The University of Nottingham

Refinement on weak or problematic small molecule data using SHELXL-97

Single Crystal and Powder Diffraction Software Workshop

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Problem structures

- twinning
- crystal size
- voids
- ADPs
- disorder
- pseudosymmetry
- residual e^-
- absorption
- H atoms
- etc

Restraints and constraints

➔ **Restraints: formally, add extra observations**

Example: all B-F distances in BF_4^- are similar

➔ **Constraints: formally, fix parameters**

Example: atoms fixed on special positions

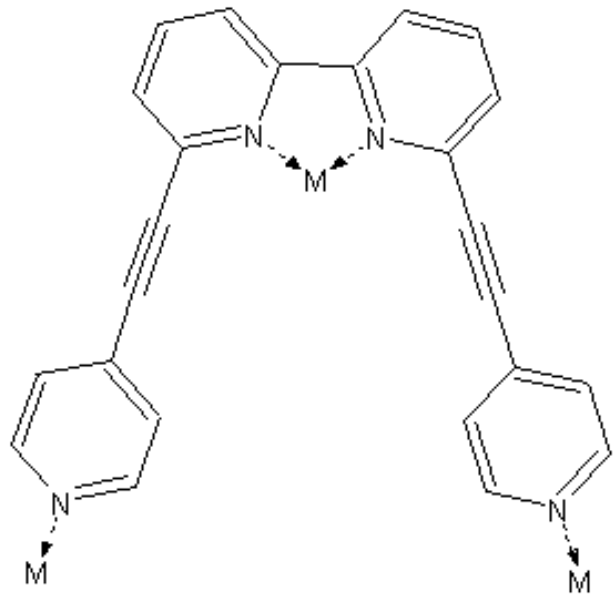
The use of either must be justifiable

The system

a range of hexanuclear supramolecular cages

utilising

a ligand which is both blocking and chelating



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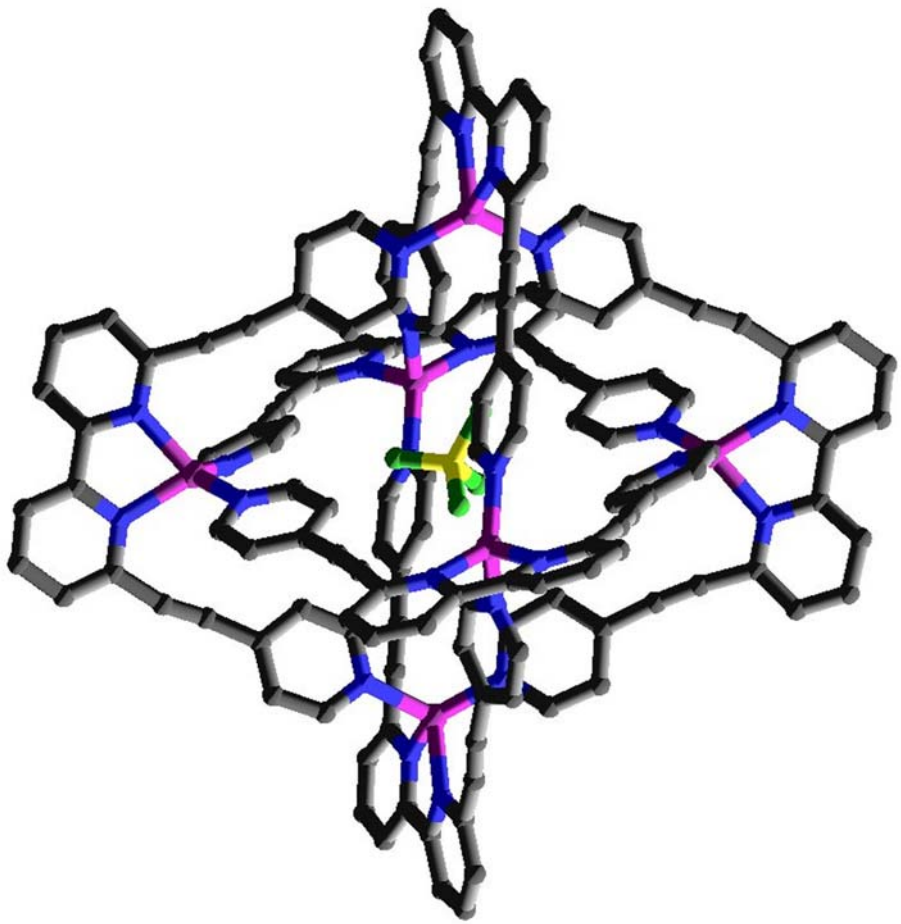
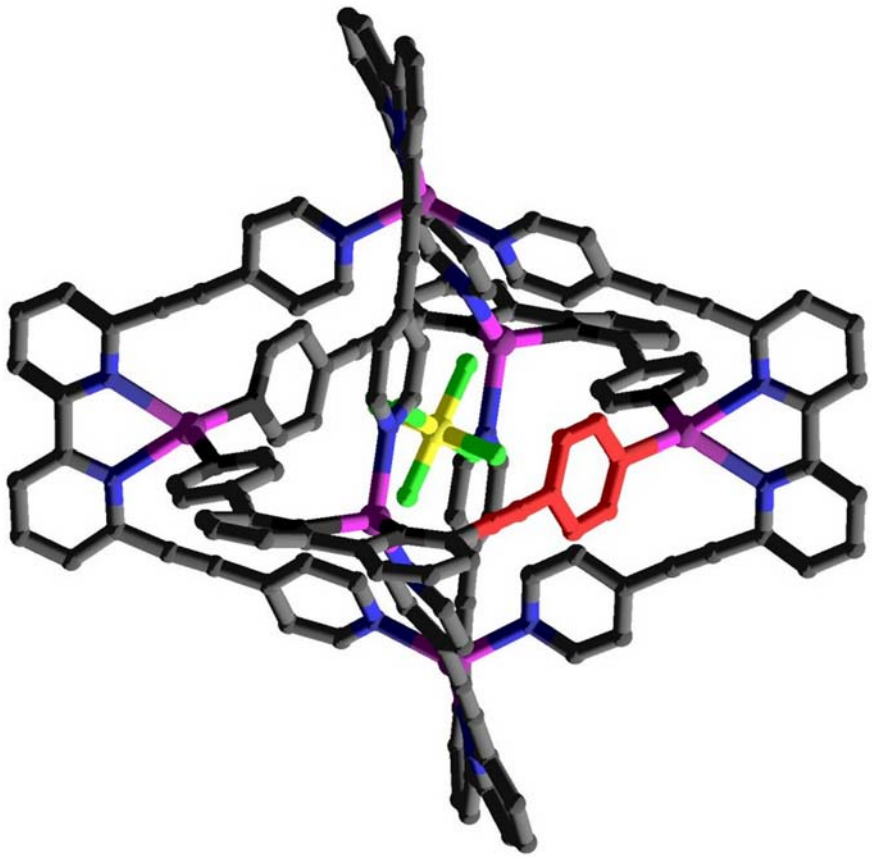
A hexanuclear cage

