A Metal-organic Framework with Paddle-wheel $Zn_2(CO_2)_4$ Secondary Building Units and Cubane-1,4-dicarboxylic Acid Linkers

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Abstract

A new crystal structure of catena-(bis((μ_4-cubane-1,4-dicarboxylato)-(N-methyl-2-pyrrolidone)-zinc(II)) N-methyl-2-pyrrolidone solvate) (**1**) was prepared by solvothermal method. The crystal structure of the compound was analyzed by single-crystal X-ray diffraction. It has a $P\bar{1}$ space group, with lattice parameters a = 10.7190(4) Å, b = 10.8245(5) Å, c = 10.8403(8) Å, α = 80.291(5)°, β = 70.0015(5)°, γ = 77.531(4)°, V = 1147.97(12) Å^3. The secondary building units of **1** consist of 2 central Zn ions, coordinated by 4 carboxylate groups in a bis-monodentate way, forming a square planar configuration of $Zn_2(CO_2)_4$, known as paddle-wheel units. The paddle-wheels are connected by cubane-1,4-dicarboxylic acid linkers at the edges, resulting in a two-dimensional coordination polymer with a square lattice (**sql**) underlying network topology. The axial sites of the zinc atoms are occupied by N-methyl-2-pyrrolidone molecules. In this new crystal structure the two-dimensional polymer planes are interstacked by weak dispersion bonds. The axial N-methyl-2-pyrrolidone solvent molecules determine the distances of planar polymer planes. The thermal properties of this new structure were studied by thermogravimetry/mass spectrometry in inert atmosphere. It was found, that the organic linkers in the framework structure do not decompose below 200 °C. The stochiometry of the activated compound is $Zn_2[C_8H_6(COO)_2]_2(C_5H_9NO)_2$, as determined by thermogravimetry in oxidative atmosphere.

Keywords

metal-organic frameworks, cubane, reticular chemistry, single-crystal X-ray diffraction, thermogravimetry/mass spectrometry

1 Introduction

Metal-organic frameworks are porous coordination polymers with crosslinks [1]. Multifunctional linkers, for example carboxylates can form strong covalent-like multidentate bonding with the metal centers, resulting in robust coordination polymer structures with high thermal stability [2, 3]. In the crystalline MOF structures, the rigid, metal-containing clusters, the so-called secondary building units (SBUs) at the vertices are interconnected by organic linkers. The most important metal-organic framework is MOF-5 [2], which builds up from $Zn_4O(CO_2)_6$ SBUs at the nodes and terephthalate linkers at the edges. Since the discovery of MOF-5 more than 20000 MOF structures were reported [3]. The combination of hundreds of SBUs and thousands of organic linkers led to discover of thousands of new MOF structures each year. Metal-organic-frameworks are typically microporous compounds with exceptional high porosity and surface area enabling many potential industrial applications, for example gas-storage, heterogeneous catalysis, molecular separation, molecular sensing or drug delivery. For a common description of the family of MOFs, Yaghi and coworkers introduced the principle of reticular chemistry based on the design of topology of framework structures [4]. For example, MOF-5 has $Zn_4O(CO_2)_6$ SBUs with six points of extension (carboxylate groups) and ditopic terephtalate linkers, so MOF-5 has a 6-c primitive cubic (**pcu**) underlying topology with

only one kind of edges (links). MOFs are highly modular structures: the organic linkers or the metallic centers can be changed without changing the underlying network topology, so the pore size, surface area and chemical reactivity of the materials can be fine-tuned. The so-called isoreticular structures are frameworks with the same underlying network topologies. The most important isoreticular series is the IRMOF-n (n=1-16) family [5], which is an isoreticular series to MOF-5 with **pcu** underlying network topology. The inorganic SBUs and the organic linkers determine the underlying topology of the periodic networks. Inorganic SBUs can be discrete objects or infinitive chains. Organic linkers (e.g. tritopic linkers) also can act as nodes (organic SBUs).

