Acta Cryst E
CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

# Crystal structures of dimetal terephthalate dihydroxides, $M_2(C_8H_4O_4)(OH)_2$ ($M$ = Co, Ni, Zn) from powder diffraction data and DFT calculations

**Emma L. Markun, Drew A. Jensen, Joshua D. Vegetabile and James A. Kaduk***

Department of Chemistry, North Central College, 131 S. Loomis, St., Naperville IL, 60540 , USA. *Correspondence e-mail: kaduk@polycrystallography.com

Received 6 May 2022
Accepted 10 May 2022

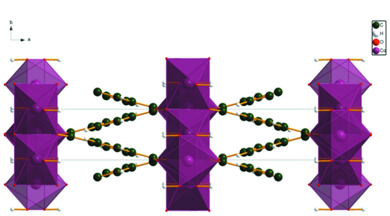
Edited by W. T. A. Harrison, University of Aberdeen, Scotland

**Keywords:** powder diffraction; density functional theory; terephthalate; hydroxide; cobalt; nickel; zinc.

**CCDC references**: 2171929; 2171928; 2171927; 2171926; 2171925; 2171924

**Supporting information**: this article has supporting information at journals.iucr.org/e

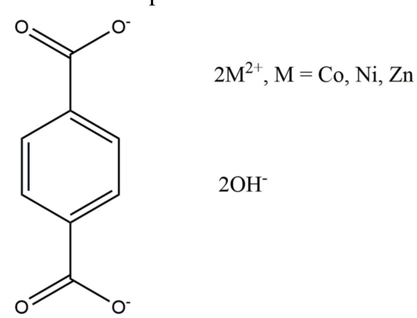
The crystal structure of poly[dihydroxido($\mu_6$-terepthalato)dizinc], $[Zn_2(C_8H_4O_4)(OH)_2]_n$, was solved and refined using synchrotron powder data, and the structures of the isostructural Co and Ni analogues were refined using laboratory powder X-ray data. The structure of $[Co_2(C_8H_4O_4)(OH)_2]_n$ has been reported previously in space group $C2/m$, which yields disordered terephthalate anions. Doubling the $c$-axis of that cell results in an ordered model in space group $C2/c$. The octahedral $M$O$_6$ coordination polyhedra of the metal cations share edges, forming chains running parallel to the $b$-axis direction. These chains share corners (hydroxyl groups), forming layers lying perpendicular to the $a$-axis direction.





## 1. Chemical context

Dicobalt terephthalate dihydroxide, $Co_2(C_8H_4O_4)(OH)_2$, was first prepared by Sherif (1970). A powder pattern was reported, but no unit cell or crystal structure were determined. The powder pattern from this reference is included in the Powder Diffraction File (Gates-Rector & Blanton, 2019) as entry 00-034-1897. A search of the nine peaks of this entry against the PDF-4 Organics 2022 database yielded no additional terephthalate compounds.




Approximately 20 years ago, one of us (JAK) solved and refined the structure of $Zn_2(C_8H_4O_4)(OH)_2$ using synchrotron powder data, first in a $C2/m$ cell with disordered terephthalate anions. It then became apparent that if the $c$-axis were doubled, the systematic absences corresponded to space group $C2/c$. This doubled unit cell removed the disorder and yielded a more satisfactory refinement. This structure was deposited in the Cambridge Structural Database (Kaduk, 2016; refcode PUCYAO01), but never otherwise published or discussed. Since that time, another polymorph of $Zn_2(C_8H_4O_4)(OH)_2$ (in space group $P2_1/c$) has been reported (Carton *et al.*, 2009; PUCYAO).

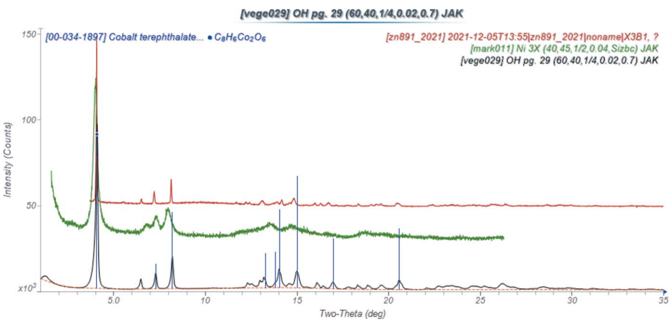



**Figure 1**
The X-ray powder diffraction patterns of $Co_2(C_8H_4O_4)(OH)_2$ (black), $Ni_2(C_8H_4O_4)(OH)_2$ (green), and $Zn_2(C_8H_4O_4)(OH)_2$ (red). The Zn pattern (measured using Co radiation) and the Zn pattern (measured using synchrotron radiation) were converted to the Mo wavelength used to measure the Co pattern using *JADE Pro* (MDI, 2021).

Some of our recent attempts to prepare Co and Ni porous metal–organic frameworks (MOFs) yielded instead cobalt and nickel terephthalate hydroxide. We took advantage of the opportunity to re-refine the structures (as well as that of Zn) in what we believe to be the correct space group, and to optimize the structures using density functional techniques.

## 2. Structural commentary

Doubling the *c*-axis of the previously reported disordered *C*2/*m* model for Co results in a chemically-reasonable ordered *C*2/*c* structure for these compounds. The X-ray powder diffraction patterns show that the three compounds are isostructural (Fig. 1). The root-mean-square Cartesian displacements of the non-H atoms in the Rietveld-refined and DFT-optimized structures are 0.125, 0.143, and 0.339 Å for Co, Ni, and Zn, respectively (Figs. 2–4). The good agreement provides strong evidence that the structures are correct (van de Streek & Neumann, 2014). This discussion concentrates on the DFT-optimized structures. The asymmetric unit (with atom numbering) is illustrated in Fig. 5. The best view of the crystal structure is down the *b*-axis (Fig. 6). A view down the *c*-axis is shown in Fig. 7.

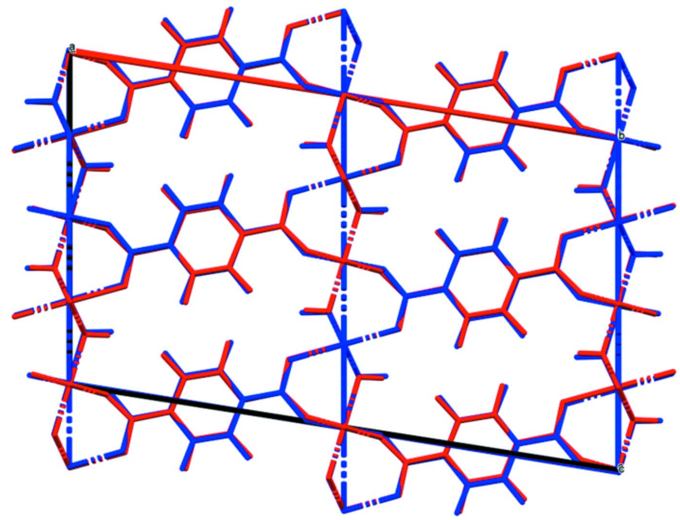


**Figure 3**
Comparison of the Rietveld-refined (red) and VASP-optimized (blue) structures of $Ni_2(C_8H_4O_4)(OH)_2$. The r.m.s. Cartesian displacement is 0.143 Å.

