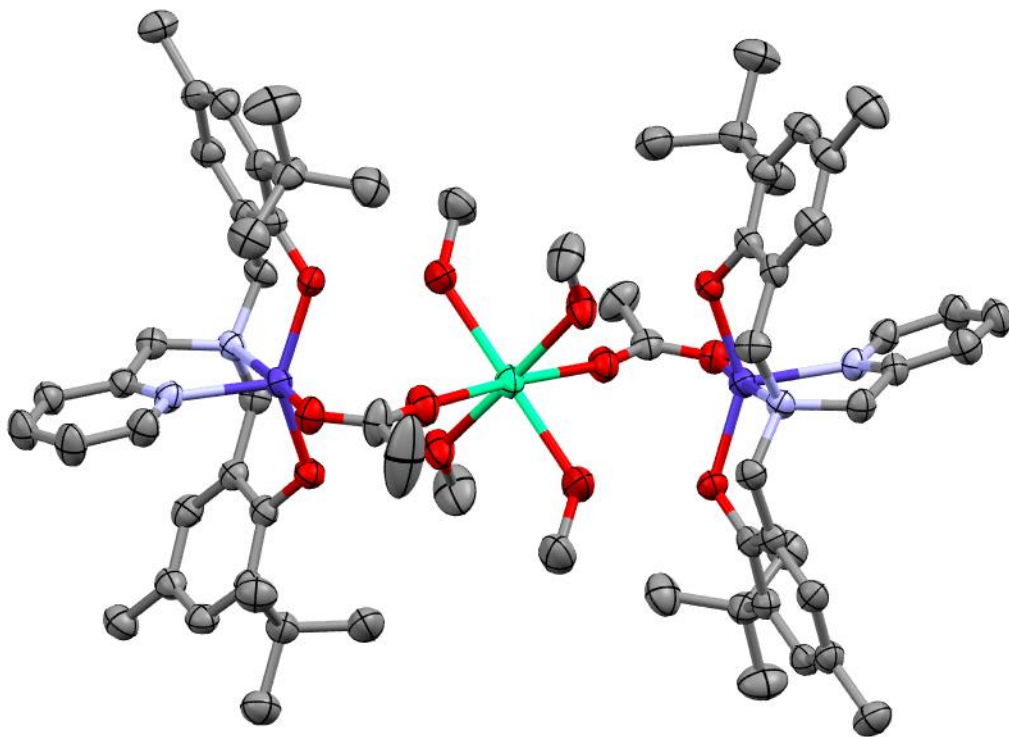


Structure Finalization: A Case Study



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ldawe@wlu.ca



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.

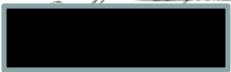
Structure Finalization Overview

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

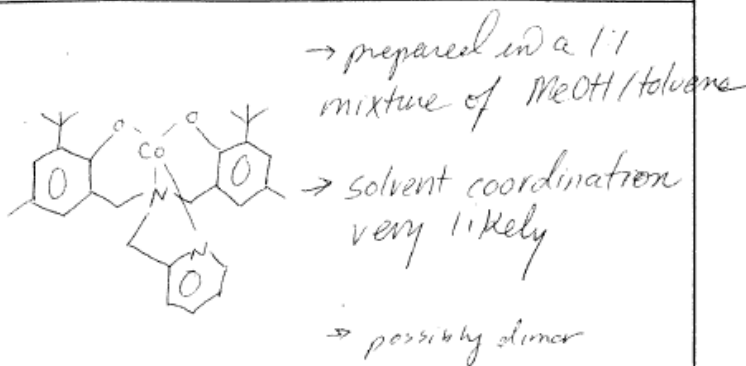
Where Problems Start...

XRD Analysis Submission Form

in a round bottom flask April 27, 11

Name	Unique Sample Code	Supervisor's signature
H_2CO_2NN <i>GuMe Py</i>	MPF03- initial filtrate	
Proposed formula	Elemental Analysis(Y/N)	Last solvent
$C_{30}H_{38}CoN_2O_2$	No	toluene/MeOH

Structure:



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

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

Date received:

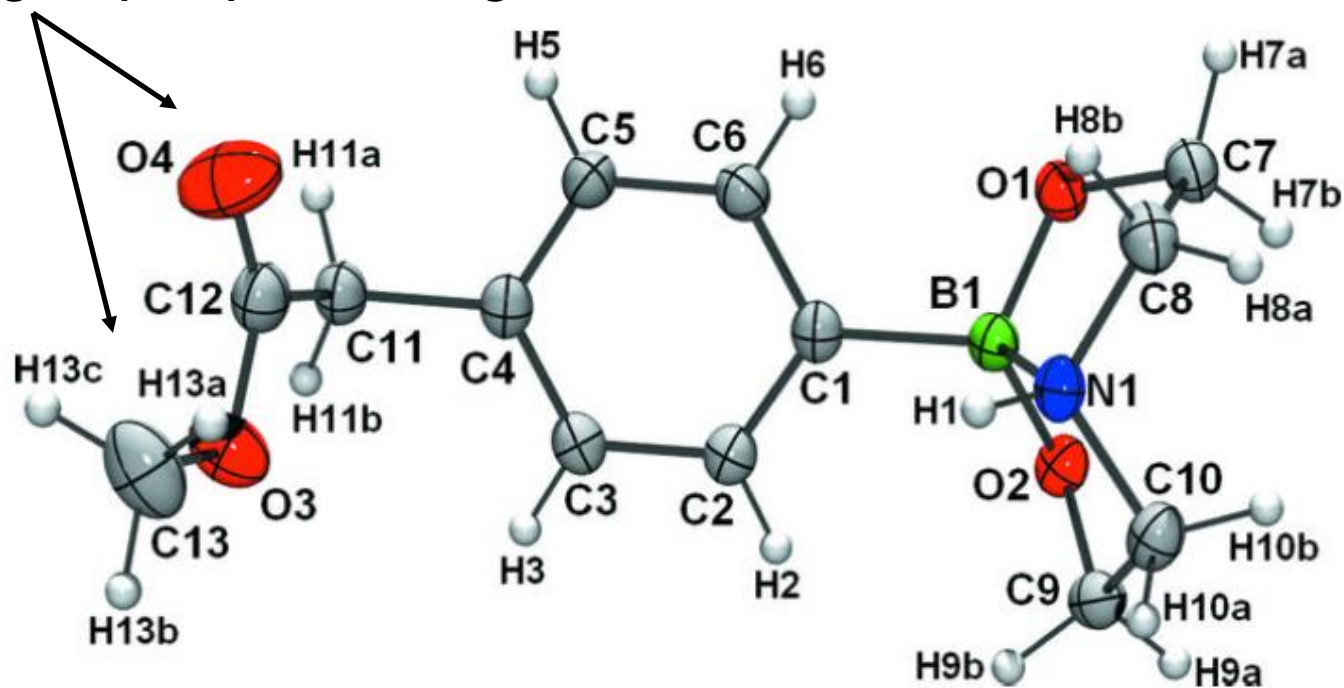
Data collection started:

Notes:

