EXAMPLES All made with XD – could be done with other programs like JANA, Valray, Molly etc.

K₂SO₄ - ongoing work





Schmøkel, M. S. Unpublished results

K₂SO₄ - ongoing work



SO₄-tetrahedra surrounded by K⁺; Oxygen: Octahedral coordination sphere; K: 9-coordinated to O-atoms

	<u>APS</u>
Space group	Pnma
Detector	Apex2
Wavelength, Å	0.41327
μ*r	0.0078
Temperature, K	18
Crystal size	30x30x20 μm³
Resolution, Å	0.37
# meas refl	49029
# unique refl	4393
Rint	0.044 (<n> = 11.2)</n>
# parameters	95
D/F ²) all data	0.010
$R(r^{-})$, un data	0.018

Data overview $-K_2SO_4$

Motivation:

Network structure, impossible at conventional source

Schmøkel, M. S. Unpublished results





Schmøkel, M. S. Unpublished results





Schmøkel, M. S. Unpublished results

Hydrogen bonding

Hydrogen bonds



X-N study of "biobrint"

Refinement details



Data overview – Biobrint				
	<u>NSLS</u>	<u>Huber</u>		
Space group	roup C2/c			
Detector	IP	point detector		
Wavelength, Å	0.643	0.5513		
Temperature, K	28	10(1)		
Resolution, Å	0.38	0.98		
# collected refl	98132	16382		
<i># unique refl</i>	15657	3187		
R _{int}	0.030	0.016		
# parameters	ameters 1128			
R(F²), all data	0.0	35		

Motivation:

Anomaly in HB distances, multicomponent crystal, active site analogue, excellent crystals

Overgaard et al, Chem. Eur. J 2001, 3756-3767

Biobrint – a model for the catalytic triad



- The bonding pattern resembles the geometry in the catalytic triad involved in enzymatic action.
- HB's are: d(N-H) d(N---O)
 N1A-H1A---O1A 1.046 2.613
 N3A-H3A---O8 1.056 2.685
 N1B-H1B---O1B 1.049 2.676
- An anomaly in HB2

Accuracy in synchrotron studies

Atomic Displacement Parameters

 $\frac{|U(x-ray)-U(neutron)|}{\sigma(U)} = 1.42 \quad |U(x-ray)-U(neutron)| = 0.0009\text{\AA}^2 \quad \frac{U(x-ray)}{U(neutron)} = 1.011(16)$

75 unique atoms (25 H)

Catalytic triad model



Ab initio theory



Experiment



Biobrint – electron density modelling

- <u>U-values</u>: Extracting U_{ij}'s from N study: The H atom adp's were taken directly from N without scaling (<U_{ii}(X)/U_{ii}(N)> = 1.011(16))
- <u>H-positions</u>: The positions of the H atoms were directly copied from N values
- <u>Significance:</u>



			_			
From	outp <u>ut l</u> isting		.			
				0 029107	510	2
DI+	0.129.0		0.17.2494	0.020197	512	-3 -4
D1-	0.008500	-0.000018	0.008482	0.014671	651	-3
D0	0.002000	-0.000028	0.001972	0.012943	705	-3
Q0	-0.048600	-0.000043	-0.048643	0.018678	759	-3
Q1+	0.011400	0.000029	0.011429	0.020080	813	-3
Q1-	-0.008500	-0.000024	-0.008524	0.016129	867	-3
Q2+	0.112600	-0.000010	0.112590	0.020783	932	-4
02-	0.066800	0.000021	0.066821	0.021843	996	-3

H and E_{hb} of HB's

$$G(\mathbf{r}_{bcp}) = \frac{3}{10} (3\pi^2)^{2/3} \rho(\mathbf{r}_{bcp})^{5/3} + \frac{1}{6} \nabla^2 \rho(\mathbf{r}_{bcp}) \\ V(\mathbf{r}_{bcp}) = \frac{\hbar}{4m} \nabla^2 \rho(\mathbf{r}_{bcp}) - 2G(\mathbf{r}_{bcp})$$
 \longrightarrow $\mathbf{E}_{\mathbf{HB}} = 0.5 * V(\mathbf{r}_{bcp})$



Cheiron Schob 2010

Source function from theo wavefunctions

• Useful in analysis of HB's as a tool to discriminate between types: What is important is the H contribution to the bcp:



• The trend is that the stronger HB's are followed by an increase in the contribution from the H atom.