Almost all of the bond distances, angles, and torsion angles in the terephthalate anions fall within the normal ranges indicated by a *Mercury* Mogul Geometry check (Macrae *et al.*, 2020). Only the Ni9—O11 bond distance of 2.187 Å [average = 2.007 (9) Å, *Z*-score = 20.4] and the Zn14—O16 bond of 1.970 Å [average = 2.122 (47) Å, *Z*-score = 3.2] are flagged as unusual. The carboxyl–phenyl torsion angles of 7.5, 9.8, and 6.2° for Co, Ni, and Zn, respectively, correspond to a distortion energy of only ~2 kJ mol$^{-1}$ (Kaduk *et al.*, 1999). This energy penalty can easily be compensated for by coordination to the

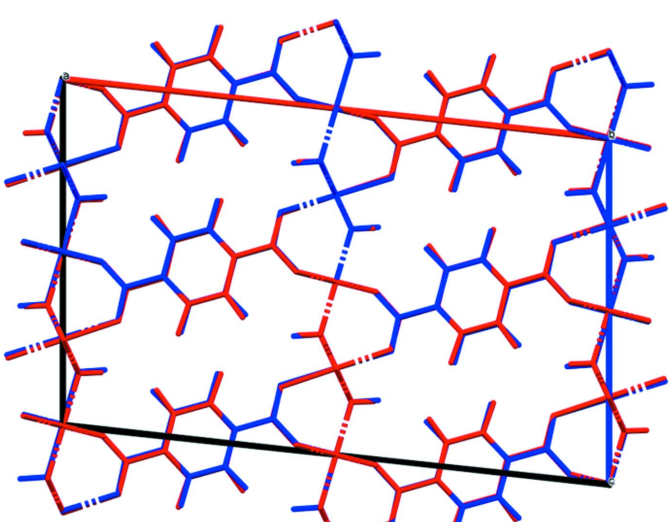


**Figure 2**
Comparison of the Rietveld-refined (red) and VASP-optimized (blue) structures of $Co_2(C_8H_4O_4)(OH)_2$. The r.m.s. Cartesian displacement is 0.125 Å.

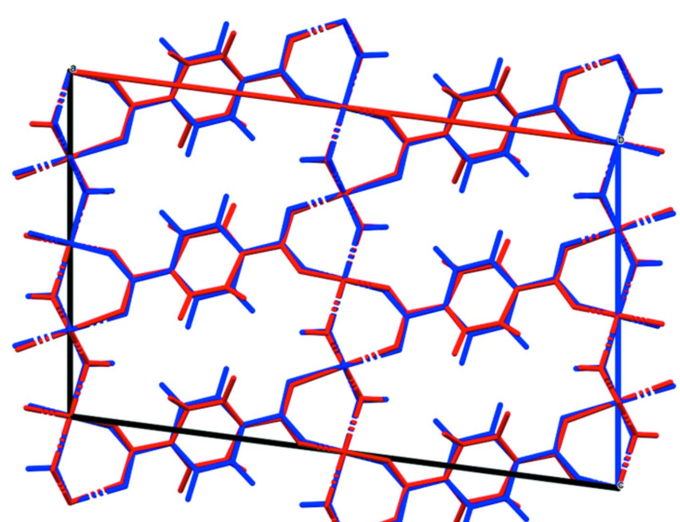


**Figure 4**
Comparison of the Rietveld-refined (red) and VASP-optimized (blue) structures of $Zn_2(C_8H_4O_4)(OH)_2$. The r.m.s. Cartesian displacement is 0.339 Å.

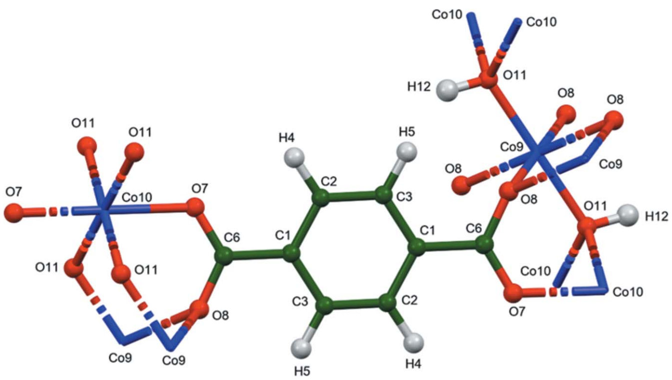



Figure 5
The asymmetric unit of $Co_2(C_8H_4O_4)(OH)_2$, with the atom numbering. The atoms are represented by 50% probability spheroids.

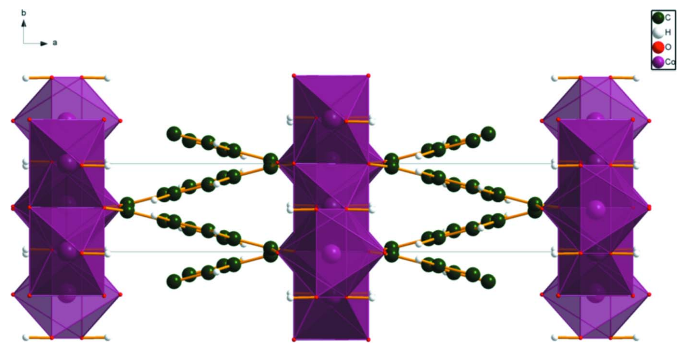



Figure 7
The crystal structure of $Co_2(C_8H_4O_4)(OH)_2$, viewed down the *c*-axis direction.

cations. The closest Miller plane of the phenyl ring is $(85\overline{1})$ for Co and Ni, and (530) for Zn. *M*9 lies on a center of symmetry, and *M*10 lies on a twofold axis. For M = Co, Co9 has two shorter Co—O distances of 2.000 Å, and four longer ones ~2.19–2.20 Å. Co10 has four distances ~2.11 Å, and two at 2.157 Å. For *M* = Ni, all six distances to Ni9 are 2.187–2.232 Å, and Ni10 has four shorter distances at 2.03–2.08 Å and two longer at 2.115 Å. For *M* = Zn, Zn9 has two short distances of 1.969 Å, and four long ones at ~2.22 Å whereas Zn10 has two distances of 2.095 Å and four at 2.14–2.18 Å. Both Co9 and Co10 exhibit octahedral coordination. The coordination sphere of Co9 contains two *trans* O7 and four equatorial O11 (hydroxyl group), while Co10 has two *trans* O11 and four equatorial O8. The hydroxyl group bridges three cobalt atoms: one Co9 and two Co10. Atom O7 coordinates to Co10, and O8 bridges two Co9 atoms; as a result each carboxyl group bridges three metal atoms. The bond-valence sums (Brown, 2002) are 1.90 and 1.84 for Co9 and Co10, respectively, 1.78 and 1.93 for Ni9 and Ni10, and 1.92 and 1.86 for Zn9 and Zn10. All cations are thus slightly under-bonded compared to their expected values of 2.00.

