

Can Z , the number of formula units per unit cell, be a fraction? A report of the IUCr Commission on Crystallographic Nomenclature

Carolyn P. Brock*‡

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055, USA. *Correspondence e-mail: cpbrock@uky.edu

‡ This report was written in consultation with all members of the Commission on Crystallographic Nomenclature.

Keywords: Commission report; Z ; number of formula units in the unit cell.

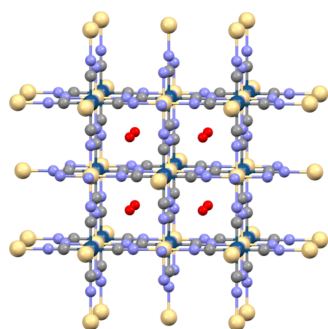
The IUCr Commission on Crystallographic Nomenclature (the CCN) has considered the question of whether fractional values of Z , the number of formula units in the unit cell, can be permitted. The consideration was initiated by a crystallographer who had determined a very unusual molecular structure, but the discussion was later broadened to cover all non-polymeric structures. Reliable structures having a fractional Z were located in the structural databases and in the literature, and were studied carefully. The CCN concluded that in some rare cases the Z value reported for a structure of a stoichiometric compound may be a fraction, but that that choice would have to be justified very carefully and convincingly. For solid solutions Z should be an integer.

The contents of the unit cell are given by the product of the chemical formula and Z , the number of formula units in the unit cell. Usually both Z and all the subscripts in the chemical formula unit are integers, but sometimes they are not. When the unit cell contains a non-integral number of one or more atoms (usually as a result of disorder and/or non-stoichiometry), the fractions are nearly always included in the specification of the formula unit so that Z remains integral. Both the CIF Dictionaries and the Online Dictionary of Crystallography currently describe Z as an integer.

There are, however, exceptions to that description in the published literature (including in the IUCr journal *Acta Crystallographica*), in the Cambridge Structural Database (the CSD; Groom *et al.*, 2016) and in the Inorganic Crystal Structure Database (the ICSD; Zagorac *et al.*, 2019). In mid-2024 a new molecular example was brought to the IUCr's Commission on Crystallographic Nomenclature (the CCN) by a crystallographer who had determined a structure for which he thought Z should be a fraction. The crystallographer, George Whitehead at the University of Manchester, asked that the definition of Z be changed to allow fractional values.

The commission webpage of the CCN (<https://www.iucr.org/resources/commissions/crystallographic-nomenclature>) says that 'Nomenclature problems arising in specific fields of crystallography that come to the attention of, and are recognized as important by, the Commission are studied by *ad hoc* committees of experts appointed by the Commission'. The definition of Z is of such wide significance that all members of the CCN were invited to participate in the discussion and vote; 60% of the voting members did so. The two CCN consultants and seven former members of the CCN also took part. Three additional experts were consulted.

The statutory members of the CCN are the Commission Chair, the Editors of the International Union of Crystal-



lography journals, the Editors of the volumes of *International Tables for Crystallography*, the Chair of the IUCr/OUN Book Series Committee, the Chair of the Teaching Commission, the Chair of the Committee for the Maintenance of the Crystallographic Information File Standard, and both the IUCr President and General Secretary. In 2025 the number of voting members is 52.

