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
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.

“Large Black” Crystals
\[
\{[L-2H]Co^{III}\}_2[(CH_3COO)(OH)]\cdot2.5\text{tol}
\]

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

Solved in P-1 using SHELXS based on the proposed formula, \( \text{C}_{50}\text{H}_{50}\text{Co}_3\text{N}_5\text{O}_{10} \)

Not a great first trial structure, but ligands look okay.
Has it assigning Co at oxygen sites? Or are they “doubled”? 
“Small Violet” Crystals

\[
\{[\text{L}-2\text{H}]\text{Co}^\text{?}\}_2[\text{Co}^\text{?}\text{(CH}_3\text{COO)}_2\text{(CH}_3\text{OH)}_4]\cdot3\text{tol}
\]

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

All lattice solvent is disordered. I modeled it, but it was tangly, so maybe this is okay?
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 CCD detectors (potential to collect 1000 datasets/year – depending on availability of quality crystals and need for sleep!)
- Crystal structures solved using “Black-Box” crystallographic software

checkCIF
http://checkcif.iucr.org/

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

**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

Sometimes alerts cannot be eliminated, but instead have valid reasons for their presence. In these cases validation reply form (vrf) statements can be inserted into a .cif, which acknowledge and account for checkCIF alerts.
CIF & FCF validation! Why?

A few different reasons, for example, future data analysis, detection problems with raw data, etc..

Major Advantage for Editors: Fraud Detection

checkCIF
http://checkcif.iucr.org/

checkCIF is a service of the International Union of Crystallography.

checkCIF reports on the consistency and integrity of crystal structure determinations reported in CIF format.

Please upload your CIF using the form below.

File name:

Select form of checkCIF report:
- HTML
- PDF

Select validation type:
- Full validation of CIF and structure factors
- Validation of CIF only (no structure factors)

Output Validation Response Form:
- Level A alerts only
- Level A and B alerts
- None

Send CIF for checking

Information about this version of checkCIF ...

Useful links:
- Prepublication check for submissions to IUCr Journals
- Details of checkCIF/PLATON tests
- CIF dictionary
- Download CIF editor (pubCIF) from the IUCr
- Download CIF editor (enCIFer) from the CCDC
checkCIF
http://checkcif.iucr.org/
Large Black Crystals

**Alert level A** = Most likely a serious problem - resolve or explain
**Alert type 2** Indicator that the structure model may be wrong or deficient

---

**Alert level A**

CHEMW03_ALERT_2_A ALERT: The ratio of given/expected molecular weight as calculated from the _atom_site* data lies outside the range 0.90 ↔ 1.10

- From the CIF: _cell_formula_units_Z = 8
- From the CIF: _chemical_formula_weight = 1341.55

TEST: Calculate formula weight from _atom_site*

<table>
<thead>
<tr>
<th>atom</th>
<th>mass</th>
<th>num</th>
<th>sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>12.01</td>
<td>62.00</td>
<td>744.68</td>
</tr>
<tr>
<td>H</td>
<td>1.01</td>
<td>80.00</td>
<td>80.64</td>
</tr>
<tr>
<td>Co</td>
<td>58.93</td>
<td>2.00</td>
<td>117.87</td>
</tr>
<tr>
<td>N</td>
<td>14.01</td>
<td>4.00</td>
<td>56.03</td>
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<tr>
<td>O</td>
<td>16.00</td>
<td>7.00</td>
<td>111.99</td>
</tr>
</tbody>
</table>

Calculated formula weight = 1111.21

---

Reported: Calculated from the atomic contents of the .cif

Why the discrepancy?
checkCIF
http://checkcif.iucr.org/
Large Black Crystals

# start Validation Reply Form
_vrf_CHEMW03_MPFO3-Filtrate
;
PROBLEM: ALERT: The ratio of given/expected molecular weight as
RESPONSE: This structure was treated via Platon's Squeeze
procedure. Please see platon_squeeze_details for full details.
The 2.5 lattice solvent toluene molecules that were
omitted from the model were included in the formula for
calculation of the intensive properties.
;