Multiple different crystals present in submitted sample

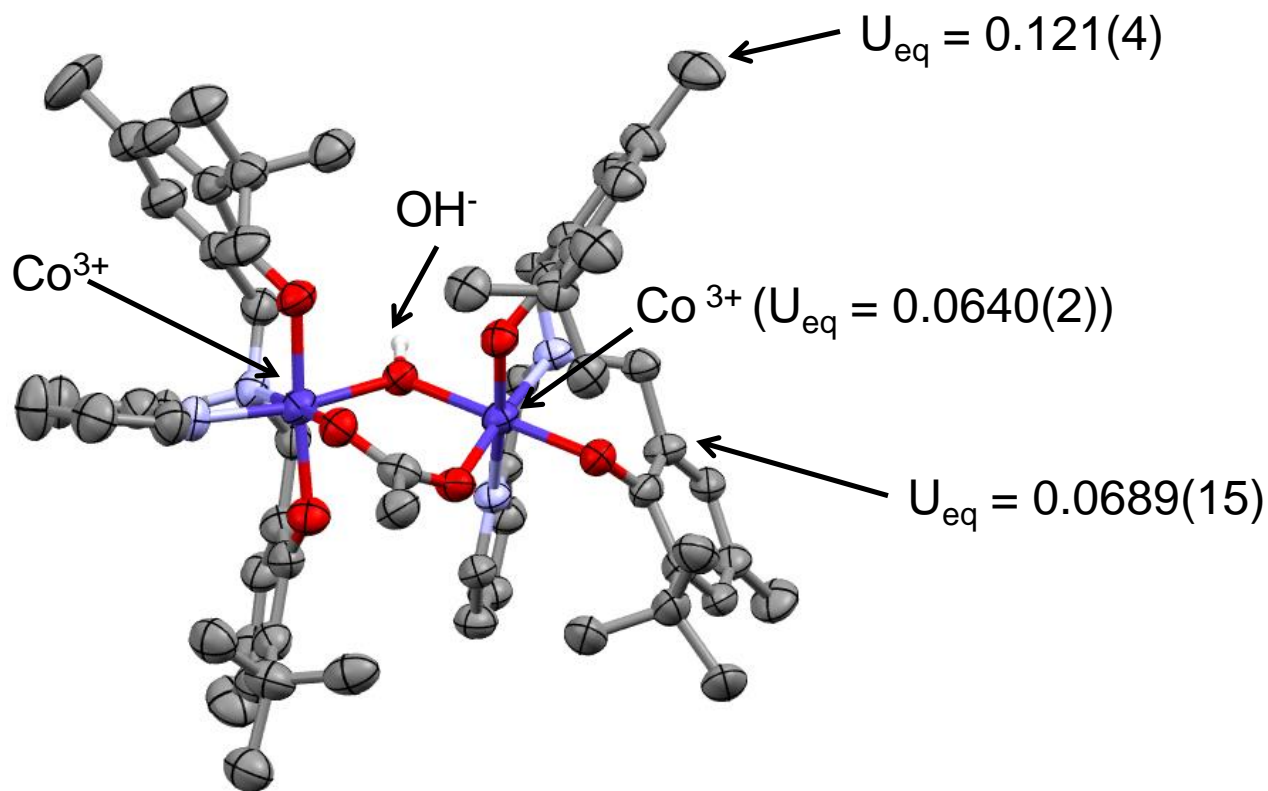
Electron Density, Ellipsoid Shape

- 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



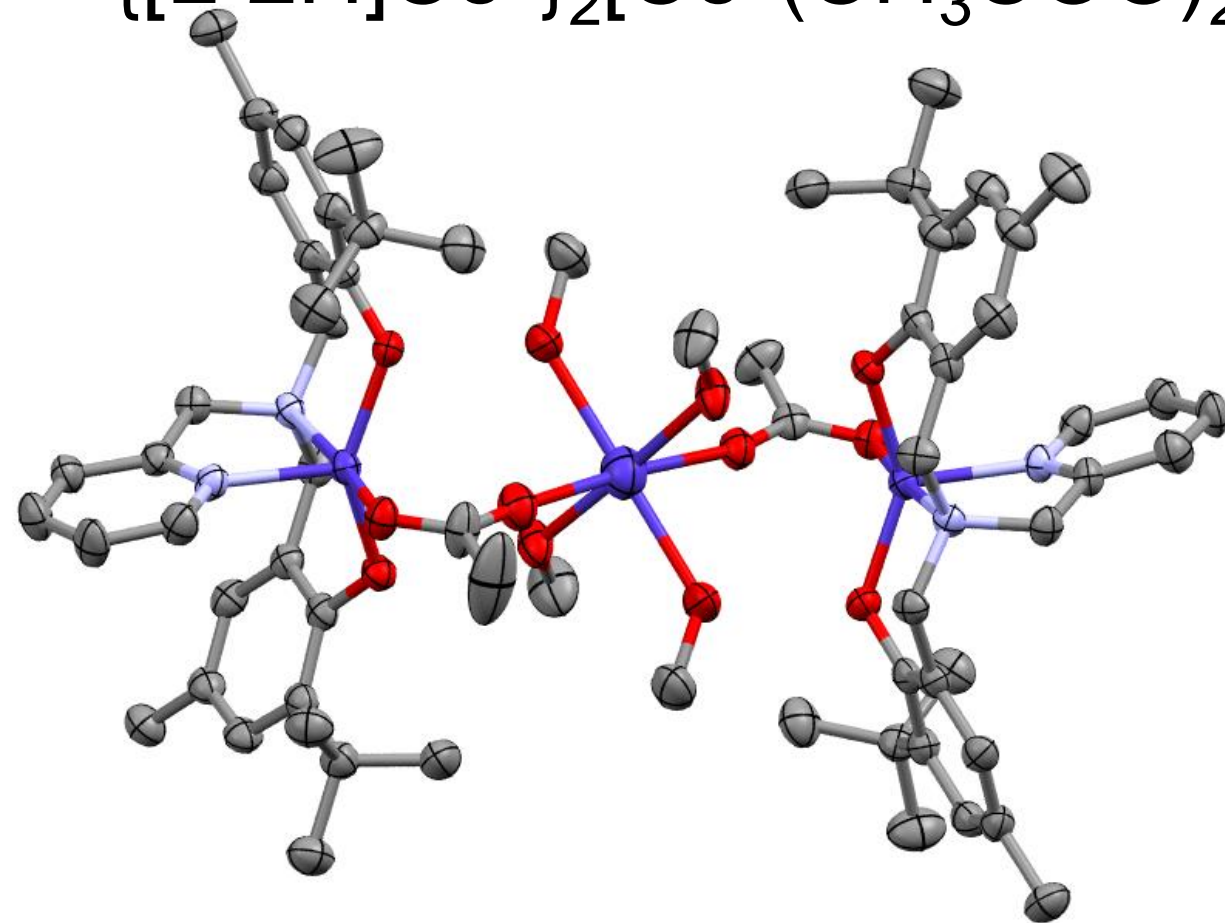
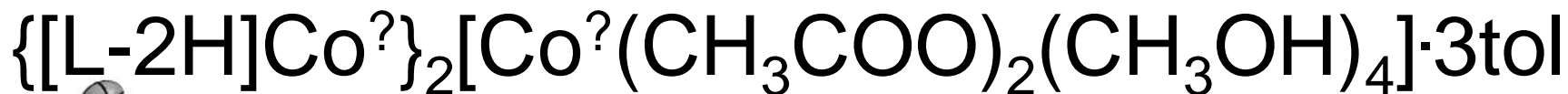
“Large Black” Crystals

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



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

“Small Violet” Crystals



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?

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 Å from C93]

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

What does this mean?

