Structures of dicobalt and dinickel 4,4′-biphenyldicarboxylate dihydroxide, $M_2(\text{O}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{CO}_2)(\text{OH})_2$, $M = \text{Co}$ and $\text{Ni}$, and diammonium 4,4′-biphenyldicarboxylate from powder diffraction data

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The triclinic structures of poly[(μ₄-4,4′-biphenyldicarboxylato)di-μ-hydroxido-dicobalt], [Co₂(\text{C}_1₄\text{H}_₈\text{O}_₄)(\text{OH})₂]ₙ, and poly[(μ₄-4,4′-biphenyldicarboxylato)di-μ-hydroxido-dinickel], [Ni₂(\text{C}_1₄\text{H}_₈\text{O}_₄)(\text{OH})₂]ₙ, were established using laboratory X-ray powder diffraction data. These structures, as well as that of poly[(μ₄-4,4′-biphenyldicarboxylato)di-μ-hydroxido-dimanganese], [Mn₂(\text{C}_1₄\text{H}_₈\text{O}_₄)(\text{OH})₂]ₙ, were optimized using density functional techniques. The structure of diammonium 4,4′-biphenyldicarboxylate, 2\text{NH}_₄⁺\text{C}_₁₄\text{H}_₈\text{O}_₄⁻, was also solved using laboratory powder data. The Mn and Co compounds are isostructural: the octahedral MO₆ groups share edges to form chains running parallel to the $c$-axis. These chains share corners (OH groups) to link into layers lying parallel to the $bc$ plane. The hydroxyl groups do not participate in hydrogen bonds. The structure of (\text{NH}_₄)₂\text{BPDC} consists of alternating layers of BPDC and ammonium ions lying parallel to the $ab$ plane. Each hydrogen atom of the ammonium ions in (\text{NH}_₄)₂\text{BPDC} participates in a strong N–H···O hydrogen bond.

1. Chemical context

Metal–organic frameworks (MOFs) are a class of compounds that have both organic (linker molecule) and inorganic (metal node) components. MOFs are used in many applied areas of science, such as gas separation and catalysis, but often the crystal structures of these MOFs are not reported. Knowing the crystal structures of MOFs lets us understand them at a molecular level as well as identify them more efficiently.

From an attempt to prepare a porous Co-BPDC (BPDC = 4,4′-biphenyldicarboxylate, C₁₄H₈O₄⁻) MOF we obtained a dense Co-BPDC phase previously synthesized by Ipadeola & Ozoemena (2020). They reported a powder pattern, but did not otherwise characterize the compound, as it was decomposed to make nano-Co₃O₄. Their XRD pattern was similar to ours, but they did not measure to a low-enough angle to observe the strongest peak of the pattern (Fig. 1).

The magnetic properties of Co₂BPDC(OH)₂ were studied by Kurmoo & Kumagai (2002) and an X-ray powder pattern was provided (Fig. 2). They stated that the compound was isostructural to the analogous terephthalate. That structure was reported to crystallize in space group C2/m, which we believe to be incorrect (Markun et al., 2022).

Most syntheses involving BPDC use H₂BPDC and a base. We prepared diammonium 4,4′-biphenyldicarboxylate as an
alternative (and more soluble) reagent, characterized its crystal structure, and used it to prepare Ni$_2$BPDC(OH)$_2$.

2. Structural commentary

The X-ray powder patterns show that the $M_2$BPDC(OH)$_2$ phases for $M = \text{Mn, Co, and Ni}$ are isostructural (Fig. 3). The root-mean-square Cartesian displacements between the experimental (single crystal or Rietveld-refined) and DFT-optimized structures are 0.133, 0.264, and 0.563 Å for $M = \text{Mn, Co, and Ni}$, respectively (Figs. 4–6). The value for nickel is outside of the normal range for correct structures (van de Streek & Neumann, 2014). The behavior of the structure during various refinements and optimizations suggests that there might be alternate orientations of the BPDC ligand and alternate coordination of the Ni cations. Sorting out these details is not supported by the relatively poor diffraction data on the Ni compound. This discussion concentrates on the DFT-optimized structures.

