

reproducible as tetragonal bipyramides. Diffraction images of different crystals show split or smeared spots but symmetry is clearly visible. Indexing works properly using different programs suggesting a primitive tetragonal lattice with $a = b = 66.8 \text{ \AA}$ and $c = 113.2 \text{ \AA}$ and one molecule in the asymmetric unit. Merging statistics and automatic space group assignment in various program packages suggests point group 422 with a $4_{1/3}$ screw axis along the fourfold and also a twofold screw axis (space group $P4_12_12$ or $P4_32_12$). But some strong violations of systematic absences at low resolution along the fourfold and one twofold axis indicate that space group $P4_{1/3}2_12$ may not actually be correct. Despite this, a three-wavelength SeMet-MAD dataset was measured with a resolution of 2.8 \AA and useable anomalous signal to about 3.5 \AA . SHELXD [1] consistently found a solution for the Se-substructure in space group $P4_12_12$ (4 out of 5 Se atoms with CC all of 52.9 and CC weak of 33.6). After solvent flattening with SHELXE [1], the experimental electron density revealed the expected three helical bundle. No improvement was achieved in further attempts of density modification using different programs from the CCP4 program suite [2].

Using the Se positions as anchors for sequence assignment, around 80 amino acids (out of a total of 221) could be built, another 40 could be placed with some uncertainty. The free R-factor stalled at $\sim 46\%$ with a FOM of $\sim 50\%$, and little difference density that would have allowed to extend the model. This model was taken for molecular replacement with PHASER [3] into the single datasets of the MAD experiment and other datasets from the native protein. Single solutions were found but with rather low Z-scores of ~ 3.6 (rotation function) and ~ 6 (translation function). We also tried molecular replacement with lower symmetry down to $P4_1$, $P2_12_12$ and $C222_1$ as well as experimental phasing in these space groups. But this did not result in better phases that allowed extending the structure or refining it to lower R-factors.

Apparently, this is a case of severe pseudosymmetry as refinement of an initial model in the suggested high symmetry spacegroup $P4_12_12$ did not work. Pseudo-merohedral twinning in a lower symmetry space group seems possible but analysis with PHENIX Xtriage [4] did not detect any indication for this. Experimental phasing in space groups $P2_1$ or $P1$ did not work due to lower multiplicity of the data. After all, other crystallographic or biochemical approaches may be required to determine the structure of this protein.

[1] G.M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122. [2] Collaborative Computational Project, Number 4, *Acta Cryst.* **1994**, *D50*, 760-763. [3] A.J. McCoy, R.W. Grosse-Kunstleve, P.D. Adams, M.D. Winn, L.C. Storoni, R.J. Read, *J. Appl. Cryst.* **2007**, *40*, 658-674. [4] P.D. Adams, P.V. Afonine, G. Bunkóczy, V.B. Chen, I.W. Davis, N. Echols, J.J. Headd, L.W. Hung, G.J. Kapral, R.W. Grosse-Kunstleve, A.J. McCoy, N.W. Moriarty, R. Oeffner, R.J. Read, D.C. Richardson, J.S. Richardson, T.C. Terwilliger and P.H. Zwart. *Acta Cryst.* **2010**, *D66*, 213-221.

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Low energy SAD experiments performed at the photon factory BL-1A

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Recent developments in SAD (single anomalous dispersion) phasing techniques facilitate to solve macromolecular crystal structures using light atoms such as sulfurs or phosphors. Longer wavelength beam

ranging from 1.7 \AA to Cr K-edge ($\sim 2.3 \text{ \AA}$) has been mainly used in data collection to enhance the weak anomalous signals. The method would be attractive for de-novo structure solutions without any derivatives, including membrane proteins or macromolecular complexes, for which heavy atom or selenomethionine derivative crystals are difficult to prepare.

We have developed a synchrotron beamline dedicated to long wavelength SAD experiments. The beamline is designed to take full advantage of a long wavelength X-ray beam at around 3 \AA to further enhance anomalous signals. The light source is an in-vacuum short gap undulator optimized at around the wavelength with the fundamental harmonics to obtain maximum brilliance. The vacuum section of the beamline has only one terminal beryllium window, followed by a diffractometer equipped with a helium cryostream and a specially designed helium chamber to minimize the attenuation of the lower energy beam and background noises. A cryo-cooled channel-cut monochromator and bimorph KB focusing mirrors compose a simple optics to deliver a focused beam with a good stability. The focused beam size (FWHM) at the sample position is 70 \mu m (H) x 10 \mu m (V), and the measured beam intensity is in the order of 10^{10} photons/sec on the area of 10 \mu m square.

Diffraction experiments using the wavelength of 2.7 \AA was performed against various protein or nucleic acid crystals. X-ray detector was the commonly used CCD area detector (ADSC Quantum 270). Some of the crystals are mounted in the 'mother-liquor free' condition following the method developed by Hokkaido University [2][3] to decrease the background noise and anisotropic absorptions. Fully automated structural solutions were obtained for some crystals. In the presentation, the effectiveness of the mounting method, the helium cryostream and variable beam sizes are discussed. The exploration of the parameters used for phasing (resolution cut-off, number of frames, etc.) will be presented in the relationship with the radiation damage.

