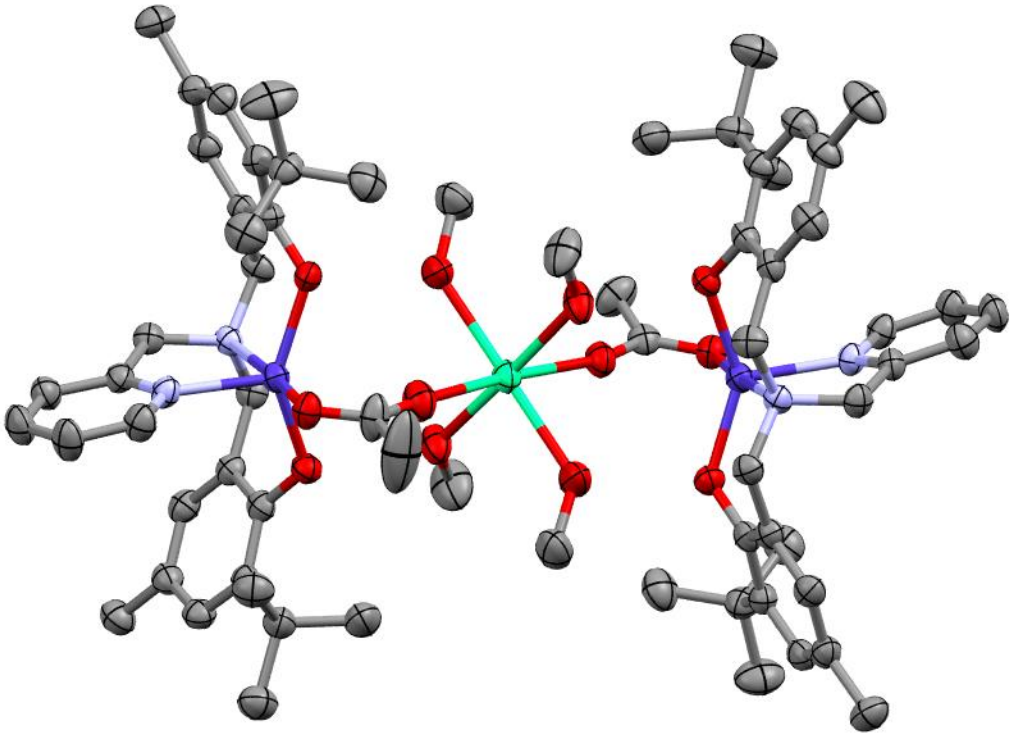
Structure Finalization: A Case Study



LOUISE DAWE, Ph.D., B.Ed.
Associate Professor
Department of Chemistry and Biochemistry
Faculty of Science

WILFRID LAURIER UNIVERSITY
75 University Ave. W, Waterloo
Ontario, Canada N2L 3C5
Office: N3020D
519.884.0710 x4963
ldawe@wlu.ca

$\{[L\text{-}2H]Co^{II}\}_2[Ca(CH_3COO)_2(CH_3OH)_4]\cdot 3tol$

Saunders, L. N. Pratt, M.E., Hann, S. E., Dawe, L.N., Decken, A., Kerton, F.M., Kozak, C.M. (2012) Structural variations in the coordination chemistry of amine-bis(phenolate) cobalt(II/III) complexes. *Polyhedron*, *46*(1), 53-65.

Structure Finalization Overview

- Things to check
  - ellipsoids (size, shape, continuity)
  - space group
  - bond valence sum calculations and charge balance
  - precedent (database searching)
  - other supporting characterizations

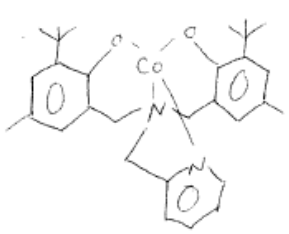
Where Problems Start…

in a Round bottom flask April 27, 11

XRD Analysis Submission Form

Name	Unique Sample Code	Supervisor's signature
$H_2[Co_2NN'J^{BuMePy}$	MPF03- initial filtrate	[redacted]
Proposed formula	**Elemental Analysis(Y/N)**	**Last solvent**
$C_{30}H_{38}Co_2N_2O_2$	No	toluene / MeOH

Structure:



→ prepared in a 1:1 mixture of MeOH/toluene

→ solvent coordination very likely

→ possibly dimer

Would you like the sample returned? (Y/N): yes

Is the compound optically pure? (Y/N) : yes

What is the melting point? (if <150°C) : /

Is the sample likely to undergo loss of solvent? : yes

Other information (i.e. toxicity, reactivity, radioactivity, etc.): /

For XRD lab use only:

Date received:

Data collection started:

Notes: - Appears to contain large black crystals, small green + small violet crystals

My bad - the submission form could really use some improvements! I should be asking for:

1.Other supporting characterizations?

2.Preparation conditions, including starting materials (not just solvent)

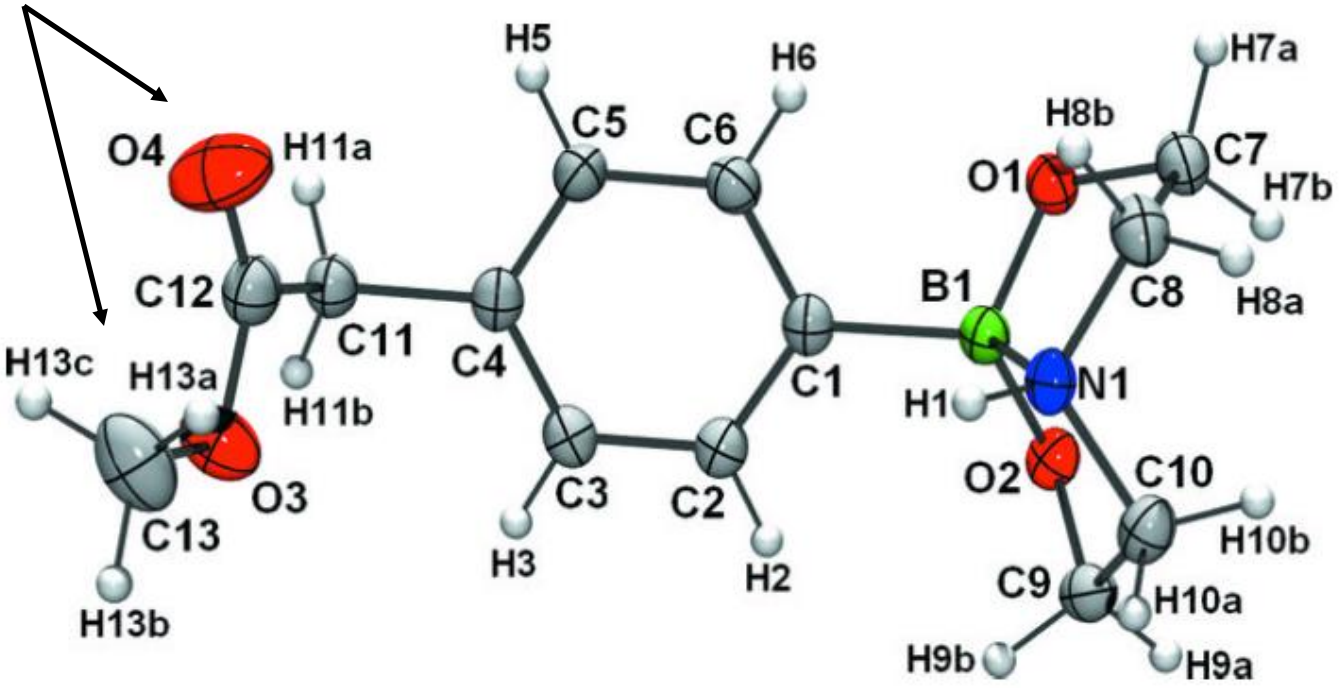
3.Sample codes of any related structures done in-house, or CCDC# for literature comparables

Multiple different crystals present in submitted sample

Electron Density, Ellipsoid Shape

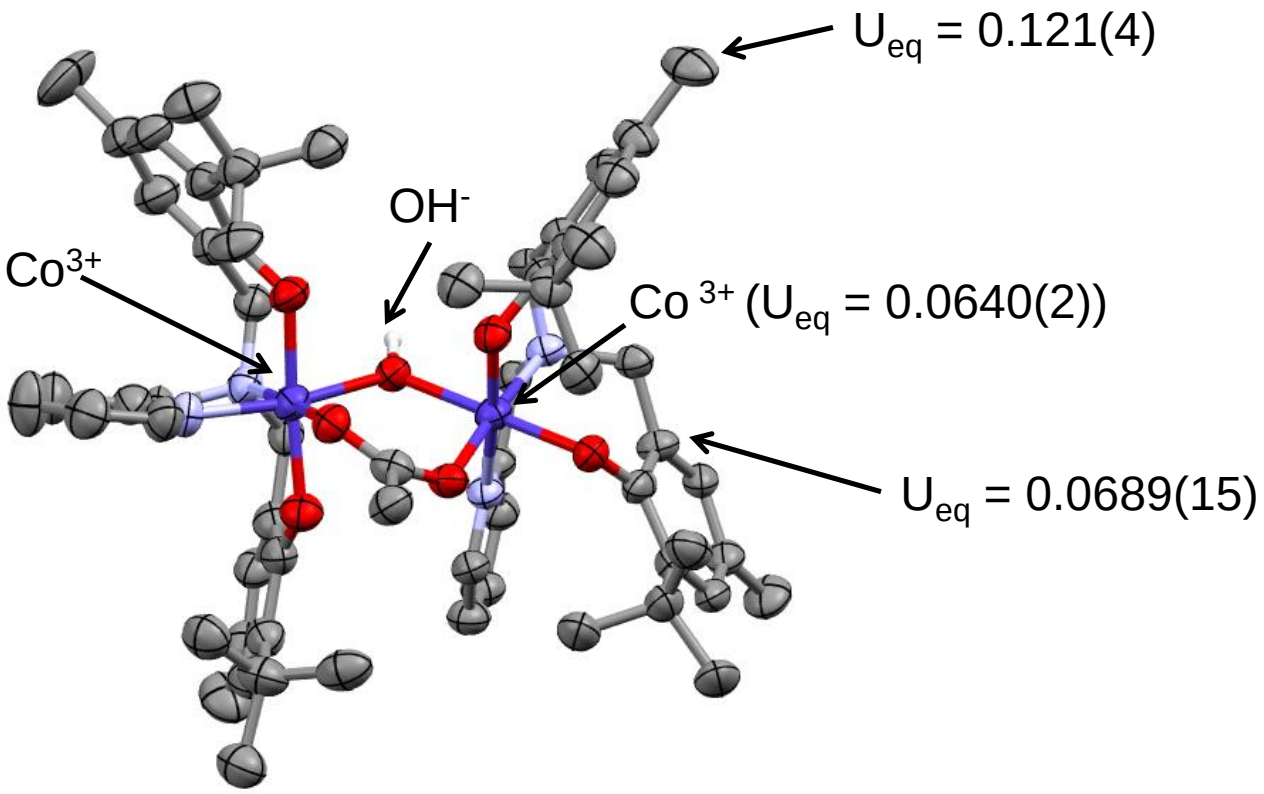
- Regions of heavier electron density correspond to the heaviest atoms present in a structure

- One normally expects the anisotropic displacements of adjacent atoms to be continuous, with ellipsoid size increasing in peripheral regions



Zein, A.L., Dawe, L.N., Georghiou, P.E. *Acta Cryst*. **2010,** *E66*, o2646.

