

Kinetics and other systematic probing of electron density at transition metal centres for application in chemical processes

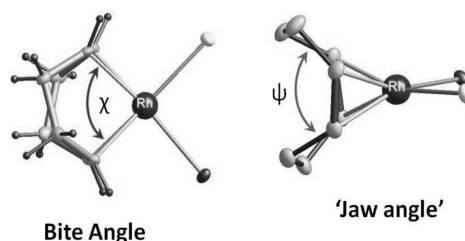
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Small molecule chemical crystallography is sometimes considered as trivial due to the phenomenal developments in hardware, computing power, and its application in, e.g. molecular biology. However, here we emphasize the continued importance of small molecule crystallography in coordination chemistry for the understanding of processes from a structural perspective. Our central focus is an integrated mechanistic approach to evaluate bonding and structures using spectroscopic techniques and reaction kinetics, to counteract trivialized conclusions based on thermodynamic observations alone.¹ Thus, since many dynamic processes (still) occur at the molecular level, fundamental understanding of structural behavior, and the associated influence on (kinetic) properties are still of prime importance. Two 'case studies' are briefly presented and discussed.

The first example focuses on applications in radiopharmacy, where the 4th and 5th row elements of the manganese triad, and in particular the ^{99m}Tc, ¹⁸⁸Re, ¹⁸⁶Re isotopes, find widespread application.^{1,2} The *fac*-[M(CO)₃]⁺ core (M = Tc, Re) has particular potential in e.g. biomedical, photo- and chiral catalytic applications. This versatile synthon exhibits a low-valent, kinetically inert and *in vivo* stable core, coordinates many ligands, and enables the design of different chelators. Although many characteristics of radiopharmaceuticals are imperative for successful application (including stability, redox and acid base properties, synthesis and more), the kinetic stability/ reactivity is also very important and can be quite diverse. Structural and other aspects thereof will be discussed to enable further understanding, and consequent potentially more accurate prediction of *in vivo* behavior and reactivity of models associated with these metals.^{2,3}

Secondly, in certain petrochemical downstream processes, diolefins may coordinate and trap the catalyst in the actual catalytic cycle.⁴ We thus identified 1,5-cyclooctadiene as a diolefin model and ligand to evaluate its bonding mode in a range of middle to late transition metal complexes, and investigated the opening/ closing of the 'Venus fly-trap' jaw angle (ψ) and the bite angle (χ) as defined here, as a function of variants such as metal centre, trans ligand donor atoms and metallocycle size.⁵ The data from a number of X-ray and accompanying DFT optimised structures, will be discussed.



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The Challenge of Crystal Structure Solution by Powder Diffraction Data: the EXPO Software

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Not always crystalline material, natural or synthetic, is available as single crystal of quality and/or dimension suitable to be studied by single crystal diffraction technique but, often, as fine-grained powder. In this case, X-ray powder diffraction (XRPD) technique¹ is the most appropriate approach for attaining the atomic structure of the sample under study.

The interpretation of the experimental powder diffraction profile is not straightforward. The difficulties, ascribed mainly to peak overlap, background and preferred orientation of microcrystallites often hinder the accurate interpretation of the pattern and, consequently, the success of the structure solution.

In spite of the recent surprising progress (experimental, theoretical, methodological and computational), structure solution by XRPD is still a challenge even in case of simple structures (less than 30 non-hydrogen atoms in the asymmetric unit).

Among several available software packages devoted to powder solution, we mention *EXPO2013*² which has given a great push towards the success in structure solution. *EXPO2013* is continuously updated, by graphical and computing tools, in order to efficiently solve structures in short time and in an automatic as possible way.

EXPO2013 is able to carry out the full pathway of the solution process: indexing, space group determination, estimation of the integrated intensities, structure solution by using reciprocal as well as direct space methods, Rietveld refinement.

Among the *EXPO2013* solution strategies we quote:

- the approaches for enhancing the *ab-initio* solution process by the optimization and completion of the structure model provided by Direct Methods³: *e.g.*, the resolution bias correction method (*RBM*) and the covariance principle based method (*COVMAP*);
- the very recent random-model-based method (*RAMM*) which processes a fully random structure model;
- the direct space methods [by using the Simulated Annealing (*SA*) and/or the *Hybrid Big Bang-Big Crunch (HBB-BC)* algorithms], particular effective when the expected molecular geometry information on the structure to be solved is available.

We give the main theoretical concepts of each step of the powder solution process and examples of application of *EXPO2013*.

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From molecular sociology to functional materials

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Chemistry is the science of communication and change, and these interrelated processes are primarily initiated and controlled by reversible interactions between molecules. Our ability to design and synthesize discrete molecular species has been developed and refined for over a century, and today we are capable of making extraordinary molecules that rival some of Nature's best efforts when it comes to structural complexity and chemical reactivity. However, the synthesis of supramolecular assemblies composed of many different molecular fragments held together by non-covalent forces, is far less advanced.

Intermolecular forces provide the conduits through which molecules communicate and exchange information. As a consequence thereof, these forces also provide the means by which molecules can be deliberately combined and organized into assemblies with specific architectures, stoichiometries, and dimensionalities, all of which play key roles in determining fundamental properties of the resulting assemblies.

In this contribution, several strategies for direct supramolecular synthesis, based upon systematic structural studies are presented, and some practical applications thereof are also examined.

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The importance of collecting and investigation of mineral samples from ore deposits - example of Stari Trg (Trepča) mine

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People usually use gathered mineral samples in different ways. Most of collected samples are destroyed in technological processes. Very few mineral samples are collected to be preserved as very nice objects. Such objects are placed in mineralogical collections of museums, collections for study or in private collections.