Source function from experiment

• Added in XD2006 is the TOPINT keyword to calculate source function contributions – to be compared to theoretical values.

SOURCE	refpoint	5.673506	2.156185	2.299098	! 0(1	A)-H(1A)
SOURCE	refpoint	9.897701	0.896144	4.688383	! 0(8) -H(3A)
SOURCE	refpoint	13.550304	2.847093	0.784550	! 0(1	B)-H(1B)
TOPINT	spheres H(2B)	0.256 H(4B)	0.257	(FOR ALL A	TOMS)	
TOPINT	atoms *all se	lect N(1B) H(1B)			



%-contributions to HB2

	EXP	THEO
H3A	6.1	4.9
08	34.8	35.0
N3A	18.3	21.8
09	8.4	8.3
N1A	4.3	3.9

Hydrogen atomic charges

• One could reasonably ask what the integrated charge within the H atomic basin is?

```
CGEN alim -0.5 1.5 blim -0.5 1.5 clim -0.5 1.5
ATBP Spheres O(8) 0.806 O(9) 0.824 N(7) 0.867 C(12) 0.424 C(13) 0.636
ATBP *atoms H(1A) iZFS nvi 100 IRsur 0 *IRSav Rest Debug Phi 48 Th 36 Rad 120 Accur
1.D-3
```

• The value of the integrated Laplacian describes the accuracy of the integration



Cheiron Schobs 2010



Refinement details

Data overview – OxHy			
	<u>D3</u>	<u>Huber</u>	
Space group	P-1		
Detector	Apex2	point detector	
Wavelength, Å	0.45	0.5513	
Temperature, K	15	11(1)	
Resolution, Å	0.38	0.357	
# collected refl	160430	15020	
# unique refl	14266	10210	
R _{int}	0.077	0.0111	
# parameters	483	548	
R(F ²), all data	0.052	0.034	

Residuals close to K⁺, which are reduced significantly by refinement of anharmonicity on the K atom

Motivation:

Very strong hydrogen bonds, test example for D3

W. Morgenroth, J. Appl. Cryst., 2008, 41, 846-853.

Parameter comparisons



UIJXN comparison D3

<∆U>	0.00050(30)
<∆U²> ^{1/2}	0.00059
<ΔU _{x,ii} /ΔU _{N,ii} >	0.89(11)
$<(\Delta U / \sigma (\Delta U))^2 >^{1/2}$	6.66

IAM parameters:

The average difference in position is, $\langle \delta X \rangle = 0.0002(5)$ while the average difference in Uvalue is $\langle \delta U_{ii} \rangle = 0.007(23)$

Multipole parameters:

307 multipole parameters refined, and $\langle \delta P_{lm} \rangle = 0.06(9)$. For the monopoles only, the average deviation, $\langle \delta P_v \rangle = 0.05(14)$

How well do the data fit?



How well do the data fit?



Laplacian map



d(O-H)=1.089 Å, d(O---O)=2.471 Å, d(H--O)=1.382 Å

Cobalt dimer

Refinement details



Data overview $- Co_2(CO)_6(HC_2C_6H_{10}OH),$ Z' = 2				
	<u>D3</u>	<u>Apex2</u>		
Space group	Space group P-1			
Detector	MarCCD1	65 Apex2		
Wavelength, Å	0.4769	0.7107		
Temperature, K	15	100		
Resolution, Å	0.42	0.45		
# unique refl	40270	31948		
# parameters	1228	785		
R(F²), all data	0.024	0.026		

Motivation:

Presence or not of Co-Co & details of Co-C₂ bonding

J. Overgaard, H. F. Clausen, J. A. Platts, B. B. Iversen, JACS, 2008, 130, 3834.

Agreement factors & redundancy



Based on the internal agreement factors, the two systems behave relatively equal

Data statistics



Significance of synchrotron data higher. Effect of thermal smearing visible on Apex2 data.