$\{[Cu_6L_6(BF_4)](BF_4)_5\}$



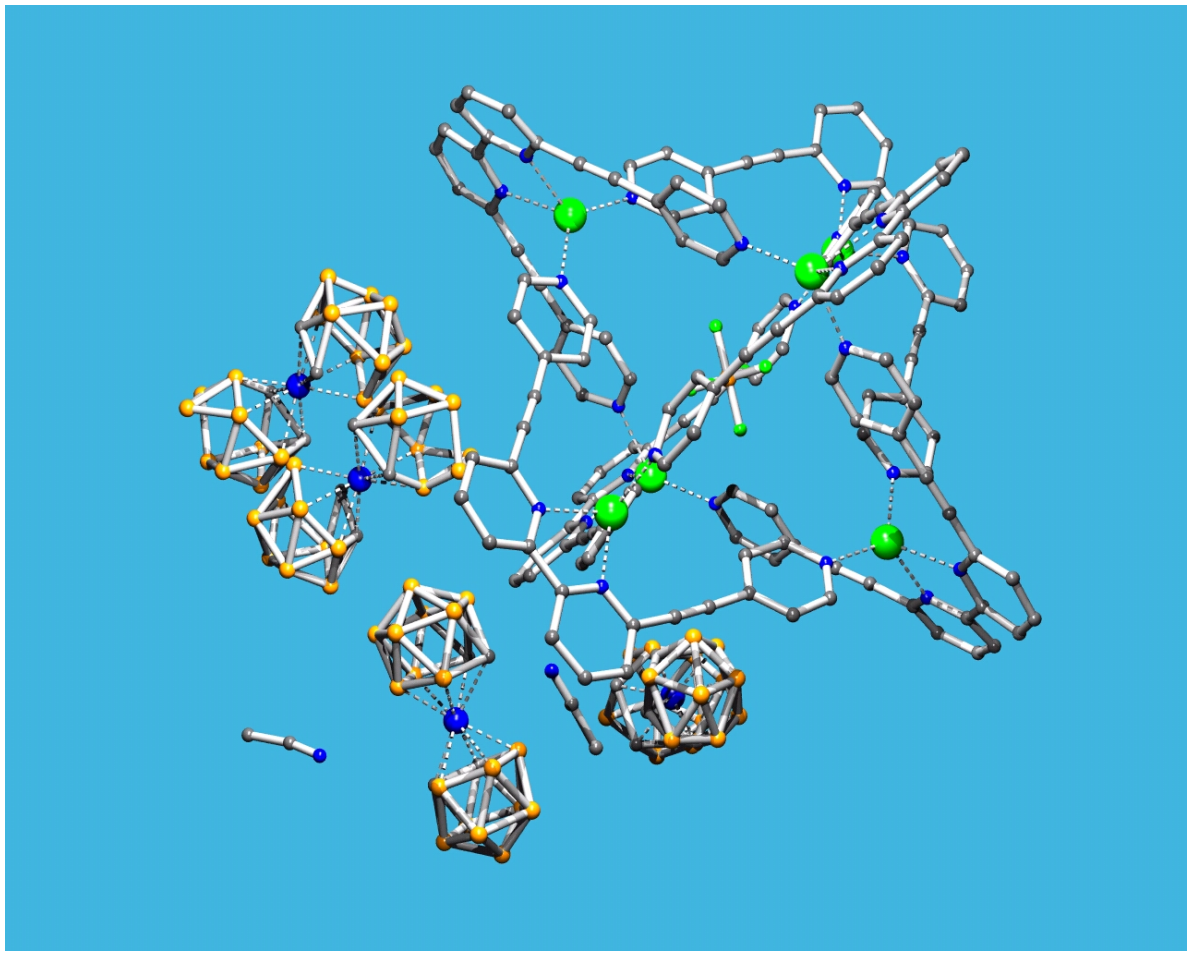
A hexanuclear cage

$\{[Ag_6L_6(SbF_6)](SbF_6)_5\}$



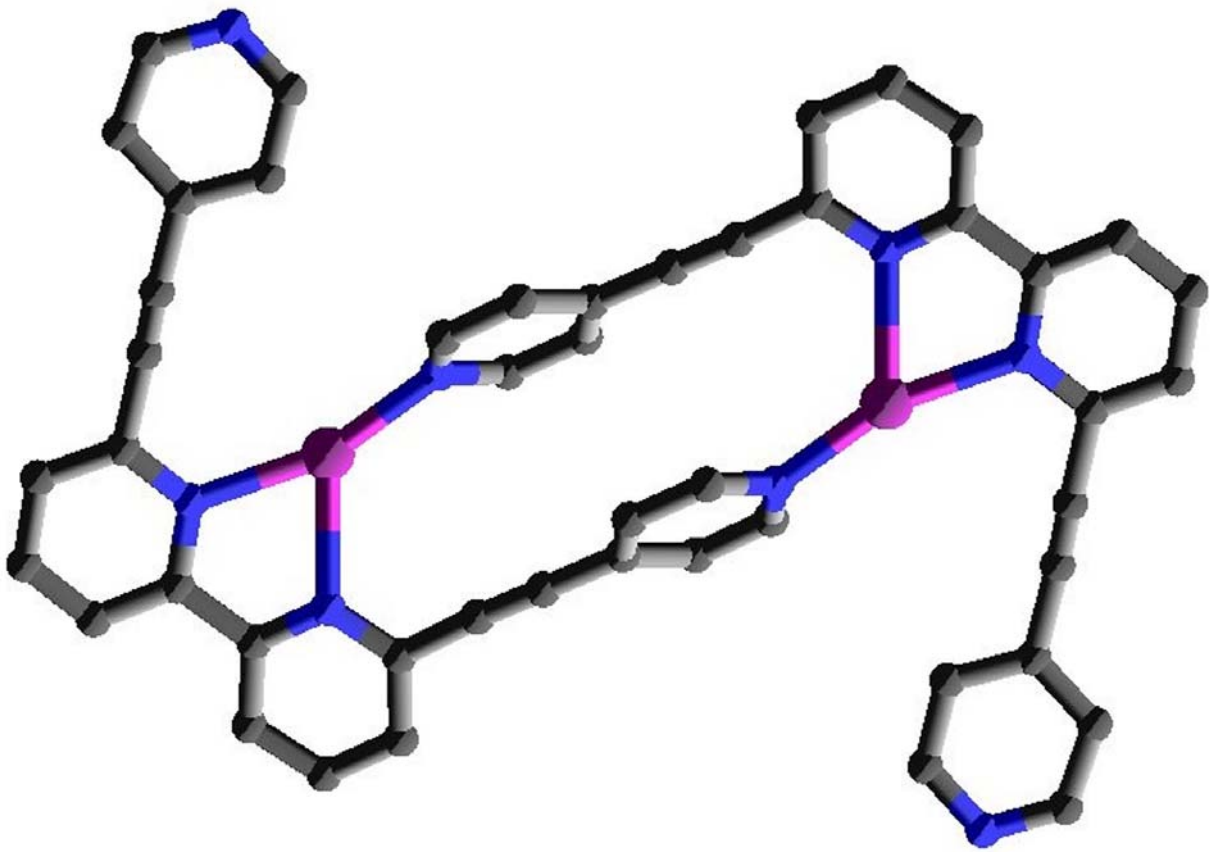
A hexanuclear cage

$[Ag_6L_6(BF_4)][Co(C_2H_{11}B_9)_2]_5$



A dinuclear cation

$(AgL)_2[Co(C_2H_{11}B_9)_2]_2$



The problems

- Disorder in many anions
- Partial occupancy of some anions
- Low resolution, low r/p ratios

The (template) anions are important

Some of the tools – a brief survey

EXYZ atomnames

The same x, y and z parameters are used for all the named atoms.

EADP atomnames

The same isotropic or anisotropic displacement parameters are used for all the named atoms.

PART n sof

The following atoms belong to PART n of a disordered group.

The tools ...

DFIX d s[0.02] atom pairs

The distance pairs of atoms are restrained to a specified target value of d(s).