Hirshfeld Tests

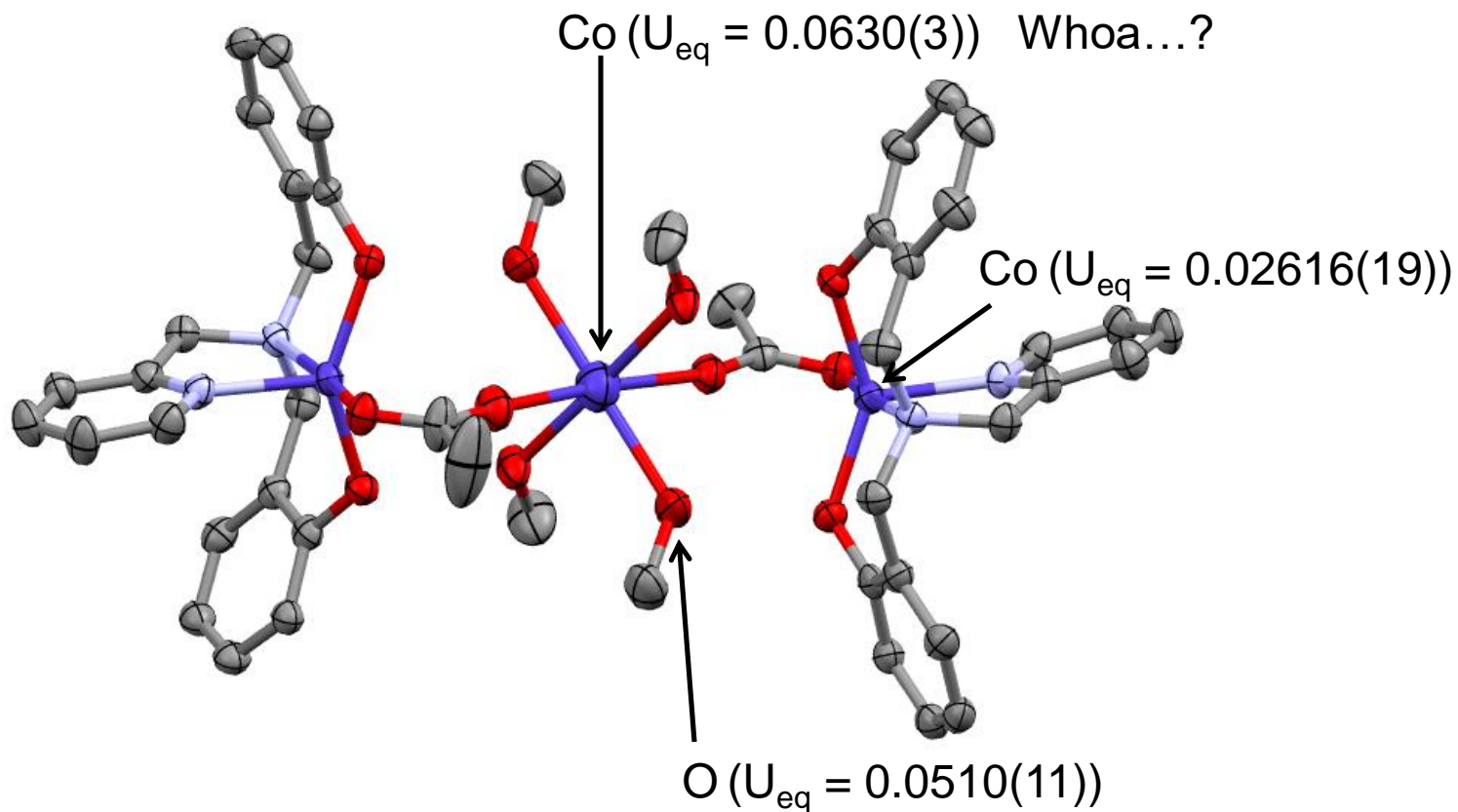
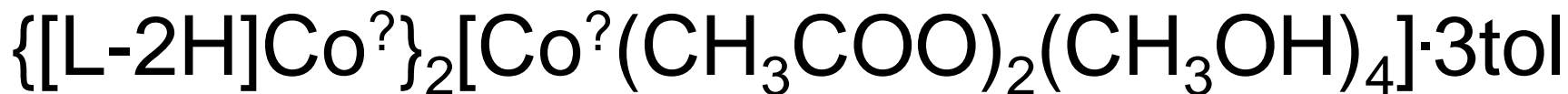
The components of the anisotropic displacement parameters along chemical bonds are assumed to be equal in magnitude. Large differences might indicate contamination of these parameters with other (unresolved) effects such as (substitutional) disorder, model or data errors and/or over-refinement.

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



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 be 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	ABSPalScan	ASYM-VIEW	fcf2hkl
NewmanPlot	Calc Inter	SQUEEZE	ADDSYM-EXT	ABSTempa	FCF-Valid	Expand2P1
Ring-Plots	Calc Coord	CalcFCF-SQ	ADDSYM-PLT	ABSGauss	Dlffourier	FCF-Gener
Plane-Plot	Calc Metal	Contour-SQ	ADDSYM-SHX	ABSXtal	ANALofVAR	HKL-Gener
Polyhedra	Calc Geom	Solv F3D	NEWSYM	ABSSphere	ByvoetPatr	HKL-Transf
ContourDlf	Calc Hbond	Solv Plot	NONSYM	SHXABS	ASYM-EXPCT	EXOR-RES
Contour-Fo	Calc TMA	CavityPlot	LePage	AnomDlsVal	ASYM-Valid	ANIS-RES
AutoMolFlt	L.S.-PLANE		DeRed	AnomDlsPlt	SupplMater	Rename-RES
HKL2Powder	DihedAngle		MOLSYM	MuPlot	EXPECT-HKL	Auto-Renum
GlmPowderP	AngleLines	FLIP MENU	SPGRfromEX		CSD-CELL	Create-spf
RadDistFun	AngLspLLn	Flip Show	ASYM		CSD-QUEST	Create-res
Patterson	CremerPopl	Flip Patt	ASYMaverFR		StructTidy	Create-clf
ShelxtPlot	BondValenc	FLIPPER 25	LePageTwin	XtLPlanAgl	StrainAnal	Create-pdb
PLUTONatlv	HFIX - RES	STRUCTURE?	TwinRotMat	Xtal Habit	LocCIF-acc	clf2shelxl

Xtal Data (CIF) shelxl.cif- Set 1(): shelxl

RefL Data (SHELXL) shelxl.fcf [FCF] (): shelxl

No check.def file found for CIF-Validation

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 NonFlt 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 Angle Flt MaxDev. x y z
-1 ===== 100 0 at 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 Lave
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 Ln ( 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