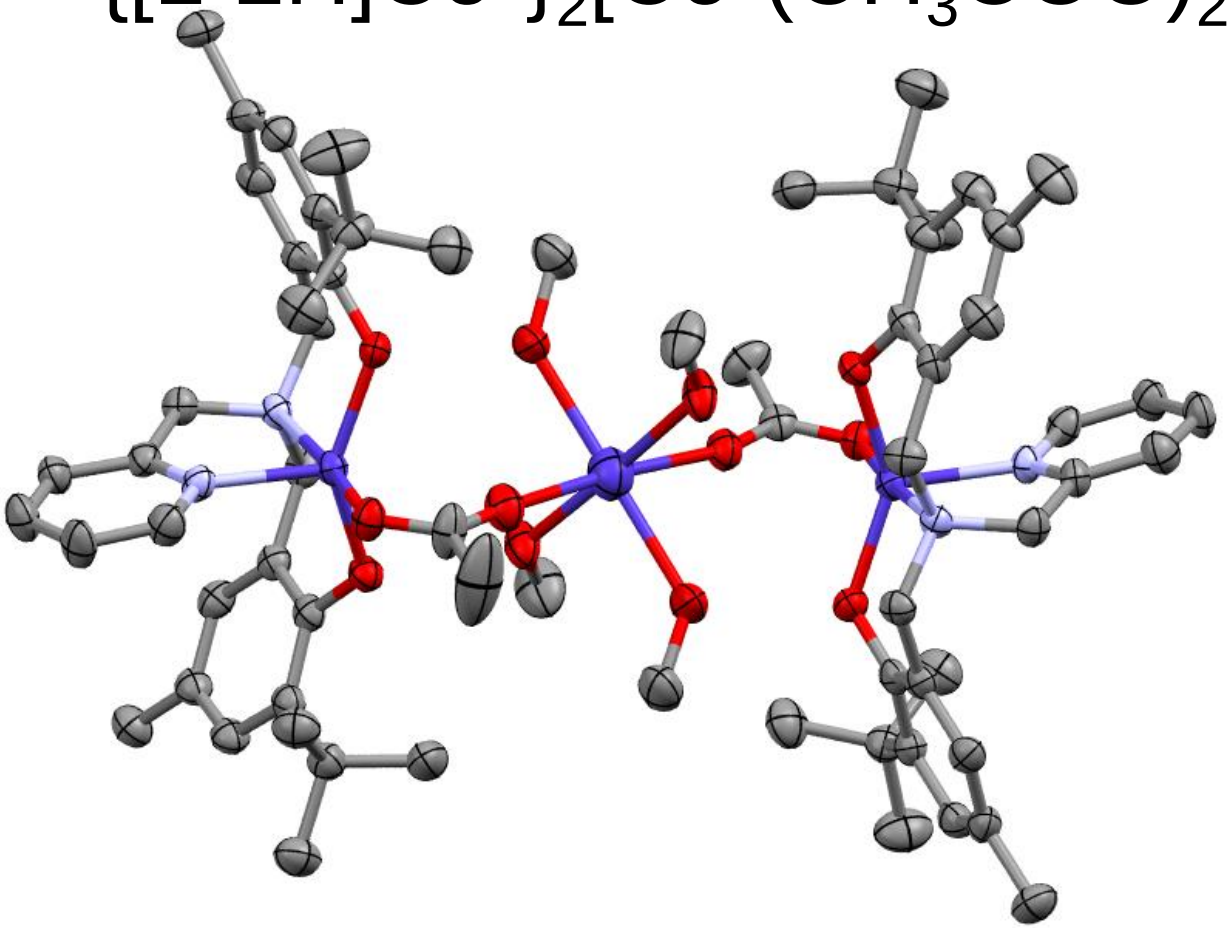
“Large Black” Crystals $\{[L\text{-}2H]Co^{III}\}_2[(CH_3COO)(OH)]\cdot 2.5tol$



30 % probability ellipsoids; H-atoms omitted for clarity. Solvent treated using PLATON’s SQUEEZE routine

“Small Violet” Crystals

$\{[L\text{-}2H]Co^{?}\}_2[Co^{?}(CH_3COO)_2(CH_3OH)_4]\cdot 3tol$



All lattice solvent is disordered. I modeled it, but it was tangly, so maybe this is okay?

50 % probability ellipsoids; H-atoms and lattice solvent omitted for clarity

Refinement Indicators

R1(Fo > 4sig(Fo))	0.1005	R1(all data)	0.1315
wR2	0.2955	GooF	1.4660
GooF(restr)	1.4910	Highest peak	1.5300
Deepest hole	-3.0700	Params	1047
Refs(total)	38218	Refs(uniq)	33512
Refs(Fo > 4sig(Fo))	12201	R(int)	0.0416
R(sigma)	0.0618	F000	1708.0
ρ/g*mm^{-3}	1.226	μ/mm^{-1}	0.50

checkCIF

http://checkcif.iucr.org/

X-ray Crystallography – How it “used” to be

- Single crystal structures determined by professional crystallographers
- Using serial detectors (~ 50 datasets/year).
- Using (open source) software they knew in detail.
- Structures were analyzed and discussed in great detail.
- Papers containing crystallographic results were refereed by fellow crystallographers.

http://www.cryst.chem.uu.nl/spek/

checkCIF

http://checkcif.iucr.org/

X-ray Crystallography – How it “is” now

- Fewer professional small molecule crystallographers
- Many crystal structures done by chemists with limited crystallographic background.
- Using modern detectors (ex. CCD: potential to collect 1000 datasets/year – depending on availability of quality crystals and need for sleep!)
- Crystal structures solved using “Black-Box” crystallographic software

http://www.cryst.chem.uu.nl/spek/

checkCIF

http://checkcif.iucr.org/

Single Crystal Structure Validation examines three questions:

1 – Is the reported information complete?

2 – What is the quality of the analysis?

3 – Is the structure correct?

Validation prior to structure finalization and submission will help you achieve the best possible model.

http://www.cryst.chem.uu.nl/spek/

checkCIF

http://checkcif.iucr.org/

ALERT level A = Most likely a serious problem - resolve or explain

ALERT level B = A potentially serious problem, consider carefully

ALERT level C = Check. Ensure it is not caused by an omission or oversight

ALERT level G = General information/check it is not something unexpected

ALERT type 1 CIF construction/syntax error, inconsistent or missing data

ALERT type 2 Indicator that the structure model may be wrong or deficient

ALERT type 3 Indicator that the structure quality may be low

ALERT type 4 Improvement, methodology, query or suggestion

ALERT type 5 Informative message, check

checkCIF

http://checkcif.iucr.org/

Small Violet Crystals

Alert level B

DIFMN02_ALERT_2_B The minimum difference density is < -0.1*ZMAX*1.00
_refine_diff_density_min given = -3.071
Test value = -2.700
Crystal system given = triclinic

PLAT098_ALERT_2_B Large Reported Min. (Negative) Residual Density -3.07 eA-3

PLAT232_ALERT_2_B Hirshfeld Test Diff (M-X) Co3 -- O6 .. 11.0 su

PLAT232_ALERT_2_B Hirshfeld Test Diff (M-X) Co3 -- O8 .. 10.5 su

From shelx.lst

Electron density synthesis with coefficients Fo-Fc

Highest peak 1.53 at 0.7008 0.5568 0.3778 [0.56 A from C93]

Deepest hole -3.07 at 0.2732 0.6223 0.2476 [0.52 A from CO3]

What does this mean?

Hirshfeld Tests

The components of the anisotropic displacement parameters along chemical bonds are assumed to be equal in magnitude. Large differences might indicate contamination of these parameters with other (unresolved) effects such as (substitutional) disorder, model or data errors and/or over-refinement.

