

27 May, 2002

MATERIAL FOR DEPOSIT

SOME ERRORS FROM THE CRYSTALLOGRAPHIC LITERATURE, SOME AMPLIFICATIONS AND A QUESTIONABLE RESULT

Frank H. Herbstein^a, Shengzhi Hu^b and Moshe Kapon^a

^aDepartment of Chemistry, Technion-Israel Institute of Technology, Haifa, Israel 32000 (chr03fh@tx.technion.ac.il), and

^bDepartment of Chemistry, Xiamen University, Xiamen, China (szhu@xmu.edu.cn),

Dedicated to Dr. R. E. Marsh (Caltech), teacher and friend, on the occasion of his eightieth birthday.

Synopsis

Correction of space-group errors for some crystals leads to clarification of relationships among chemically-similar but apparently crystallographically-different crystal structures. There are new examples of the ‘centrosymmetric—non-centrosymmetric’ ambiguity, and also straightforward revisions of space groups. Finally, a questionable structure presents evidence either for a new type of N–H...Cl hydrogen bonding, or an error.

Abstract.

The space groups of $[(\text{Mo}_2(\text{O}_2\text{CCH}_3)_4(\text{'linker'}))_n]$ are corrected from $\bar{P}1$ to $C2/m$, for ‘linker’ = pyrazine and 1,4-diazabicyclo[2.2.2]-octane (dabco), and from $\bar{P}1$ to $C2/c$ for ‘linker’ = 4,4'-bipyridine. Also $[(\text{tris}-(2\text{-pyridylmethyl})\text{amine})\text{BrV}(\text{?}-\text{O})\text{VBr}(\text{tris}-(2\text{-pyridylmethyl})\text{amine})\text{Br}\cdot\text{H}_2\text{O}]$ is corrected from $\bar{P}1$ to $C2/c$. These Laue group changes allow more reliable crystallochemical comparisons to be made among families of related structures. Space groups are corrected for 4-methyl-2,6-bis(4-methylbenzylidene)-cyclohexanone, 2,6-bis(4-dimethylaminobenzylidene)-cyclohexanone, $\text{K}[\text{Cr}(\text{tetra-methylenediamine-N,N,N',N'}\text{-tetraacetate.})]\cdot\text{H}_2\text{O}$, and $\{2(11,11\text{-dimethyl-3,4:8,9-dibenzo-bicyclo}[4.4.1]\text{undeca-3,8-diene})\text{--}(\text{tetracyanoethylene})\}$. The conflicting reports for $\text{Cu}(\text{H}_2\text{O})(\text{phenanthroline})_2(\text{X})_2$, where $\text{X} = \text{ClO}_4, \text{NO}_3, \text{BF}_4$ are resolved. Three related examples of open framework host-guest structures with space groups ‘ Cc or $C2/c$ ’ are discussed. Adding centers to 2,2'-Bi-1H-imidazolium dipicrate and $\{\text{tris}(2,2'\text{-bi-1H-imidazole})\text{ bis}(2\text{-}(2\text{-1H-imidazolyl})\text{-1H-imidazolium})\text{ bis}(\text{iodide})\}$ corrects discrepancies of up to 0.38 Å between chemically-similar hydrogen bond distances. Mis-identified atoms are corrected in $\text{?-(bis(ethylenedithio)tetrafulvalene)}_2$ ($\text{CsCd}(\text{SCN})_4$ and (purported) diaquadihydroxotetrakis(*m*-nitrobenzene-sulfonate)-discandium(III)). The reported difference between the crystal structure of $(\text{CH}_3\text{NH}_3)_4\text{YbCl}_7$ and those of the other members of this family of $(\text{CH}_3\text{NH}_3)_4\text{MX}_7$ ($\text{M} = \text{In, Fe, V}$; $\text{X} = \text{Cl, Br}$).structures is pointed out in the context of possibly-different N–H...Cl hydrogen bonding in the Yb structure.

Discussion of anomalous N...Cl distances given in CSD

The procedure was as follows: the $d(\text{N}\dots\text{Cl})$ values are those obtained from a CSD search in the range 2.701–2.900 Å i.e. these are values before any check or correction has been made (apart from CSD-inserted corrections). Then each ‘delinquent’ structure was examined in detail, and corrections made where possible, or comments added.

1. BAXVAX Beta angle acute (80.42°). “The structure consists of cations and chloride ions held together by two weak hydrogen bonds N–H...Cl- of 3.15 Å”. N present as $-\text{NH}_2^+-$.