Paddle-wheel-like binuclear metal (Cu, Mo, Rh, Cr…) carboxylate complexes are well known for decades [6-8]. In these structures two metallic centers are connected by four bis-monodentate carboxylate bridges, forming a rigid, binuclear, paddle-wheel-like cluster structure. The axial coordination sites of the metals can be free or can be occupied by other ligands, for example solvents (water, DMF, THF…). Discrete monomer molecules, one-, two-, or three-dimensional MOF structures were also prepared with paddle-wheel $M_2(CO_2)_4$ units [9]. In the CSD database [10] 2567 hits were found with $M_2(CO_2)_4$ units[1]. Among these structures 722 polymer structures and 1845 discrete molecules were found. One of the earliest carboxylate-based metal-organic framework structures, MOF-2 [11] was the first metal-organic framework which was studied for gas-adsorption. MOF-2 is a two-dimensional, porous coordination polymer with paddle-wheel $Zn_2(CO_2)_4$ SBUs at the nodes and terephthalates at the edges. The axial sites of the two zinc atoms are occupied by water molecules. The adjacent polymer layers are inter-stacked by hydrogen-bonding of axial water molecules and the carboxylate oxygen atoms of the adjacent layers. MOF-2 has a two-dimensional square-lattice (**sql**) underlying network topology. The two-dimensional polymer planes can be bonded by replacing the axial terminating ligands (for example water) to bridge-ligands, for example 1,4-diaza-bicyclo[2.2.2]octane or 4,4'-bipyridine, forming three-dimensional framework structures [12].

The combination of paddle-wheel SBUs with organic SBUs led to the discovery of many important MOF structures with complicated multi-nodal topologies, for example

HKUST-1 [13] with excellent methane storing capacity, or NU-110 [14], the reported highest surface area material.

Many isoreticular structures were prepared to MOF-2 with $Zn_2(CO_2)_4$ nodes and aromatic, or non-aromatic dicarboxylic acids, for example 4,4'-biphenyl-dicarboxylate [15], naphthalene-2,6-dicarboxylate in MOF-105 [16], dihydro-benzocyclobutadiene-3,6-dicarboxylate (MOF-103) [16] or cubane-1,4-dicarboxylate (MOF-104) [16]. MOF-104 [16] has $Zn_2(CO_2)_4$ SBUs at the nodes and cubane-1,4-dicarboxylate linkers at the edges, similar to our new crystal structure (1). In MOF-104 the polymer planes are stacked by weak dispersion bonds. On the other hand, the solvents and the crystal structure of MOF-104 and **1** are different and the thermal properties of MOF-104 were not studied.

In this paper, we describe the preparation, structure and thermal stability of **1**, a new solvate of MOF-104 [16] with the same underlying topology and linkers, but different structure and different coordination of the solvent.

2 Experimental
2.1 Materials and methods
Cubane-1,4-dicarboxylic acid (Sigma Aldrich), zinc nitrate hexahydrate (Sigma Aldrich, purum p.a. ≥99.0 %), N-methyl-2-pyrrolidone (Sigma Aldrich) and acetone (VWR Chemicals, HiPerSolv CHROMANORM ≥99.8 %) were used as received for the synthetic work.

The solvothermal synthesis was performed in a PARR Teflon-lined high pressure vessel. Heat treatment was carried out in a Memmert UR30 electric oven.

2.2 Solvothermal synthesis
231.1 mg (0.779 mmol) zinc nitrate hexahydrate and 50.3 mg (0.262 mmol) cubane-1,4-dicarboxylic acid were stirred in 6.9 ml of N-methyl-2-pyrrolidone for 1 hour at room temperature under an argon atmosphere. After all the starting materials were dissolved, the reaction mixture was filtered by a 0.2 μm PTFE filter and the solution was annealed in a PTFE lined high pressure vessel at 105 °C for 30 hours. Irregular shaped single-crystals were formed with hundreds of microns edge lengths and the solution became yellowish. After sampling some crystals together with the mother liquor for single-crystal X-ray diffraction, the crystals were settled and washed by 2 x 10 ml NMP and 3 x 3 ml acetone and the sample was dried in vacuum. The yield of the dried sample was 65 milligrams (70 % of theoretical yield).

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1 ConQuest Version 1.20 (CSD Ver. 5.39) was used for structural search. The O-M-O bond angles in the $M_2(CO_2)_4$ units were limited to the range between 85° and 95°.

2.3 Single-crystal X-ray diffraction

The single-crystal X-ray diffraction measurements were carried out at room temperature by an Agilent Supernova diffractometer, equipped with dual microfocal source, Kappa goniometer and CCD detector.

The crystal structure was solved with OLEX2 [17] and SHELX [18] software.