Unlike the metal complexes, in diammonium BPDC, the aromatic rings are nearly perpendicular ($C_2—C_4—C_{11}—C_{14} = 85.7°$). One carboxylate group lies nearly in the ring plane ($O_{25}—C_{21}—C_{12}—C_{15} = 4.6°$), while the other ($O_{24}—C_{22}—C_6—C_3 = 85.6°$) is nearly perpendicular to its ring. The r.m.s. Cartesian displacement of the non-H atoms in the BPDC anion is 0.384 Å (Fig. 7).
Analysis of the contributions to the total crystal energy of the structures using the Forcite module of Materials Studio (Dassault Systèmes, 2021) suggests that bond and angle distortion terms dominate the intramolecular deformation energy in all three metal compounds. The intermolecular energy in all three compounds is dominated by electrostatic attractions, which represent the $M-O$ coordinate bonds.

The density of states (DOS) calculated by VASP (Kresse & Furthmüller, 1996) indicate that all three $M$-BPDC compounds are semiconductors, with band gaps of 1.695, 1.407 and 0.856 eV for Mn, Co and Ni respectively. Both the HOMO and LUMO consist mainly of metal $d$ states. For Mn and Co, the DOS for the up and down spins differ, while for Ni they are very similar. Thus, the bonding in the Ni compound seems to be different than that in the other two.

A uniaxial microstrain model (100 as the unique axis) was used to model the peak profiles. The axial and equatorial microstrains for Co are $7.4 \times 10^4$ and $5.6 \times 10^4$ ppm, while those for Ni show a greater difference, at $1.1 \times 10^5$ and $1.5 \times 10^4$ ppm, respectively. This possibly indicates that the Ni compound also contains some alternate metal-ion coordinations (different orientations of the carboxyl groups). During some refinements of the Ni compound, the orientation of the carboxyl groups changed considerably, and/or the displacement coefficients became very large. The very broad peaks of the Ni powder pattern certainly limit the structural information that can be obtained.

The Bravais–Friedel–Donnay–Harker (Bravais, 1866, Friedel, 1907; Donnay & Harker, 1937) morphology suggests that we might expect a platy (with $\{100\}$ as the major faces) morphology for the compounds. No preferred orientation correction model was necessary in the Co and Ni refinements.

3. Supramolecular features

The Mn and Co compounds are isostructural (Fig. 8). Both $M14$ and $M15$ exhibit an octahedral coordination, and occupy centers of symmetry. For $M14$, the coordination consists of trans carboxylate O12 atoms and four equatorial hydroxyl groups. For $M15$ there are trans hydroxyl groups and four equatorial carboxylate O13 atoms. The bond-valence sums are 1.94 and 2.09 for Mn and 1.80 and 1.85 for Co, in acceptable agreement with the expected values of 2.00. The carboxylate O12 atom bonds to one $M14$, and O13 bridges two $M15$. The hydroxyl group O16 bridges two $M14$ and one $M15$. 
The M14 octahedra share edges to form chains running parallel to the c-axis. The M15 octahedra also share edges to form chains parallel to the c-axis. These chains share corners (the O16 OH groups), linking into layers lying parallel to the bc plane. The hydroxyl groups do not participate in hydrogen bonds.

The coordination in the Ni compound is different from the other two (Fig. 9). Ni14 is square planar, with trans carboxylate O12 atoms and two trans hydroxyl groups. Ni15 is also square planar, with trans hydroxyl O16 and carboxylate O13 atoms. Atom O12 is bonded to Ni14 (same), and O13 is bonded to Ni15 (different). Each carboxyl group bridges two metal atoms (not three), and the hydroxyl group O16 bridges one Ni14 and one Ni15. Both Ni ions share hydroxyl corners to form chains lying parallel to the [011] axis. The result is layers, but not connected (Fig. 10).