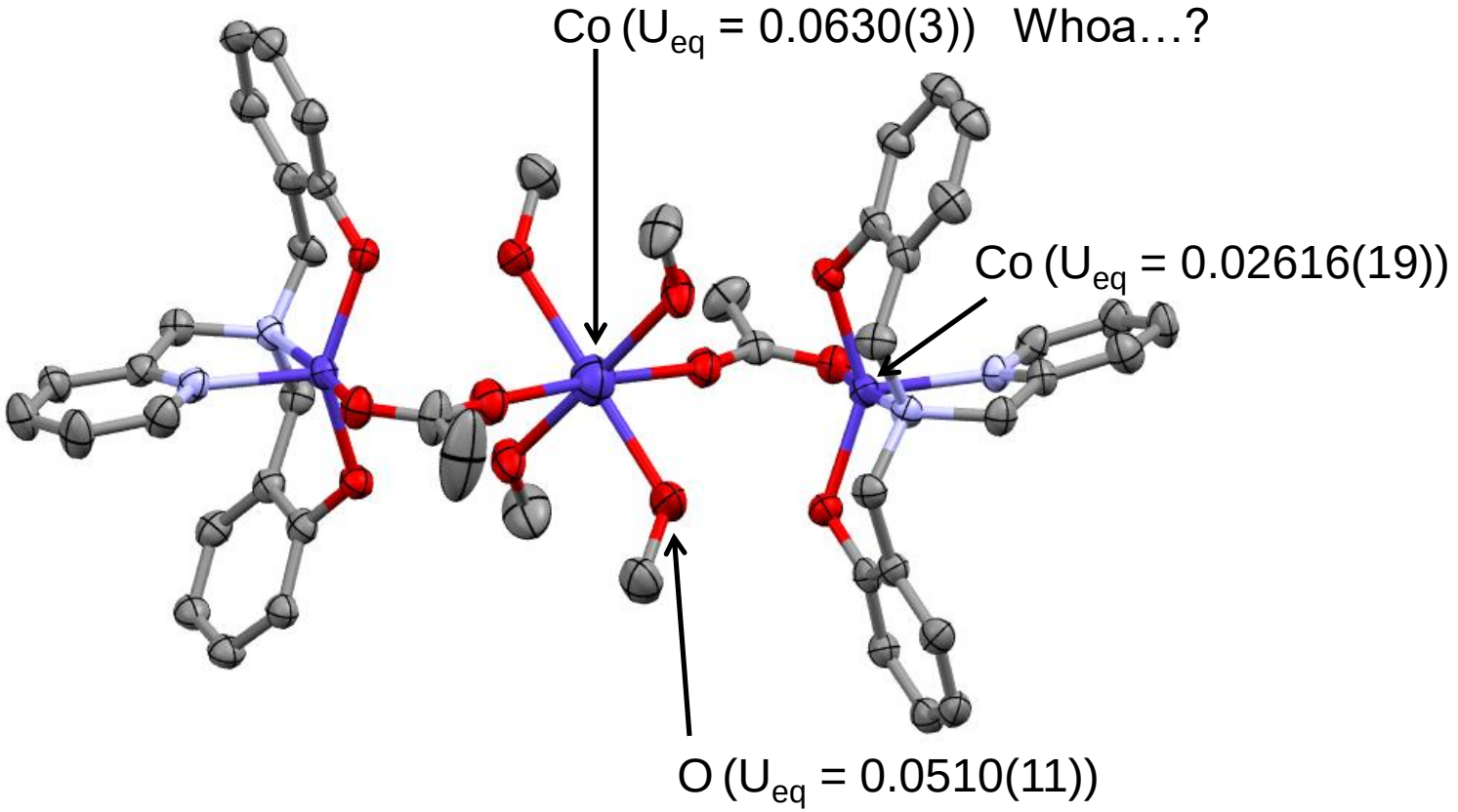
Atomic sites assigned the wrong scattering type (e.g. Ag versus Br) should generate 'problem signals' with this test.

The original 'Hirshfeld-test' was defined in absolute terms (see F.L.Hirshfeld, Acta Cryst. (1976). A32, 239-244). The current test is with reference to the associated standard uncertainty.

http://journals.iucr.org/services/cif/checking/PLAT234.html

“Small Violet” Crystals

$\{[L\text{-}2H]Co^{?}\}_2[Co^{?}(CH_3COO)_2(CH_3OH)_4]\cdot 3tol$

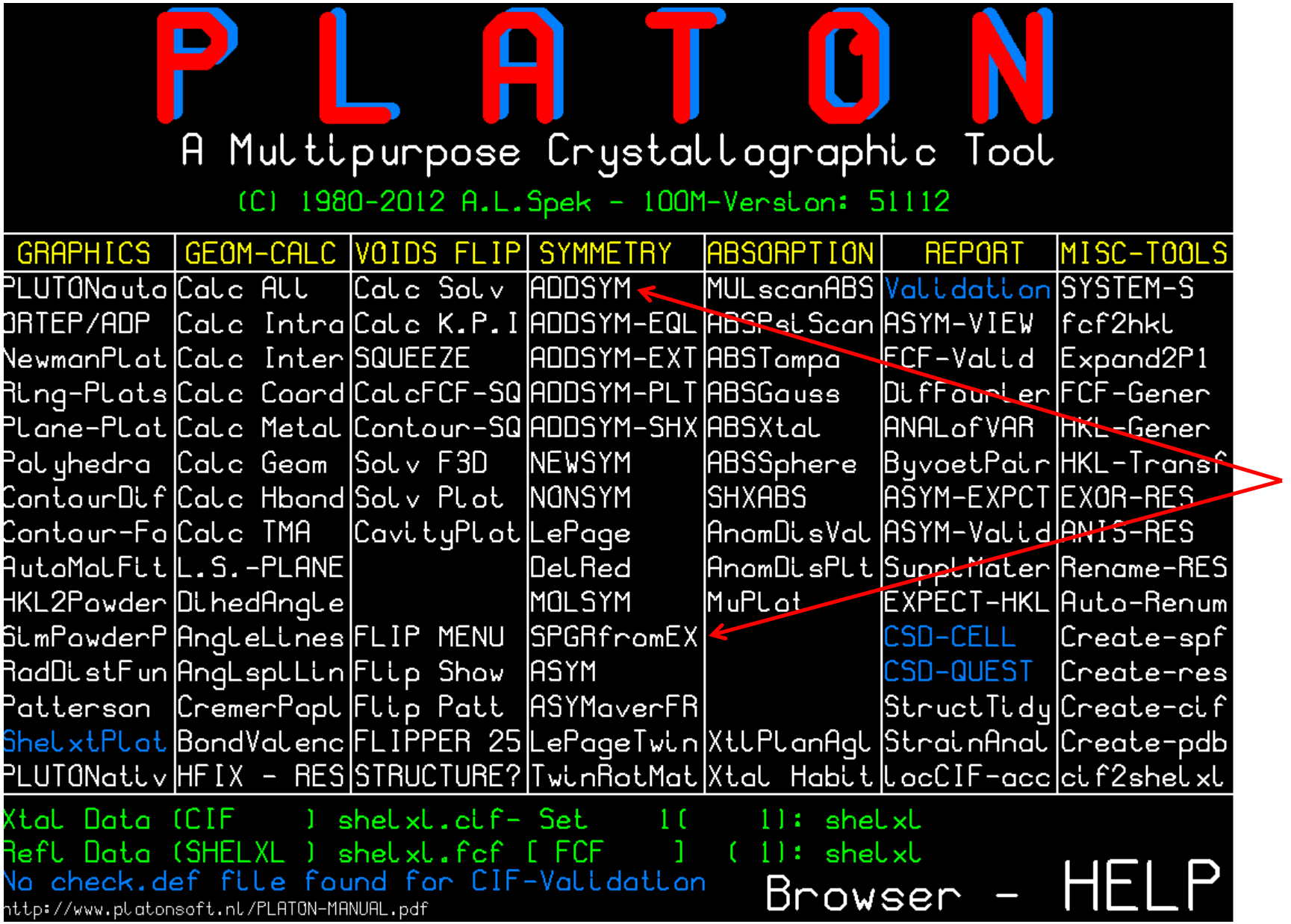


50 % probability ellipsoids; H-atoms, solvent and terminal ring substituents omitted for clarity

Space Group

- PLATON will look for missed symmetry elements and suggest alternate space groups based on your model (ADDSYM)
- ADDSYM will also looked for the presence of non-crystallographic pseudo-symmetry
- This check is also performed by checkCIF
- PLATON can also evaluate likely space groups from the reflection data (systematic absences; SPGRfromEX)

Space Group


PLATON
A Multipurpose Crystallographic Tool
(C) 1980-2012 A.L.Spek - 100M-Version: 51112
GRAPHICS
GEOM-CALC
VOIDS FLIP
SYMMETRY
ABSORPTION
REPORT
MISC-TOOLS
PLUTONauto
Calc All
Calc Solv
ADDSYM
MULscanABS
Validation
SYSTEM-S
ORTEP/ADP
Calc Intra
Calc K.P.I
ADDSYM-EQL
ABSPslScan
ASYM-VIEW
fcf2hkl
NewmanPlot
Calc Inter
SQUEEZE
ADDSYM-EXT
ABSTampa
FCF-Valid
Expand2P1
Ring-Plots
Calc Coord
CalcFCF-SQ
ADDSYM-PLT
ABSGauss
DiffFourier
FCF-Gener
Plane-Plot
Calc Metal
Contour-SQ
ADDSYM-SHX
ABSXtal
ANALofVAR
HKL-Gener
Polyhedra
Calc Geom
Solv F3D
NEWSYM
ABSSphere
ByvoetPair
HKL-Transf
ContourDif
Calc Hbond
Solv Plot
NONSYM
SHXABS
ASYM-EXPCT
EXOR-RES
Contour-Fo
Calc TMA
CavityPlot
LePage
AnomDisVal
ASYM-Valid
ANIS-RES
AutoMolFit
L.S.-PLANE
DelRed
AnomDisPlt
SupplMater
Rename-RES
HKL2Powder
DihedAngle
MOLSYM
MuPlot
EXPECT-HKL
Auto-Renum
SimPowderP
AngleLines
FLIP MENU
SPGRfromEX
CSD-CELL
Create-spf
RadDistFun
AngLsplLin
Flip Show
ASYM
CSD-QUEST
Create-res
Patterson
CremerPopl
Flip Patt
ASYMaverFR
StructTidy
Create-cif
ShelxtPlot
BondValenc
FLIPPER 25
LePageTwin
XtlPlanAgl
StrainAnal
Create-pdb
PLUTONativ
HFIX - RES
STRUCTURE?
TwinRotMat
Xtal Habit
LocCIF-acc
cif2shelxl
Xtal Data (CIF) shelxl.cif- Set 1(1): shelxl
Refl Data (SHELXL) shelxl.fcf [FCF] (1): shelxl
No check.def file found for CIF-Validation
http://www.platonsoft.nl/PLATON-MANUAL.pdf
Browser - HELP

