Acta E Articles: Frequently Encountered Problems and Hints for Evaluating Structures of Inorganic and Metal-Organic Compounds

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Category

Although the wrong category is a minor problem (without consequences; the wrong category is usually corrected at the proof stage by technical editors or section editors), co-editors are encouraged to check the correct category:

_publ_requested_category
EI for inorganics
(no C—C and/or C—H bonds)

EM for metal organics
(at least one metal and C—C and/or C—H bonds must be present)

EO for organics
(no metals, but semi-metals like Se, Te can be present)

Disorder

Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.005 Å; disorder in solvent or counterion; R factor = 0.043; wR factor = 0.112; data-to-parameter ratio = 13.3.

Key indicators in the published paper

Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.004 Å; disorder in main residue; R factor = 0.028; wR factor = 0.056; data-to-parameter ratio = 16.9.

Treatment of disorder should be reported in the Abstract with numerical values for the occupancies (including s.u.) and in more detail in _publ_section_exptl_refinement

An easy way to check disorder: Just look into the review *.pdf

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
O3W	0.2685 (6)	0.07326 (15)	0.00654 (18)	0.0889 (12)	
H3WA	0.2790	0.1069	0.0349	0.133*	
H3WB	0.2908	0.0402	0.0355	0.133*	
O4W	0.0439 (13)	0.3920 (4)	0.0141 (4)	0.0793 (16)	0.479 (6)
H4WA	0.1206	0.3496	0.0243	0.119*	0.479 (6)
H4WB	0.0705	0.3718	−0.0225	0.119*	0.479 (6)
O4W'	0.1795 (12)	0.4147 (3)	0.0175 (4)	0.0793 (16)	0.521 (6)
H4WD	0.1938	0.3757	0.0273	0.119*	0.521 (6)
H4WF	0.0831	0.4181	−0.0182	0.119*	0.521 (6)

Special positions

Special positions or symmetry should be reported in the Abstract!

E.g. : … the Fe(II) atom is located on an inversion centre …;

… the MgO_6 octahedron has .*m*. symmetry …

But not: The asymmetric unit contains one ligand molecule and *half of a metal atom* (there are no half-/quater/- *etc*. atoms!)

How to spot special positions in an easy way?

Check coordinates in the review *.pdf → Wyckoff positions in *IT* **A**

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.48061 (6)	0.7500	0.49255 (3)	0.05827 (17)
N1	0.4523 (5)	0.7500	0.3651 (2)	0.0754 (10)
C1	0.4513 (5)	0.7500	0.2879 (3)	0.0606 (9)
S1	0.44866 (18)	0.7500	0.18058 (7)	0.0784 (3)
N2	0.2888 (5)	0.7500	0.5693 (3)	0.0792 (10)
C2	0.1682 (5)	0.7500	0.6084 (3)	0.0663 (10)
S2	−0.00054 (18)	0.7500	0.66536 (11)	0.1021 (5)
N11	0.6137 (3)	0.63122 (14)	0.52674 (13)	0.0549 (5)
C11	0.6306 (3)	0.60498 (19)	0.61208 (16)	0.0608 (6)

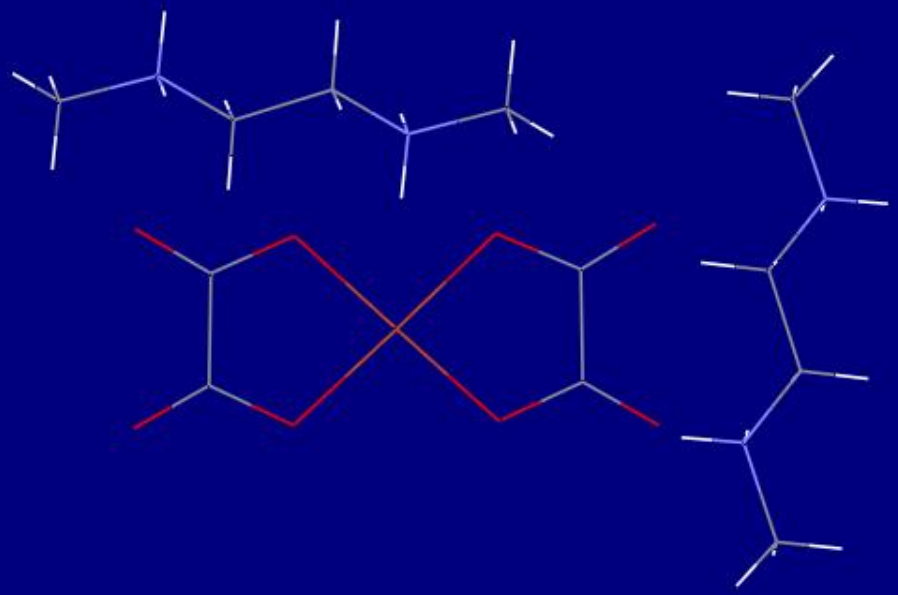
Or check the structure visually with *PLATON* or the freely downloadable ***Mercury***