SADI s[0.02] atom pairs

The distances between pairs of atoms are restrained to be equal with an effective standard deviation s (cf. DFIX)

SAME s1[0.02] s2[0.02] atomnames

The atoms specified here are linked to the same number of atoms which follow.

The tools ...

FLAT s[0.1] four or more atoms

The named atoms are restrained to lie in a plane.

SUMP c sigma c1 m1 c2 m2 ...

The linear restraint: c = c1*fv(m1) + c2*fv(m2) + ... is applied to the specified free variables.

DELU/SIMU/ISOR

Applies various restraints to ADPs.

The tools ...

FRAG code[17] a ... γ

Enables a fragment to be input using an input cell and coordinates.

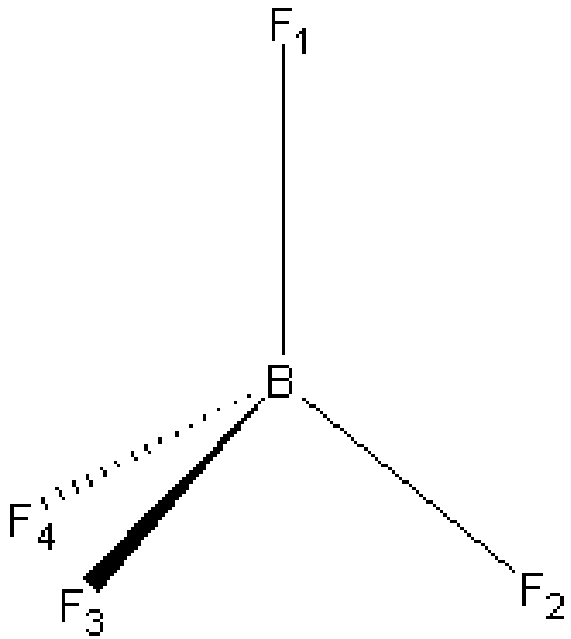
FEND

This must immediately follow the last atom of a FRAG fragment.

AFIX n>16

Applies geometry of fragment with this n value.