Space Group for the Small Violet Crystals

ADDSYM

```
                          PLATON/ADDSYM for shelxl    P -1
ADDSYM Search on ALL NON-H Chemical Types [Max NonFit 20 Perc]
Criteria 1.00 Deg (Metric), 0.25 Ang (Rot.), 0.45 Ang (Inv), 0.45 Ang (Transl)
Symm.  Input  Reduced  (Ang)        (Deg) Perc AvrDev.(Ang)          Input Cell
ECem Cell Row Cell Row   d  Typ Dot AngCe Fit  MaxDev.              x     y     z
-1   ================================== 100       0  at            0     0     0
                                         0

  Reduced-to-Convent       Input-to-Reduced     T = Input-to-Convent:   a' = T a
(    1     0     0 )   (    1     0     0 )   (    1     0     0 )     Det(T)
(    0     1     0 ) X (    0     1     0 ) = (    0     1     0 )       =
(    0     0     1 )   (    0     0     1 )   (    0     0     1 )     1.000
Cell Lattice  a       b       c     Alpha   Beta  Gamma Volume CrystalSystem Laue
Input   aP 15.141  17.471  17.927 110.63 100.49  93.08   4328    -1     -1
Reduced  P 15.141  17.471  17.927 110.63 100.49  93.08   4328
Convent aP 15.141  17.471  17.927 110.63 100.49  93.08   4328    Triclinic    -1
:: SpaceGroup = P-1          - No Obvious Spacegroup Change Needed/Suggested
```

SPGRfromEX

```
Candidate Space Groups in ( 1.00 0.00 0.00/ 0.00 1.00 0.00/ 0.00 0.00 1.00) Cell
Name       #  AbsFreq StandSet.      R(av)Perc. N  A/C-Prob
P1         1    799  P1       :ABC      0.00     0  17 Chiral A
P-1        2  15327  P-1      :ABC      0.00     0  83         C
```

Bond Valence Sum (BVS) Calculations

Bond Valence Sum calculations are used mostly by mineralogists and inorganic chemists to assess structure correctness.

The bond valence model is based on several assumptions (I.D. Brown, *Acta Cryst.* **1992**. *B48,* 553-572):

1. Any chemical structure can be considered as a network in which the nodes are atoms and the edges are bonds.

2. Atoms are characterized by three properties: atomic number (Z, defining the chemical element), valence (V, defining the oxidation state) and electronegativity (χ).

3. Bonds occur only between neighbouring atoms whose valences have opposite sign.

4. Bonds are characterized by their bond valences (s) and their bond lengths (R).

Bond Valence Sum (BVS) Calculations

Bond valences (s) are calculated from the bond lengths (R) using the equation

$$s = \exp[(R_o - R)/B],$$

where R is the observed bond length, R_0 is a tabulated parameter expressing the ideal bond length when the element has exactly valence 1, and b is an empirical constant, typically 0.37 Å.

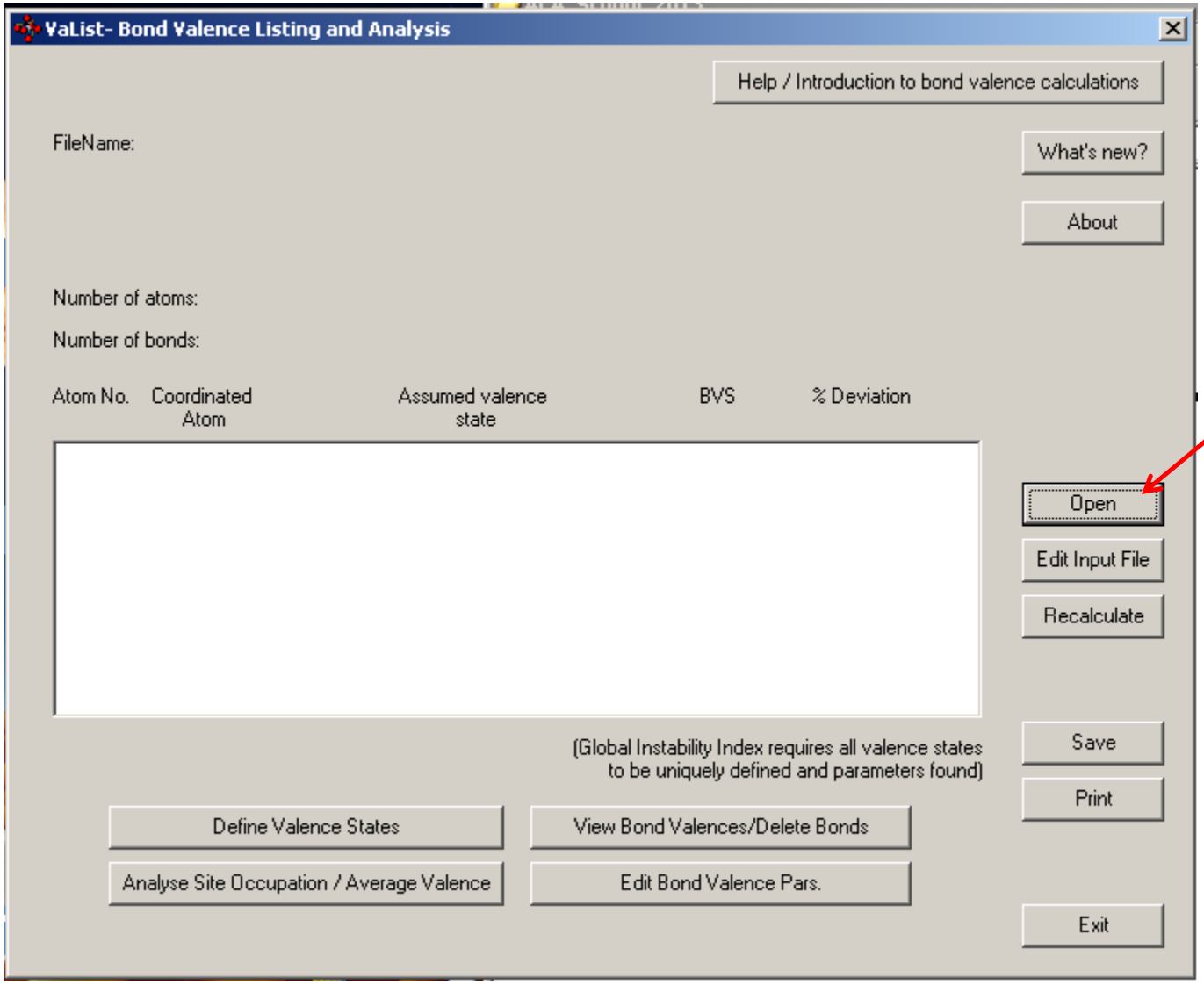
For a comprehensive review on Recent Developments in the Methods and Applications of the Bond Valence Model**,** see I.D. Brown, *Chem. Rev*. **2009**,*109*(12), 6858–6919.

- VaList is an excellent program for performance of BVS calculations, that is compatible with CIF, GSAS (*.LST), ICSD (*.CGI) Fullprof (*.DIS), TOPAS (*.INP) files.

- A.S. Wills, VaList, Program available from www.ccp14.ac.uk

- With supporting documentation available from: ftp://ftp.ucl.ac.uk/pub/users/uccaawi/VaList_instructions.pdf

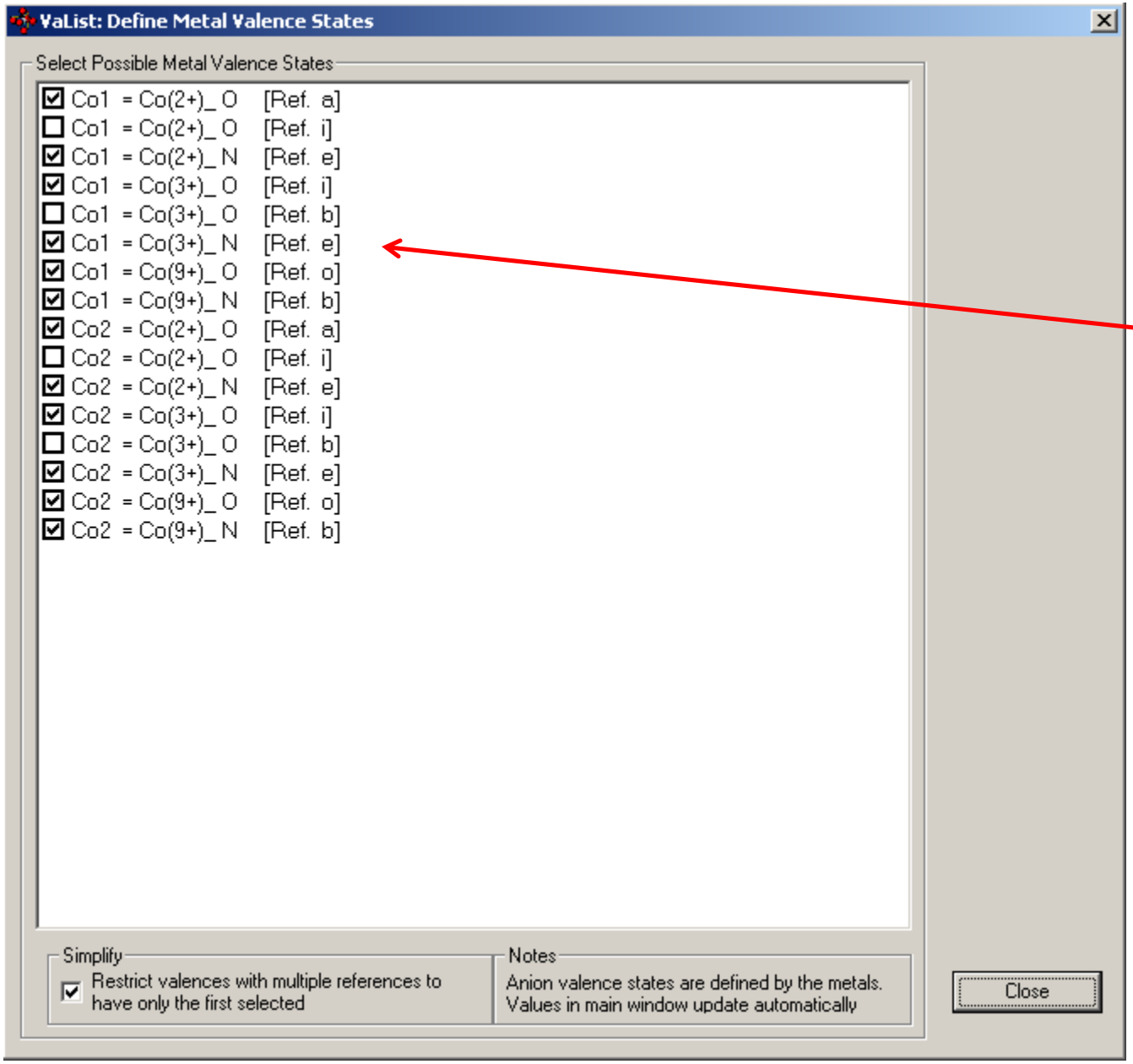
Bond Valence Sum (BVS) Calculations



Open .cif

Tip: Since I am only interested in the metal sites, I normally delete all the atoms except the metals and the atoms to which they are coordinated, before running this program