Whitehead's structure (Martínez-Crespo *et al.*, 2024) was added to the CSD in 2025 with the refcode XUJWOS. The structure (Fig. 1) is of a trimer that was well characterized by non-crystallographic methods. The trimers form columns along **a** in a space group of symmetry $P\bar{1}$. It happens that the $\text{CH}\cdots\text{HC}$ distance between trimers adjacent in a column is the same to less than 0.01 Å as the length of the intramolecular $\text{C}\equiv\text{C}\cdots\text{C}\equiv\text{C}$ link that connects monomers. That link is within 1° of being parallel to **a**. Assuming space is filled densely, the molecules must be ordered within a single column along **a**, but there is no reason that adjacent columns need be in register. As a result of the disorder, the length *a* determined from the 3D diffraction pattern is shorter by a factor of 3 than the translation in a 1D ordered column. The measured unit cell then contains $\frac{1}{3}$ each of two inversion-related trimers. If *Z* is required to be an integer, then the chemical formula must differ from the known molecular formula ($\text{C}_{88}\text{H}_{128}\text{N}_6\text{O}_9$) by a factor of $\frac{1}{3}$. The formula would have to be written as $\frac{1}{3}(\text{C}_{88}\text{H}_{128}\text{N}_6\text{O}_9)$ or $(\text{C}_{88}\text{H}_{128}\text{N}_6\text{O}_9)_{1/3}$ or $\text{C}_{88/3}\text{H}_{128/3}\text{N}_2\text{O}_3$. None of these follow IUPAC guidelines.¹

Consideration of the matter involved two steps. First, two expert crystallographers confirmed Whitehead's structure by re-refining it using the original data, which had been collected at 100 K with Cu $K\alpha$ radiation from a rotating-anode source. The resulting *R* factors, bond lengths and atomic ellipsoids are unremarkable. Reconstructed reciprocal-lattice slices supplied by Whitehead were scanned for signs of diffuse scattering and extra diffraction peaks but none was found. A crystallographer with expertise in diffuse scattering confirmed that it would be difficult to observe diffuse scattering in this structure, even if it were studied with neutrons.

One of the experts involved was certain that *Z* must always be integral; another was certain that for this structure a fractional *Z* is necessary. The important difference between the two viewpoints is the relative importance given to the chemical formula as determined by non-crystallographic methods and the formula obtained from the size of the unit cell as determined by diffraction methods. Summaries of their views, which they had approved, were forwarded to the CCN.

The second step was searching the CSD (version of November 2024) for non-polymeric structures in which *Z* is fractional. (Polymeric structures were excluded because they present special problems.) The search found 38 structures having archived coordinates, $R \leq 0.075$, and no error flag set.

¹ From section IR-4.2.1 of the IUPAC Red Book (IUPAC, 2005; https://iupac.org/wp-content/uploads/2016/07/Red_Book_2005.pdf). For stoichiometric compounds 'The empirical formula of a compound is formed by juxtaposition of the atomic symbols with appropriate (integer) subscripts to give the simplest possible formula expressing the composition'. See also sections IR-4.2.4, 11.1.2 and 11.6.1.

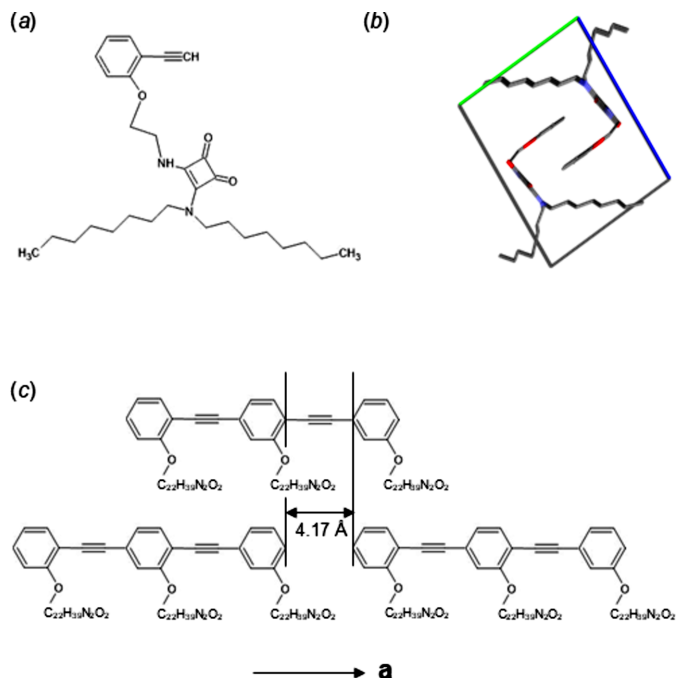


Figure 1

(a) Chemical line drawing of the XUJWOS monomer. (b) View along **a** of the $P\bar{1}$ structure of XUJWOS (Martínez-Crespo *et al.*, 2024). (c) Diagram showing the similarity of the length of a link between monomers and the $\text{C}\cdots\text{C}$ distance between trimers in a column along **a**.