We find the following short distances:

Cl1.....N1(65601) 2.811

Cl1.....N1(55601) 2.847

Cl1.....C4(65601) 2.985.

Comparison of CSD coordinates with those in the paper do not show any transcription errors. Perhaps Cl1 should have $y = 0.0$ instead of 0.1 (this parameter has to be fixed in P2(1); this gives $d(\text{N}\dots\text{Cl}) = 3.175$ Å.

2. CUGBUB We find the following short distances:

Cl1.....N1(56502) 2.868 Å.

$x(\text{Cl1})$ given incorrectly in CSD as 0.1341 instead of 0.1641. After correction, the (not anomalous) $d(\text{N}\dots\text{Cl})$ values given in the paper are reproduced.

3. DOWNAE 2.868

There is a later publication (DOWNAE01; 1986 instead of 1985) with shortest $d(\text{N}\dots\text{Cl}) = 3.019$ Å.

4. FOLJOF N3.....Cl2(46404) 2.200 Å, and other short distances.

The CSD incorrectly transcribed the space group as P21/n, while it is given as P21/c in the paper. The latter gives correct distances. There is another difference in that the CSD gives $a = 10.578$, $b = 10.747$, whereas these values are 10.548 and 10.474 in the paper. The CSD values are given as corrections and presumably should be accepted.

5. FOXTIV10 2.734, 2.795, 2.770

This is discussed in our paper; we do not have a clearcut explanation for these unusually short distances.

6. IQUINC 2.818

$R = 0.15$. Redetermination desirable as the paper

was published in 1965.

7. KEMWUU 2.775

Beta acute (81.28°).

Cl2, which is involved in the short distances, was reported with an occupancy factor of 0.5. Also, the two Cl’s were described as ‘atoms’ in the original paper, which cannot be correct. The melamine and cyanuric acid moieties were shown to be present as uncharged molecules. We suggest that there is one HCl and that the so-called half-occupied Cl(2) is actually a neutral water molecule, the arrangement .

presumably being $\text{H}_3\text{O}^+\cdot\text{Cl}^-$. This change brings about charge balance, which was not true of the original description. If these remarks are correct, then the distance of 2.775 Å is for an N–H...O hydrogen bond, and is normal. We plan repeat the refinement of this structure if we can obtain. F values.

8. NAGJIO 2.720 Cl's extensively disordered; Cc, Z = 8.. Further checking is not possible because this is a 'private communication'.

9. NOKGOJ 2.763, 2.766

"The position of the Cl(-) ion could not be ascertained unambiguously on account of it being disordered as was evident from the abnormally high isotropic temperature factor of this atom (Fig. 2)."

The Cl(-) ion was not inserted in Fig. 2; no numerical value for B(Cl-) is available.

It is possible that the disordered Cl- ion is actually a hydroxyl (cf. #7) but this cannot be tested as F's are not available..

10. POXRAV 2.878, also O...Cl given as 2.562, 2.323 Å.

The original paper has been seen. Some of the atoms with questionable distances have B_{equiv} values of 10–20 Å². Parts of this structure are reliably determined and other parts not. There are no obvious errors (e.g. wrong transcription of space group or coordinates) but the short distances cannot be considered as established. The onus is on the authors to confirm their unusual results.

11. TANDOB 2.704 Other short N...Cl distances are 2.19 and 2.70 Å. The reason is a CSD transcription error in z(Cl1) which should be –0.6135 and not –0.3165. After insertion of this correction, and of the other corrections noted by the CSD, the distances are found to be normal.

12. TOCQUX 2.701 Incorrectly entered in CSD as P2(1)/n. Isomorphous with YUDFUY. No problems remain after correction of CSD transcription error.

13. VISPAO After insertion of the corrections given by the CSD and use of the CSD coordinates, $d(\text{N4}(1655401)\dots\text{Cl2}) = 2.805$ and $d(\text{N4}(1656502)\dots\text{Cl5}) = 2.917$ Å, and $\angle\text{N4-C4-C5} = 83.2^\circ$. The value given in the paper is $113.4(2)^\circ$. There is some error in the coordinates of N(4) but we have not been able to identify this. The problem has been referred back to the CSD.

14. VOHDEB 2.788 Cl- to O4W* is 2.24 Å.

There is a CSD transcription error: x(Cl1) is –0.099616, not positive as given by the CSD. No problems after correction.

15. YUDFUY 2.720 Anomalies disappear after correction of space group from P2(1)/n (given incorrectly by CSD) to P2/n.