Practical application 1

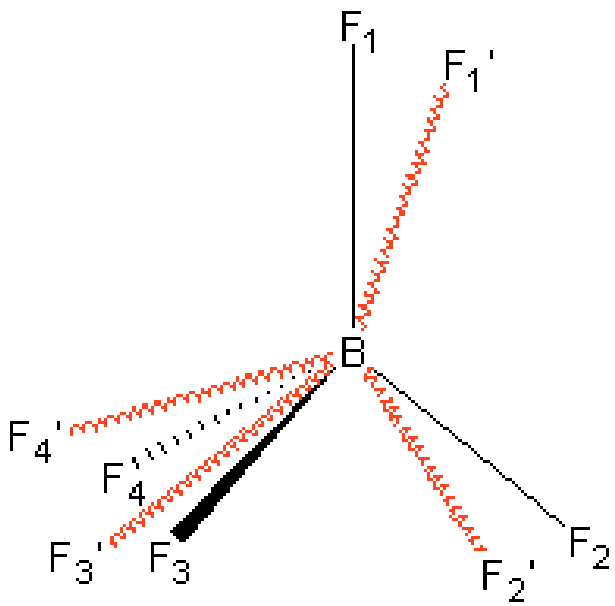



```
DFIX 1.38 0.01  B F1  B F2  B F3  B F4

DFIX 2.25 0.02  F1 F2  F1 F3  F1 F4  =
     F2 F3  F2 F4  F3 F4
```

This is often a prelude to disorder modelling ...

Practical application 1



DFIX 1.38 0.01 B F1 B F2 B F3 B F4

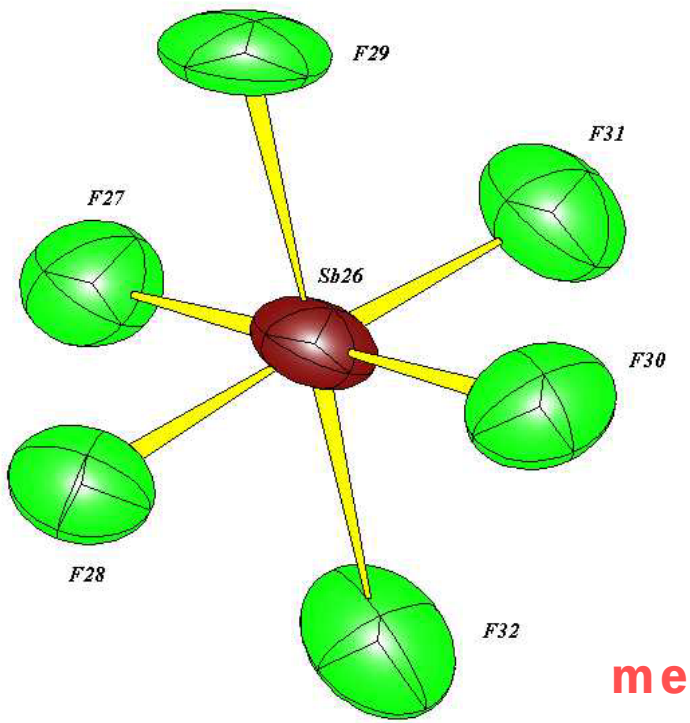
DFIX 2.25 0.02 F1 F2 F1 F3 F1 F4 =
F2 F3 F2 F4 F3 F4

DFIX 1.38 0.01 B F1' B F2' B F3' B F4'

DFIX 2.25 0.02 F1' F2' F1' F3' F1' F4' =
F2' F3' F2' F4' F3' F4'

+ refine occupancy of F1—F4 versus F1'—F4'

Practical application 2



SADI 0.01 SB26 F27 SB26 F28 ...

SADI 0.02 F27 F28 F27 F29 ...

(*cis* angles only)

SADI 0.02 F27 F30 F28 F31 F29 F32

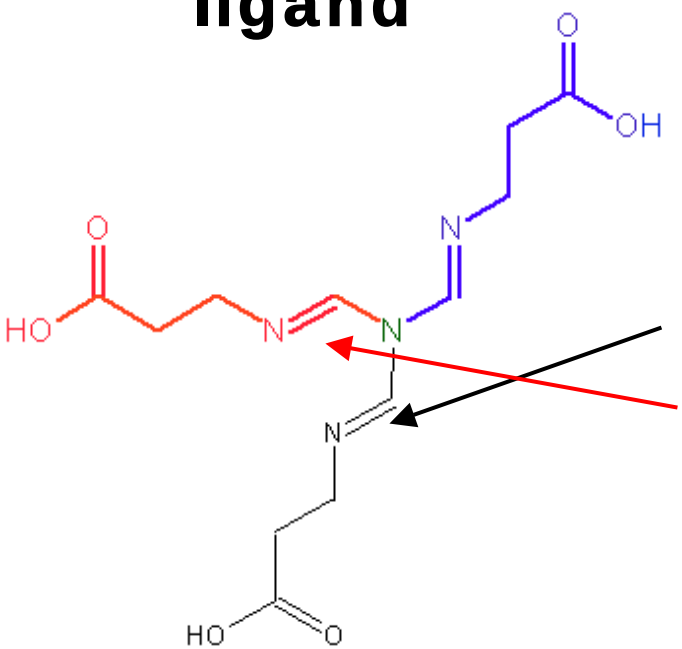
(*trans* angles)