Private collections were prohibited many times through history. It is obvious today that variety of collections have not just esthetic, artistic or educational value, but also scientific importance. Exploitation of mineral deposits influences to the environment and destroy minerals, crystals and their parageneses.

Economic crises enhance possibilities to extract and collect mineral samples. Local society sometimes does not recognize the importance of museums and mineral collections placed in them. Closing important museum could save some money during crisis time, but it could be uncountable damage for future. Such example is National museum in Sarajevo.

Investigation of old samples placed in curated collections lead to new scientific results. Some of these old specimens are very rare or it is not possible to find it anymore. Such situation enlarges importance of continuous collecting mineral samples, formation of collections and careful scientific and museologic investigation.

Example of mineral collection which is continuously collected for more than 100 years is collection of mineral samples from Trepča mine in Natural History Museum in Zagreb. This collection is investigated and more than 700 samples are listed with careful description of found minerals. Catalogue of this, probably the best in the World, collection of mineral samples from Trepča mine is recently published in monographic edition dedicated to this deposit.

Nanocrystalline metal oxides: synthesis, characterisation and application

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The synthesis of nanoparticles has been studied extensively in order to understand physics and chemistry at a ‘small’ scale and because of promising applications due to their size-dependent properties.¹ There are two major reasons why nanocrystals and their bulk counterparts differ from each other: (i) in nanocrystals the number of surface atoms is a large fraction of the total, (ii) the size of the nanocrystal interior causes a systematic transformation in the density of electronic energy levels.² Namely, in any material the surface atoms make a distinct contribution to the free energy, so the changes in thermodynamic properties of the nanocrystals compared to the crystalline bulk material of same composition can appear (e.g. melting temperature depression, solid-solid phase transition elevation). Also, changes in thermodynamic stability associated with size can induce modification of cell parameters and/or structural transformations. To display mechanical or structural stability, a nanoparticle must have a low surface free energy. As a consequence of this requirement, phases that have a low stability in bulk materials can become very stable in nanostructures. This structural phenomenon has been detected in TiO₂, VO_x, Al₂O₃ or MoO_x oxides. For (semi)conductors, as the particle get smaller an additional effect, the so-called quantum-size effect or confinement effect which essentially arise from the presence of discrete, atom-like electronic states which influences the energy shift of exciton levels and optical band gap.³ Therefore, synthesis of nanoparticles with controlled size and shape has been found to be demanding for tailoring the desired materials properties since the thermal, electric, optical, catalytic and magnetic properties are strongly composition-, structure-, but also, size- and shape-dependent.⁴ Our work is focused on development of new synthetic routes for oxide materials preparation, namely, direct molecular-to-materials pathways which include heterometallic complexes as single-molecular precursors. Generally, preparation method from single-molecular precursor,⁵ as compared to conventional methods, has several advantages: (i) the obtained material is more homogeneous because the metals are mixed at the molecular level; (ii) the resulting materials are characterized by relatively high specific surface areas because they are usually formed under milder; and (iii) bridging or chelating ligands in the precursor can prevent unwanted metal separation during the oxide formation. Structural and microstructural characterisation of Ba₄Nb₂O₉, Ba₄Ta₂O₉, CoMn₂O₄ and CaCr₂O₄ will be discussed in details.

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Inclusions in Gemstones – origin, identification and valuation

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An inclusion in a precious or ornamental stone is any inner part or area that differs from the rest of the gemstone and is completely or partly enclosed within it. The formation of inclusions depends on a number of geological processes, e.g. shifting of plates in the earth's lithosphere, and on the type of rock forming process and hence the conditions of mineral crystallization. Thus, we can use inclusions to identify the conditions of crystallization and determine the geological processes that shaped and still shape our planet. Inclusions of minerals, which are by far the most common type of inclusions in gemstones, are investigated from the geochemical and the chronological points of view. From the geochemical point of view we determine the conditions of crystallization (temperature, pressure and the abundance of individual chemical elements present in a given environment), and from the chronological point of view we determine the age of minerals, as inclusions may have been formed before or after the crystallization of the host mineral or simultaneously with it (protogenetic, syngenetic and epigenetic inclusions respectively, or primary, secondary and pseudo-secondary inclusions). Minerals and mineral inclusions reflect the geochemical environment and variations in the physicochemical conditions of their formation. Combinations of inclusions in gemstones formed in a natural environment often differ from inclusions in synthetic gemstones that are made in laboratories using different methods. Therefore, inclusions help us to determine the authenticity of gemstones. Inclusions can have a significant influence on the colour of the host mineral. Some inclusions are very typical and can be used to identify gemstones without using other methods. Some inclusions are so typical that they can tell us where a gemstone comes from. Optical phenomena are a common – or even the most important – reason for the attractiveness of a gemstone, and in such cases inclusions often play a decisive role.

Highly detailed standards and criteria for the identification of gemstone inclusions are an integral part of gemmology in the context of gemstone evaluation. This includes not only the evaluation of diamond purity, which is governed by the most detailed standards for the classification of purity, but also the evaluation of other gemstones. In fact, inclusions have a significant impact on the value of all gems. Generally speaking, the more inclusions in a gemstone, the lower its quality and thus its value. However, there are some exceptions, since inclusions may be the very features that emphasize the rare, unique qualities of a particular gemstone. Furthermore, it is important to note that no two gemstones have the exact same inclusions in the same location. This fact is important when it comes to gemstone certification, as precise and correct identification and mapping of inclusions in the cutting diagram create a kind of fingerprint of a gemstone.

In gemmological practice, the world of gemstones is the world of inclusions. Indeed, inclusions in gemstones are a valuable source of information; they affect the appearance and the value of a gemstone and help us identify it.