The structure of (NH4)2BPDC consists of alternating layers of BPDC dianions and ammonium cations lying parallel to the ab plane (Fig. 11). As expected, each hydrogen atom of the ammonium ions in (NH4)2BPDC participates in a strong N—H···O hydrogen bond (Table 1). The energies of these hydrogen bonds were calculated using the correlation of Wheatley & Kaduk (2019).

4. Database survey
We attempted to solve the structure of Co2BPDC(OH)2 from the powder data without success. Previous searches of the Cambridge Structural Database [CSD version 5.43 June 2022 (Groom et al., 2016); ConQuest 2022.2.0 (Bruno et al., 2002)] did not yield suitable analogues, but searches of CSD release 2021.3 using a BPDC fragment and the chemistry CHO and Ni, Zn, Fe, Mn, or Mg only yielded a few hits, among which was Mn2BPDC(OH)2, refcode UBUPEQ (Sibille et al., 2021).

This compound has a similar powder pattern to our Co and Ni compounds (Fig. 3), and provided a suitable starting model for Rietveld refinements.

5. Synthesis and crystallization
Cobalt(II) nitrate hexahydrate (0.4383 g, 1.5 mmol) and biphenyl-4,4'-dicarboxylic acid (0.3645 g, 1.5 mmol) were added to a flask with 1.5 ml of triethanolamine and ~60 ml of...
dimethylformamide (DMF). The mixture was stirred on a hot plate (343 K) until the solution appeared to be homogenous (∼15 min). A 5 ml aliquot of this solution was transferred to a Pyrex microwave vial and 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 off. Automatic cooling was turned off and the vial was left in the microwave until it cooled to 343 K. The solution was filtered using vacuum filtration and washed with DMF (10 ml). The remaining purple solid was dried in a vacuum oven at ∼343 K.

Nickel(II) acetate tetrahydrate (0.0880 g, 0.35 mmol) and diammonium biphenyl-4,4'-dicarboxylate (0.1278 g, 0.5 mmol) were added to a flask and ∼20 ml of DMF was added. The reaction was stirred on a hot plate (343 K) until solution appeared to be homogenous (∼15 min). A 5 ml aliquot of this solution was transferred to a Pyrex microwave vial and heated using a CEM Discover microwave with power set to 200 W using a ramp time of 5 min to reach 423 K with a hold time of 30 min and internal stirring on high. Automatic cooling was turned on. The solution was filtered using vacuum filtration and washed with DMF (10 ml). The remaining green solid was dried in a vacuum oven at ∼343 K.

0.8990 g (4.1 mmol) of biphenyl-4,4'-dicarboxylic acid (Aldrich Lot #BCCF5104) were placed into a 50 ml beaker. About 50 ml of 15 M aqueous ammonia were placed in a 250 ml beaker, and the 50 ml beaker placed in the larger beaker. The large beaker was covered with a Petri dish, and allowed to stand at ambient conditions overnight. The white recovered solid weighed 1.0257 g, corresponding to the expected quantitative yield for (NH₄)₂BPDC.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

The powder pattern of (NH₄)₂BPDC was indexed using DOCVOL14 (Louër & Boultif, 2014). All attempts to solve and refine the structure in space group P1 were unsuccessful, so P1 was used. The structure was solved by Monte Carlo simulated-annealing techniques as implemented in EXPO2014 (Altomare et al., 2013), using a BPDC anion and two N atoms as fragments.

Rietveld refinements (Figs. 12–14) were carried out using GSAS-II (Toby & Von Dreele, 2013). All non-H bond distances and angles in the BPDC dianion 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 χ². The Uiso parameters were grouped by chemical similarity: given the complex, low-symmetry structures and poor data quality, these values should be treated with caution. The Uiso for the H atoms were fixed at 1.3×Uiso of the heavy atoms to which they are attached. The peak profiles were described using the generalized microstrain model and the backgrounds were modeled using a 3–12-term shifted Chebyshev polynomial. For Co, the value of μ-R used was 0.37. For the ammonium salt, no absorption correction was necessary. For Ni, the geometry was reflection, so no absorption correction was appropriate.