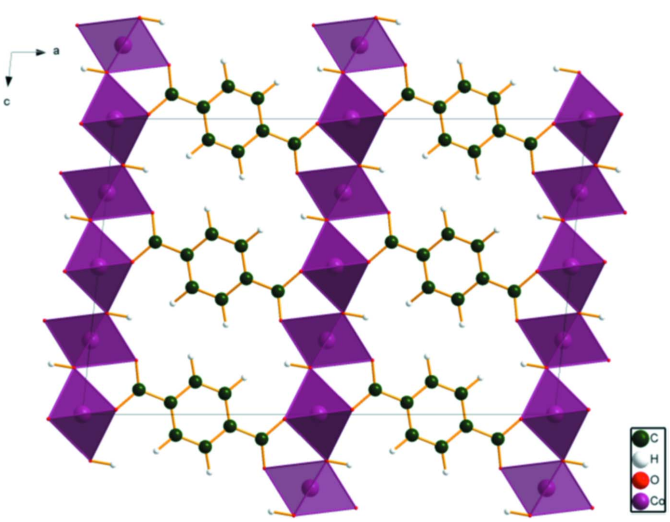



Figure 6
The crystal structure of $Co_2(C_8H_4O_4)(OH)_2$, viewed down the *b*-axis direction.

The peak profiles are dominated by microstrain broadening. The generalized microstrain model was used for Co and Zn, but the limited Ni data supported refinement of only an isotropic broadening coefficient. The average microstrain is similar for Co and Zn (21042 and 20094 ppm, respectively), while that for Ni is much larger, at 114830 ppm. Perhaps this greater microstrain indicates that some square-planar Ni coordination also occurs. Analysis of the contributions to the total crystal energy of the structure using the Forcite module of *Materials Studio* (Dassault Systèmes, 2021) suggests that for Co and Ni, the bond and angle distortion terms dominate intramolecular deformation energy, but that torsion terms are also significant. For Zn, the angle distortion terms dominate the intramolecular deformation energy. The intermolecular energy in all three compounds is dominated by electrostatic attractions, which represent the *M*—O bonds.

The Bravais–Friedel–Donnay–Harker (Bravais, 1866; Friedel, 1907; Donnay & Harker, 1937) morphology suggests

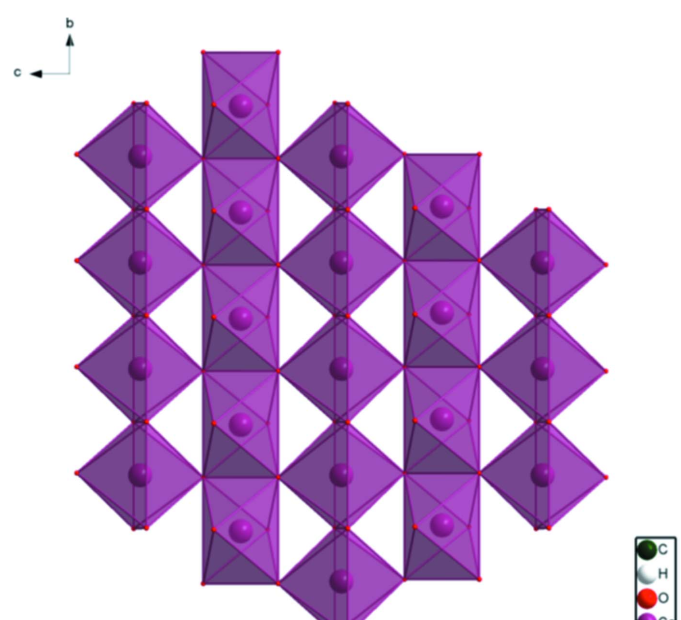



Figure 8
The layers in the crystal structure of $Co_2(C_8H_4O_4)(OH)_2$, viewed down the *a*-axis direction.

**Table 1**
Experimental details.

| | $[Co_2(C_8H_4O_4)(OH)_2]$ | $[Ni_2(C_8H_4O_4)(OH)_2]$ | $[Zn_2(C_8H_4O_4)(OH)_2]$ |
|---|---|---|---|
| Crystal data | | | |
| $M_r$ | 316 | 315.53 | 328.89 |
| Crystal system, space group | Monoclinic, *C*2/*c* | Monoclinic, *C*2/*c* | Monoclinic, *C*2/*c* |
| Temperature (K) | 300 | 300 | 300 |
| *a*, *b*, *c* (Å) | 19.9554 (10), 3.2883 (2), 12.6139 (8) | 20.35 (5), 3.364 (6), 12.19 (4) | 20.165 (2), 3.3273 (5), 12.5956 (16) |
| $\beta$ (°) | 96.059 (5) | 98.9 (2) | 97.431 (10) |
| $V$ (Å$^3$) | 823.08 (6) | 824.6 (15) | 837.99 (14) |
| $Z$ | 4 | 4 | 4 |
| Radiation type | Mo $K\alpha_{1,2}$, $\lambda$ = 0.70932, 0.71361 Å | Co $K\alpha_{1,2}$, $\lambda$ = 1.78892, 1.79278 Å | Synchrotron, $\lambda$ = 1.15008 Å |
| Specimen shape, size (mm) | Cylinder, 12 × 0.7 | Flat sheet, 16 × 16 | Cylinder, ? × ? |
| Data collection | | | |
| Diffractometer | PANalytical Empyrean | PANalytical X'Pert | NSLS beamline X3B1 |
| Specimen mounting | Glass capillary | Si zero-background plate with well | Kapton capillary |
| Data collection mode | Transmission | Reflection | Transmission |
| Scan method | Step | Step | Step |
| $2\theta$ values (°) | $2\theta_{min}$ = 1.002, $2\theta_{max}$ = 49.991, $2\theta_{step}$ = 0.008 | $2\theta_{min}$ = 4.007, $2\theta_{max}$ = 69.983, $2\theta_{step}$ = 0.017 | $2\theta_{min}$ = 6.0, $2\theta_{max}$ = 60.0, $2\theta_{step}$ = 0.01 |
| Refinement | | | |
| *R* factors and goodness of fit | $R_p$ = 0.045, $R_{wp}$ = 0.063, $R_{exp}$ = 0.020, $R(F^2)$ = 0.05751, $\chi^2$ = 10.414 | $R_p$ = 0.084, $R_{wp}$ = 0.107, $R_{exp}$ = 0.070, $R(F^2)$ = 0.14454, $\chi^2$ = 2.369 | $R_p$ = 0.092, $R_{wp}$ = 0.121, $R_{exp}$ = 0.097, $R(F^2)$ = 0.14121, $\chi^2$ = 1.573 |
| No. of parameters | 42 | 12 | 57 |
| No. of restraints | 15 | 0 | 14 |
| $(\Delta/\sigma)_{max}$ | 0.025 | 97.398 | 1.459 |

The same symmetry and lattice parameters were used for the DFT calculations as for each powder diffraction study. Computer programs: *GSAS-II* (Toby & Von Dreele, 2013), *Mercury* (Macrae *et al.*, 2020), *DIAMOND* (Crystal Impact, 2015), and *publCIF* (Westrip, 2010).

that we might expect elongated (with [010] as the long axis) or platy (with {200} as the major faces) morphology for these compounds. A 2nd order spherical harmonic model was included in the refinement. The texture indices were 1.003, 1.417, and 1.016 for Co, Ni, and Zn respectively, showing that preferred orientation was significant only for the flat-plate Ni specimen.