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[1] K. Djinović Carugo, J.R. Helliwell, H. Stuhmann, M.S. Weiss, *J. Synchr. Rad.* **2005**, *12*, 410-419. [2] Y. Kitago, N. Watanabe, I. Tanaka, *Acta Cryst.* **2005**, *D61*, 1013-1021. [3] Y. Kitago, N. Watanabe, I. Tanaka, *J. Appl. Cryst.* **2010**, *43*, 341-346.

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Coordinated ligand effects in the substitution kinetics of $[\text{Re}(\text{CO})_3]^+$ complexes

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The coordination chemistry of rhenium gained a lot of interest in the last few years, since Alberto's *fac*- $[\text{Re}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ complex were remarkably synthesized from $[\text{Re}(\text{CO})_4]^+$ in water and under mild conditions [1].

Synthetically, a lot of work has been published on $[\text{M}(\text{CO})_3]^+$ ($\text{M} = \text{Re}, \text{Tc}$) systems with a huge variation in ligand systems [2 - 7]. The aqua ligands on the starting synthon, $[\text{Re}(\text{CO})_3(\text{H}_2\text{O})_3]^+$, can readily be substituted by a variety of combinations of ligands to produce potential radiopharmaceuticals with many different characteristics.

Our interest lies with the *fac*- $[\text{Re}(\text{CO})_3]^+$ moiety and adopting the [2+1] approach [8]. The solid state behaviour and different effects like charge of the complexes and the influence of coordinated bidentate ligands on the rate of substitution can be explored.

Poster Sessions

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 substitution kinetics of these 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.

[1] R. Alberto, R. Schibli, R. Waibel, U. Abram, A.P. Schubiger, *Coord. Chem. Rev.* **1999**, 192, 901. [2] M. Schutte, H.G. Visser, *Acta Cryst.* **2008**, E64, m1226-m1227. [3] M. Schutte, H.G. Visser, A. Brink, *Acta Cryst.* **2009**, E65, m1575-m1576. [4] R. Alberto, R. Schibli, P.A. Schubiger, U. Abram, T.A. Kaden, *Polyhedron* **1996**, 15, 1079. [5] U. Abram, S. Abram, R. Alberto, R. Schibli, *Inorg. Chim. Acta.* **1996**, 248, 193. [6] R. Schibli, R. Alberto, U. Abram, S. Abrams, A. Egli, P.A. Schubiger, T.A. Kaden, *Inorg. Chem.* **1998**, 37, 3509. [7] R. Alberto, A. Egli, R. Schibli, U. Abram, T.A. Kaden, A.O. Schaffland, R. Schwarzath, P.A. Schubiger, *Q. J. Nucl. Med.* **1998**, 42, 9. [8] S. Mundwiler, M. Kundig, K. Ortner, R. Alberto, *Dalton Trans.* **2004**, 1320. [9] B. Salignac, P.V. Grundler, S. Cayemittes, U. Frey, R. Scopelliti, A.E. Merbach, *Inorg. Chem.* **2003**, 42, 3516. [10] L. Helm, *Coord. Chem. Rev.* **2008**, 252, 2346. [11] R. Alberto, A. Egli, U. Abram, K. Hegetschweiler, V. Gramlich, P.A. Schubiger, *J. Chem. Soc. Dalton Trans.* **1984**, 2815.

Keywords: Kinetics, Rhenium

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

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X-PhonyH (X = aromatic substituents; PhonyH = 4-(phenylamino)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.

[1] W. Pyżuk, A. Krówczynski, E. Górecka, *Mol. Cryst. Liq. Cryst.* **1993**, 237, 75-84. [2] M. Xia, B. Wu, G. Xiang, *J. Flu. Chem.* **2008**, 129, 402-408. [3] H.Y. Tan, W.K. Loke, Y.T. Tan, N.-T. Nguyen, *Lab Chip* **2008**, 8, 885-891. [4] W.J. Fanshawe, L.S. Crawley, S.R. Safir, G.E. Wiegand, E.C. Cooley, *Substituted enaminoketones* **1974**, US3997530 (Patent). [5] V.A. Nair, M.M. Suni, K. Sreekumar, *Proc. Indian Acad. Sci. (Chem. Sci.)* **2002**, 114, 481-486. [6] G.J.S. Venter, G. Steyl, A. Roodt, *Acta Cryst* **2009**, E65, m1321-m1322. [7] G.J.S.

Venter, G. Steyl, A. Roodt, *Acta Cryst* **2009**, E65, m1606-m1607.

Keywords: rhodium, enaminoketone, dicarbonyl

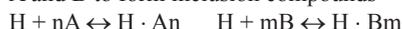
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Measuring selectivity in host-guest systems

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When a host compound, H, is dissolved in a mixture of liquid guest A and B to form inclusion compounds



then one may write the equilibrium constants

$$K_1 = [H \cdot nA] / [H] [A]^n \quad K_2 = [H \cdot mB] / [H] [B]^m$$

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

$$\text{selectivity} = K_1 / K_2$$

However, if the host forms an inclusion compound which incorporates both guests



where generally $n \neq m'$, $m \neq m'$, 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 dimensional system, comprising the host H and three competing guests A, B and C.

[1] A.M. Pivovar, K.T. Holman, M.D. Ward, *Chem. Mater.* **2001**, 13, 3018.

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Dinuclear Gadolinium(III) complexes constructed by monocarboxylate ligands

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