mean Sb—F 1.85(1) Å (175 CCDC entries)

Practical application 3

- unrealistic bonds and angles
- poor agreement between arms
- looks unsatisfactory

Ill-defined tripodal ligand



Similarity restraints (distances+angles)

SAME 0.01 C1 > O7

C11 …

…

O17 …

➔ “average out” the discrepancies

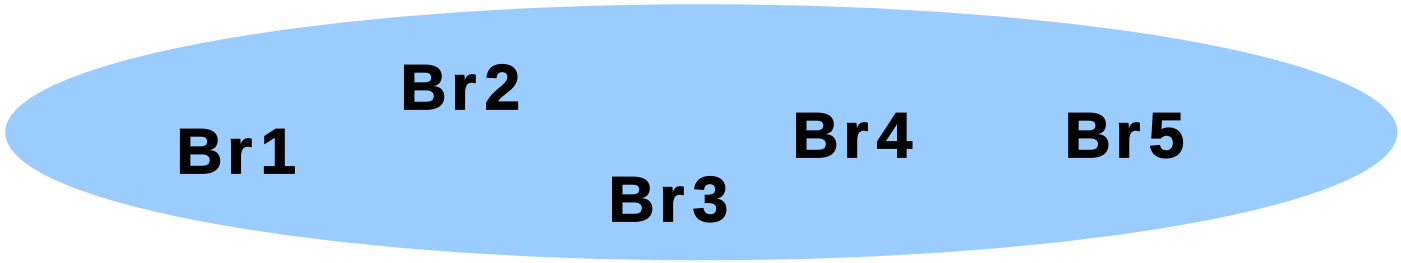
Practical application 4

Disorder over multiple (>2) sites

- **with two sites just use a free variable**
- **with more it is a bit more complicated**

- **SUMP instruction**
- **several free variables on FVAR instruction**
- **free variable references in ATOM instructions**

Practical application 4 ...



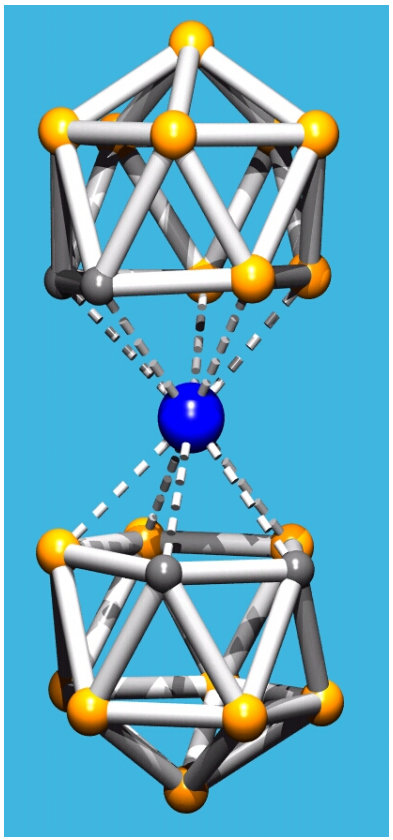

```
SUMP 1.00 0.01  1 2  1 3  1 4  1 5  1 6

FVAR  osf   0.2  0.2  0.2  0.2  0.2

Br1     5       x y z   21      ...
Br2     5       x y z   31      ...
Br3     5       x y z   41      ...
Br4     5       x y z   51      ...
Br5     5       x y z   61      ...
```