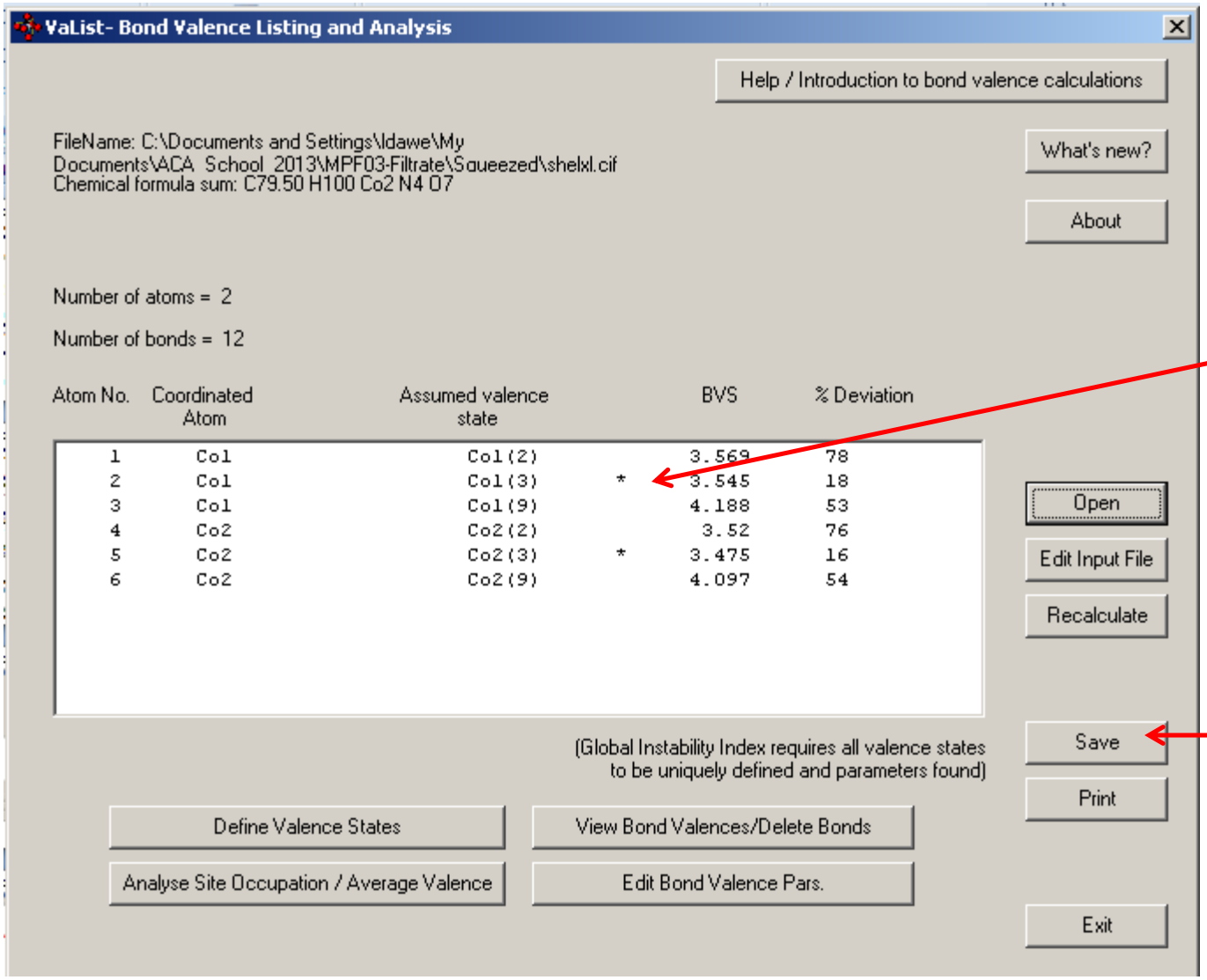
Bond Valence Sum (BVS) Calculations



I opened the .cif for the ‘sensible’ large black crystals.

Define your metal valence states

Bond Valence Sum (BVS) Calculations



I opened the .cif for the 'sensible' large black crystals.

The most consistent valence states are indicated by an asterisk.

If you hit 'Save' you will get a detailed output in .txt format with Ro, B, and references.

Bond Valence Sum (BVS) Calculations

For the small violet crystals...

Selected bond valence sums:

Atom no.	Valence state assumed	Most consistent valence state	Bond Valence Sum	% Deviation from assumed valence state
Co1	Co1(2)	*	1.841	8
Co1	Co1(3)		1.816	39
Co2	Co2(2)	*	1.863	7
Co2	Co2(3)		1.838	39
Co3	Co3(2)	*	1.181	41
Co3	Co3(3)		1.017	66
Co3	Co3(4)		1.272	68

The middle Co is +1?

Does this make sense?

Charge Balance

- Absolute requirement – the contents of your asymmetric unit MUST be overall neutral.
- If you cannot account for charge balance, you have ‘mis’sed something – misassigned, misinterpreted
- This should be your number one priority when using SQUEEZE or another solvent masking procedure

From http://www.cryst.chem.uu.nl/spek/platon/pl000303.html:

Potential Problems and Pitfalls

Be aware of charge balance problems: SQUEEZED density in the disordered solvent area might contain a charge that can have consequences for the charge, valence and interpretation of the ordered structure part.

Charge Balance

- For the large black crystals

  $\{[L\text{-}2H]Co^{III}\}_2[(CH_3COO)(OH)]\cdot 2.5tol$

  $2(-2) + 2(+3) + (-1) + (-1) = (-4) + (+6) + (-2) = 0$

Overall charge neutral

- For the small violet crystals

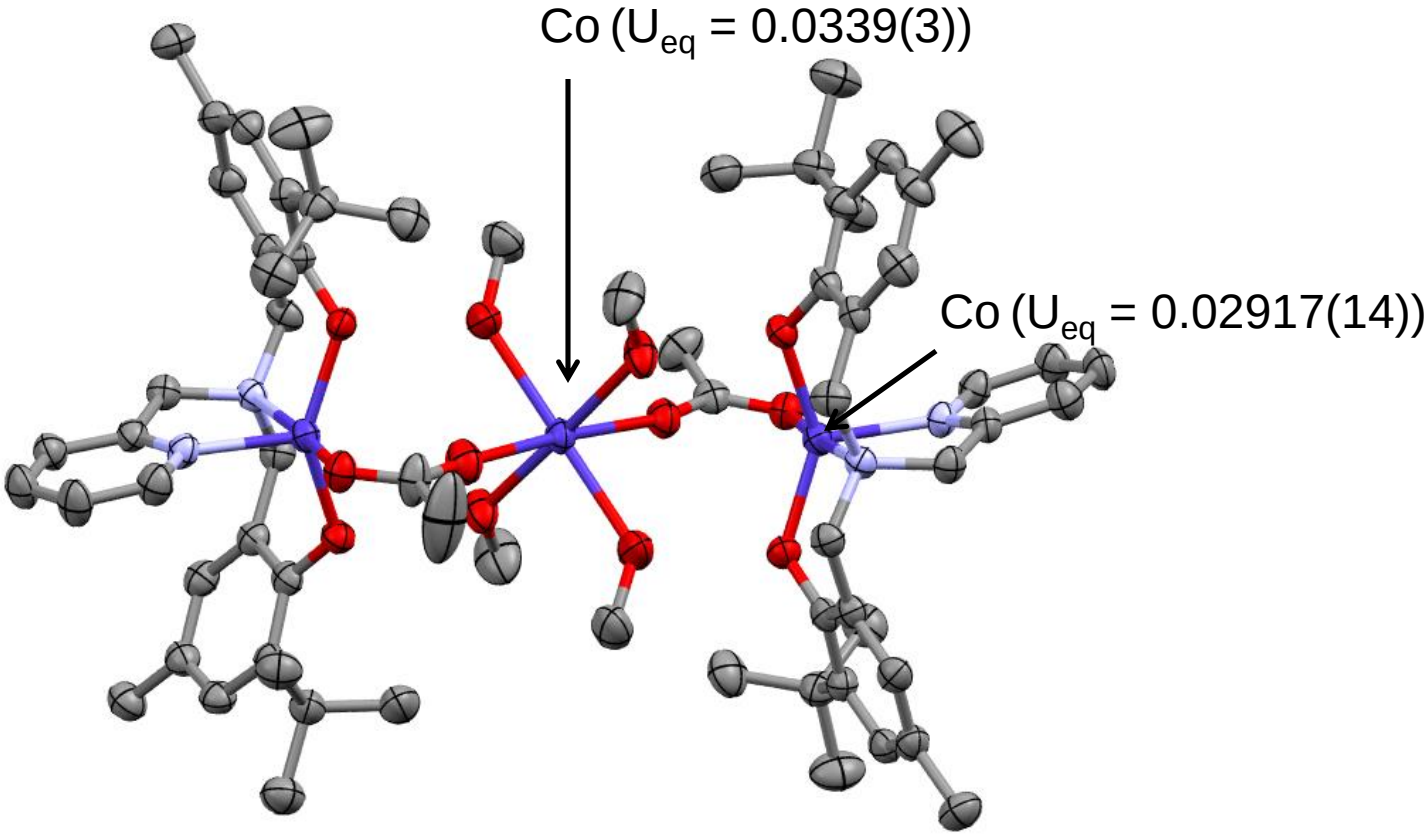
  $\{[L\text{-}2H]Co^{II}\}_2[Co^{I}(CH_3COO)_2(CH_3OH)_4]\cdot 3tol$

  $2(-2) + 2(+2) + (+1) + 2(-1) = (-4) + (+4) + (+1) + (-2) = -1$

Overall charge -1?