The structures were optimized with density functional techniques using VASP (Kresse & Furthmüller, 1996) (fixed experimental unit cells) through the MedeA graphical inter-
Table 2
Experimental details.

|                          | Co$_2$(O$_2$CC$_6$H$_4$C$_6$H$_4$CO$_2$)(OH)$_2$ | Ni$_2$(O$_2$CC$_6$H$_4$C$_6$H$_4$CO$_2$)(OH)$_2$ | (NH$_4$)$_2$BPDC |
|-------------------------|-----------------------------------------------|-------------------------------------------------|-----------------|
| Crystal data            |                                               |                                                 |                 |
| Chemical formula        | [Co(C$_6$H$_5$)$_2$(OH)$_2$]                   | [Ni(C$_6$H$_5$)$_2$(OH)$_2$]                     | 2NH$_4^+$C$_6$H$_5$O$_2$$_2^-$ |
| $M_r$                   | 392.09                                        | 391.63                                          | 276.29          |
| Crystal system, space group | Triclinic, P$ar{T}$                        | Triclinic, P$ar{T}$                          | Triclinic, P$ar{T}$ |
| Temperature (K)         | 300                                           | 300                                             | 300             |
| $a$, $b$, $c$ (Å)       | 14.16 (5), 6.269 (3), 3.332 (4)               | 15.0 (11), 6.04 (12), 4.04 (9)                 | 4.6770 (6), 5.2306 (14), 14.387 (6) |
| $\alpha$, $\beta$, $\gamma$ (°) | 91.43 (2), 98.46 (7), 90.0 (3)                | 82.7 (2), 72.3 (8), 82 (2)                     | 90.57 (7), 91.41 (4), 92.775 (11) |
| $V$ (Å$^3$)             | 291.6 (2)                                     | 345 (2)                                         | 351.43 (17)     |
| $Z$                     | 1                                             | 1                                               | 1               |
| Radiation type          | $K\alpha_2, \lambda = 0.70932, 0.71361$ Å   | $K\alpha_2, \lambda = 1.54059, 1.54445$ Å      | $K\alpha_1, \lambda = 0.70932, 0.71361$ Å |
| Specimen shape, size (mm) | Cylinder, 12 x 0.7                            | Flat sheet, 16 x 16                            | Cylinder, 12 x 0.7 |

Data collection

|                          |                  |                  |                  |
|-------------------------|-----------------|-----------------|-----------------|
| Diffractometer          | PANalytical Empyrean | PANalytical X'Pert | PANalytical Empyrean |
| Specimen mounting       | Glass capillary  | Si zero-background cell with well | Glass capillary  |
| Data collection mode    | Transmission    | Reflection       | Transmission     |
| Scan method             | Step            | Step             | Step             |
| 2θ values (°)           | $2\theta_{\text{max}} = 49.991$, $2\theta_{\text{step}} = 0.008$ | $2\theta_{\text{max}} = 99.998$, $2\theta_{\text{step}} = 0.017$ | $2\theta_{\text{max}} = 49.982$, $2\theta_{\text{step}} = 0.008$ |

Refinement

|                          |                  |                  |                  |
|-------------------------|-----------------|-----------------|-----------------|
| $R$ factors and         | $R_p = 0.065$, $R_{exp} = 0.092$, $R_{exp} = 0.022$, $R(F^2) = 0.11340$, $\chi^2 = 21.977$ | $R_p = 0.042$, $R_{exp} = 0.059$, $R_{exp} = 0.011$, $R(F^2) = 0.09176$, $\chi^2 = 30.426$ | $R_p = 0.033$, $R_{exp} = 0.043$, $R_{exp} = 0.015$, $R(F^2) = 0.09394$, $\chi^2 = 14.055$ |
| goodness of fit         |                  |                  |                  |
| No. of parameters       | 49              | 47              | 93              |
| No. of restraints       | 64              | 30              | 55              |
| $(\Delta/\sigma)_{\text{max}}$ | 2.587           | 4.433           | 0.723           |