Based on the multipole models, the average ratio in 0.05 Å⁻¹ shells of reciprocal space are closer to ideal 1.0 for D3 data.

Geometry comparison



Geometr	Geometry – Co ₂ (CO) ₆ (HC ₂ C ₆ H ₁₀ OH)			
	<u>D3</u>	Apex2		
Co-Co	2.4633(1),2.4653(1)	2.4648(1), 2.4666(1)		
Co-C(O)	1.791-1.836	1.791-1.836		
C(11)-C(12)	1.3421(4), 1.3399(4)	1.3433(7), 1.3401(6)		
Comparison the average 0.06%!!	Comparison of D3 vs Apex2 structural models is 0.2%, and the average difference between same bond lengths is 0.06%!!			

Multipole model



Карра ра	Kappa parameters:				
	D3/Apex2	<u>Theory</u>			
Со	0.999(2), 0.95(2)	0.9721(4), 1.014			
	1.012(1), 0.865(5)				
O(CO)	0.985(1), 0.78(1)	0.9901(3), 0.998			
	1.014(1), 1.00(1)				
C(sp3)	0.914(2), 0.827(5)	N/A			
	1.009(1), 0.834(5)				
C(CO)	0.940(2), 0.883(7)	0.966,0.863			
	1.066(1), 0.897(6)				
C(alkyne)	0.912(2), 0.75(1)	0.9218, 0.774			
	1.023(2), 0.758(8)				

Topology comparison



For comparison a theoretical calculation was done using CAS-SCF methods. This showed the molecule to be a singlet diradical.

Quantum Topological Molecular Similarity showed the two models to be rather different (QTMS-value of 3.5; for $p-NH_2$ and $p-NO_2$ it is 0.37). However, without the C-O bonds, the value is much lower at 0.8.Why?

J. A. Platts, G. J. S. Evans, M. P. Coogan, J. Overgaard, *Inorg. Chem.* **2007**,*46*, 6291. P. L. A. Popelier, *J. Phys. Chem. A* **1999**, *103*, 2883.

Electron density in the "infamous" polar carbonyl bond



In such a polar bond, the sign of the Laplacian is strongly dependent on the exact position of the bcp. Here: Synchrotron model: $\nabla^2 \rho$ +40 eÅ⁻⁵ Conventional model: $\nabla^2 \rho$ -10 eÅ⁻⁵

Electron density in the Co-C₂ triangles

In this region, the density is extremely flat and the topology is affected by small errors in the data as well as model insufficiencies. Not all Co-C bond paths found.



Electron density in the Co-C₂ triangles

This is illustrated by the density curvatures along paths in this plane. Only small valleys are found to show minima.
Possible explanations:
➢ Crystal packing
➢ Asymmetric ligand
➢ Model dependency
➢ Measurement errors
➢ ...



Electron density in the Co-C₂ triangles



Coordination polymers

Refinement details



Data overview – Mn ₂ C ₄ H ₁₂ O ₁₂			
	<u>D3</u>	<u>Apex2</u>	
Space group	P2 ₁ /	Ċ	
Detector	MarCCD1	65 Apex2	
Wavelength, Å	0.55	0.7107	
Temperature, K	100	100	
Resolution, Å	1.56	1.18	
<i># unique refl</i>	15080	7212	
# parameters	263	263	
R(F²), all data	0.043	0.024	

Motivation:

Magnetic interaction pathways. Comparison with APS (6).

R. D. Poulsen et al, Chem. Eur. J. 2007, 13, 9775.

Data comparisons



The HO data are relatively higher at the synchrotron, despite identical temperatures.



The significance in Apex compared to D3 is higher for the weak data but lower for the strong data.

Thermal parameters

The thermal parameters are lower for the D3 by ca 10% which relates well to the relatively higher intensities for D3 HO data.