Alert level A
CHEMW03_ALERT_Z_A ALERT: The ratio of given/expected molecular weight as
calculated from the _atom_site* data lies outside
the range 0.90 <-> 1.10
From the CIF: _cell_formula_units_Z
From the CIF: _chemical_formula_weight 1341.55
TEST: Calculate formula weight from _atom_site_*

<table>
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</table>

Calculated formula weight 1111.21

Author Response: This structure was treated via Platon’s Squeeze procedure. Please see
platon_squeeze_details for full details. The 2.5 lattice solvent toluene molecules that were
omitted from the model were included in the formula for calculation of the intensive properties.
# start Validation Reply Form
_vrf_CHEMW03_MPF03-Filtrate
;
PROBLEM: ALERT: The ratio of given/expected molecular weight as
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From the CIF: _cell_formula_units_Z 8
From the CIF: _chemical_formula_weight 1341.55
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</tr>
</tbody>
</table>

Calculated formula weight 1111.21

Ugh. How many of these alerts do I have to answer?
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
$\{[L-2H]Co?\}_2[Co?{(CH_3COO)}_2(CH_3OH)_4]\cdot3\text{tol}$

50 % probability ellipsoids; H-atoms, solvent and terminal ring substituents omitted for clarity
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
- Did I get the space group wrong?
Space Group

• PLATON will look for missed symmetry elements and suggest alternate space groups based on your model (ADDSYM)

• ADDSYM will also look 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)
<table>
<thead>
<tr>
<th>GRAPHICS</th>
<th>GEOM-CALC</th>
<th>VOIDS FLIP</th>
<th>SYMMETRY</th>
<th>ABSORPTION</th>
<th>REPORT</th>
<th>MISC-TOOLS</th>
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<td>PLUTONauto</td>
<td>Calc All</td>
<td>Calc Solv</td>
<td>ADDSYM</td>
<td>MULscanABS</td>
<td>Validation</td>
<td>SYSTEM-S</td>
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<tr>
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<td>Calc Intra</td>
<td>Calc K.P.I</td>
<td>ADDSYM-EQL</td>
<td>ABSPsTScan</td>
<td>ASYM-VIEW</td>
<td>fcf2hkl</td>
</tr>
<tr>
<td>NewmanPlat</td>
<td>Calc Inter</td>
<td>SQUEEZE</td>
<td>ADDSYM-EXT</td>
<td>ABSTampa</td>
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<td>Expand2P1</td>
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<td>Alng-Plats</td>
<td>Calc Caard</td>
<td>CalcFCF-SQ</td>
<td>ADDSYM-PLT</td>
<td>ABSSGauss</td>
<td>DlfF4wler</td>
<td>FCF-Gener</td>
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<td>Contour-SQ</td>
<td>ADDSYM-SHX</td>
<td>ABSXtal</td>
<td>ANALofVAR</td>
<td>HKL-Gener</td>
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<td>Calc Geam</td>
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<td>ByvoetPatr</td>
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<td>Calc Hband</td>
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<td>SupplMater</td>
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<td>ASYMaverFR</td>
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<td>FLIPPER 25</td>
<td>LePageTwin</td>
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<tr>
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<td>HFIX - RES</td>
<td>STRUCTURE?</td>
<td>TwinRotMat</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Xtal Data (CIF ) shelxl.cif- Set 1( 1): shelxl
Refi Data (SHELXL ) shelxl.fcf [ FCF ] ( 1): shelxl
No check.def file found for CIF-Validation

http://www.platonsoft.nl/PLATON-MANUAL.pdf
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
Etem Cell Raw Cell Raw d Typ Dot Angle Flt MaxDev. 0 0 0 0 0

Reduced-to-Convert   Input-to-Reduced   T = Input-t0-Convert:  a' = T a
{ 1 0 0 }   { 1 0 0 }   { 1 0 0 }   Det(T) =
{ 0 1 0 }   { 0 1 0 }   =
{ 0 0 1 }   { 0 0 1 }   1.000

Cell Lattice a b c Alpha Beta Gamma Volume Crystal System 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(avg)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
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)

No more Hirshfeld alerts from checkCIF

How many electrons is a 0.64 occupancy Co?