The deconstruction of the crystal structure and the topology analysis of the underlying network were carried out with ToposPRO [19].

2.4 Thermogravimetry and thermogravimetry/mass spectrometry (TG/MS)

The TG/MS measurements were performed with a modified Perkin Elmer TGS-2 thermobalance coupled to a Hiden HAL 301/PIC2 quadrupole mass spectrometer. The TG/MS measurement for determining the heat stability was acomplished in an inert argon atmosphere using about 4 mg sample size and 10 °C min^{-1}. The thermogravimetry measurement for stoichiometry determination was carried out in dry synthetic air atmosphere using about 1 mg sample and 5 °C min^{-1} heating rate. Before the experiments, the thermobalance was purged by the carrier gas for 45 minutes.

3 Results and discussion
3.1 Crystal structure

The material has a $P\bar{1}$ space group and lattice parameters $a = 10.7190(4)$ Å, $b = 10.8245(5)$ Å, $c = 10.8403(8)$ Å, $\alpha = 80.291(5)°$, $\beta = 70.015(5)°$, $\gamma = 77.531(4)°$, $V = 1147.97(12)$ Å^3. Two zinc atoms are connected by four cubane-1,4-dicarboxylates in a bis-monodentate fashion. Zn1-Zn1 distances in the SBUs are 2.9484(6) Å. The carboxylate oxygen-zinc distances are 2.0340(19) Å (Zn1-O1), 2.0526(19) Å (Zn1-O2), 2.032(2) Å (Zn1-O3) and 2.039(2) Å (Zn1-O4). **1** is composed of two-dimensional polymer sheets with paddle-wheel Zn$_2$(CO$_2$)$_4$ SBUs at the vertices and cubane-1,4-dicarboxylate linkers at the edges (Fig. 1, and also see the supplementary cif file). Oxygen atoms of N-methyl-2-pyrrolidone (NMP) molecules are coordinated to the axial sites of pentacoordinated zinc atoms with 1.9804(19) Å Zn1-O5 distances, so the coordination of solvents is relatively strong. The planar polymer layers are interstacked by dispersion bonds (Fig. 2), the distance of adjacent layers is 9.91 Å. Ordered and disordered solvent molecules (NMP) are also stacked in the voids of MOF structure by weak dispersion bonds. The disordered solvent content was modeled with a superposition of 2 NMP molecules that were also doubled by inversion symmetry.
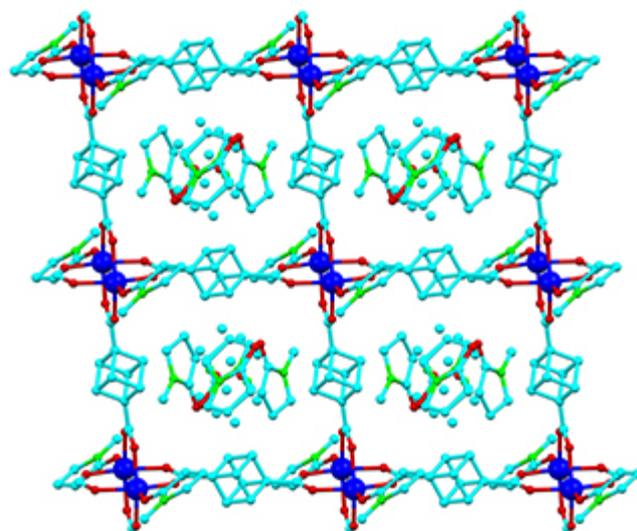

Fig. 1 Crystal structure of **1**, view down crystallographic *a* axis. H atoms are omitted for clarity. Blue: Zn, red: O, green:N, cyan: C.
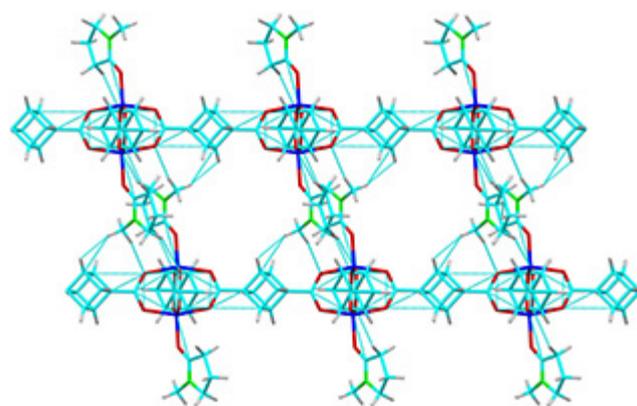

Fig. 2 Intermolecular stacking of adjacent polymer layers. The weakly bonded solvents in the voids are omitted for clarity. View down crystallographic *c* axis. Blue: Zn, red: O, green:N, cyan: C, white:H.

