Charge-Density Analysis of a disordered Aluminium Dihydride Complex

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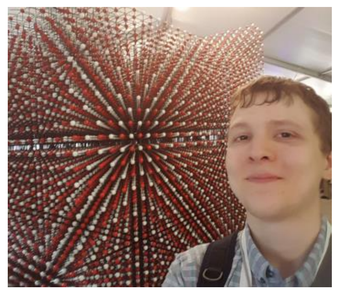
FCI FONDS DER CHEMISCHEN INDUSTRIE



Introduction

- Bis(benzoxazol-2-yl)methanide (BOX) ligands are considered a promising alternative to the ubiquitous NacNac ligand family. Our investigated compound AlH2-MeBOX is the BOX equivalent of an analogous NacNac complex showing catalytic activity.[1]
- Charge-density analysis based on high-resolution data with subsequent topological analysis[2] is an advanced single crystal x-ray diffraction technique that allows for modelling of electron density (ED) even in interatomic regions and thereby provides many useful insights for synthetic chemists.
- Compared to standard IAM refinements, the method is highly susceptible to otherwise easily resolved complications such as disorder. AlH2-MeBOX shows a minor molecular disorder of below 5%, which we tried to overcome in this investigation using two different approaches.

Multipole Formalism[3]

$$\underbrace{\rho_{atom}(\boldsymbol{r})}_{\text{Atomic electron density}} = \underbrace{P_c\rho_c(\boldsymbol{r})}_{\text{Core density}} + \underbrace{P_v\kappa^3\rho_v(\kappa\boldsymbol{r})}_{\text{Spherical Valence density}} + \underbrace{\rho_d(\kappa'\boldsymbol{r})}_{\text{Aspherical Valence density}}$$

Methods for describing the disorder

"2Part"

1. Disorder refinement in SHELXL.[4]
2. Hirshfeld Atom Refinement of the disorder using Olex2/NoSpherA2.[5]
3. Refinement of ADPs in SHELXL against high order data.
4. Starting model generation in XD2016.[6]
5. Transfer of multipole parameters from refinement against theor. data.
6. Iteration over several site occupancy factors (SOFs) for both molecules.
7. Final refinement with SOFs and experimental starting multipoles from 6.
8. Occupancy and multipoles of main component are scaled to 100% and written to a parameter file with only one component.
9. Calculation of structural properties.

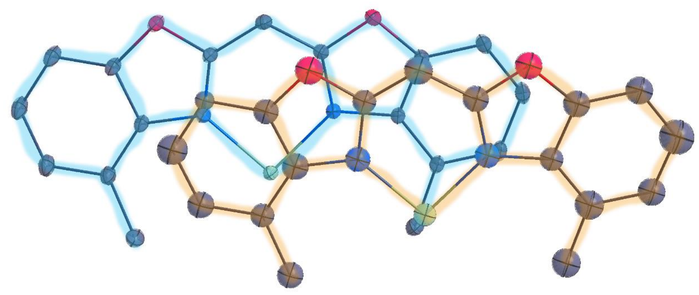
"1Part"

1. Disorder refinement in SHELXL.
2. Calculation of structure factors of the minor component.
3. Starting model generation in XD2016 based on the main component.
4. Contribution of disorder is subtracted from observed structure factors. This is akin to the treatment of disordered solvent with BYPASS, which is the predecessor of the now commonly used PLATON SQUEEZE.[7]

$$F^o_{h,\mathrm{corr}} = s \cdot \left|F^o_{h,\mathrm{all}}\right| \cdot \exp\left(i\varphi^c_{h,\mathrm{all}}\right) - F^c_{h,\mathrm{Part2}}$$

5. Refinement against the corrected data.
6. Calculation of structural properties.

AlH_2-MeBOX
N,N'-bis[(4-methyl-benzoxazol-2-yl)-methanido]-dihydridoaluminum



Space Group : $P2_1/c$
$\sin(\vartheta)/\lambda_{\max}$: 1.00 Å^{-1}
$R(F^2)_{\mathrm{IAM}}$ = 0.0824

SOF minor component:
0.0338(7)
0.0413(7)

- Two molecules in asymmetric unit.
- Small molecular disorder for both molecules. Site occupancy factors of minor components are below 5 %.
- Minor component was modelled using only isotropic thermal displacement parameters and refined as rigid group.