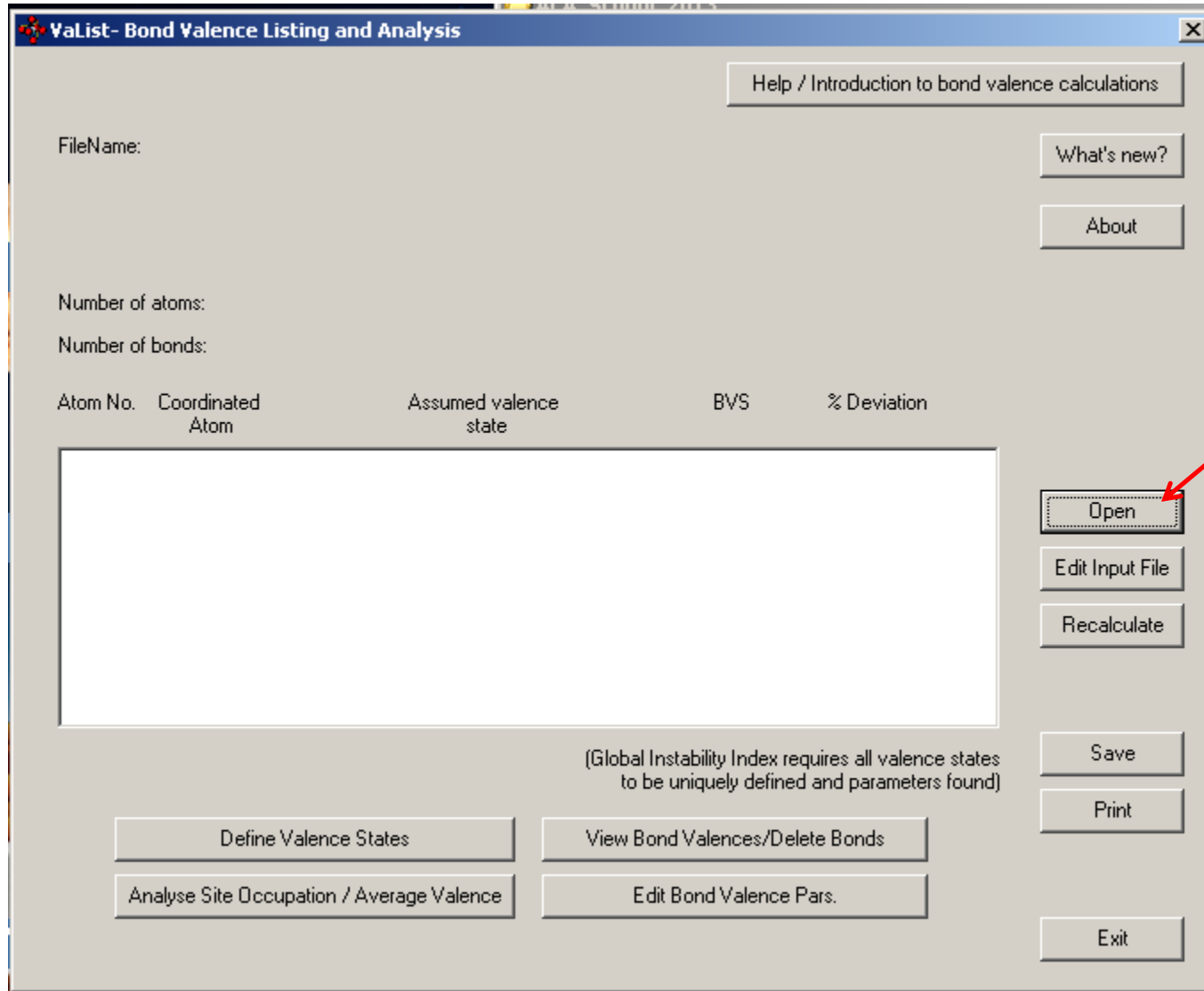
$$s = \exp[(R_0 - R)/B],$$

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

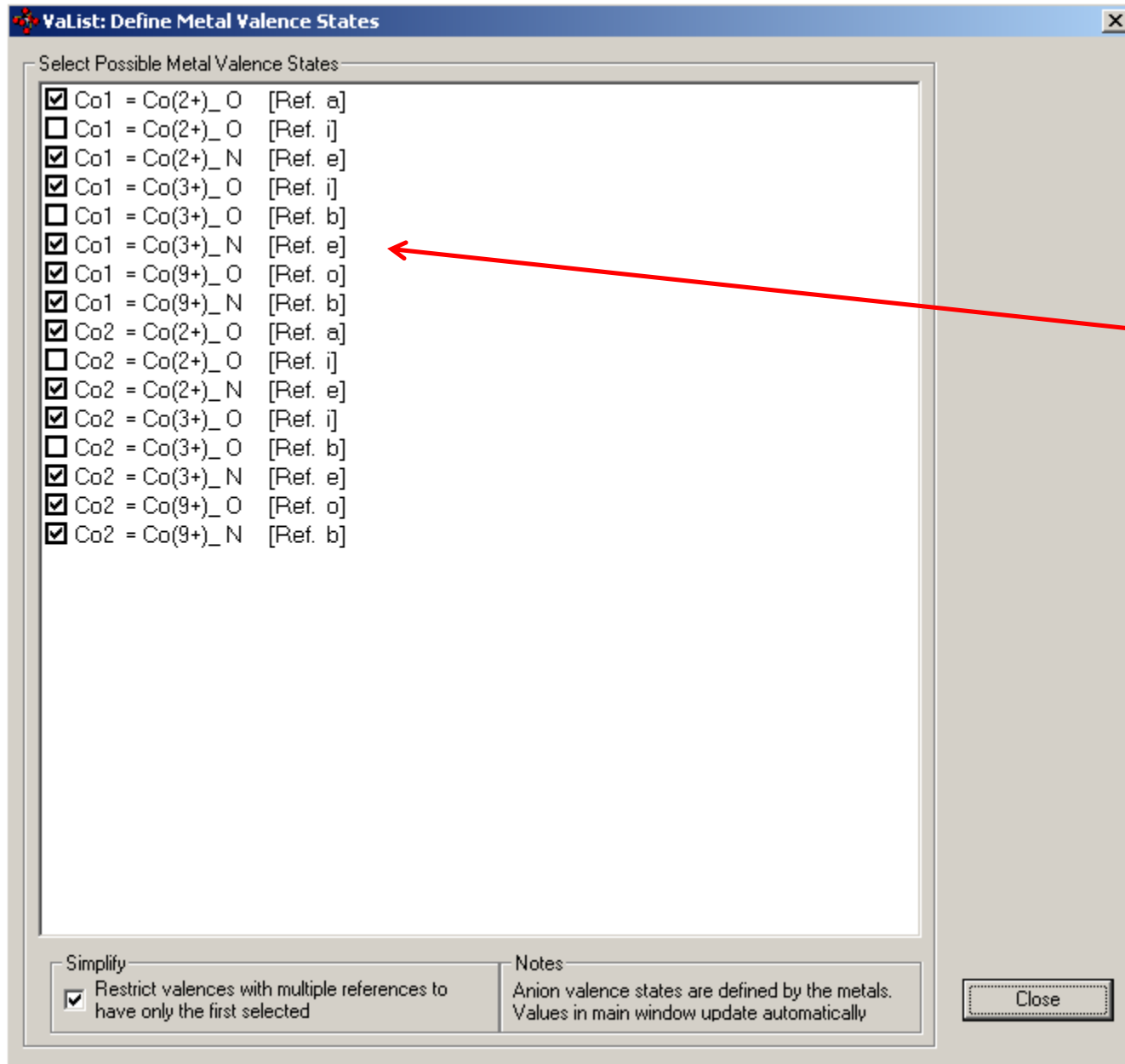
Bond Valence Sum (BVS) Calculations



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

Help / Introduction to bond valence calculations

FileName: C:\Documents and Settings\ldawe\My Documents\ACA_School_2013\MPF03-Filtrate\Squeezed\shelxl.cif
Chemical formula sum: C79.50 H100 Co2 N4 O7

Number of atoms = 2
Number of bonds = 12

Atom No.	Coordinated Atom	Assumed valence state	BVS	% Deviation
1	Co1	Co1 (2)	3.569	78
2	Co1	Co1 (3) *	3.545	18
3	Co1	Co1 (9)	4.188	53
4	Co2	Co2 (2)	3.52	76
5	Co2	Co2 (3) *	3.475	16
6	Co2	Co2 (9)	4.097	54

(Global Instability Index requires all valence states to be uniquely defined and parameters found)

Buttons: Define Valence States, View Bond Valences/Delete Bonds, Analyse Site Occupation / Average Valence, Edit Bond Valence Pars., Open, Edit Input File, Recalculate, Save, Print, Exit.