← these occupancies will refine subject to their sum staying close to 1.00

Practical application 5



Multiple DFIX instructions

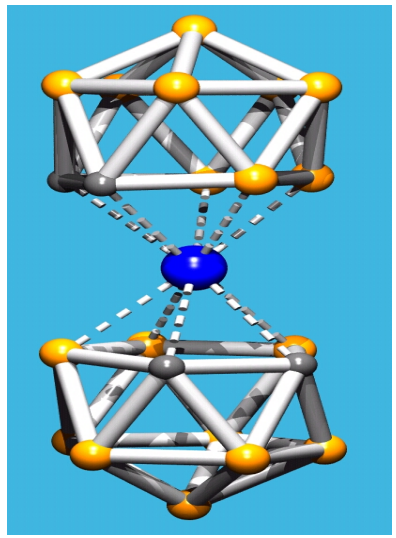
Co—B Co—C B—B B—C

Manual or automatic generation

+ similarity restraints between cages

Complicated

(and no angle restraints)



A hexanuclear cage

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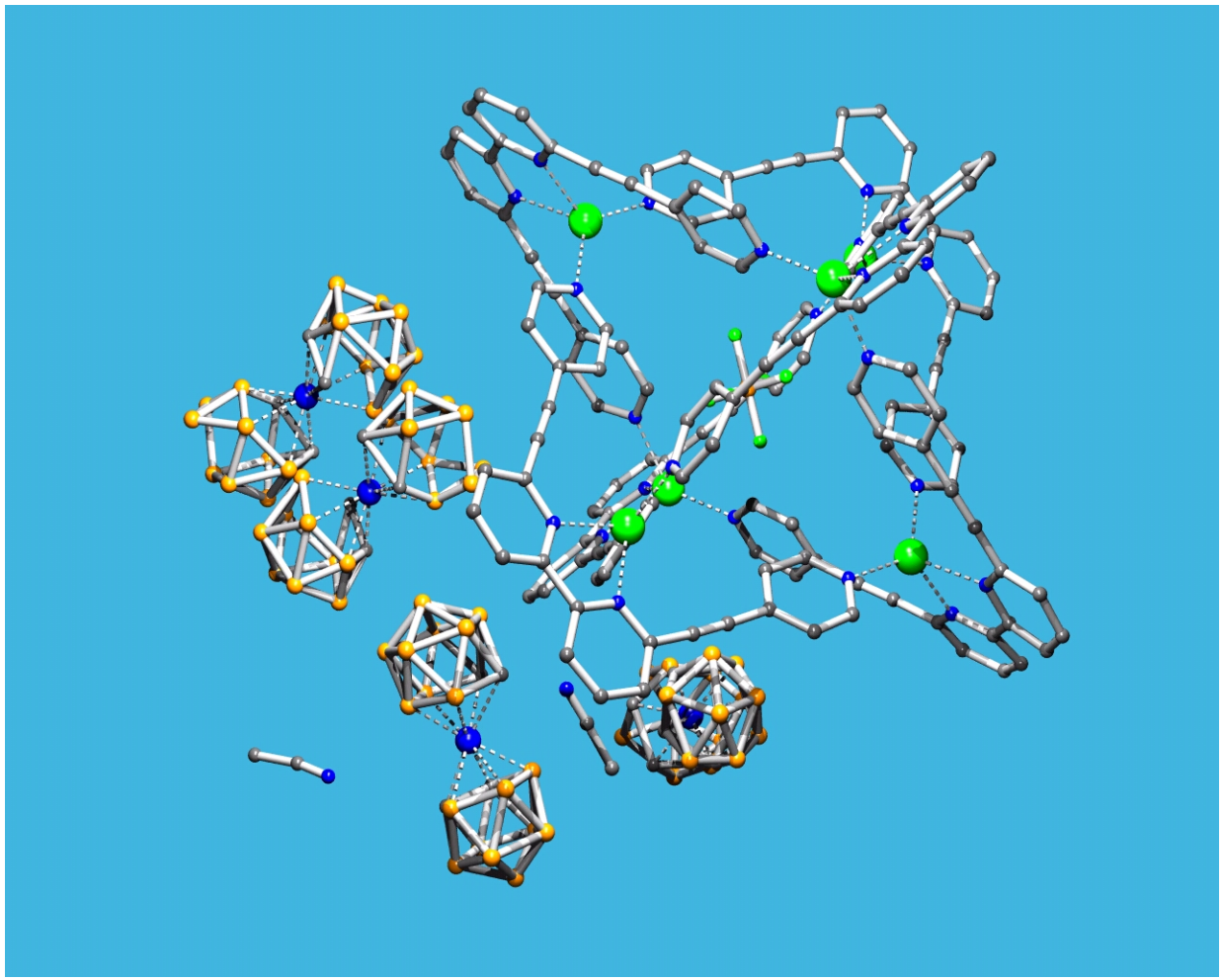


Practical application 5 ...

