Only a few crystal structures of these complexes with O,O' bidentate ligand systems are published. Also, very few kinetic studies have been undertaken on these fascinating complexes [9-10]. Alberto et al. [11] focussed on the pH dependence of different polymeric species of the rhenium, but very little attention has been given to the subsitution kinetcis of therse tricarbonyl compounds.

Crystal structures of the aqua substituted Re(I) tricarbonyl complexes with various monodentate incoming ligands, thus the kinetic end products, were obtained and will be discussed in this presentation.

The current available knowledge of these Re(I) tricarbonyl complexes were expanded and contributed to the pool of available crystallographic data.

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Keywords: Kinetics, Rhenium

MS24.P02

Enaminoketones: Influencing Rh(I) dicarbonyl complexes with halogen substituents

Gertruida J.S. Venter, Gideon Steyl, Andreas Roodt. *Department of Chemistry, University of the Free State, Bloemfontein, 9300, (South Africa).* E-mail: truidie@hotmail.com

X-PhonyH (X = aromatic substituents; PhonyH = 4-(phenyl-amino)pent-3-en-2-one) compounds belong to the group of enaminoketones. Since these contain nitrogen and oxygen donor atoms as well as an alkene functionality, these electron-rich compounds are of interest in various areas, including application as liquid crystals [1], in fluorescence studies [2], the medical field [3,4] and with significant potential in homogeneous catalysis [5].

This study is therefore concerned with the synthesis of PhonyH derivatives as ligand system and the influence of halide substitution on such ligands with regard to rhodium(I) complex formation. A range of thirteen crystal structures of the (i) free ligands, (ii) complexes of the type [Rh^I(X-Phony)(CO)$_2$] (X-Phony = 4-(phenylamino)pent-3-en-2-onato derivatives), and (iii) [Rh^I(X-Phony)(CO)(PPh$_3$)] (substitution of a CO group in (ii) by PPh$_3$ complexes [6, 7] as catalyst precursors will be discussed. Furthermore, iodomethane oxidative addition, as key step in the catalytic cycles of olefin hydroformylation and methanol carbonylation and the influence of structure/ reactivity relationships therein, will be highlighted.

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Keywords: rhodium, enaminoketone, dicarbonyl

MS24.P03

Measuring selectivity in host-guest systems

Luigi Renzo Nassimbeni,[a] Nikoletta Bathori,[b] Ayesha Jacobs,[b] [a]*Departament of Chemistry, University of Cape Town, Rondebosch, (South Africa).* [b]*Chemistry Department, Faculty of Applied Sciences, Cape Peninsula University of Technology, Cape Town, (South Africa).* E-mail: luigi.nassimbeni@uct.ac.za

When a host compound, H, is dissolved in a mixture of liquid guest A and B to form inclusion compounds
H + nA ↔ H · An   H + mB ↔ H · Bm
then one may write the equilibrium constants
$K_1 = [H \cdot An] / [H] [A]^n$ $K_2 = [H \cdot Bm] / [H] [B]^m$
with the standard state defined as 1 mol dm^{-3}.

The selectivity of the host H is given as the ratio of the equilibrium constants
selectivity = K_1 / K_2
However, if the host forms an inclusion compound which incorporates both guests
H + nA + mB ↔ H · n'A · m'B
where generally n ≠ m', m ≠ m', then the selectivity cannot be so defined.

We have therefore elected to employ the selectivity coefficient
$K_{A:B} = (K_{B:A})^{-1} = Z_A / Z_B * X_B / X_A$ [1]
where X_A, X_B are the mole fractions of the guest in the mother liquor and Z_A, Z_B are the mole fractions in the resulting crystal.

We have studied a series of host-guest systems comprising bulky diol-hosts with pairs of related guests and have measured their selectivity curves. The results are rationalised by NMR results, crystal structure analysis, examination of the non-bonded interactions and evaluation of the volume of the voids which accommodate the guest molecules.

Examples are given of poor versus good selectivity as well as when the selectivity is concentration dependent, giving rise to sigmoid selectivity curves. We demonstrate the possibility of mapping the enclathration process of a four dimentional system, comprising the host H and three competing guests A, B and C.

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MS24.P04

Dinuclear Gadolinium(III) complexes constructed by monocarboxylate ligands

Laura Cañadillas-Delgado,[a,b,c] Wilson Rodriguez-DeLeón,[c] Carla Martinez-Benito,[c] Pau Díaz-Gallifa,[c] Mariadel Déniz,[c] Jorge Pasán,[c] Óscar Fabelo,[a,b,c] Catalina Ruiz-Pérez,[c] [a]*Instituto de Ciencia de Materiales de Aragón. CSIC-Universidad de Zaragoza (Spain).* [b]*Institute Laue Langevin. Grenoble (France).* [c]*Laboratorio de Rayos X y Materiales Moleculares, Depto. Física Fundamental II, Universidad de La Laguna. Tenerife. (Spain).* E-mail: canadillas-delgado@ill.fr

The chemistry of gadolinium(III) carboxylate complexes, especially those with direct interaction between Gd(III) centres, has been the

topic of research of several recent papers within the field of magneto-structural correlations. [1] Symmetry rules [2] give an explanation of the occurrence of ferro- or antiferromagnetic interactions in polynuclear compounds with transition metals; however the application of them to *f*-block elements is still unclear. The main advantage of the use of Gd(III) resides in its spin-only formalism, since its first excited state is well separated from its ground state. However the shielding of the inner electron orbits by the *f*-electrons promotes that the values of magnetic coupling are weak, which means that are hard to measure and easily confused with other interactions as the ligand field.