## 3. Supramolecular features

The octahedral coordination spheres of Co9 share edges, forming chains running parallel to the *b*-axis direction; the shared edges are parallel the *a*-axis direction. The octahedral coordination spheres of Co10 share edges, forming chains propagating along the *b*-axis; in this case, the shared edges lie parallel to the *c*-axis direction. Co9 and Co10 share corners (*via* O11 = the hydroxyl group), forming layers lying perpendicular to the *a*-axis direction (Fig. 8). The hydroxyl group does not participate in hydrogen bonds.

## 4. Database survey

The crystal structure of the 'new terephthalate-based cobalt hydroxide $Co_2(OH)_2(C_8H_4O_4)$' was reported by Huang *et al.* (2000), and its crystal structure determined [Cambridge Structural Database (Groom *et al.*, 2016) refcode QASLIF] by *ab initio* methods using X-ray powder diffraction data. The reported space group is *C*2/*m* with *a* = 19.943 (1), *b* = 3.2895 (1), *c* = 6.2896 (3) Å, $\beta$ = 95.746 (3)°, *V* = 410.545 Å$^3$, and *Z* = 2. The structure consists of alternating Co-hydroxide and terephthalate layers, and the terephthalate anions are disordered about an inversion center. Antiferromagnetic ordering in this compound was studied using neutron powder diffraction by Feyerherm *et al.* (2003), using the same unit cell (QASLIF02). The structure was also determined by Kurmoo *et al.* (2001; QASLIF01) in the same unit cell, as well as the structure of cobalt terephthalate dihydrate. The structures of a series of $(Co,Fe)_2(C_8H_4O_4)(OH)_2$ solid solutions were refined in the same unit cell by Mesbah *et al.* (2010) (UJIMOQ, UJIMOQ01, UJINAD, UJINAD01) using synchrotron and neutron powder data. A reduced cell search in the Cambridge Structural Database yielded in addition the structures of $Ni_2(C_8H_4O_4)(OH)_2$ (Mesbah *et al.*, 2014, NIWQOB; Han *et al.*, 2018, NIWQOB01).

## 5. Synthesis and crystallization

Cobalt(II) nitrate hexahydrate (0.0364 g, 0.125 mmol) and terephthalic acid (0.0208 g, 0.125 mmol) were added to a flask followed by 0.125 ml of triethylamine and approximately 5 ml of dimethylformamide. The reaction was stirred for 10 min until a homogenous mixture was obtained. The reaction was heated using a CEM Discover microwave with power set to 150 W using a ramp time of 2 min to reach 423 K with a hold time of 30 min and internal stirring switched off. The vial remained in the microwave until it cooled to 323 K, and the reaction mixture was filtered using vacuum filtration, washed

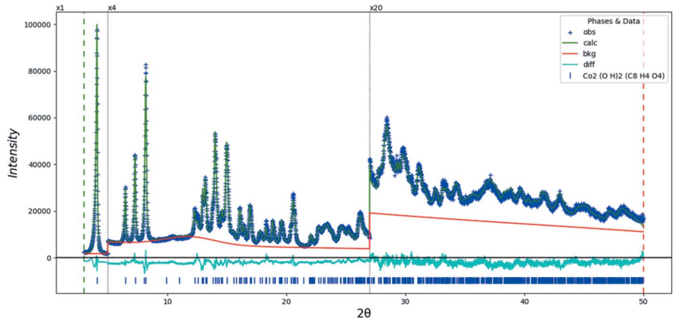



**Figure 9**
The Rietveld plot for the refinement of $Co_2(C_8H_4O_4)(OH)_2$. The blue crosses represent the observed data points, and the green line is the calculated pattern. The cyan curve is the normalized error plot. The row of tick marks indicates the calculated reflection positions. The vertical scale has been multiplied by a factor of 4× for $2\theta > 5.0°$, and by a factor of 20× for $2\theta > 27.0°$.

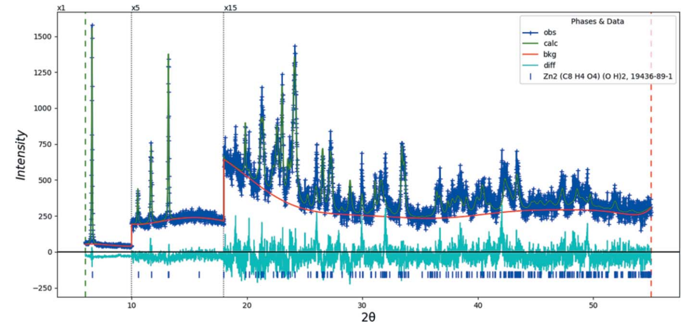



**Figure 11**
The Rietveld plot for the refinement of $Zn_2(C_8H_4O_4)(OH)_2$. The blue crosses represent the observed data points, and the green line is the calculated pattern. The cyan curve is the normalized error plot. The row of tick marks indicates the calculated reflection positions. The vertical scale has been multiplied by a factor of 5× for $2\theta > 10.0°$, and by a factor of 15× for $2\theta > 18.0°$.

with DMF and deionized water (10 ml each). The remaining solid was dried in an oven at 343 K under vacuum.

Nickel(II) nitrate hexahydrate (0.1948 g, 0.67 mmol) and terephthalic acid (0.2492 g, 1.5 mmol) were dissolved in 10 ml of DMF in a microwave vial. The solution was stirred until homogenous. The solution was then heated using a CEM Mars 6 microwave reactor at 750 W for a total of 85 s, in increments of 25 and 60 s. The resulting green solid was isolated using vacuum filtration, washed with water, methanol, and acetone, and allowed to air dry.

Information on the synthesis of $Zn_2(C_8H_4O_4)(OH)_2$ from prior to 1997 is no longer available.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

Rietveld refinements (Figs. 9–11) were carried out using *GSAS-II* (Toby & Von Dreele, 2013). All non-H bond distances and angles in the terephthalate anions were subjected to restraints, based on a *Mercury* Mogul Geometry Check (Sykes *et al.*, 2011; Bruno *et al.*, 2004). The Mogul average and standard deviation for each quantity were used as the restraint parameters. The restraints contributed 0–2.3% to the final $\chi^2$. The $U_{iso}$ were grouped by chemical similarity. The $U_{iso}$ values for the H atoms were fixed at 1.3 × the $U_{iso}$ of the heavy atoms to which they are attached. The peak profiles were described using the generalized microstrain model. The background was modeled using a 3–12-term shifted Chebyshev polynomial.