$[Co(C_2B_9H_{11})_2]^-$ is a 3D-rigid anion

- can treat it as a rigid group

Can take model from

- ❑ a better version in the same structure
- ❑ a better version from another structure
- ❑ a calculated or optimised version
- ❑ a typical or average database structure

Practical application 5 ...

First import the model into the INS file

```
FRAG 17  15.72  20.15 20.39 74.8 70.75 86.50
Co    4      x y z  ...
C1    1      x y z  ...
C2    1      x y z  ...
B3    3      x y z  ...
...
B19   3       x y z ...
FEND
```

Practical application 5 ...

Then apply this model to your structure

```
AFIX 17
Co1   7  0.33250   0.76245   0.52909 11.000   0.0608 0.1389 =
        0.0396  -0.0183  -0.0212   0.0153
C1    1  0.37668   0.84367   0.54903 11.00000   0.155
C2    1  0.41382   0.84350   0.45796 11.00000   0.089
...
B3    3  0.31680   0.82455   0.43612 11.00000   0.117
B19   3  0.20793   0.79538   0.51437 11.00000   0.138
AFIX  0
```

Practical application 5 ...

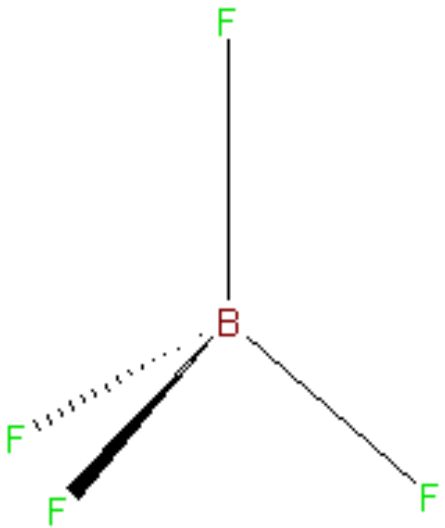
- Your model is idealised to the input model
- FRAG ... FEND lines disappear in the RES file
- AFIX 17 is replaced by a simple AFIX 3
- Positional parameters reduced from 69 to 6

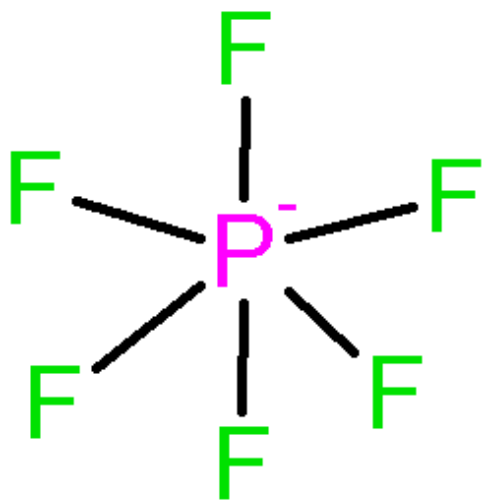
❖ The 3D matching requirements are rigorous

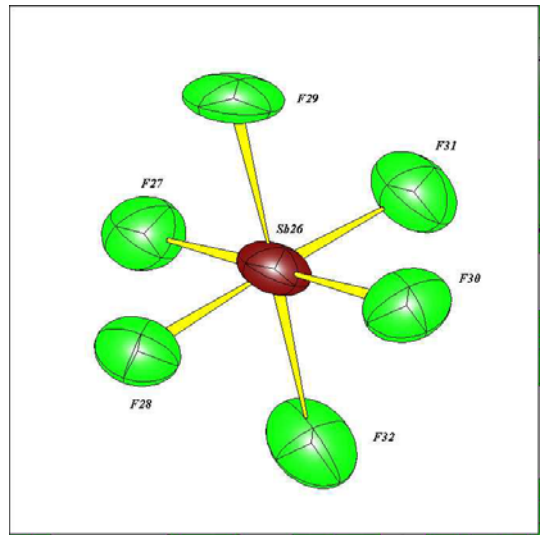
❖ The input model must be valid

❖ Check the refinement indicators for warnings

Could also be applied to …







+ benzene solvent, phenyl rings,

other rigid anions, etc …

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