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

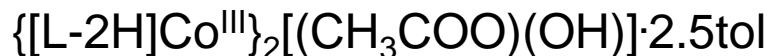
From <http://www.cryst.chem.uu.nl/spek/platon/pl000303.html>:

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

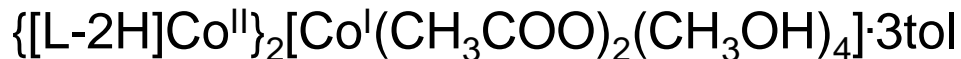
- For the large black crystals



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

Overall charge neutral

- For the small violet crystals

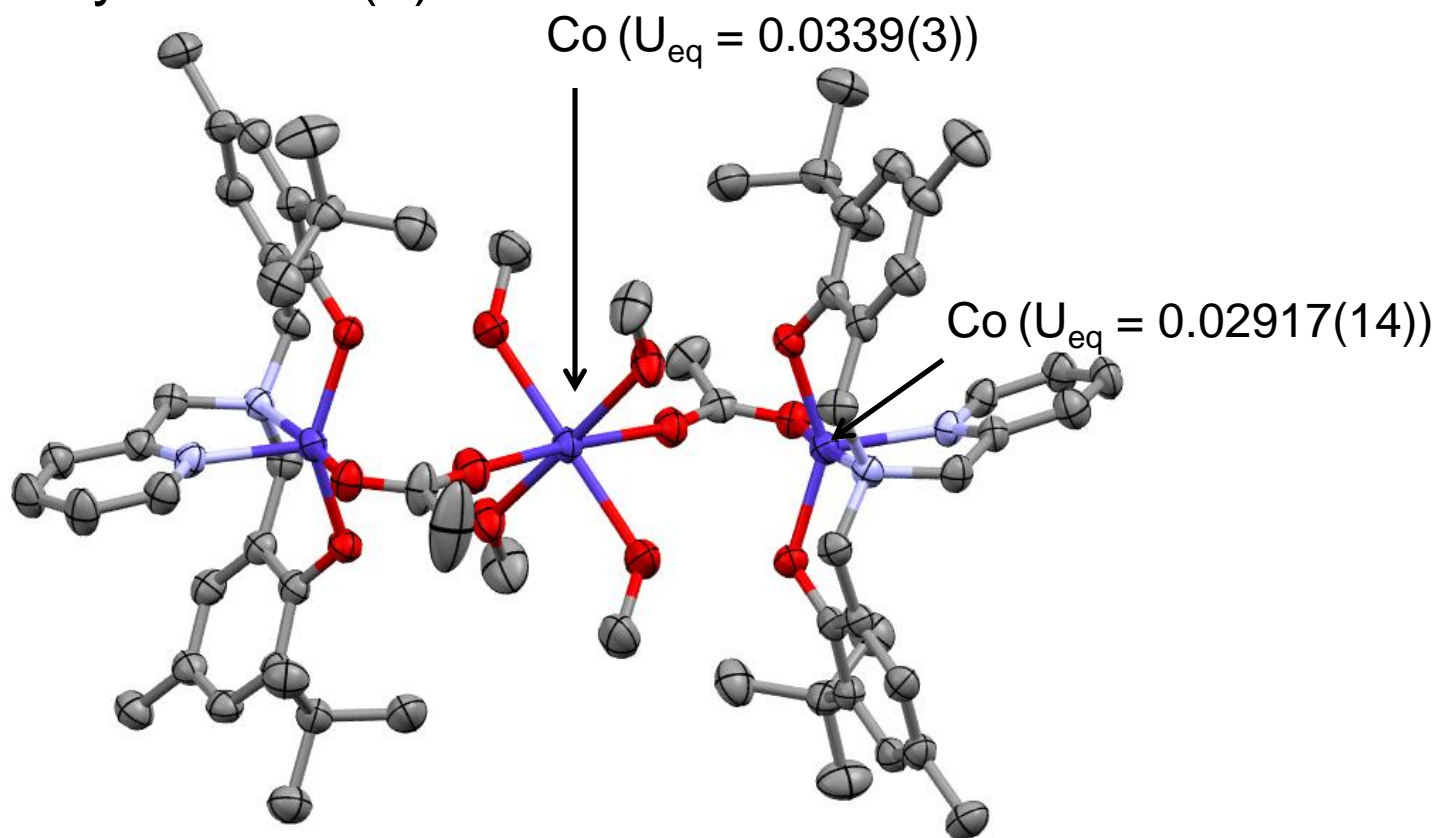


$$2(-2) + 2(+2) + (+1) + 2(-1) = (-4) + (+4) + (+1) + (-2) = -1$$

Overall charge -1?

Site-Occupancy

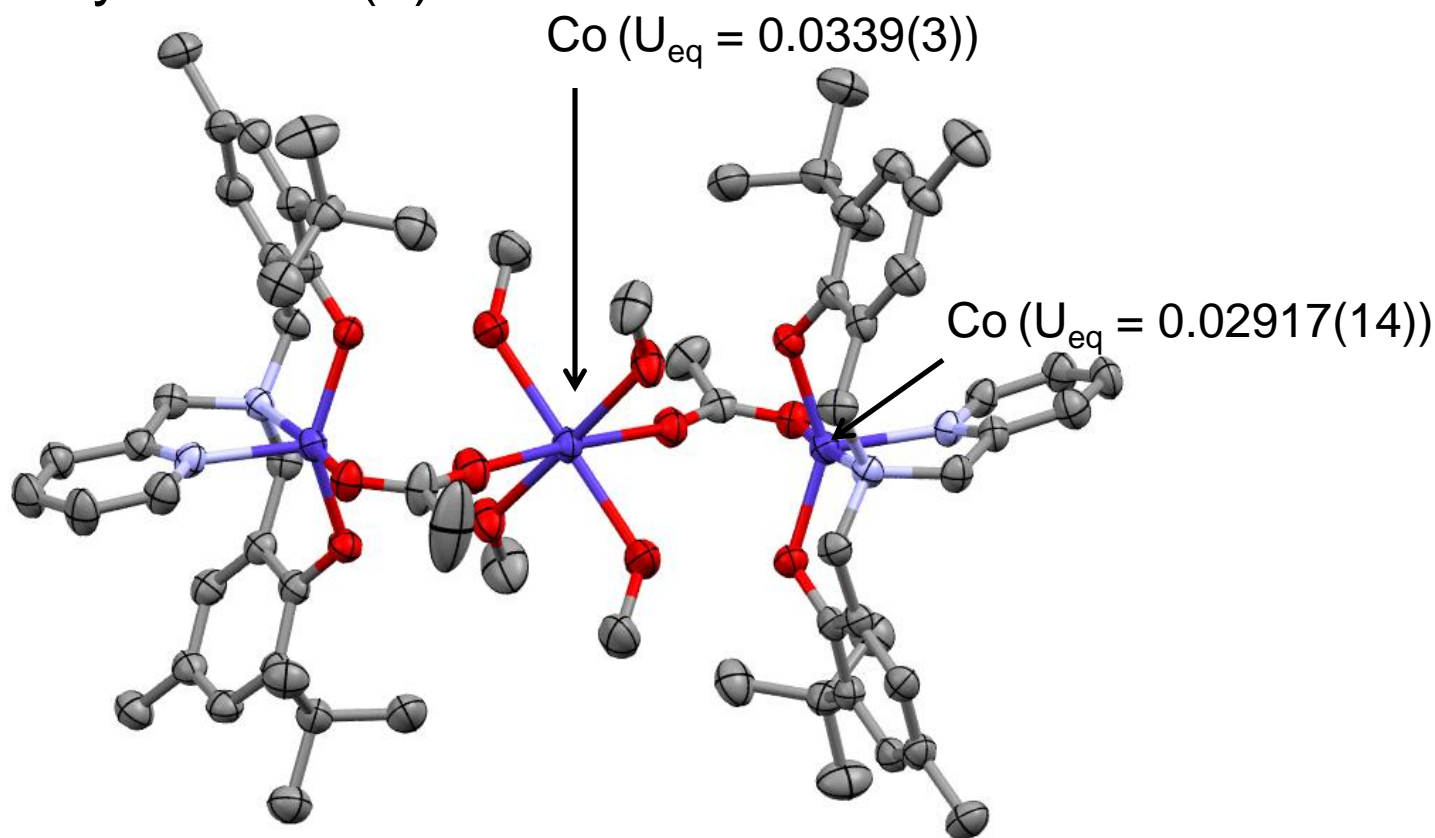
- Tied the occupancy of the central Co to a free variable and refined the occupancy
- Occupancy = 0.642(3)