http://www.ccdc.cam.ac.uk/products/mercury/

Load CIF

Display
Symmetry Elements

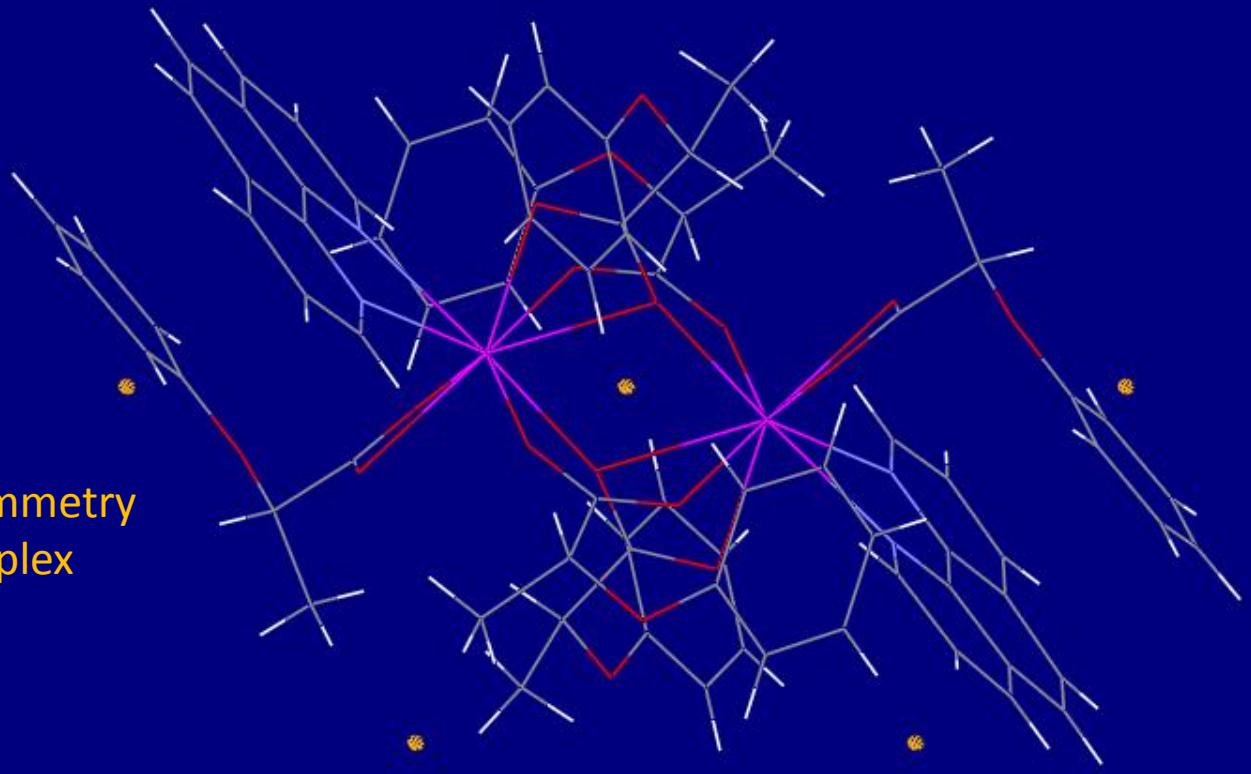
N,*N*'-Dimethylethylenediammonium dioxalatocuprate(II)



N,*N*'-Dimethylethylenediammonium dioxalatocuprate(II)