In a few structures there were errors, but most fitted one of the three following categories:

(1) Columns of *n*-mers that are ordered in 1D but disordered in 3D because of the near equivalence of the intramolecular distances between monomers and the intermolecular distances between *n*-mers.

This category includes XUJWOS (Fig. 1) and the structures ITUWIF (Hasegawa *et al.*, 2016) and ITOFUV (and ITOFIJ, $R = 0.099$) (Teng *et al.*, 2021).

(2) Disorder at a single site of residues that cannot be distinguished crystallographically but are present in a fixed ratio.

A good example is the $P4/mcc$ structure (refcode BEGSUB; Martinsen *et al.*, 1982) of a triiodide salt of a Ni-tetra-benzoporphyrin (or NiTBP) cation that is disordered with its neutral molecule on a site of symmetry $4/m$. The 1:2 ratio of cations and neutral molecules (both $\text{C}_{36}\text{H}_{20}\text{N}_4\text{Ni}$) was determined by charge balance. Diffuse scattering was observed, but was attributed to disorder in the triiodide chains that extend along **c**. The diffuse scattering, which supports the identification of the anions as triiodide rather than iodide ions, had been investigated carefully in the case of the isostructural compound NIPHTI (Schramm *et al.*, 1980).

In the CSD BEGSUB is formulated as $[\text{Ni}(\text{TBP})^+](\text{I}_3^-) \cdot 2[\text{Ni}(\text{TBP})]$ with $Z = \frac{2}{3}$. The best alternatives with integral *Z* would be $(\frac{1}{3})[\text{Ni}(\text{TBP})^+](\text{I}_3^-) \cdot \frac{2}{3}\text{Ni}(\text{TBP})$ and $\text{Ni}(\text{TBP})\text{I}$, both with $Z = 2$, but the latter is uninformative and the former is unconventional. The IUPAC guidelines (IUPAC, 2005) for addition compounds (IR-4.2.4) specify that the chemical formulae of the components should be preceded by Arabic

numerals. The isostructural compound NIPHTI is, however, given in the CSD as $0.34[\text{Ni}(\text{Pc})^+]\cdot 0.34(\text{I}_3^-)\cdot 0.66[\text{Ni}(\text{Pc})]$, Pc = phthalocyanine, with $Z = 2$. In both papers the table of crystallographic data gives the empirical formula only and $Z = 2$.

In some of the structures in this category the ratio of occupancies was established not by charge balance but by steric considerations. The isostructural crystals of $[\text{M}(\text{en})_2]\cdot [\text{M}(\text{en})_2\text{X}_2](\text{ReO}_4)_4$, en = ethylenediamine, $M = \text{Pt}$, $X = \text{Cl}$ (SETSES), Br (SETSIW), I (SETSAO), and $M = \text{Pd}$, $X = \text{Br}$ (SETRUH) (Kumagai *et al.*, 2018) are good examples. Along **a** there are chains $X\text{--}M(\text{en})_2\text{--}X\cdots M(\text{en})_2\cdots X\text{--}M(\text{en})_2\text{--}X\cdots$ (Fig. 2); the chains must be ordered because there is not enough space for a contact $M(\text{en})_2\text{--}X\cdots X\text{--}M(\text{en})_2$ but there would be too much empty space in a contact $M(\text{en})_2\cdots M(\text{en})_2$. There is no evidence of correlation between adjacent chains.