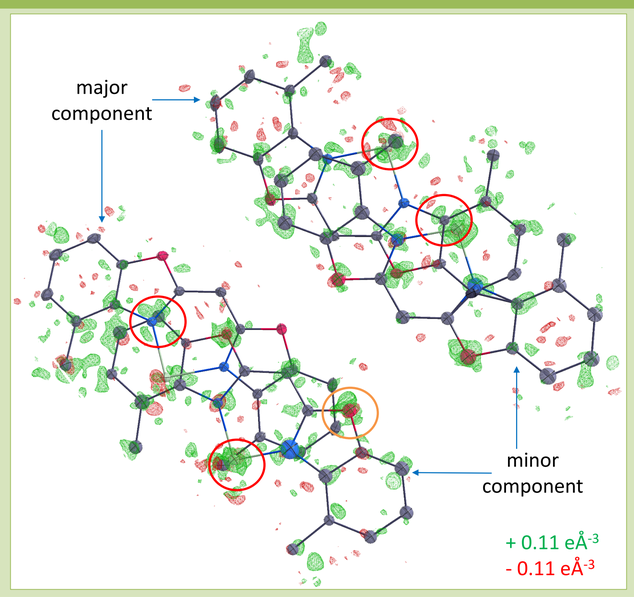
Final Multipole Model

2Part

	Quality Indicators
wR2	0.0318
GoF	2.8065
$\rho_{\min}, \rho_{\max}$	-0.722 ; 0.624 eÅ^{-3}
e_{gross}	46

- Residual density concentrated near overlap between components and several oxygen atoms of the minor component.
- Best results from residual density analysis with SOFs of 2.75%, 2.75%.

Sub-optimal description of the molecular disorder!

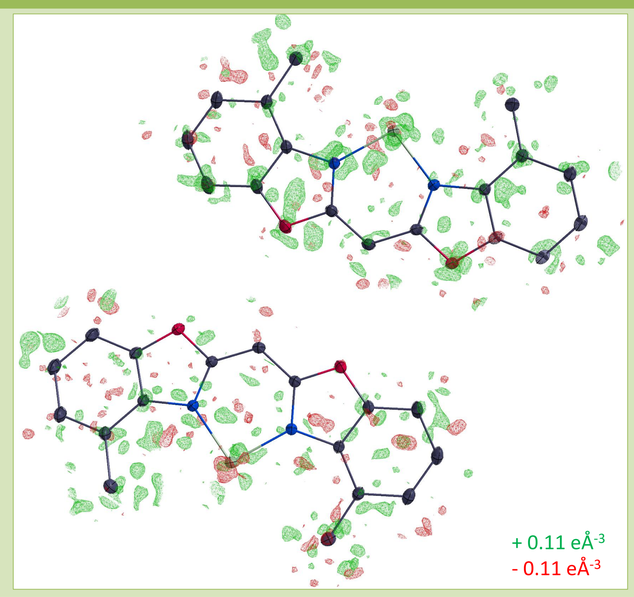


1Part

	Quality Indicators
wR2	0.0289
GoF	2.1002
$\rho_{\min}, \rho_{\max}$	-0.325 ; 0.591 eÅ^{-3}
e_{gross}	44.4

- Overall residual density level is lower, with all of the critical regions from the 2Part approach improving.
- Correction based on SOFs from SHELXL.

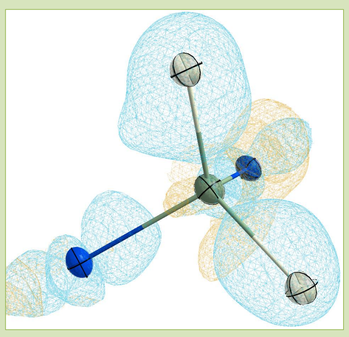
1Part approach yields better model quality!