Inversion symmetry cation

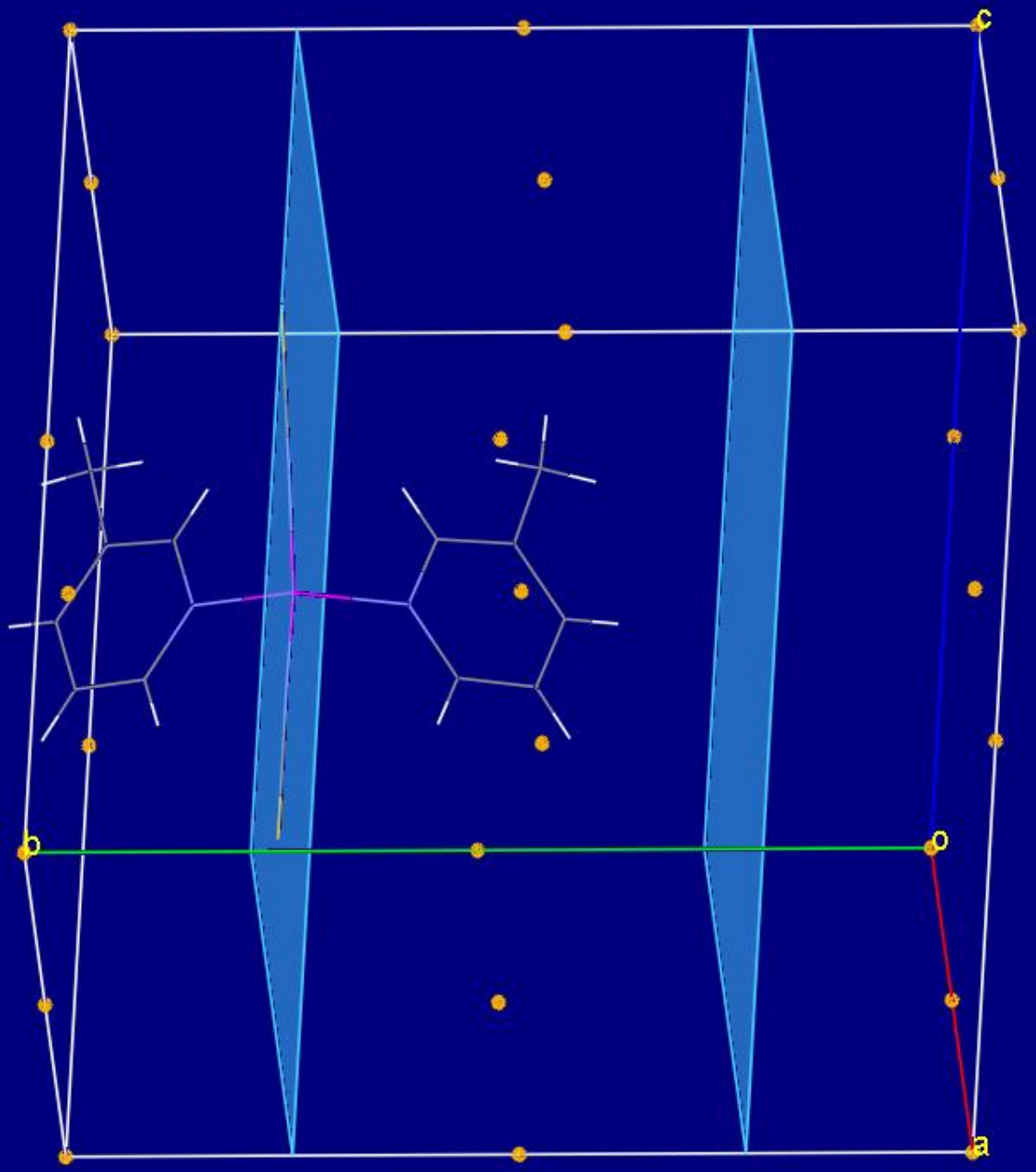
Tetrakis(μ_2-2-phenoxypropionato-κ^3-O,O,O‘,-κ^3O,O,O,-κ^4O,O,)-bis[(2-phenoxypropionato-κ^2-O,O')(1,10-phenanthroline-κ^2-N,N‘) gadolinium(III)]



Inversion symmetry
dimeric complex

Bis(3-methylpyridine- κ*N*)bis(thiocyanato- κ*N*)zinc

Mirror symmetry
for the entire complex



Coordination numbers and polyhedra

Report coordination number(s) and/or corresponding polyhedra for metal atoms in the Abstract. This can be supplemented by flagged metal—ligand atom distances to be published in Table 1

