) and Ni(III) complexes with the same ligand (3,6-dichlorobenzene-1,2-dithiolate) shows similar and typical square-planar coordination. In the experimental results, we see two combined effects. One effect is that the positive charge on the central atom is always lower than the formal oxidation state, and the other is that one part of electron density is shifted from the central atom to the non-innocent ligand. Thus, the non-innocent ligand can adapt to the requirements of the central atom [3]. In nitrosyl a μ_3^- Oxido Trinuclear Diiron(III)-Ruthenium(II) complex we have studied whether such a complex can release NO photolytically [4]. We will discuss also tetrahedral Cu(I) and pseudo-octahedral Cu(II) complexes with biphenyldiimino dithioether as the blue copper protein model structures. The real challenge is a compound with the Cr-Cr distance of 1.8077(7) Å [5]. Is there a sufficient electron density for one , two and two bonds?

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PRESENTATION OF THE FUNDAMENTALS OF CHEMICAL CRYSTALLOGRAPHY TEXTBOOK

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Crystallography is an important scientific field that helps the development of other scientific fields such as physics, chemistry, biology and material sciences. The importance of crystallography grows over time with the development of more sophisticated and technically demanding studies, which are also accompanied by the development of crystallography itself on the theoretical, experimental and instrumental side. Despite the importance of crystallography and structural analysis in Slovak literature, no textbook dealing with crystallography or structural analysis has been written so far, with the exception of the outdated university scripts written by Pavelčík and Kuchta in 1995 [1]. The development of both crystallography and structural analysis forced their differentiation for the needs of other scientific fields. The development of chemistry also requires knowledge of crystallography and structural analysis, with claims to knowledge of growth from the development of chemistry. This is due to the need to write a textbook dedicated to crystallography oriented for students of chemistry and related fields, as well as workers in these fields. The aim of the textbook is to bring basic information about chemical crystallography as well as other specific information from crystallography and structural analysis interesting and important for chemists and chemistry.

The textbook is written in the Slovak language and corrected using the Slovak crystallographic dictionary [2]. The inspiration for writing the textbook in terms of content and scope was several modern textbooks written in English in the last edition [3-6] and supplemented with additional information from other sources and primary literature. The textbook is divided into 16 chapters and one additional chapter. The introductory chapter 1 of the textbook introduces the reader to the history of modern crystallography. The following chapter 2 will introduce the reader to basic concepts such as lattice, unit cell, crystallographic systems and others. The following chapter 3 is devoted to crystal symmetry, symmetry operations, crystallographic point groups and space groups. The chapter 4 is devoted to the geometric aspect of diffraction, introduces the concept of the reciprocal Lattice, deals with Laue diffraction conditions, the Bragg equation, and the Ewald construction. The following chapter 5 is devoted to X-ray diffraction, X-ray radiation, radiation scattering and diffraction theory. This is followed by chapter 6 dedicated to the structural factors. The chapter 7 introduces the reader to the issue of intensity diffraction.

The following chapters are devoted to solving the crystal structure. The chapter 8 is devoted to the solution of the phase problem by various methods and their implementation in the software. The following chapter 9 is devoted to the refinement of the structure, the geometric analysis of the structure, and the determination of the absolute structure by various methods. This is followed by the chapter 10, which is dedicated to finalizing the structure, validating the crystal structure, rendering the structure in imaging programs, archiving the crystal structure and the CIF file.

In the chapter 11, the reader will learn about problem structures such as disorders, twinning and modulated structures. The following chapter 12 is devoted to quantum crystallography: charge densities, the Kappa and Multipole models of refinement, Hirshfeld Atom Refinement and other methods of quantum crystallography, as well as topological analysis of charge densities.

The more extensive chapter 13 discusses the experimental technique in more detail, starting with the preparation, selection and montage of crystals. The next chapter deals with sources of X-ray radiation, including modern microfocused sources, metal-jet anodes and synchrotron sources. Chapter 13 further deals with the issue of monochromatization and collimators, and the measurement of the intensity of X-ray radiation using various detectors, including the newest semiconductor flat detectors. The chapter continues with the collection of diffraction data from single crystal diffractometers and their techniques. This is followed by chapter 14 dedicated to advanced measurement techniques: structural analysis at low temperatures and observed physical events, structural analysis at high pressures, use of anomalous scattering to determine unknown atoms, photocrystallographic methods, neutron diffraction of single crystals, and neutron diffraction of single crystals .

Chapter 15 is devoted to crystallographic databases. Chapter 16 is devoted to the issue of burst diffraction from the point of view of chemistry. The last supplementary chapter 17 supplements the mathematical apparatus.

The textbook with the title *" Základy chemickej kryštalografie "* and the English translation of the title *" Fundamentals of chemical crystallography "* has the ambition to be a basic textbook for students of chemistry and related fields studying the subjects Diffraction methods in crystal chemistry, Structural crystallography, Structural analysis and similar study courses, but it can also be useful for workers in chemistry who do not have sufficient knowledge or need to supplement their knowledge.

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PRESENTATION OF THE FUNDAMENTALS OF STRUCTURAL CRYSTALLOGRAPHY (OBJECT LESSON GUIDEBOOK)

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The aim of Chemical Crystallography course at our faculty is to introduce non-specialists to basics of single crystal structure determination instead of creation of expert crystallographers. The course offers possibility of full hands-on experience from the data collection to structure refinement and validation, analysis of results and manuscript preparation – and learn them when to ask for expert advice.

The introduction of *Olex2* [1, 2] as an integrated package for crystal structure solution, refinement and molecular graphics available for *Windows*, *macOS* and *Linux* operation systems substantially simplified the course setup and solved the problem of using too many computer programs.

Although *Olex2* package is close in its capabilities to *SHELX* [3], the structure solution module *olex2.solve* has no counterpart within *SHELX* package and there are some, albeit mostly subtle, differences in the capabilities and workflow details between *olex2.refine* and *SHELXL*. As a result, the vast amount of available teaching materials for *SHELX* cannot be directly used. There is also a problem of language barrier when beginners studying crystallography in their native Slovak or Czech language would try to use online or built-in documentation. Similarly to *SHELX* manuals, which are intended to be used by more experienced crystallographers, even using materials like Ilia Guzei's *Notes on Olex2* [4] is not really beginner friendly.

A result of the need of such beginner friendly teaching material, *Základy štruktúrnej kryštalografie* (*Fundamentals of Structural Crystallography*) guidebook [5] focused on a series of object lessons was published in 2019. In Chapter 1, it covers preparation methods for single crystals – often overlooked art. Chapter 2 is a key chapter dealing with crystal structure solution, refinement, validation and analysis. Chapter 3 is dedicated to working with molecular graphics. In Chapter 4, students find how to write the description of crystallographic experiment in crystallographic articles. Chapter 5 consists of detailed description of the CIF file.

As a working examples, two datasets were used. One of them is focused on absolute structure determination, second towards hydrogen atoms treatment and working with hydrogen bonds. The use of the book is allowed during the exam.

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