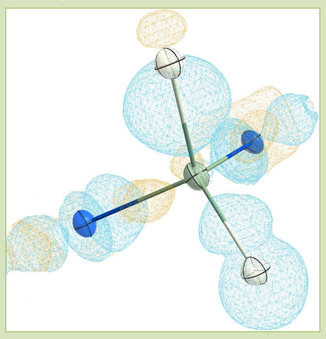
Model Evaluation

Deformation Density

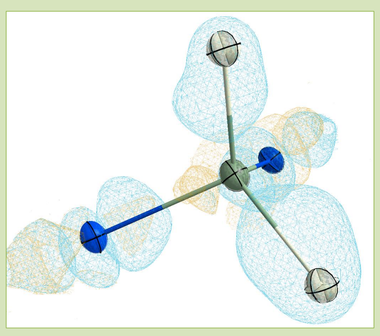
- Correction of the disorder visibly improves the overall residual density in areas of overlap, especially the aluminium centre and bonded hydrogen atoms.



uncorrected

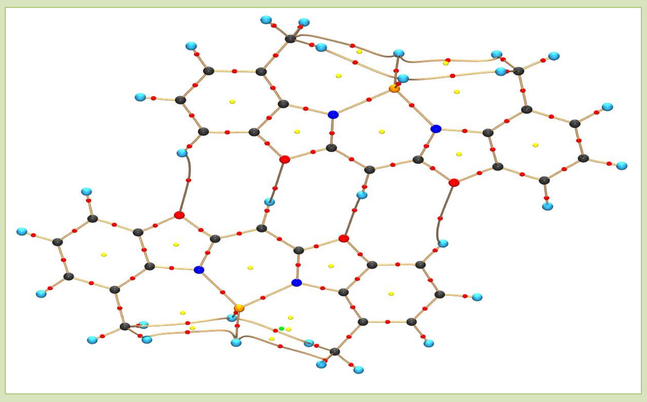


2Part



1Part

Molecular Graph



- Some minor problems were identified in the molecular graphs of all models.
- In regions of lower electron density, there are problems with identification of all critical points.
- This includes the areas between the two molecules and between the hydrogen atoms of methyl groups and aluminium atoms.

Under Investigation!

Comparison of selected Structural Properties

Bader Charges

- Charges of integrated atomic basins ("Bader charges") were calculated for all atoms in the structure. Results from both disorder approaches, a refinement with untreated disorder and refinement against theoretical structure factors (theoMM) were compared.
- As the compound is neutral, the sum of *all charges should amount* to zero.

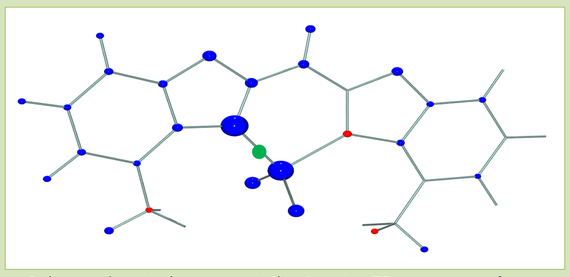
Bader charges	uncorrected	2Part	1Part	theoMM
Al(1)	1.89	2.13	2.07	2.21
Al(2)	2.17	2.11	1.98	2.21
⟨Hydride H⟩	-0.99	-0.91	-0.79	-0.67
⟨Methyl Groups⟩	-0.48	-0.03	0.07	0.09
$\Sigma_{\mathrm{Structure}}$	0.00	-1.00	0.06	0.04

- In the uncorrected refinement, as expected, aluminium and methyl group charges are clearly affected by the undescribed second component.

Source Function Investigations[8]

- The source function descriptor can be used to quantify delocalisation of electron density from the ligand to the metal centre.
- The calculation could only be successfully carried out in the 1Part approach. In the 2Part approach and the uncorrected refinement, the calculation crashed.

1Part approach enhances property determination!



Larger Spheres denote larger contributions to ED at green reference point.
Blue denotes positive contributions, red denotes negative contributions

Conclusion

- A small-scale molecular disorder could be successfully treated in the charge-charge density study of AlH2-MeBOX, as well as disorder of three methyl groups.
- Subtracting the calculated contribution of the disorder from the experimentally obtained structure factors turned out be superior to actually modelling the disorder itself in XD.

References & Acknowledgement

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