- No more Hirshfeld alerts from checkCIF

Site-Occupancy

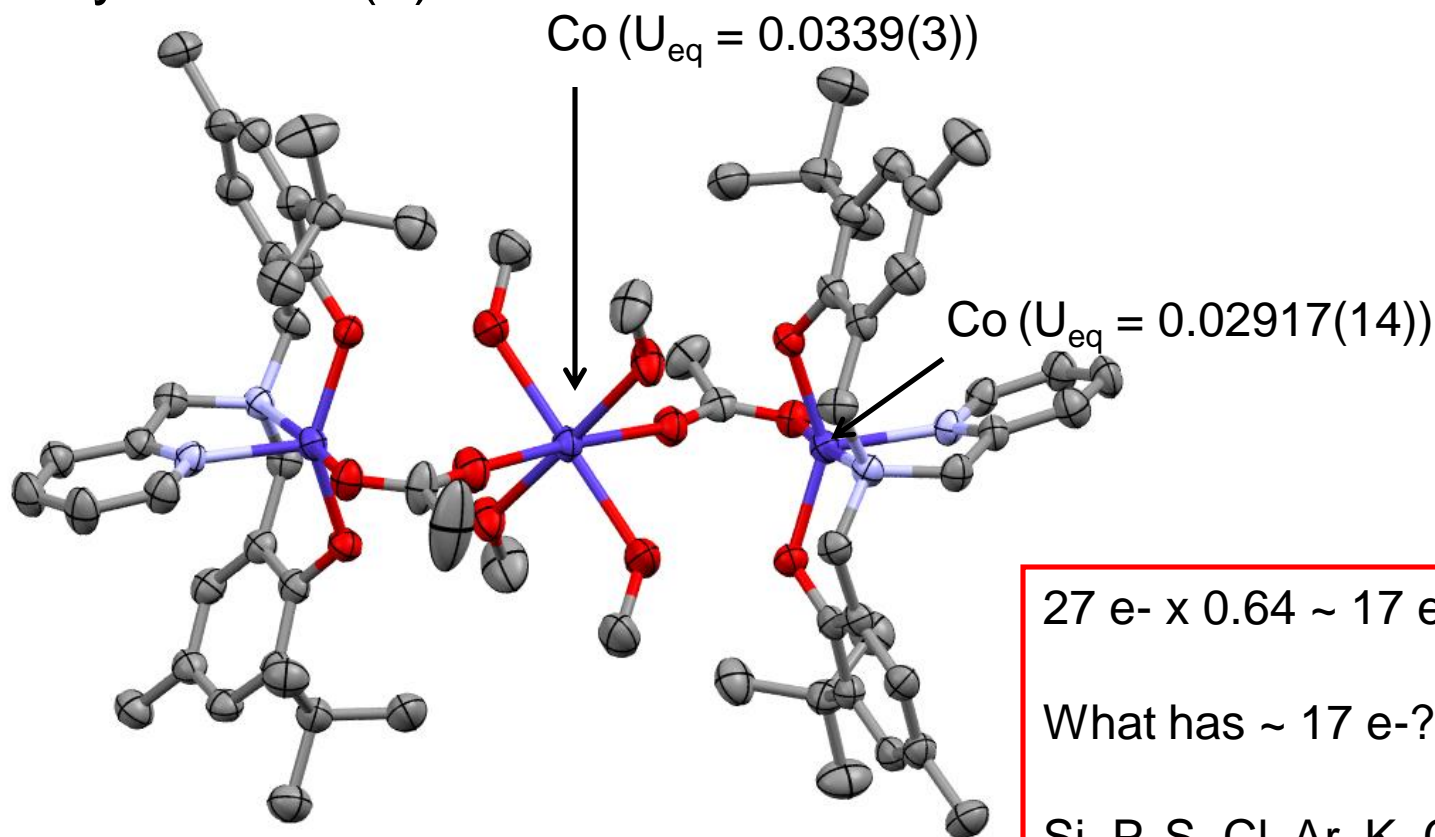
- Tied the occupancy of the central Co to a free variable and refined the occupancy
- Occupancy = 0.642(3)



- 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)



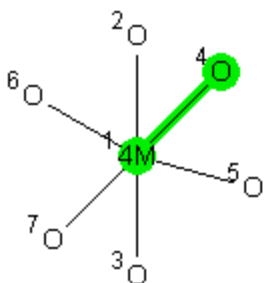
- No more Hirshfeld alerts from checkCIF
- **How many electrons is a 0.64 occupancy Co?**

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)



3D Limits and Options

PARAMETER: DIST2 (Distance)

Modify options and hit 'OK' when done.

LIMIT: Value 2.2360 +/- 0.05 (Å)

Range
 Value +/- tolerance

RENAME: DIST2

Cancel OK

Geometric Parameters

To construct Parameter/Object:
3D Options dialog box displayed.....

Current Selection:

Valid Parameters

Distance: DIST2

Options...

Valid Objects

Defined Objects:

Delete

Reset Done

Groups... 4M Bond: Single

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

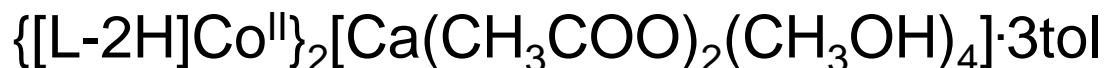
15 structures containing Ce

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:



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 $A \pm 0.4\%$ 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.

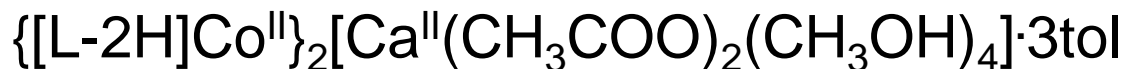
However, it should be noted that, in general, mass spectrometric and spectroscopic data do not constitute proof of purity, and, in the absence of elemental analyses, additional evidence of purity should be provided (melting points, PXRD data, etc.)