Site-Occupancy

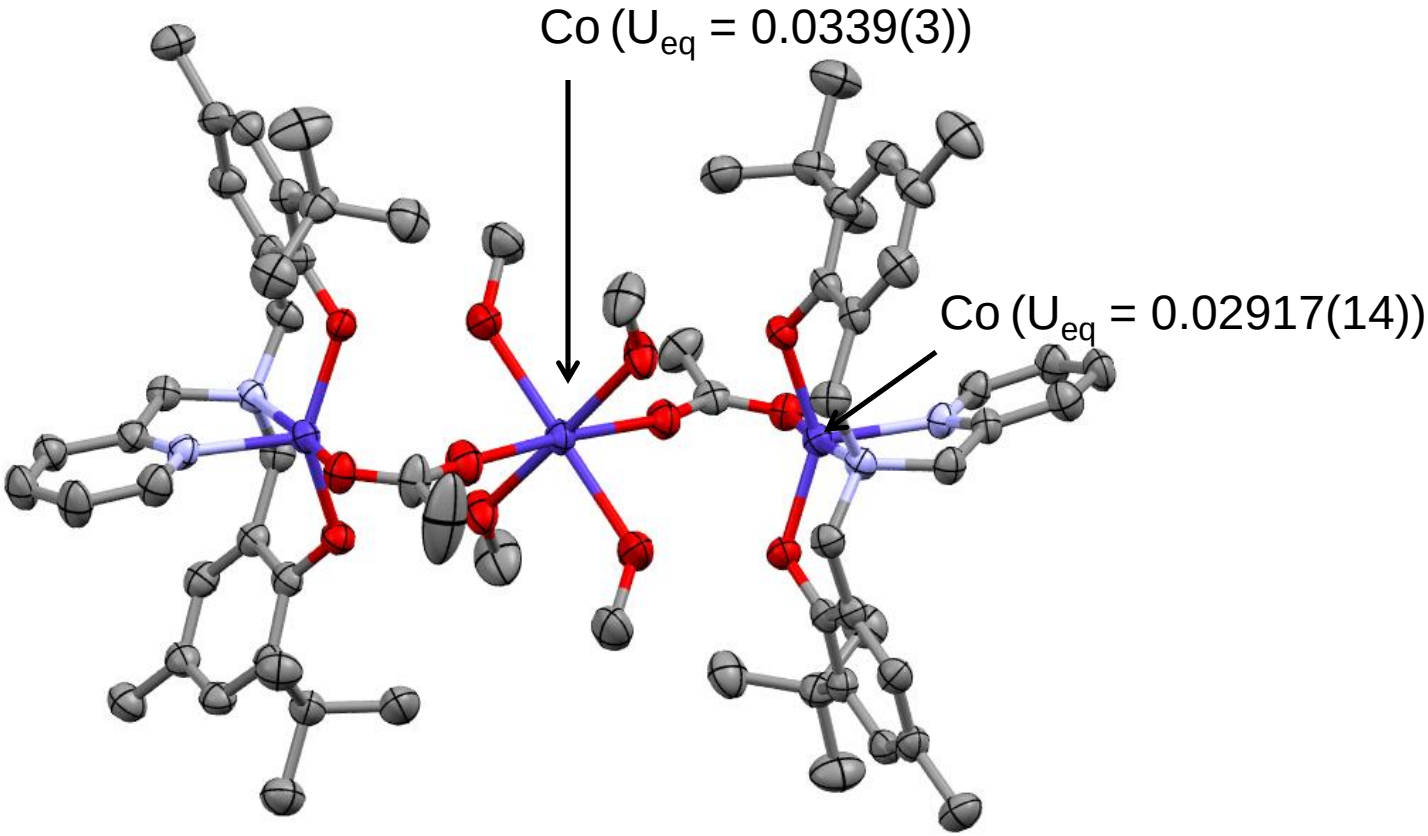
- Tied the occupancy of the central Co to a free variable and refined the occupancy
- Occupancy = 0.642(3)



- No more Hirshfeld alerts from checkCIF

Site-Occupancy

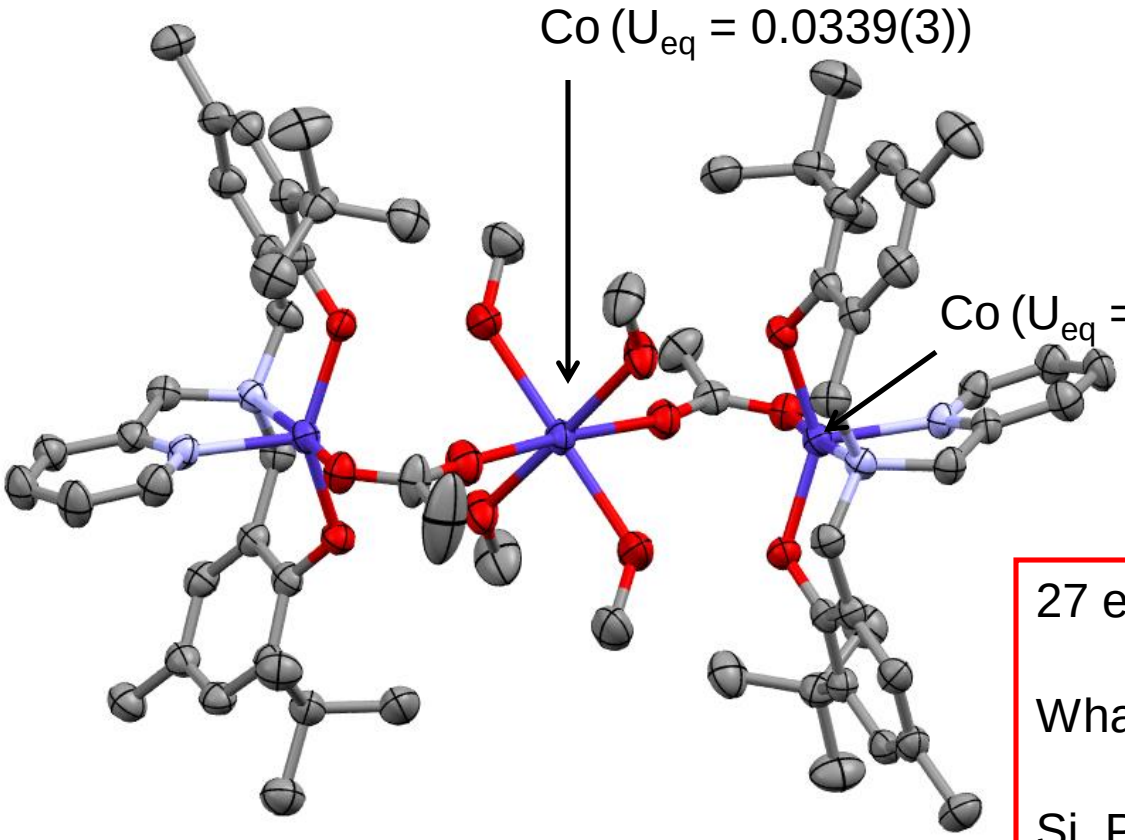
- Tied the occupancy of the central Co to a free variable and refined the occupancy
- Occupancy = 0.642(3)



- No more Hirshfeld alerts from checkCIF
- **How many electrons is a 0.64 occupancy Co?**

Site-Occupancy

- Tied the occupancy of the central Co to a free variable and refined the occupancy
- Occupancy = 0.642(3)



27 e- x 0.64 ~ 17 e-

What has ~ 17 e-?

Si, P, S, Cl, Ar, K, Ca

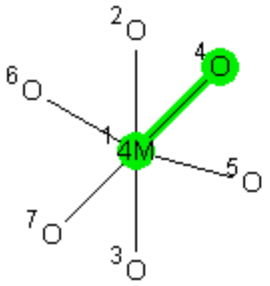
- No more Hirshfeld alerts from checkCIF
- **How many electrons is a 0.64 occupancy Co?**

Coordination Environment Precedent: Cambridge Structural Database

- By now, no one should be convinced that the weird site is cobalt.
- If it isn't cobalt, then what is it?
- There are many ways to come up with ideas, but I did a search in the CSD for structures containing an octahedral coordination environment with the refined bond lengths for the mystery 2/3 Co.

Coordination Environment Precedent: Cambridge Structural Database

Co3-O8	2.2393(7)
Co3-O11	2.3147(6)
Co3-O9	2.3190(6)
Co3-O10	2.3275(6)
Co3-O12	2.3401(6)
Co3-O4	2.2360(8)



Coordination Environment Precedent: Cambridge Structural Database

The search returned 677 structures.
114 structures containing Cd
82 structures containing Er
50 structures containing Lu
41 structures containing Ca
15 structures containing Ce
11 structures containing Yb
8 structures containing Fe

Of the possible metals identified, only a full occupancy Ca is equivalent to ~17 electrons!

The proposed formula is now:

$$\{[L\text{-}2H]Co^{II}\}_2[Ca(CH_3COO)_2(CH_3OH)_4]\cdot 3tol$$

But how to confirm?