The structures were optimized with density functional techniques using VASP (Kresse & Furthmüller, 1996) (fixed experimental unit cells) through the MedeA graphical interface (Materials Design, 2016). The calculations were carried out on 16 2.4 GHz processors (each with 4 Gb RAM) of a 64-processor HP Proliant DL580 Generation 7 Linux cluster at North Central College. The calculations for Co and Ni were spin-polarized magnetic calculations, using the simplified LDSA + U approach, and $U_j$ = 3.7 eV for Co and Ni. The calculations used the GGA-PBE functional, a plane wave cutoff energy of 400.0 eV, and a *k*-point spacing of 0.5 $Å^{-1}$ leading to an 8 × 8 × 2 mesh.

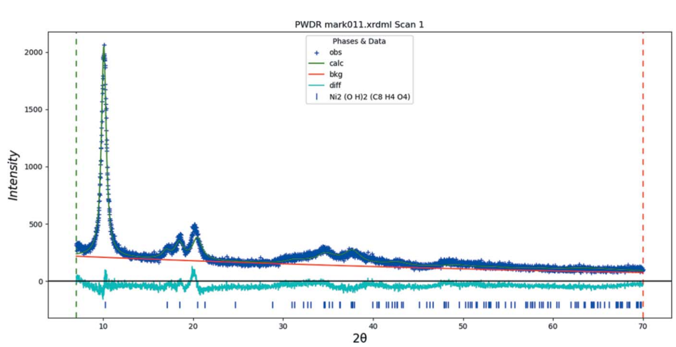



**Figure 10**
The Rietveld plot for the refinement of $Ni_2(C_8H_4O_4)(OH)_2$. The blue crosses represent the observed data points, and the green line is the calculated pattern. The cyan curve is the normalized error plot. The row of tick marks indicates the calculated reflection positions.

## Acknowledgements

We thank Professors Paul F. Brandt, Jeffrey A. Bjorklund, and Nicholas C. Boaz for their support, mentoring, and helpful discussions.

## References

Bravais, A. (1866). *Etudes Cristallographiques*. Paris: Gauthier Villars.
Brown, I. D. (2002). *The Chemical Bond in Inorganic Chemistry*. IUCr/Oxford University Press.
Bruno, I. J., Cole, J. C., Kessler, M., Luo, J., Motherwell, W. D. S., Purkis, L. H., Smith, B. R., Taylor, R., Cooper, R. I., Harris, S. E. & Orpen, A. G. (2004). *J. Chem. Inf. Comput. Sci.* **44**, 2133–2144.
Carton, A., Mesbah, A., Aranda, L., Rabu, P. & François, M. (2009). *Solid State Sci.* **11**, 818–823.
Crystal Impact (2015). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Dassault Systèmes (2021). *Materials Studio*. BIOVIA, San Diego, CA, USA.
Donnay, J. D. H. & Harker, D. (1937). *Am. Mineral.* **22**, 446–447.

Feyerherm, R., Loose, A., Rabu, P. & Drillon, M. (2003). *Solid State Sci.* **5**, 321–326.
Friedel, G. (1907). *Bull. Soc. Fr. Mineral.* **30**, 326–455.
Gates-Rector, S. & Blanton, T. (2019). *Powder Diffr.* **34**, 352–360.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.
Han, B., Ou, X., Deng, Z., Song, Y., Tian, C., Deng, H., Xu, Y.-J. & Lin, Z. (2018). *Angew. Chem. Int. Ed.* **57**, 16811–16815.
Huang, Z.-L., Drillon, M., Masciocchi, N., Sironi, A., Zhao, J.-T., Rabu, P. & Panissod, P. (2000). *Chem. Mater.* **12**, 2805–2812.
Kaduk, J. A. (2016). *CSD Communication* (refcode PUCYAO01). CCDC, Cambridge, England.
Kaduk, J. A., Golab, J. T. & Leusen, F. J. J. (1999). *Cryst. Eng.* 1(3/4), 277-290.
Kresse, G. & Furthmüller, J. (1996). *Comput. Mater. Sci.* **6**, 15–50.
Kurmoo, M., Kumagai, H., Green, M. A., Lovett, B. W., Blundell, S. J., Ardavan, A. & Singleton, J. (2001). *J. Solid State Chem.* **159**, 343–351.
Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). *J. Appl. Cryst.* **53**, 226–235.
Materials Design (2016). *MedeA 2.20.4*. Materials Design Inc., Angel Fire, NM, USA.
MDI (2021). *JADE Pro* 8.1. Materials Data, Livermore CA, USA.
Mesbah, A., Malaman, B., Mazet, T., Sibille, R. & François, M. (2010). *CrystEngComm*, **12**, 3126–3131.
Mesbah, A., Rabu, P., Sibille, R., Lebègue, S., Mazet, T., Malaman, B. & François, M. (2014). *Inorg. Chem.* **53**, 872–881.
Sherif, F. (1970). *Ind. Eng. Chem. Prod. Res. Develop.* **9**(3), 408–412.
Streek, J. van de & Neumann, M. A. (2014). *Acta Cryst.* B**70**, 1020–1032.
Sykes, R. A., McCabe, P., Allen, F. H., Battle, G. M., Bruno, I. J. & Wood, P. A. (2011). *J. Appl. Cryst.* **44**, 882–886.
Toby, B. H. & Von Dreele, R. B. (2013). *J. Appl. Cryst.* **46**, 544–549.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

# supporting information

*Acta Cryst.* (2022). E**78**, 584-589 [https://doi.org/10.1107/S2056989022005023]

## Crystal structures of dimetal terephthalate dihydroxides, $M_2(C_8H_4O_4)(OH)_2$ ($M$ = Co, Ni, Zn) from powder diffraction data and DFT calculations

Emma L. Markun, Drew A. Jensen, Joshua D. Vegetabile and James A. Kaduk

### Computing details

Program(s) used to refine structure: *GSAS-II* (Toby & Von Dreele, 2013) for Co_Riet, Ni_Riet, Zn_Riet. Molecular graphics: *Mercury* (Macrae *et al.*, 2020), *DIAMOND* (Crystal Impact, 2015) for Co_Riet. Software used to prepare material for publication: *publCIF* (Westrip, 2010) for Co_Riet.