In the quest of clarify magneto-structural correlations in these complexes, we have synthesized three new digadolinium(III) complexes with hexa-, hepta- and octanoate ligands [caproate (cap), enanthate (ena) and caprylate (capy), respectively] of formulae $[Gd_2(cap)_6(H_2O)_4]$ (**1**), $[Gd_2(ena)_6(H_2O)_4]$ (**2**) and $[Gd_2(capy)_6(H_2O)_4]$ (**3**) and their structures have been determined by X-ray diffraction on single crystals. Their structures consist of neutral and isolated digadolinium(III) units, containing six monocarboxylate ligands and four coordinated water molecules, where the aliphatic tails pointing to the *a* direction in all cases. The hydrophobic character of this tails avoids the inclusion of any crystallographic water molecule. The bridging skeleton within the Gd(III) units is built by a $\mu O(1){:}\kappa^2 O(1)O(2)$ framework where the values of the intramolecular Gd–Gd separation are 4.133(2) (**1**), 4.1150(13) (**2**) and 4.1378(7) (**3**) Å and those of the Gd-O-Gd angle are 113.69(15) (**1**), 113.2(2) (**2**) and 113.90(12) (**3**)º. This structural pattern has already been observed in previously reported complexes whose structure and magnetic properties were reported.[3]

Magnetic susceptibility measurements in the temperature range 1.9–300 K reveal the occurrence of a weak intramolecular antiferromagnetic interaction in **2** [$J = -0.042(2)$ cm^{-1}, the Hamiltonian being defined as $H = -JS_A{\cdot}S_B$] in contrast with the intramolecular ferromagnetic coupling which occurs in **1** and **3** [J = +0.037(3) (**1**) and +0.057(3) cm^{-1} (**3**)]. The magneto–structural data of **1**–**3** indicates a suitable relation between the magnetic coupling between two gadolinium(III) ions and the geometrical parameters at the $\mu O(1){:}\kappa^2 O(1)O(2)$ bridge.

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MS24.P05

Telling "twin molecules" apart in the solid state world: charge density approach

Yulia V. Nelyubina, Mikhail Yu. Antipin, Konstantin A. Lyssenko, *X-ray Structural Center, A.N. Nesmeyanov Institute of Organoelement Compounds, Moscow (Russia).* E-mail: unelya@xrlab.ineos.ac.ru

Chemical compounds that tend to form crystals with several independent species (Z'>1, often pseudosymmetric) or exist as several polymorphic modifications are an evergreen challenge of the solid state world. Encountering these "twins" (molecules or crystals of the same chemical nature) significantly complicates the scientific efforts of many crystallographers. In the case of Z'>1, however, they mostly have to go to the efforts of averaging, as such molecules are usually believed to be identical. Meanwhile, the self-association of these species, like the interactions between counterions, can cause the

electron density redistribution that makes them distinct. As a result, the crystal structures and thus the related properties cannot be predicted based on the quantum chemical calculations of an isolated molecule.

Theoretical methods were elaborated to rationalize the crystal structures with Z'=2 [1], but many systems have more than two independent species; therefore, to assess the degree to which they are different and how it is related to the crystal environment can be a challenge difficult to overcome. The similar questions can be addressed to the polymorphic modifications. Judging whether a distinction between the "twins" is significant is still based mostly on the comparison of geometrical parameters; interconnecting a molecular or crystal structure with the physicochemical properties of the resulting materials (e.g., their stability), on some empirical principles of crystal formation (dense packing, strength of interactions between species, etc. [1]). These approaches are, however, too rough approximations of the complex situation in a real crystal and provide no quantitative information on the matter. Much more powerful is the topological analysis of the electron density distribution within the "atoms in molecules" theory [2]. It allows accurately evaluating the net properties of molecules (e.g., their charge) and the energy of interactions they form in a crystal (and so the energy of a crystal lattice), hence distinguishing the "twins" at both the molecular and supramolecular levels.

We tested this approach on a series of Z'>1 crystals and polymorphs with intermolecular interactions of various strength: from classical H-bonds (as in paracetamol [3]) to weak van-der-Waals contacts (as in a sidnone imine derivative [4]). It proved to be an effective tool to identify and quantify even subtle differences between the molecules and their crystal environments [4] and thus to correlate the charge transfer and mutual polarization due to the self-association with the interaction energy, while revealing some important implications for crystal engineering. In summary, Z'>1 systems should be dealt with care, as neglecting even faint distinction between the independent species (those caused by the weakest interactions) can have measurable consequences; the "cost" for a crystal structure being sometimes high [5]. This approach also allowed estimating the stability of polymorphic modifications, the isoenergetic ones and those violating the "density rule"; in the latter case it helped to reveal the interactions that are responsible for this [3].

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MS24.P06

Looking at nanoscale properties in macro-systems with x-ray diffraction imaging

Andrei Nikulin,[a] Daniele Pelliccia,[a] Barry Muddle,[b] *[a]School of Physics, Monash University, Wellington Road, Clayton, Victoria 3800 (Australia). [b]Department of Materials Engineering, Monash University, Wellington Road, Clayton, Victoria 3800 (Australia).* E-mail: Andrei.Nikulin@monash.edu

A feature of emerging nanotechnology is the development of novel materials based on the dispersion of nano-particles in a broad variety of matrices. Applications of such materials range from novel paints and coatings, to a new generation of light alloys, advanced photonics and telecommunication devices, cosmetics and novel biomedical