(3) Avoidance of fractional coefficients for molecules or ions in stoichiometric compounds (*i.e.* compounds in which the relative atomic proportions can be expressed as ratios of integers).

Consider the very carefully written report of the closely related structures with refcodes REVS OA, REVS IU and REVS UG (Babian-Kibala *et al.*, 1996). The compounds in these structures were formulated as $[\text{Al}(\text{MeCN})_6]^{3+}\cdot [\text{MCl}_6]^{3-}\cdot 3(\text{MeCN})$, with $M = \text{Ta}$ ($P4/mbm$, $Z = \frac{2}{3}$), and $M = \text{Nb}$ and Sb (both $P4/mnc$, $Z = 4/3$). The cations lie on sites of symmetry $4/m$, the Ta anion lies on a site of symmetry mmm , and the Nb and Sb anions lie on sites of symmetry 222 . All atoms of the acetonitrile molecules lie either on a site of

symmetry 4 or of symmetry m . When the anion contains Nb or Sb the ratio of the multiplicities of the two ion sites is $2/4 = 1/2$, but the chemistry indicates the ratio must be $1/3$. Refinement with an Al^{3+} occupancy of $\frac{2}{3}$ and acetonitrile molecules that are end-for-end disordered when the Al^{3+} site is empty was successful. When the anion contains Ta the ratio of ion multiplicities is $4/4 = 1$ so that the occupancy factor of the Al^{3+} ions must be $\frac{1}{3}$.

If Z were required to be an integer then these structures would have to be written as $\frac{1}{3}[\text{Al}(\text{MeCN})_6]^{3+}\cdot [\text{MCl}_6]^{3-}\cdot 3(\text{MeCN})$ with $Z = 2$ for the Ta compound and $Z = 4$ for the Nb and Sb compounds.

These three structures are analogous to WUXLAE (Mullica *et al.*, 1996) in having partial, but stoichiometric, occupancy of an atom on a special position. The formula of WUXLAE is $[\text{Cd}^{2+}]_3[\text{Ir}(\text{CN})_6]^{3-}\cdot 12\text{H}_2\text{O}$, the space group is of symmetry $Fm\bar{3}m$, and the Ir and Cd atoms both lie on $m\bar{3}m$ sites. The occupancy of the Ir site must therefore be $\frac{2}{3}$. When the Ir atom is missing it and the six CN^- ions are each replaced by water molecules (Fig. 3). WUXLAE is isostructural with $[\text{M}^{2+}]_3\cdot [\text{Co}(\text{CN})_6]^{3-}\cdot 12\text{H}_2\text{O}$, $M = \text{Mn}$ and Cd (Beall *et al.*, 1977), with the Mn structure having been determined by single-crystal neutron diffraction. For the formula given, $Z = 4/3$. If Z were 1 the formula would be, *e.g.*, $[\text{Cd}^{2+}]_4[\text{Co}(\text{CN})_6]^{3-}\cdot 16\text{H}_2\text{O}$.

Some of the structures in this category are very complicated. A good example is the molecular double perovskite