### Poly[dihydroxido($\mu_6$-terepthalato)dicobalt] (Co_Riet)

*Crystal data*

$[Co_2(C_8H_4O_4)(OH)_2]$
$M_r$ = 316
Monoclinic, $C2/c$
$a$ = 19.9554 (10) Å
$b$ = 3.2883 (2) Å
$c$ = 12.6139 (8) Å
$\beta$ = 96.059 (5)°
$V$ = 823.08 (6) Å$^3$
$Z$ = 4
$D_x$ = 2.550 Mg m$^{-3}$
Mo $K\alpha_{1,2}$ radiation, $\lambda$ = 0.70932, 0.71361 Å
$T$ = 300 K
pink
cylinder, 12 × 0.7 mm

*Data collection*

PANalytical Empyrean diffractometer
Specimen mounting: glass capillary
Data collection mode: transmission
Scan method: step
$2\theta_{min}$ = 1.002°, $2\theta_{max}$ = 49.991°, $2\theta_{step}$ = 0.008°

*Refinement*

Least-squares matrix: full
$R_p$ = 0.045
$R_{wp}$ = 0.063
$R_{exp}$ = 0.020
$R(F^2)$ = 0.05751
5864 data points
Profile function: Finger-Cox-Jephcoat function parameters U, V, W, X, Y, SH/L: peak variance(Gauss) = Utan(Th)$^2$+Vtan(Th)+W: peak HW(Lorentz) = X/cos(Th)+Ytan(Th); SH/L = S/L+H/L U, V, W in (centideg)$^2$, X & Y in centideg 30.816, 10.768, 0.000, 1.935, 0.000, 0.033, Crystallite size in microns with "isotropic" model: parameters: Size, G/L mix 1.000, 1.000, Microstrain, "generalized" model ($10^6$ * delta Q/Q) parameters: S400, S040, S004, S220, S202, S022, S301, S103, S121, G/L mix 2180.060, 4.385767395e6, 5373.300, 103711.383, 724.789, 689333.161, -2196.502, 2609.389, 91248.973, 0.800,
42 parameters
15 restraints
H-atom parameters not defined?
Weighting scheme based on measured s.u.'s
$(\Delta/\sigma)_{max}$ = 0.025
Background function: Background function: "chebyschev-1" function with 4 terms: 1063(5), -577(6), 95(4), -25(3), Background peak parameters: pos, int, sig, gam: 11.866, 3892.401, 44425.907, 0.100,
Preferred orientation correction: Simple spherical harmonic correction Order = 2 Coefficients: 0:0:C(2,-2) = -0.0542; 0:0:C(2,0) = -0.1055; 0:0:C(2,2) = -0.0207

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.3140 (2) | 0.106 (3) | 0.0412 (4) | 0.018 (3)* |
| C2 | 0.2695 (3) | 0.269 (3) | 0.1093 (3) | 0.0184* |
| C3 | 0.2024 (3) | 0.368 (4) | 0.0686 (4) | 0.0184* |
| H4 | 0.28873 | 0.24618 | 0.19840 | 0.0220* |
| H5 | 0.17120 | 0.48125 | 0.13117 | 0.0220* |
| C6 | 0.3837 (3) | −0.024 (5) | 0.0845 (5) | 0.0200* |
| O7 | 0.3988 (3) | −0.007 (7) | 0.1799 (5) | 0.020000* |
| O8 | 0.4268 (3) | −0.031 (5) | 0.0168 (5) | 0.020000* |
| Co9 | 0.50000 | 0.50000 | 0.50000 | 0.0020 (5)* |
| Co10 | 0.00000 | 0.495 (3) | −0.25000 | 0.0020* |
| O11 | 0.0287 (3) | 0.030 (7) | 0.1569 (7) | 0.0200* |
| H12 | 0.06922 | −0.03114 | 0.16621 | 0.0260* |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C1—C2 | 1.406 (6) | O8—C6 | 1.274 (4) |
| C1—C3$^{i}$ | 1.391 (3) | O8—Co9$^{ii}$ | 2.151 (12) |
| C1—C6 | 1.501 (5) | Co9—O8$^{iii}$ | 2.151 (12) |
| C2—C1 | 1.406 (6) | Co9—O8$^{iv}$ | 2.151 (12) |
| C2—C3 | 1.421 (4) | Co9—O11$^{v}$ | 2.004 (8) |
| C3—C1$^{i}$ | 1.391 (3) | Co9—O11$^{vi}$ | 2.004 (8) |
| C3—C2 | 1.421 (4) | Co10—O7$^{i}$ | 2.119 (5) |
| C6—C1 | 1.501 (5) | Co10—O7$^{vii}$ | 2.119 (5) |
| C6—O7 | 1.211 (5) | Co10—O11$^{viii}$ | 2.072 (16) |
| C6—O8 | 1.274 (4) | Co10—O11$^{ix}$ | 2.072 (16) |
| O7—C6 | 1.211 (5) | O11—Co9$^{x}$ | 2.004 (8) |
| O7—Co10$^{i}$ | 2.119 (5) | O11—Co10$^{viii}$ | 2.072 (16) |
| | | | |
| C2—C1—C3$^{i}$ | 119.1 (3) | C1$^{i}$—C3—C2 | 119.2 (3) |
| C2—C1—C6 | 120.4 (2) | C1—C6—O7 | 118.2 (4) |
| C3$^{i}$—C1—C6 | 119.5 (3) | C1—C6—O8 | 115.2 (5) |
| C1—C2—C3 | 119.9 (3) | O7—C6—O8 | 123.5 (6) |

Symmetry codes: (i) −*x*+1/2, −*y*+1/2, −*z*; (ii) −*x*+1, *y*−1, −*z*+1/2; (iii) −*x*+1, *y*+1, −*z*+1/2; (iv) *x*, −*y*, *z*+1/2; (v) −*x*+1/2, *y*+1/2, −*z*+1/2; (vi) *x*+1/2, −*y*+1/2, *z*+1/2; (vii) *x*−1/2, −*y*+1/2, *z*−1/2; (viii) −*x*, −*y*+1, −*z*; (ix) *x*, −*y*+1, *z*−1/2; (x) −*x*+1/2, *y*−1/2, −*z*+1/2.

**(Co_DFT)**

*Crystal data*

$C_8H_6Co_2O_6$
$M_r$ = 316
Monoclinic, *C*2/*c*
*a* = 20.02520 Å
*b* = 3.30420 Å
*c* = 12.59800 Å
*β* = 96.33°
*V* = 828.49 Å³
*Z* = 4

*Data collection*

$h = \rightarrow$
$k = \rightarrow$
$l = \rightarrow$

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.31569 | 0.14758 | 0.04012 | 0.0184 |
| C2 | 0.26806 | 0.23812 | 0.11006 | 0.0184 |
| C3 | 0.20287 | 0.33955 | 0.07035 | 0.0184 |
| H4 | 0.28329 | 0.23013 | 0.19578 | 0.022 |
| H5 | 0.16565 | 0.41266 | 0.12436 | 0.022 |
| C6 | 0.38562 | 0.03773 | 0.08352 | 0.020 |
| O7 | 0.39861 | 0.98679 | 0.18301 | 0.020 |
| O8 | 0.42960 | 0.00198 | 0.01583 | 0.020 |
| Co9 | 0.00000 | 0.00000 | 0.00000 | 0.002 |
| Co10 | 0.50000 | 0.97237 | 0.25000 | 0.002 |
| O11 | 0.02838 | 0.97997 | 0.15714 | 0.020 |
| H12 | 0.07726 | 0.97414 | 0.17088 | 0.026 |