Mn OH3 1.9149(11) 3_665 y
Mn OH3 1.9149(11) 8_455 ?
Mn OH3 1.9149(11) 1_455 ?
Mn OH3 1.9149(11) 2_545 ?
Mn OH3 1.9149(11) 7_545 ?
Mn OH3 1.9149(11) 9_665 ?
Ca O2 2.3465(11) 4 y
Ca O2 2.3465(11) . ?
Ca OH3 2.456(5) 3_665 y
Ca OH3 2.456(5) 6_665 ?
Ca OH3 2.518(5) 1_455 ?
Ca OH3 2.518(5) 4_455 y
Ca OW4 2.578(9) . y
Ca OW4 2.690(9) 3_565 y

Symmetry-related distances should not be flagged since point group symmetries of the polyhedra should be indicated in the Abstract in any event. Angles around metal atoms are usually of no great insight.

Coordination numbers and polyhedra

Coordination polyhedra (coordination numbers) are very good measures for the correctness of a metal! Some metal ions are known to have peculiar coordination polyhedra (and *vice versa)*:

CN = 2

Linear coordination for ions like Ag(I), Hg(II), Au(I) …

CN = 3

Trigonal-planar (T-shaped) coordination for ions like Ag(I), Cu(I), …

CN = 4

- Tetrahedral coordination for ions like Li(I), Co(II), Al(III), Sn(IV), …
- Square-planar coordination frequent for d^8 ions (Ni(II), Pt(II), Pd(II)); sometimes for Cu(II) apparent from the *.lst file when long distances are not recognized (‚low' CONN instruction in *SHELXL*); extremely unusual (if existing at all) for ions like Fe(II/III), Co(II/III), Zn(II), …

Coordination numbers and polyhedra

CN = 5

- Trigonal-bipyramidal coordination for ions like Al(III), Sn(IV), Zn(II), …
- Square-pyramidal coordination for ions like Cu(II), Ni(II), V(V), …

CN = 6

- Octahedral coordination for ions like Mg(II), Al(III), Mn(II), Cr(III), …

Jahn-Teller effect results in a considerably tetragonally distorted octahedron ([4+2] coordination with two long metal-ligand distances) and is pronounced for ions Mn(III), Cr(II), **Cu(II)**

- Trigonal-prismatic coordination for ions like Mo(VI), Zr(IV), …

CN $\geq$ 7

Frequently very distorted polyhedra for ions with larger ionic radius like Na(I), Ca(II), *RE*(III), …

Other very useful criteria to check the correctness of a metal:

Bond lengths!
Inorganics: Bergerhoff & Brandenburg, *Int. Tables* **C**, p 771-780.
Metal-organics: Orpen *et al*., *Int. Tables* **C**, p 804-888.

Bond valence sums (BVS)!
- N.E. Brese & M. O'Keeffe (1991). *Acta Cryst*. **B**47, 192-197.
- I.D. Brown (2002). *The chemical bond in inorganic chemistry : the bond valence model*. IUCr Monographs in Crystallography 12

Software available for calculation of BVS:
http://www.ccp14.ac.uk/solution/bond_valence/index.html

PLATON also allows to calculate BVS

Crystallographic directions

In the Abstract, crystal packing features in terms of chain or layer formation are discussed, *e.g.*
– „ …and the metal atoms are bridged by the oxalate ligands, resulting in the formation of a helical chain.“
- „Intermolecular O –H…O hydrogen bonding interactions lead to a two-dimensional set up.“

Such features should always be completed by indicating the crystallographic directions:

„… of a helical chain extending parallel to [100] (to the *a* axis)“
[brackets denote a direction vector]

„ …to a two-dimensional set up parallel to (100) (to the *bc* plane)“
(parentheses denote planes)

Order of atoms

In the CIF the order

N1 Pd 2.072(9) . ?
N1 H1 0.85(2) . ?
N2 Pd 2.005(11) . ?
N2 H10 0.85(2) . ?
O1 Pd 1.976(8) . ?
O3 H8 0.86(2) . ?
O5 Pd 2.024(7) . ?
...

is often confusing 

whereas the order

Pd O1 1.976(8) . ?
Pd N2 2.005(11) . ?
Pd O5 2.024(7) . ?
Pd N1 2.0724(9) . ?
O1 C1 1.307(14) . ?
O2 C1 1.244(14) . ?
O3 C5 1.317(7) . ?
...

is much clearer 

Order of atoms in *SHELXL* *.ins (*JANA* *.m50) [or re-refining with *PLATON*]

Metal1
Metal2
Ligand atom1
Ligand atom 2
...