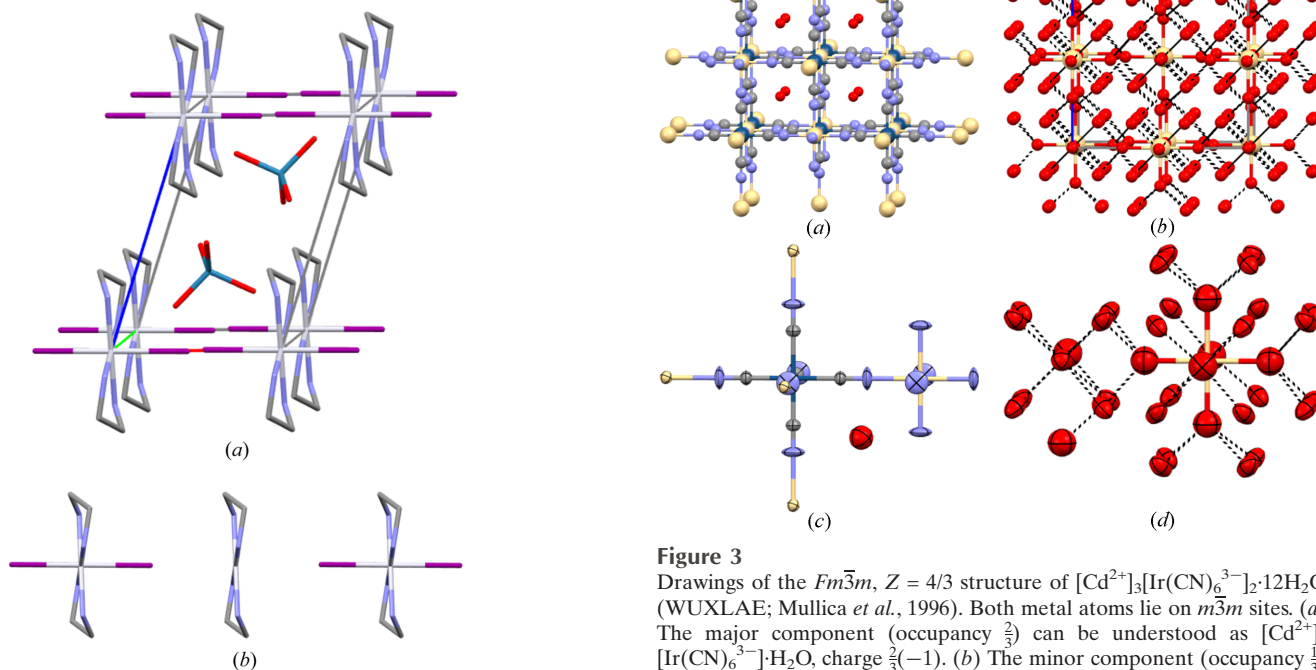


Figure 2
(a) Drawings of the $P\bar{1}$, $Z = \frac{1}{2}$, $Z' = \frac{1}{4}$ structure of $[\text{Pt}(\text{en})_2]^{2+}[\text{Pt}(\text{en})_2\text{I}_2]^{2-}(\text{ReO}_4)_4$, en = ethylenediamine (SETSAO; Kumagai *et al.*, 2018). The Pt^{II} and Pt^{IV} cations are 1:1 disordered at the origin. (b) The assumed alternation pattern of the two cations in a single column along **a**. No evidence of correlation between adjacent columns was reported.

Figure 3
Drawings of the $Fm\bar{3}m$, $Z = 4/3$ structure of $[\text{Cd}^{2+}]_3[\text{Ir}(\text{CN})_6]^{3-}\cdot 12\text{H}_2\text{O}$ (WUXLAE; Mullica *et al.*, 1996). Both metal atoms lie on $m\bar{3}m$ sites. (a) The major component (occupancy $\frac{2}{3}$) can be understood as $[\text{Cd}^{2+}]\cdot [\text{Ir}(\text{CN})_6]^{3-}\cdot \text{H}_2\text{O}$, charge $\frac{2}{3}(-1)$. (b) The minor component (occupancy $\frac{1}{3}$) can be understood as $[\text{Cd}(\text{OH}_2)_6]^{2+}\cdot 4\text{H}_2\text{O}$, charge $\frac{1}{3}(+2)$. There are then $\frac{2}{3}(1) + \frac{1}{3}(10) = \frac{1}{3}(12)$ H_2O molecules per Cd^{2+} ion and 12 for three Cd^{2+} ions. (c) The chemical units of the two components showing the atomic displacement ellipsoids. The one water molecule in the first component makes no hydrogen bonds; there is a strong hydrogen-bonding network in the second component. The cyanide ligands in the first component bridge the two metal atoms.