According to topology analysis, **1** has an uninodal, 4-c square lattice (**sql**) underlying network topology. The compound is isoreticular to MOF-2, furthermore **1** has the same topology and linkers (cubane-1,4-dicarboxylate), as that of MOF-104.

The comparison of the three isoreticular structures **1**, MOF-2 and MOF-104 is summarized in Table 1. The crystal structures have different space groups, but all of them have the same Zn$_2$(CO$_2$)$_4$ SBUs with similar Zn-Zn and carboxylate O-Zn distances and **sql** underlying network topologies. MOF-2 has aromatic terephthalate linkers, while MOF-104 and **1** have the same alicyclic cubane-1,4-dicarboxylate linkers. The isoreticular compounds have different axial ligands: NMP in **1**, water in MOF-2 and DMF in MOF-104. The distances of the polymer sheets in the three materials are also different, the
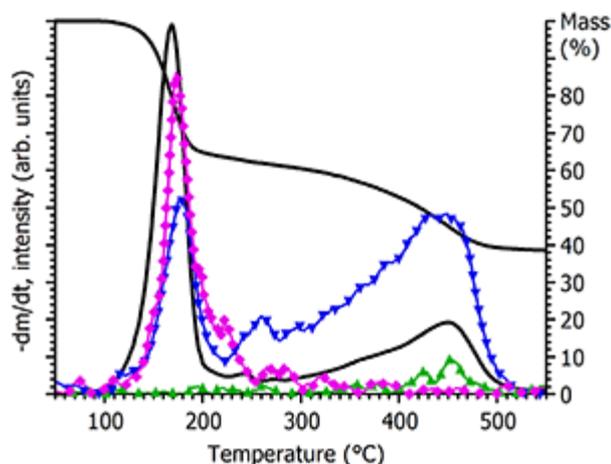
Table 1 Comparison of 1, MOF-2 [10], and MOF-104 [12]

	1	MOF-2	MOF-104
space group	$P\bar{1}$	P2$_1$/n	C2/m
underlying topology	sql	sql	sql
SBU	Zn$_2$(CO$_2$)$_4$	Zn$_2$(CO$_2$)$_4$	Zn$_2$(CO$_2$)$_4$
linker	cubane-1,4-dicarboxylate	terephthalate	cubane-1,4-dicarboxylate
distance of polymer planes	9.91 Å	5.28 Å	10.00 Å
axial sites	NMP	water	DMF
stacking of planes	dispersion	H-bond	dispersion
Zn-Zn distances in SBUs	2.9484(6) Å	2.941(2) Å	2.919(2) Å
Zn-carboxylate O distances	2.0340(19) Å 2.0526(19) Å 2.032(2) Å 2.039(2) Å	2.013(5) Å 2.024(5) Å 2.056(5) Å 2.067(4) Å	2.040(5) Å 2.018(4) Å

interactions of adjacent layers are directed by the axial ligands. Similarly to MOF-104, the planar polymer planes are stacked by dispersion bonds in **1**, while in MOF-2 the planar polymer layers are stacked by H-bonds.

3.2 TG and TG/MS measurements

The heating of the sample in inert atmosphere results in mass loss in two distinct steps. In the first step between 100 °C and 200 °C the release of solvent (NMP), while in the second step between 200 °C and 500 °C the products of cubane-1,4-dicarboxylic acid decomposition (benzene, carbon-dioxide) were detected by mass-spectrometry (Fig. 3), so the framework structure is stable up to 200 °C. The TG/MS measurement in argon atmosphere results in