Supporting Characterizations

A new chemical substance (molecule or extended solid) should have a homogeneous composition and structure. Where the compound is molecular, authors must provide data to **unequivocally** establish its homogeneity, purity and identification. In general, this should include elemental analyses that agree to within A±0.4% of the calculated values. In cases where elemental analyses cannot be obtained (e.g. for thermally unstable compounds), justification for the omission of this data should be provided. Note that **an X-ray crystal structure is not sufficient for the characterisation of a new material**, since the crystal used in this analysis does not necessarily represent the bulk sample. In rare cases, it may be possible to substitute elemental analyses with high-resolution mass spectrometric molecular weights. This is appropriate, for example, with trivial derivatives of thoroughly characterised substances or routine synthetic intermediates. In all cases, relevant spectroscopic data (NMR, IR, UV-vis, etc.) should be provided in tabulated form or as reproduced spectra.

However, it should be noted that, in general, mass spectrometric and spectroscopic data do not constitute proof of purity, and, in the absence of elemental analyses, additional evidence of purity should be provided (melting points, PXRD data, etc.)

Dalton Transactions Journal Policy 3.0 - Characterisation Guidelines
http://www.rsc.org/Publishing/Journals/guidelines/AuthorGuidelines/JournalPolicy/Journals/DT.asp

BVS Calculations and Charge Balance for Violet Crystals

Selected bond valence sums:

Atom no.	Valence state assumed	Most consistent valence state	Bond Valence Sum	% Deviation from assumed valence state
Co1	Co1(2)	*	1.837	8
Co1	Co1(3)		1.811	40
Co2	Co2(2)	*	1.86	7
Co2	Co2(3)		1.835	39
Ca1	Ca1(2)	*	2.479	24

For the small violet crystals

$$\{[L\text{-}2H]Co^{II}\}_2[Ca^{II}(CH_3COO)_2(CH_3OH)_4]\cdot 3tol$$

$$2(-2) + 2(+2) + (+2) + 2(-1) = (-4) + (+4) + (+2) + (-2) = 0$$

Overall charge is now neutral.

Supporting Characterizations

X-ray Formula: $C_{68}H_{98}CaCo_2N_4O_{12}$, $3(C_7H_8)$

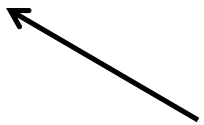
Bulk sample sent for elemental analysis was dried, and so the the solventless formula was used for comparison to the experimental results.

Anal. Calc. for $C_{68}H_{98}CaCo_2N_4O_{12}$:
C, 61.80; H, 7.47; N, 4.24.

Found: C, 61.92; H, 7.79; N, 4.22%.

What if it was calculated for $C_{68}H_{98}Co_3N_4O_{12}$?

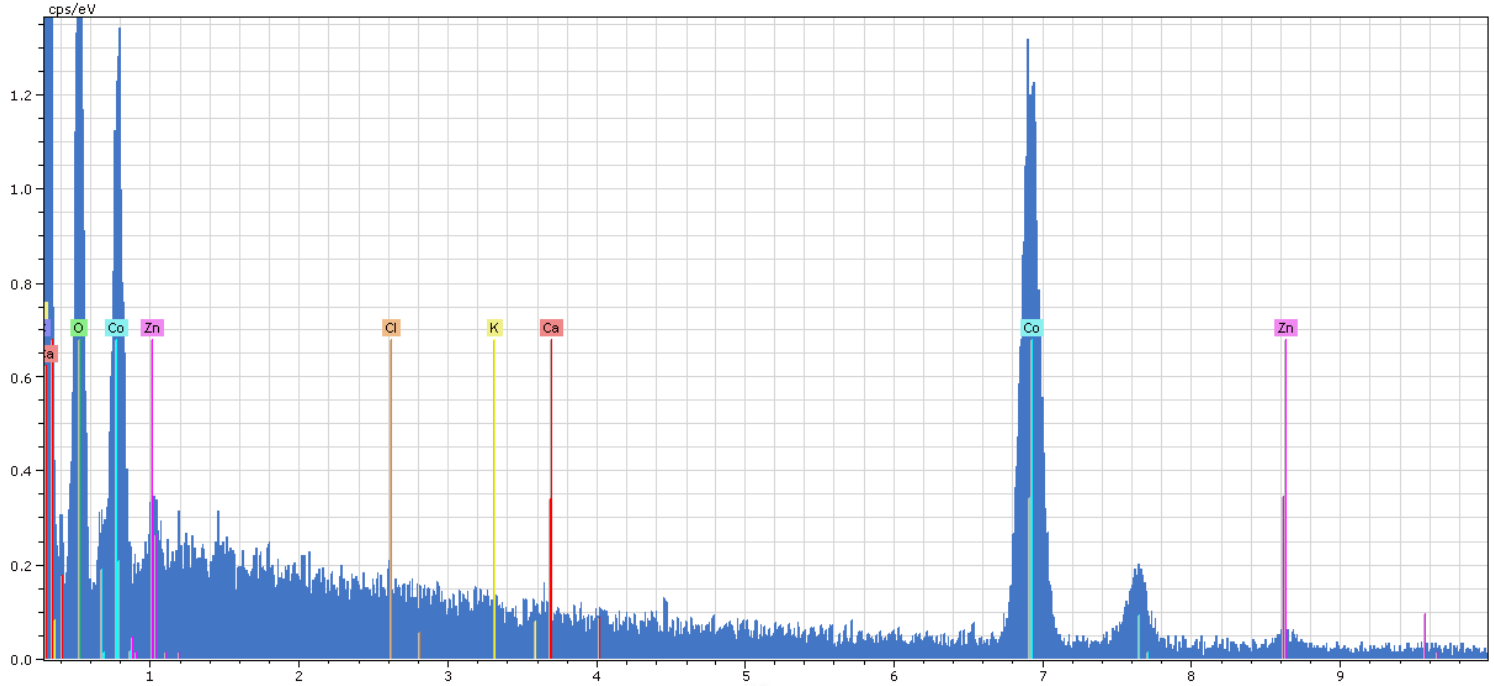
C, 60.94; H, 7.37; N, 4.18

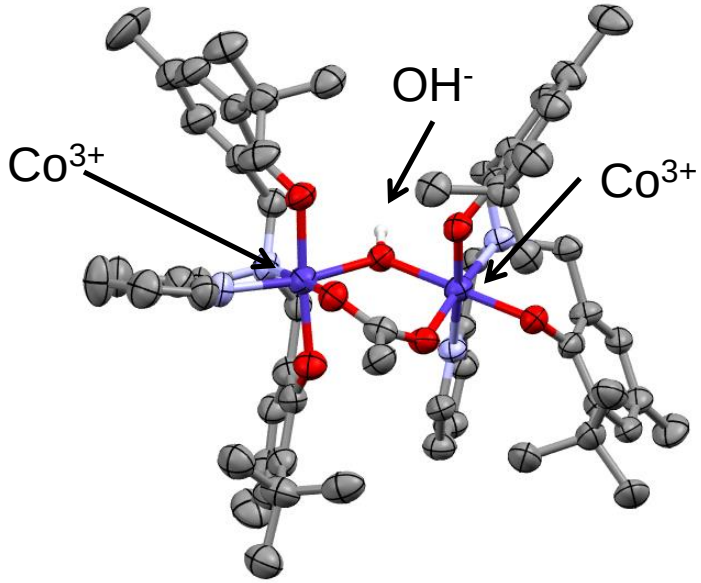


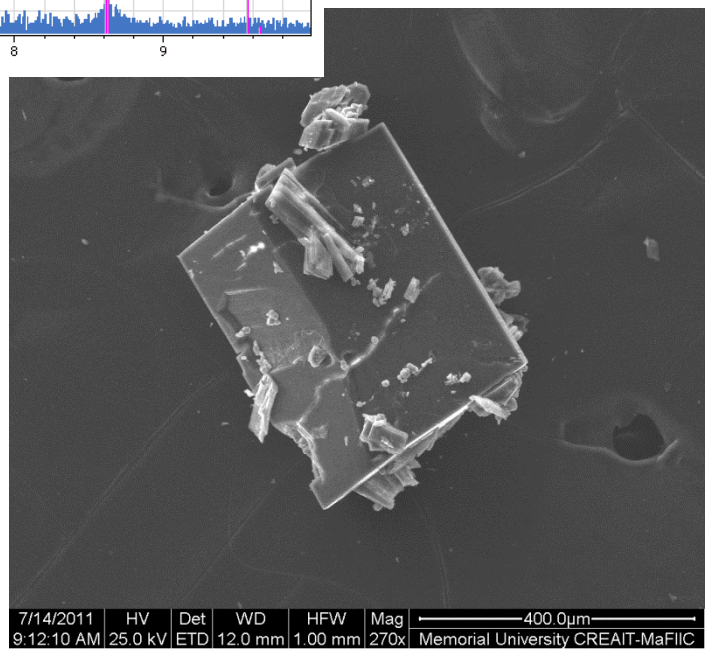
Off by 0.98! Not within limits for publication.