## Poly[dihydroxido($\mu_6$-terepthalato)dinickel] (Ni_Riet)

*Crystal data*

$[Ni_2(C_8H_4O_4)(OH)_2]$
$M_r$ = 315.53
Monoclinic, $C2/c$
$a$ = 20.35 (5) Å
$b$ = 3.364 (6) Å
$c$ = 12.19 (4) Å
$\beta$ = 98.9 (2)°
$V$ = 824.6 (15) Å³
$Z$ = 4
$D_x$ = 2.542 Mg m$^{-3}$
Co $K\alpha_{1,2}$ radiation, $\lambda$ = 1.78892, 1.79278 Å
$T$ = 300 K
pale green
flat_sheet, 16 × 16 mm

*Data collection*

PANalytical X′Pert diffractometer
Specimen mounting: Si zero-background plate with well
Data collection mode: reflection
Scan method: step
$2\theta_{min}$ = 4.007°, $2\theta_{max}$ = 69.983°, $2\theta_{step}$ = 0.017°

*Refinement*

Least-squares matrix: full
$R_p$ = 0.084
$R_{wp}$ = 0.107
$R_{exp}$ = 0.070
$R(F^2)$ = 0.14454
3949 data points
Profile function: Finger-Cox-Jephcoat function parameters U, V, W, X, Y, SH/L: peak variance(Gauss) = Utan(Th)$^2$+Vtan(Th)+W: peak HW(Lorentz) = X/cos(Th)+Ytan(Th); SH/L = S/L+H/L U, V, W in (centideg)$^2$, X & Y in centideg 2.761, 0.000, 1.090, 3.610, 0.000, 0.047,
12 parameters
0 restraints
H-atom parameters not defined?
$(\Delta/\sigma)_{max}$ = 97.398
Background function: Background function: "chebyschev-1" function with 3 terms: 139.3(6), -71.0(8), 7.7(7),
Preferred orientation correction: Simple spherical harmonic correction Order = 2 Coefficients: 0:0:C(2,-2) = -0.91(8); 0:0:C(2,0) = 0.63(8); 0:0:C(2,2) = 0.93(13)

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

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.31564 | 0.11999 | 0.03425 | 0.0100* |
| C2 | 0.27426 | 0.26556 | 0.10759 | 0.0100* |
| C3 | 0.20930 | 0.40008 | 0.07333 | 0.0100* |
| H4 | 0.28873 | 0.24618 | 0.19840 | 0.0130* |
| H5 | 0.17120 | 0.48125 | 0.13117 | 0.0130* |
| C6 | 0.38661 | −0.01497 | 0.07632 | 0.0100* |
| O7 | 0.39933 | −0.00110 | 0.17831 | 0.0100* |
| O8 | 0.43321 | −0.00173 | 0.01302 | 0.0100* |
| Ni9 | 0.50000 | 0.50000 | 0.50000 | 0.0387* |
| Ni10 | 0.00000 | 0.50145 | −0.25000 | 0.0387* |
| O11 | 0.02771 | 0.0007 | 0.15823 | 0.0063* |
| H12 | 0.06922 | −0.03114 | 0.16621 | 0.0082* |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C1—C2 | 1.4074 | O8—C6 | 1.3123 |
| C1—C3$^{i}$ | 1.3331 | Ni9—O11$^{ii}$ | 1.9246 |
| C1—C6 | 1.5251 | Ni9—O11$^{iii}$ | 1.9246 |
| C2—C1 | 1.4074 | Ni10—O7$^{i}$ | 2.0995 |
| C2—C3 | 1.3985 | Ni10—O7$^{iv}$ | 2.0995 |
| C3—C1$^{i}$ | 1.3331 | Ni10—O11$^{v}$ | 2.149 |
| C3—C2 | 1.3985 | Ni10—O11$^{vi}$ | 2.1377 |
| H5—C3 | 1.1584 | Ni10—O11$^{vii}$ | 2.149 |
| C6—C1 | 1.5251 | Ni10—O11$^{viii}$ | 2.1377 |
| C6—O7 | 1.2313 | O11—Ni9$^{ix}$ | 1.9246 |
| C6—O8 | 1.3123 | O11—Ni10$^{v}$ | 2.149 |
| O7—C6 | 1.2313 | O11—Ni10$^{vi}$ | 2.1377 |
| O7—Ni10$^{i}$ | 2.0995 | | |
| | | | |
| C2—C1—C3$^{i}$ | 117.925 | C1$^{i}$—C3—C2 | 118.448 |
| C2—C1—C6 | 121.216 | C1—C6—O7 | 111.649 |
| C3$^{i}$—C1—C6 | 120.856 | C1—C6—O8 | 121.645 |
| C1—C2—C3 | 123.601 | O7—C6—O8 | 122.291 |

Symmetry codes: (i) $-x+1/2, -y+1/2, -z$; (ii) $-x+1/2, y+1/2, -z+1/2$; (iii) $x+1/2, -y+1/2, z+1/2$; (iv) $x-1/2, -y+1/2, z-1/2$; (v) $-x, -y, -z$; (vi) $-x, -y+1, -z$; (vii) $x, -y, z-1/2$; (viii) $x, -y+1, z-1/2$; (ix) $-x+1/2, y-1/2, -z+1/2$.

**(Ni_DFT)**

*Crystal data*

$C_8H6Ni_2O_6$
$M_r$ = 315.53
Monoclinic, $C2/c$
$a$ = 20.40719 Å
$b$ = 3.27188 Å
$c$ = 12.22464 Å
$\beta$ = 99.20°
$V$ = 805.74 Å$^3$
$Z$ = 4

*Data collection*

$h = \rightarrow$
$k = \rightarrow$
$l = \rightarrow$

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

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.31659 | 0.14671 | 0.03597 | 0.010 |
| C2 | 0.27424 | 0.23178 | 0.11288 | 0.010 |
| C3 | 0.20831 | 0.33316 | 0.07742 | 0.010 |
| H4 | 0.29416 | 0.22005 | 0.20095 | 0.013 |
| H5 | 0.17519 | 0.40045 | 0.13678 | 0.013 |
| C6 | 0.38690 | 0.03143 | 0.07591 | 0.010 |
| O7 | 0.90294 | 0.45891 | 0.17836 | 0.010 |
| O8 | 0.42774 | 0.00936 | 0.00489 | 0.010 |
| Ni9 | 0.00000 | 0.00000 | 0.00000 | 0.03866 |
| Ni10 | 0.00000 | 0.45204 | 0.25000 | 0.03866 |
| O11 | 0.52764 | 0.45960 | 0.16035 | 0.00631 |
| H12 | 0.57607 | 0.45471 | 0.17494 | 0.00821 |

## Poly[dihydroxido($\mu_6$-terepthalato)dizinc] (Zn_Riet)

*Crystal data*

$[Zn_2(C_8H_4O_4)(OH)_2]$
$M_r$ = 328.89
Monoclinic, $C2/c$
$a$ = 20.165 (2) Å
$b$ = 3.3273 (5) Å
$c$ = 12.5956 (16) Å
$\beta$ = 97.431 (10)°
$V$ = 837.99 (14) Å$^3$
$Z$ = 4
$D_x$ = 2.607 Mg m$^{-3}$
Synchrotron radiation, $\lambda$ = 1.15008 Å
$T$ = 300 K
white