Crystal colour

Provides useful information, although in some cases ambiguous!

Check consistency:

_publ_section_exptl_prep

;

… . Slow evaporation of the filtrate overnight resulted in **green cystals** suitable for X-ray analysis in approximately 70% yield.

;

BUT

_exptl_crystal_colour **brown**

Ask authors when crystal colour seems to be ‚wrong' !

Crystal colour

Colour may serve as a warning sign for an incorrect metal, e.g. ‚coloured' Zn-compounds; colourless Cu(II)-compounds, *etc*.

Some first row transition metal ions are ‚chameleons' . They can adopt colours in the entire spectral range, depending on the ligand , *e.g.* Cu(II), Ni(II).

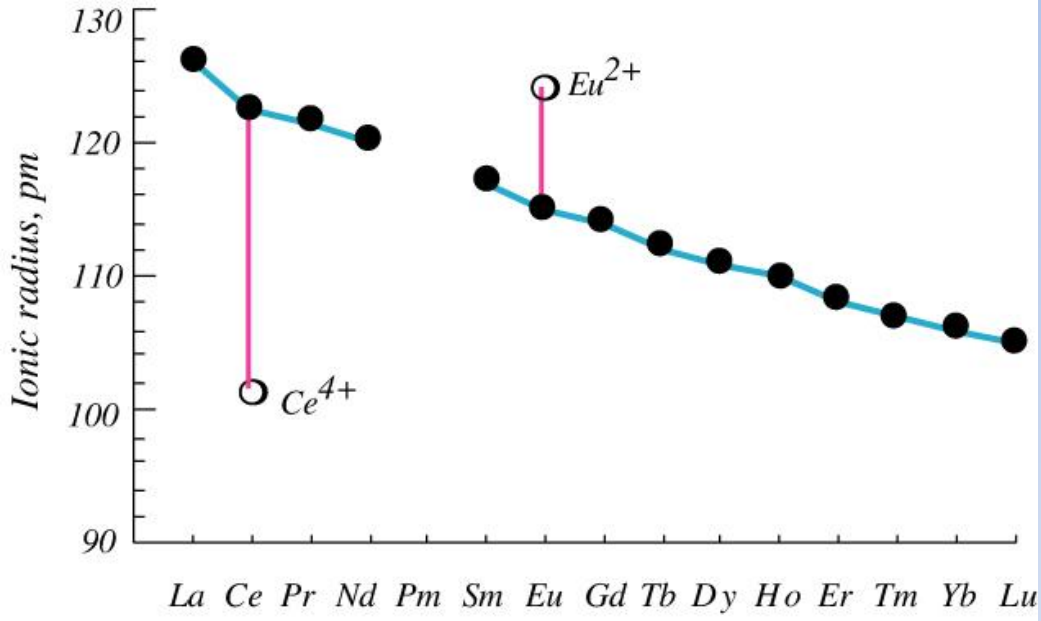
Ions with closed-shell electronic configuration (row I; row II; Zn, Cd, Hg) most frequently are colourless, except for charge-transfer complexes or where anions are coloured, *e.g.* for chromates(VI)

Rare earth ions are difficult to classify in terms of colour. Here are the most frequently observed colours:

Ox. State	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
+2						Sm^{2+}	Eu^{2+}						Tm^{2+}	Yb^{2+}	
+3	La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Pm^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}	Lu^{3+}
+4		Ce^{4+}	Pr^{4+}	Nd^{4+}					Tb^{4+}	Dy^{4+}					

Rare earth metals

Often reported in form of **isotypic series**
Correctness of the metal is difficult to check (refinement of s.o.f. ambiguous)
Use the **Check for similar reduced cells** option provided at your homepage to search for isotypic structures and consider the lanthanide contraction:



Deviation of the expected decrease of the unit cell volume with increasing atom number is a clear warning sign!

In such cases check the deposited structure factors for similarity with *PLATON*

Conclusion and Recommendation

For validation, use checkCIF output provided in the review *.pdf or at your homepage

It is recommended to always re-refine the structure (→ occupancies of metal atoms, location of H atoms from difference Fourier maps etc.) – just a few mouse clicks / keys with *PLATON*!

Using programs and tools like/within *PLATON, publCIF, Mercury*, *etc*. will make your life easier!

Nevertheless, always consider your chemical intuition!

Thanks to all of you for your work and input for the journal!