the formation of zinc oxide and amorphous carbon as end products, so the stoichiometry of the compound can not be determined this way.
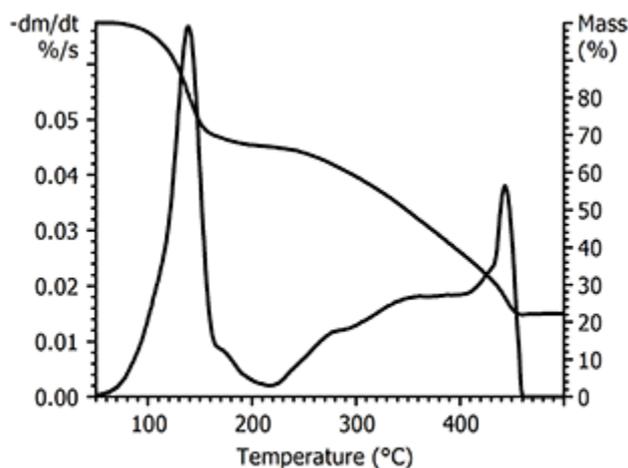
A TG measurement was carried out in an oxidative, synthetic air atmosphere (Fig. 4) to burn out the amorphous carbon and leave only zinc oxide as end product. This way the stoichiometry of the compound can be determined from the mass loss caused by the release of solvent and from the mass of ZnO residue. According to the oxidative TG measurement, the stoichiometry of **1** is Zn$_2$(C$_8$H$_6$(COO)$_2$)$_2$(C$_5$H$_9$NO)$_2$, so only the two axial NMP molecules were present.

4 Conclusion

A new solvate of MOF-104 was prepared by solvothermal method. In the new crystal structure (**1**), binuclear Zn$_2$(CO$_2$)$_4$ paddle-wheel secondary building units are interconnected by cubane-1,4-dicarboxylate linkers, resulting in a 2-dimensional coordination polymer structure with square lattice (**sql**) underlying topology. The axial sites of zinc atoms are occupied by NMP molecules. The adjacent polymer layers are interstacked by dispersion bonds and the distances of the layers are directed by the axial solvent molecules. According to TG/MS measurement, the MOF is stable up to 200 °C. The activated material has a stoichiometry of Zn$_2$[C$_8$H$_6$(COO$_2$)]$_2$(C$_5$H$_9$NO)$_2$, as determined by thermogravimetry.

Acknowledgement

Fig. 3 TG/MS measurement in argon atmosphere. Solid lines: TG and DTG curves. MS ions: -◆-, NMP (*m/z* 99); -▼-, CO$_2$ and NMP fragment (*m/z* 44); -▲-, benzene (*m/z* 78).

Fig. 4 TG and DTG curves in dry air atmosphere.

References

[1] Batten, S. R., Champness, N. R., Chen, X.-M., Garcia-Martinez, J., Kitagawa, S., Öhrström, L., O'Keeffe, M., Suh, M. P., Reedijk, J. "Coordination polymers, metal-organic frameworks and the need for terminology guidelines", CrystEngComm, 14, pp. 3001–3004, 2012.
https://doi.org/10.1039/C2CE06488J

[2] Li, H., Eddaoudi, M., O'Keeffe, M., Yaghi, O. M. "Design and synthesis of an exceptional stable and highly porous metal-organic framework", Nature, 402, pp. 276–279, 1999.
https://doi.org/10.1038/46248

[3] Furukawa, H., Cordowa, K. E., O'Keeffe, M., Yaghi, O. M. "The Chemistry and Application of Metal-Organic Frameworks", Science, 341 (6149), pp. 974–986, 2013.
https://doi.org/10.1126/science.1230444

[4] Li, M., Li, D., O'Keeffe, M., Yaghi, O. M. "Topological Analysis of Metal-Organic Frameworks with Polytopic Linkers and/or Multiple Building Units and the Minimal Transitivity Principle", Chemical Reviews, 114(2), pp. 1343–1370, 2014.
https://doi.org/10.1021/cr400392k

[5] Eddaoudi, M., Kim, J., Rosi, N., Vodak, D., Wachter, J., O'Keeffe, M., Yaghi, O. M. "Systematic Design of Pore Size and Functionality in Isoreticular MOFs and Their Application in Methane Storage", Science, 295(5554), pp. 469–472, 2002.
https://doi.org/10.1126/science.1067208

[6] van Niekerg, J. N., Schoenig, F. R. L. "A New Type of Copper Complex as found in the Crystal Structure of Cupric Acetate, $Cu_2(CH_3COO)_4 \cdot 2H_2O$", Acta Crystallographica, 6, pp. 227–232, 1953.
https://doi.org/10.1107/S0365110X53000715