*Data collection*

NSLS beamline X3B1
diffractometer
Specimen mounting: Kapton capillary
Data collection mode: transmission
Scan method: step
$2\theta_{min}$ = 6.0°, $2\theta_{max}$ = 60.0°, $2\theta_{step}$ = 0.01°

*Refinement*

Least-squares matrix: full
$R_p$ = 0.092
$R_{wp}$ = 0.121
$R_{exp}$ = 0.097
$R(F^2)$ = 0.14121
5400 data points
Profile function: Finger-Cox-Jephcoat function parameters U, V, W, X, Y, SH/L: peak variance(Gauss) = Utan(Th)$^2$+Vtan(Th)+W: peak HW(Lorentz) = X/cos(Th)+Ytan(Th); SH/L = S/L+H/L U, V, W in (centideg)$^2$, X & Y in centideg 6.427, -1.067, 0.000, 0.000, 0.000, 0.022, Crystallite size in microns with "isotropic" model: parameters: Size, G/L mix 1.000, 1.000, Microstrain, "generalized" model ($10^6$ * delta Q/Q) parameters: S400, S040, S004, S220, S202, S022, S301, S103, S121, G/L mix 807.414, 6.074702219e6, 12850.425, 116093.843, 1080.871, 214564.056, 1450.184, -4276.159, -164837.348, 0.600,
57 parameters
14 restraints
H-atom parameters not defined?
$(\Delta/\sigma)_{max}$ = 1.459

Background function: Background function: "chebyschev-1" function with 12 terms: 28.78(11), -16.88(18), 8.18(16), 0.45(16), -2.60(15), -1.04(14), 3.60(13), -1.88(13), 0.46(12), 1.97(12), -1.94(11), 1.26(10),

Preferred orientation correction: Simple spherical harmonic correction Order = 2 Coefficients: 0:0:C(2,-2) = -0.05(4); 0:0:C(2,0) = -0.18(6); 0:0:C(2,2) = -0.21(4)

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.3153 (9) | 0.132 (11) | 0.038 (2) | 0.148 (18)* |
| C2 | 0.2801 (13) | 0.369 (13) | 0.1020 (17) | 0.148* |
| C3 | 0.2145 (14) | 0.477 (16) | 0.067 (2) | 0.148* |
| H7 | 0.29840 | 0.55800 | 0.17260 | 0.192* |
| H8 | 0.18320 | 0.73700 | 0.09150 | 0.192* |
| C11 | 0.3863 (5) | 0.016 (8) | 0.0750 (18) | 0.0500* |
| O12 | 0.4045 (9) | 0.025 (16) | 0.1743 (18) | 0.050000* |
| O13 | 0.4201 (7) | −0.156 (9) | 0.008 (2) | 0.050000* |
| Zn14 | 0.50000 | 0.50000 | 0.50000 | 0.078 (4)* |
| Zn15 | 0.00000 | 0.54200 | −0.25000 | 0.078* |
| O16 | 0.0318 (13) | 0.072 (14) | 0.161 (3) | 0.0500* |
| H17 | 0.06922 | −0.03114 | 0.16621 | 0.065000* |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C1—C2 | 1.3877 (16) | O13—C11 | 1.284 (2) |
| C1—C3$^{i}$ | 1.43 (4) | O13—Zn14$^{ii}$ | 1.989 (13) |
| C1—C11 | 1.498 (3) | Zn14—O13$^{iii}$ | 1.989 (13) |
| C2—C1 | 1.3877 (16) | Zn14—O13$^{iv}$ | 1.989 (13) |
| C2—C3 | 1.385 (2) | Zn14—O16$^{v}$ | 2.06 (3) |
| C3—C1$^{i}$ | 1.43 (4) | Zn14—O16$^{vi}$ | 2.06 (3) |
| C3—C2 | 1.385 (2) | Zn15—O12$^{i}$ | 2.048 (17) |
| C11—C1 | 1.498 (3) | Zn15—O12$^{vii}$ | 2.048 (17) |
| C11—O12 | 1.2573 (14) | Zn15—O16$^{viii}$ | 1.87 (4) |
| C11—O13 | 1.284 (2) | Zn15—O16$^{ix}$ | 1.87 (4) |
| O12—C11 | 1.2573 (14) | O16—Zn14$^{x}$ | 2.06 (3) |
| O12—Zn15$^{i}$ | 2.048 (17) | O16—Zn15$^{viii}$ | 1.87 (4) |
| | | | |
| C2—C1—C3$^{i}$ | 119.81 (12) | C1—C11—O12 | 116.6 (2) |
| C2—C1—C11 | 120.4 (2) | C1—C11—O13 | 118.59 (19) |
| C3$^{i}$—C1—C11 | 119.6 (4) | O12—C11—O13 | 123.42 (15) |
| C1—C2—C3 | 120.20 (17) | O16$^{viii}$—Zn15—O16$^{xi}$ | 93 (2) |
| C1$^{i}$—C3—C2 | 119.83 (12) | | |

Symmetry codes: (i) −*x*+1/2, −*y*+1/2, −*z*; (ii) −*x*+1, *y*−1, −*z*+1/2; (iii) −*x*+1, *y*+1, −*z*+1/2; (iv) *x*, −*y*, *z*+1/2; (v) −*x*+1/2, *y*+1/2, −*z*+1/2; (vi) *x*+1/2, −*y*+1/2, *z*+1/2; (vii) *x*−1/2, −*y*+1/2, *z*−1/2; (viii) −*x*, −*y*+1, −*z*; (ix) *x*, −*y*+1, *z*−1/2; (x) −*x*+1/2, *y*−1/2, −*z*+1/2; (xi) *x*, −*y*+1, *z*+1/2.

**(Zn_DFT)**

*Crystal data*

$C_8H_6O_6Zn_2$
$M_r$ = 328.89
Monoclinic, $C2/c$
$a$ = 20.15960 Å
$b$ = 3.32510 Å
$c$ = 12.59470 Å
$\beta$ = 97.52°
$V$ = 837.00 Å$^3$
$Z$ = 4

*Data collection*

$h$ = →
$k$ = →
$l$ = →

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

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.31537 | 0.14052 | 0.03973 | 0.14798 |
| C2 | 0.26900 | 0.22410 | 0.11036 | 0.14798 |
| C3 | 0.20398 | 0.33320 | 0.07087 | 0.14798 |
| H7 | 0.28504 | 0.20470 | 0.19624 | 0.19231 |
| H8 | 0.16745 | 0.40076 | 0.12504 | 0.19231 |
| C11 | 0.38529 | 0.02740 | 0.08247 | 0.050 |
| O12 | 0.39938 | 0.97473 | 0.18247 | 0.050 |
| O13 | 0.42745 | 0.99381 | 0.01434 | 0.050 |
| O16 | 0.02778 | 0.97322 | 0.15570 | 0.050 |
| H17 | 0.07652 | 0.96489 | 0.16886 | 0.065 |
| Zn14 | 0.00000 | 0.00000 | 0.00000 | 0.07842 |
| Zn15 | 0.50000 | 0.96690 | 0.25000 | 0.07842 |