Supporting Characterizations – SEM with EDX

Black crystals: $\{[L\text{-}2H]Co^{III}\}_2(CH_3COO)(OH)]\cdot 2.5tol$

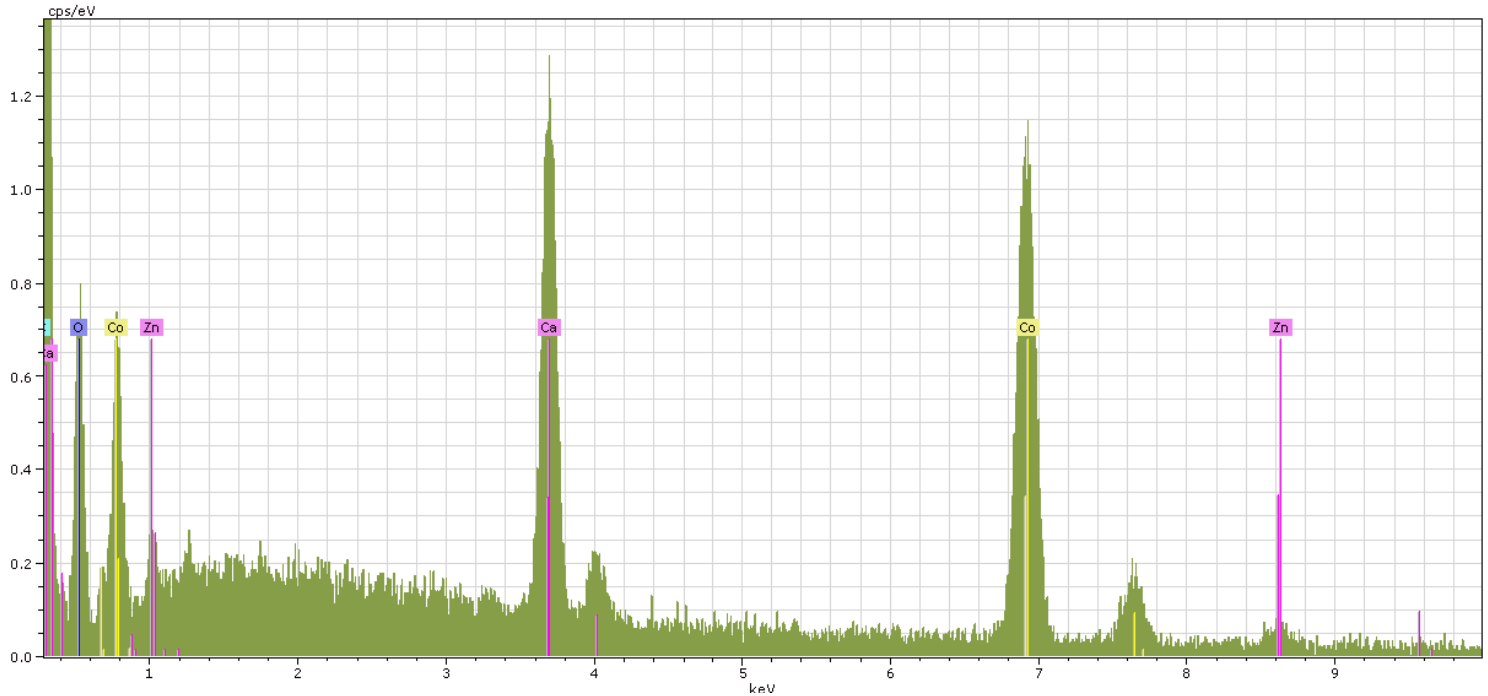


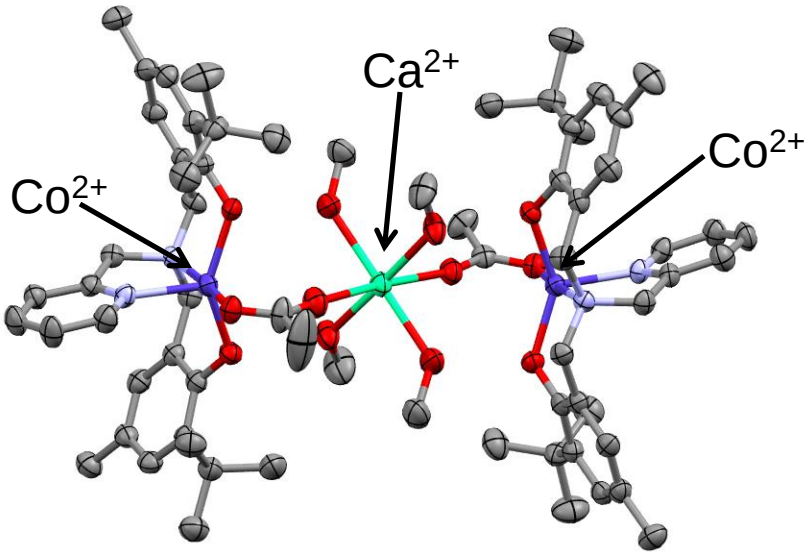


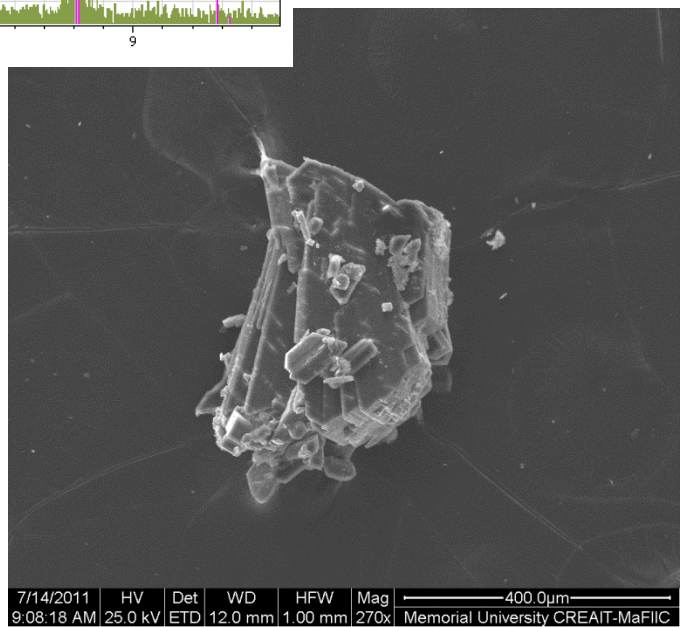


Supporting Characterizations – SEM with EDX

Violet Crystals: $\{[L\text{-}2H]Co^{II}\}_2[Ca(CH_3COO)_2(CH_3OH)_4]\cdot 3tol$





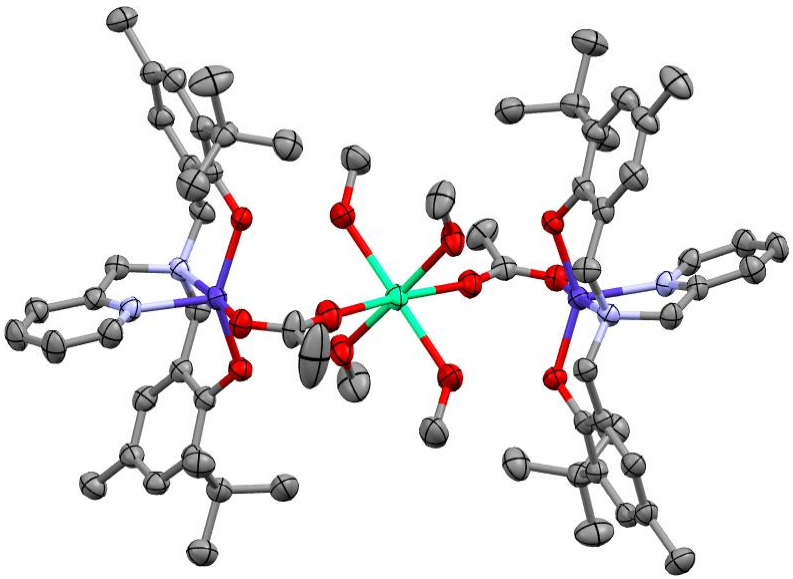


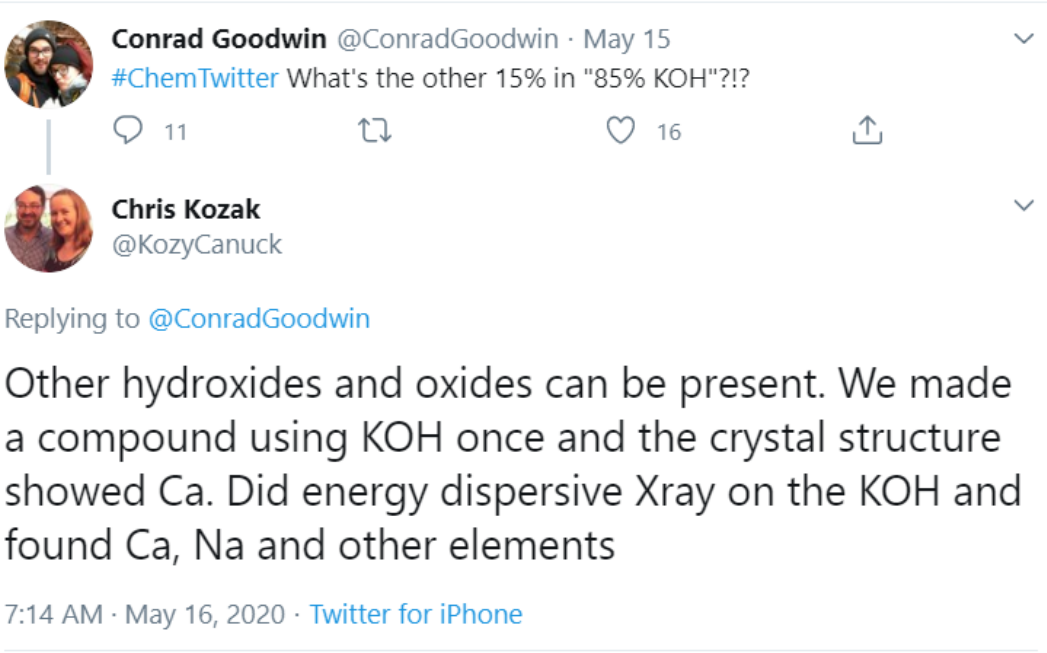
Structure Finalization Summary

Things to check

- space group
- ellipsoids (size, shape, continuity)
- bond valence sum calculations and charge balance
- precedent (database searching)
- other supporting characterizations

Structure Finalization: A Case Study





$\{[L\text{-}2H]Co^{II}\}_2[Ca(CH_3COO)_2(CH_3OH)_4]\cdot 3tol$

Saunders, L. N. Pratt, M.E., Hann, S. E., Dawe, L.N., Decken, A., Kerton, F.M., Kozak, C.M. (2012) Structural variations in the coordination chemistry of amine-bis(phenolate) cobalt(II/III) complexes. *Polyhedron*, *46*(1), 53-65.

Additional Resources

Website of (Emeritus) Prof. Dr. Anthony L. Spek: http://www.cryst.chem.uu.nl/spek/

(Emeritus) Prof. Dr. Anthony L. Spek's PowerPoint Presentations: http://www.cryst.chem.uu.nl/spek/ppt.html

Taylor, R.; Kennard, O. Accuracy of Crystal Structure Error Estimates**.** *Acta Cryst.* **1986**, *B42*, 112-120.

http://www.xrayforum.co.uk/

http://shelx.uni-ac.gwdg.de/SHELX/shelxl_html.php