[7] Lawton, D., Mason, R. "The Molecular Structure of Molybdenum(II) Acetate", Journal of the American Chemical Society, 87(4), pp. 921–922, 1965.
https://doi.org/10.1021/ja01082a046

[8] Cotton, F. A., DeBoer, B. G., LaPrade, M. D., Pipal, J. R., Ucko, D. A. "The Crystal and Molecular Structure of Dichromium Tetra-acetate Dihydrate and Dirodium Tetra-acetate Dihydrate", Acta Crystallographica, B27, pp. 1664–1671, 1971.
https://doi.org/10.1107/S0567740871004527

[9] Köberl, M., Cokoja, M., Herrmann, W. A., Kühn, F. E. "From molecules to materials: Molecular paddle-wheel synthons of macromolecules, cage compounds and metal-organic frameworks", Dalton Transactions, 40(26), pp. 6834–6859, 2011.
https://doi.org/10.1039/C0DT01722A

[10] Groom, C. R., Bruno, I. J., Lightfoot, M. P., Ward, S. C. "The Cambridge Structural Database", Acta Crystallographica, B72, pp. 171–179, 2016.
https://doi.org/10.1107/S2052520616003954

[11] Li, H., Eddaoudi, M., Groy, T. L., Yaghi, O. M. "Establishing Microporosity in Open Metal−Organic Frameworks: Gas Sorption Isotherms for Zn(BDC) (BDC = 1,4-Benzenedicarboxylate)", Journal of the American Chemical Society, 120(33), pp. 8571–8572, 1998.
https://doi.org/10.1021/ja981669x

[12] Chun, H., Dybtsev, D. N., Kim, H., Kim, K. "Synthesis, X-ray Crystal Structures, and Gas Sorption Properties of Pillared Square Grid Nets Based on Paddle-Wheel Motifs: Implications for Hydrogen Storage in Porous Materials", Chemistry A European Journal, 11(12), pp. 3521–3529, 2005.
https://doi.org/10.1002/chem.200401201

[13] Chui, S. S.-Y., Lo, S. M.-F., Charmant, J. P. H., Orpen, A. G., Williams, I. D. "A Chemically Functionalizable Nanoporous Material $[Cu_3(TMA)_2(H2O)_3]_n$", Science, 283(5405), pp. 1148–1150, 1999.
https://doi.org/10.1126/science.283.5405.1148

[14] Farha, O. K., Eryazici, I., Jeong, N. C., Hauser, B. G., Wilmer, C. E., Sarjeant, A. A., Snurr, R. Q., Nguyen, S. T., Yazaydın, A. Ö. and Hupp, J. T. "Metal–Organic Framework Materials with Ultrahigh Surface Areas: Is the Sky the Limit?", Journal of the American Chemical Society, 134(36), pp.15016–15021, 2012.
https://doi.org/10.1021/ja3055639

[15] Tao, J., Yin, X., Huang, R., Zheng, L., Ng, S. W. "Assembly of a microporous metal-organic framework [Zn(bpdc)(DMSO)] (bpdc=4,4′-biphenyldicarboxylate) based on paddle-wheel units affording guest inclusion", Inorganic Chemistry Communications, 5(11), pp. 975–977, 2002.
https://doi.org/10.1016/S1387-7003(02)00623-8

[16] Eddaoudi, M., Kim, J., Vodak, D., Sudik, A., Wachter, J., O'Keeffe, M., Yaghi, O. M. "Geometric requirements and examples of important structures in the assembly of square building blocks", PNAS, 99(8), pp. 4900–4904, 2002.
https://doi.org/10.1073/pnas.082051899

[17] Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K., Puschmann, H. "OLEX2: a Complete Structure Solution, Refinement and Analysis Program", Journal of Applied Crystallography, 42, pp. 339–341, 2009.
https://doi.org/10.1107/S0021889808042726

[18] Sheldrick, G. M. "A Short Hystory of SHELX", Acta Crystallographica, A64(Pt 1), pp. 112–122, 2008.
https://doi.org/10.1107/S0108767307043930

[19] Blatov, V. A., Shevchenko, A. P., Proserpio, D. M. "Applied Topological Analysis of Crystal Structures with the Program Package ToposPro", Crystal Growth and Design, 14(7), pp. 3576–3586, 2014.
https://doi.org/10.1021/cg500498k