$27 \text{ e-} \times 0.64 \sim 17 \text{ e-}$

What has $\sim 17 \text{ e-}$?

Si, P, S, Cl, Ar, K, Ca
Bond Valence Sum (BVS) Calculations

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


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

\[ s = \exp\left(\frac{R_0 - R}{B}\right) \]

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.


- 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](http://www.ccp14.ac.uk)

Bond Valence Sum (BVS) Calculations

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

Define your metal valence states
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...

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

The middle, ~2/3 occupancy Co is +1? Is this a common oxidation state for Co?
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
  \[
  \{[\text{L-2H}]\text{Co}^{\text{III}}\}_2\text{[(CH}_3\text{COO})(\text{OH})]\cdot 2.5\text{tol} \\
  2(-2) + 2(+3) + (-1) + (-1) = (-4) + (+6) + (-2) = 0
  \]

  Overall charge neutral

- For the small violet crystals
  \[
  \{[\text{L-2H}]\text{Co}^{\text{II}}\}_2\text{[Co}^{1/2/3}(\text{CH}_3\text{COO})_2(\text{CH}_3\text{OH})_4]\cdot 3\text{tol} \\
  2(-2) + 2(+2) + 2/3(+1) + 2(-1) = (-4) + (+4) + (+2/3) + (-2) = -4/3
  \]

  Overall charge -1.33?

- What is on the go with that central 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

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Co3-O8</td>
<td>2.2393(7)</td>
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<tr>
<td>Co3-O11</td>
<td>2.3147(6)</td>
</tr>
<tr>
<td>Co3-O9</td>
<td>2.3190(6)</td>
</tr>
<tr>
<td>Co3-O10</td>
<td>2.3275(6)</td>
</tr>
<tr>
<td>Co3-O12</td>
<td>2.3401(6)</td>
</tr>
<tr>
<td>Co3-O4</td>
<td>2.2360(8)</td>
</tr>
</tbody>
</table>
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:

\[ \{[L-2H]Co^{II}\}_{2}[Ca(CH_3COO)_2(CH_3OH)_4]\cdot3tol \]

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
### BVS Calculations and Charge Balance for Violet Crystals

#### Selected Bond Valence Sums:

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<tr>
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</thead>
<tbody>
<tr>
<td>Co1</td>
<td>Co1(2)</td>
<td>*</td>
<td>1.837</td>
<td>8</td>
</tr>
<tr>
<td>Co1</td>
<td>Co1(3)</td>
<td></td>
<td>1.811</td>
<td>40</td>
</tr>
<tr>
<td>Co2</td>
<td>Co2(2)</td>
<td>*</td>
<td>1.86</td>
<td>7</td>
</tr>
<tr>
<td>Co2</td>
<td>Co2(3)</td>
<td></td>
<td>1.835</td>
<td>39</td>
</tr>
<tr>
<td>Ca1</td>
<td>Ca1(2)</td>
<td>*</td>
<td>2.479</td>
<td>24</td>
</tr>
</tbody>
</table>

For the small violet crystals

\[
\{[L-2H]Co^{ll}\}_2[Ca^{ll}(CH_3COO)_2(CH_3OH)_4]\cdot3tol
\]

\[
2(-2) + 2(+2) + (+2) + 2(-1) = (-4) + (+4) + (+2) + (-2)
\]

\[
= 0
\]

Overall charge is now neutral.
Supporting Characterizations

X-ray Formula: $\text{C}_{68}\text{H}_{98}\text{CaCo}_2\text{N}_4\text{O}_{12}, 3(\text{C}_7\text{H}_8)$

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

Anal. Calc. for $\text{C}_{68}\text{H}_{98}\text{CaCo}_2\text{N}_4\text{O}_{12}$:

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 $\text{C}_{68}\text{H}_{98}\text{Co}_3\text{N}_4\text{O}_{12}$?

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-2H]Co^{III}\}_2(CH_3COO)(OH)]\cdot2.5tol
Supporting Characterizations – SEM with EDX
Violet Crystals: \([L\cdot 2H]Co^{ll}\)_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
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


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

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