Deformation density maps

The static deformation density maps in the plane of the water molecule show interestingfeatures.Apex2Hasylab D3



Refinement details



Data overview – $M_2C_4H_{12}O_{12}$				
	Zn	<u>Fe</u>		
Space group	P2 ₁ /0	2		
Detector	MarCCD	165		
Wavelength, Å	0.50	0.47686		
Temperature, K	15	15		
Resolution, Å	0.45	0.44		
# meas refl	154531	50762		
# unique refl	7314	8212		
Rint	0.045	0.040		
# parameters	342	344		
R(F²), all data	0.0215	0.0254		

Motivation:

Magnetic interaction pathways. Comparison with Mn-complex.

Refinement details

Almost exactly parabolic in shape in the residual density analysis



Mads R. V. Jørgensen et al, unpublished results

Atomic charges

Atom	Ρ _Ω	V ₀₀₁	Dipole moment	Quadrupole Moments
Zn(1)	2.04	51.8	0.0	-4.80, -4.81, -4.79
Fe(1)	1.69	60.8	0.0	-5.41, -5.42, -5.22
Mn(1)	1.68	66.8	0.0	-5.52, -5.43, -5.54
Zn(2)	2.00	52.8	0.0	-4.84, -4.86, -4.80
Fe(2)	1.96	62.4	0.0	-5.40, -5.49, -5.05
Mn(2)	1.60	71.2	0.0	-5.67, -5.74, -5.77

Mads R. V. Jørgensen et al, unpublished results

d-orbital populations

	d _{x²-y²}	d _{z2}	d _{xy}	d _{yz}	d _{xz}	SUM	Max. unpaired
Zn1	1.97	2.00	1.91	1.98	1.97	9.83	N/A
	(20.0)	(20.3)	(19.4)	(20.1)	(20.0)		
Fe1	1.03	1.22	1.39	1.37	1.21	6.21	3.79
	(16.6)	(19.6)	(22.4)	(22.0)	(19.5)		
Fe1 (ERD ⁽⁶⁾)	1.30	0.99	1.34	1.19	1.39	6.21	3.77
	(21.0)	(15.9)	(21.6)	(19.1)	(22.4)		
Mn1	1.12	1.19	1.09	0.92	0.91	5.23	4.43
	(21.5)	(22.7)	(20.8)	(17.6)	(17.4)		
Mn1 (ERD)	0.91	1.32	0.91	1.25	0.84	5.23	4.09
	(17.4)	(25.2)	(17.4)	(23.9)	(16.1)		
Zn2	2.12	1.94	1.88	1.98	1.94	9.87	N/A
	(21.5)	(19.7)	(19.0)	(20.1)	(19.7)		
Fe2	1.23	0.95	1.55	1.19	1.03	5.95	3.95
	(20.7)	(16.0)	(26.0)	(20.0)	(17.3)		
Fe2 (ERD)	0.98	1.18	1.09	1.80	0.92	5.95	3.86
	(16.4)	(19.8)	(18.3)	(30.0)	(15.6)		
Mn2	1.06	1.11	1.07	1.07	1.02	5.32	4.67
	(19.8)	(20.9)	(20.0)	(20.1)	(19.1)		
Mn2 (ERD)	0.89	1.37	0.89	1.26	0.92	5.32	4.43
	(16.7)	(25.7)	(16.8)	(23.6)	(17.3)		

Mads R. V. Jørgensen et al, unpublished results

Cr-wheel complex

Refinement details



Data overview – $Cr_8F_8(C_5H_9O_2)_{16}$				
	<u>NSLS</u>			
Space group	P2 ₁ /c			
Detector	SMART1000			
Wavelength, Å	0.643			
Temperature, K	16(5)			
Resolution, Å	0.55			
# meas refl	165264			
<i># unique refl</i>	37733			
# parameters	1582			
R(F²), all data	0.039			

Motivation:

Electrostatic potential, host-guest chemistry

Overgaard et al, Chem Eur. J. 2002, 12, 2775-2786

Host-guest chemistry



Host-guest chemistry



Residual density Single crystal synchrotron data



Deformation density map

Inorganic analogue to the cyclodextrins



Cyclodextriner

d anf f electrons may lead to novel chemistry (including magnetism) Fantastic inclusion properties, stable, cheap, non-toxic => used for molecular protection in pigments, food etc







X-ray Electrostatic Potential