ULUYEI ($Pn\bar{3}$; Lee *et al.*, 2021). A fractional $Z = \frac{2}{3}$ again allows the coefficients in the chemical formula to be integral, which emphasizes that the compound is stoichiometric.

These seven examples are all stoichiometric salts in which an ion lying on a high-symmetry special position has a fractional occupancy factor that is determined by the chemical formula. No evidence of correlations of the disordered sites has been reported.

Structures of solid solutions of molecules and/or ions that can be distinguished crystallographically are sometimes reported with fractional Z values (*e.g.* refcode JUMTET). The coefficients of the components of a solid solution are normally determined by refinement of occupancy factors and are rarely ratios of simple integers. Furthermore, compositional variation between samples is expected. It therefore seems reasonable that those coefficients should be fractions that add to one, and that Z for solid solutions should be an integer.

After considering these structures the CCN voted on the following options: (A) Z must be an integer. (B) Z must be an integer except for a small number of defined exceptions. (C) A fractional value of Z can be allowed if the authors of the paper make a convincing case for it.

Thirty-one of the 52 statutory members of the CCN voted; 28 voted for option C and 3 for option B. Of the 9 other participants 8 preferred option C and 1 preferred option B. Option C was favored over B because of the possibility that situations would arise that the CCN had not foreseen.

While the CCN has voted to allow fractional Z values, it is anticipated that they will be rare and will have to be justified very carefully. Attempts to identify very weak diffraction peaks and to record diffuse scattering may be expected.

Acknowledgements

We thank H.-B. Bürgi, A. Linden and V. G. Young, Jr for their contributions to the discussion.

References

- Babian-Kibala, E., Chen, H., Cotton, F. A., Daniels, L. M., Falvello, L. R., Schmid, G. & Yao, Z. (1996). *Inorg. Chim. Acta* **250**, 359–364.
- Beall, G. W., Milligan, W. O., Korp, J. & Bernal, I. (1977). *Inorg. Chem.* **16**, 2715–2718.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Hasegawa, M., Nakamura, K.-I., Tokunaga, S., Baba, Y., Shiba, R., Shirahata, T., Mazaki, Y. & Misaki, Y. (2016). *Chem. Eur. J.* **22**, 10090–10101.
- IUPAC (2005). *Nomenclature of Inorganic Chemistry, IUPAC Recommendations 2005 (IUPAC Red Book)*. Cambridge: RSC Publishing.
- Kumagai, S., Takaishi, S., Gao, M., Iguchi, H., Breedlove, B. K. & Yamashita, M. (2018). *Inorg. Chem.* **57**, 3775–3781.
- Lee, J. Y., Ling, S., Argent, S. P., Senn, M. S., Cañadillas-Delgado, L. & Cliffe, M. J. (2021). *Chem. Sci.* **12**, 3516–3525.
- Martínez-Crespo, L., Whitehead, G. F. S., Vitorica-Yrezabal, I. J. & Webb, S. J. (2024). *Chem. Sci.* **15**, 17120–17127.
- Martinsen, J., Pace, L. J., Phillips, T. E., Hoffman, B. M. & Ibers, J. A. (1982). *J. Am. Chem. Soc.* **104**, 83–91.
- Mullica, D. F., Hayward, P. K. & Sappenfield, E. L. (1996). *Acta Cryst.* **C52**, 502–504.
- Schramm, C. J., Scaringe, R. P., Stojakovic, D. R., Hoffman, B. M., Ibers, J. A. & Marks, T. J. (1980). *J. Am. Chem. Soc.* **102**, 6702–6713.
- Teng, P., Zheng, M., Cerrato, D. C., Shi, Y., Zhou, M., Xue, S., Jiang, W., Wojtas, L., Ming, L.-J., Hu, Y. & Cai, J. (2021). *Commun. Chem.* **4**, 58.
- Zagorac, D., Müller, H., Ruehl, S., Zagorac, J. & Rehme, S. (2019). *J. Appl. Cryst.* **52**, 918–925.