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



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

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.

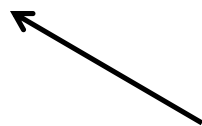
Anal. Calc. for $C_{68}H_{98}CaCo_2N_4O_{12}$:

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 $C_{68}H_{98}Co_3N_4O_{12}$?

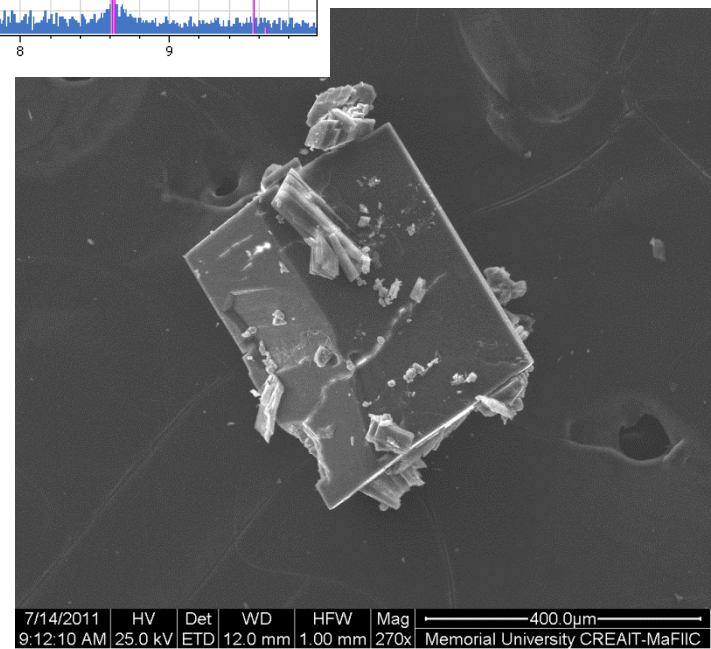
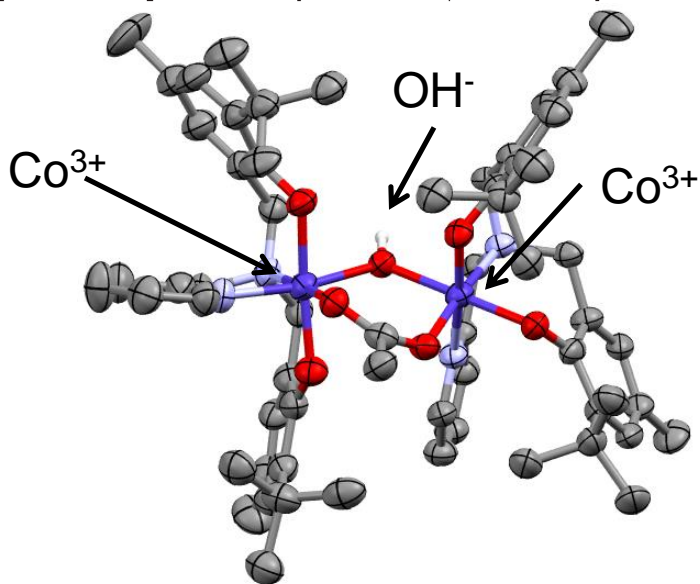
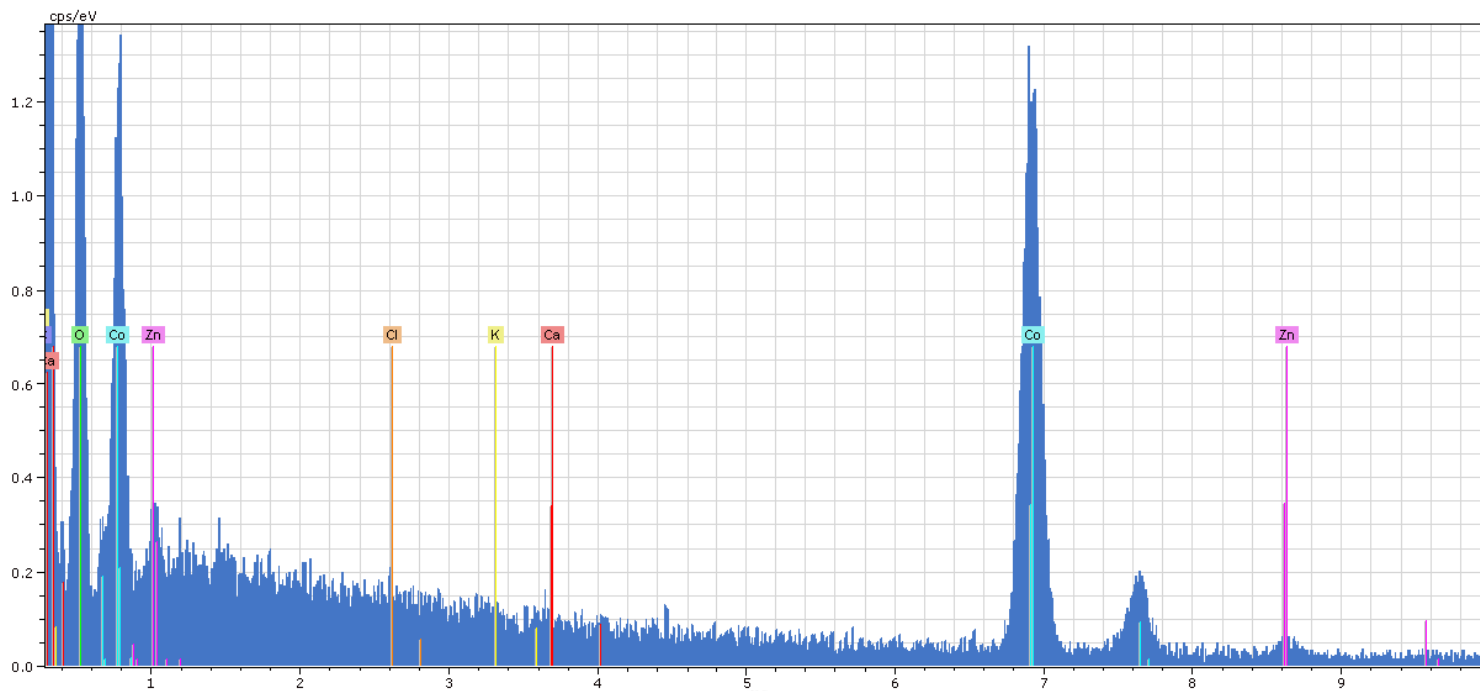
C, 60.94; H, 7.37; N, 4.18



Off by 0.98! Not within limits for publication.

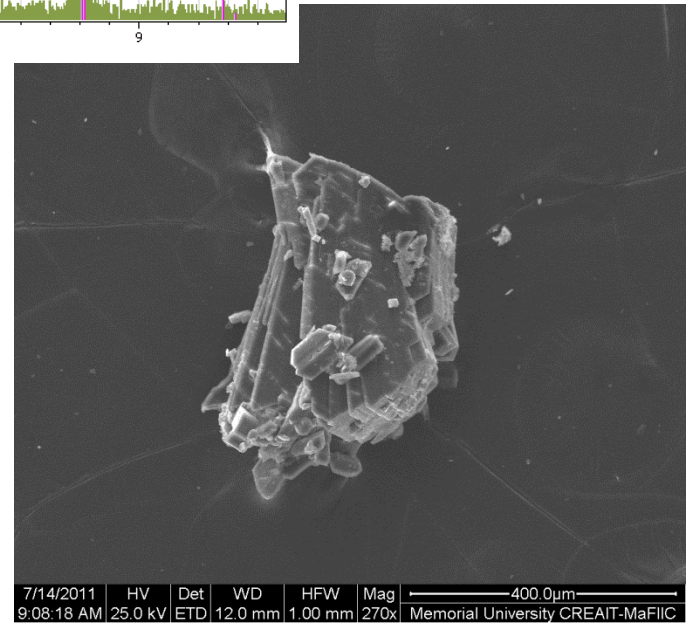
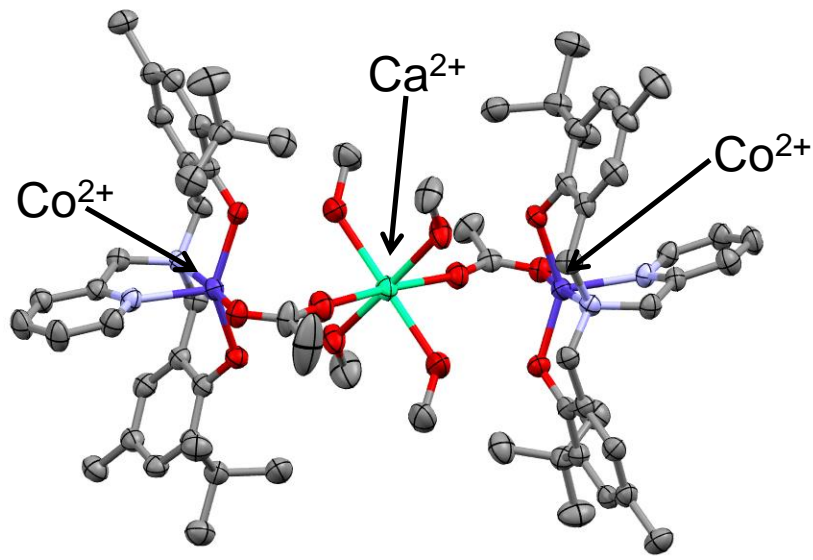
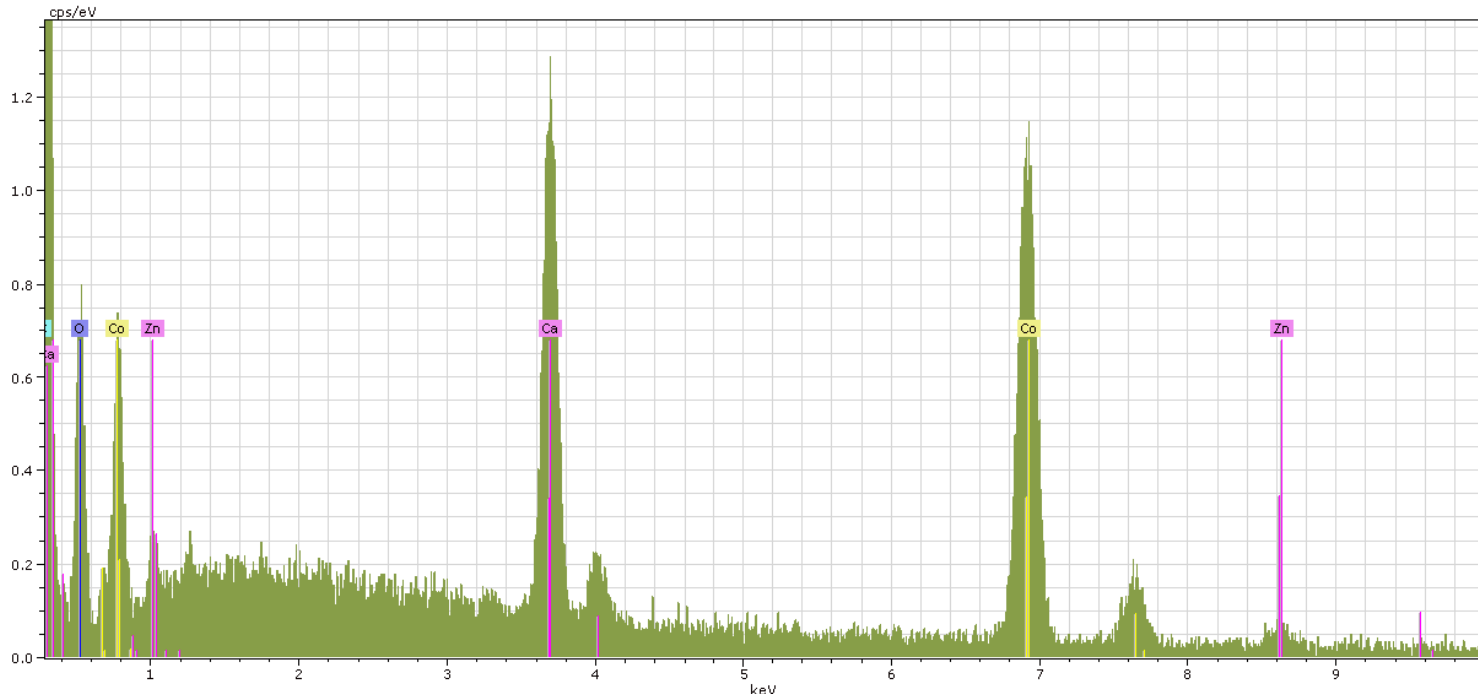
Supporting Characterizations – SEM with EDX

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



Supporting Characterizations – SEM with EDX

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

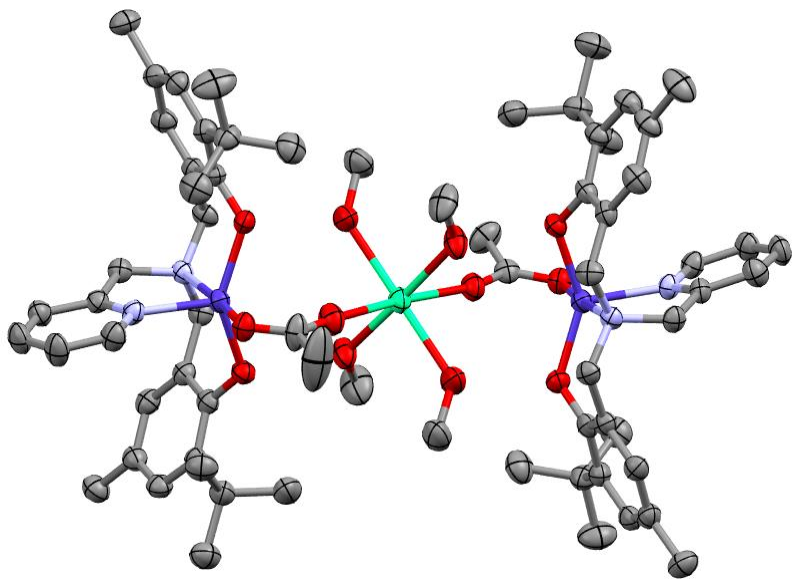


Structure Finalization Summary

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



Conrad Goodwin @ConradGoodwin · May 15
#ChemTwitter What's the other 15% in "85% KOH"?!?

11



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Chris Kozak
@KozyCanuck

Replying to @ConradGoodwin

Other hydroxides and oxides can be present. We made a compound using KOH once and the crystal structure showed Ca. Did energy dispersive Xray on the KOH and found Ca, Na and other elements

7:14 AM · May 16, 2020 · Twitter for iPhone



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