The same symmetry and lattice parameters were used for the DFT calculations as for each powder diffraction study. Computer program: GSAS-II (Toby & Von Dreele, 2013).

face (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 LSDA+U approach, and $U_{\text{f}} = 3.7$ for Mn, 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 a $1 \times 3 \times 4$ mesh.

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Vegetable and Kaduk • M$_2$(O$_2$CC$_6$H$_4$C$_6$H$_4$CO$_2$)(OH)$_2$ and (NH$_4$)$_2$BPDC 1071
Supporting Information

**Acta Cryst.** (2022). E78, 1066-1071  [https://doi.org/10.1107/S2056989022009288]

Structures of dicobalt and dinickel 4,4′-biphenyldicarboxylate dihydroxide, $M_2(O_2CC_6H_4C_6H_4CO_2)(OH)_2$, $M = \text{Co and Ni}$, and diammonium 4,4′-biphenyldicarboxylate from powder diffraction data

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Computing details

Program(s) used to solve structure: DFT for Co_DFT, NH4_DFT. Program(s) used to refine structure: GSAS-II (Toby & Von Dreele, 2013) for Co_X, Ni_X, NH4_X.

Poly[(µ4-4,4′-biphenyldicarboxylato)di-µ-hydroxido-dicobalt] (Co_X)

**Crystal data**

\[[\text{Co(C}_14\text{H}_8\text{O}_4)_{0.5}(\text{OH})]\]

\[M_r = 392.09\]

Triclinic, $P\bar{1}$

Hall symbol: -P 1

\[a = 14.16 (5) \text{ Å}\]

\[b = 6.269 (3) \text{ Å}\]

\[c = 3.323 (4) \text{ Å}\]

\[\alpha = 91.43 (2)^\circ\]

\[\beta = 98.46 (7)^\circ\]

\[\gamma = 90.0 (3)^\circ\]

\[V = 291.6 (2) \text{ Å}^3\]

\[Z = 1\]

\[D_x = 2.233 \text{ Mg m}^{-3}\]

Ka_{1,2} radiation, $\lambda = 0.70932, 0.71361$ Å

\[T = 300 \text{ K}\]

**Data collection**

PANalytical Empyrean diffractometer

Specimen mounting: glass capillary

Data collection mode: transmission

Scan method: step

\[2\theta_{\text{min}} = 1.002^\circ, 2\theta_{\text{max}} = 49.991^\circ, 2\theta_{\text{step}} = 0.008^\circ\]

**Refinement**

Least-squares matrix: full

\[R_p = 0.065\]

\[R_{wp} = 0.092\]

\[R_{exp} = 0.022\]

\[R(F^2) = 0.11340\]

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,

49 parameters

H-atom parameters not defined?

\[(\Delta/\sigma)_{\text{max}} = 2.587\]

Background function: Background function: "chebyschev-1" function with 4 terms: 1205(8), -655(9), 147(7), -88(6), Background peak parameters: pos, int, sig, gam: 11.72(4), 4.94(12)e5, 3.12(13)e4, 0.100,

Preferred orientation correction: March-Dollase correction coef. = 1.000 axis = [0, 0, 1]
Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|      | x     | y     | z     | U(eq) |
|------|-------|-------|-------|-------|
| C1   | 0.613 (3) | 0.625 (7) | 0.90 (3) | 0.26 (3)* |
| C3   | 0.704 (3) | 0.560 (8) | 0.84 (3) | 0.26 (3)* |
| C5   | 0.7409 (16) | 0.364 (3) | 0.97 (2) | 0.26 (3)* |
| C6   | 0.688 (3) | 0.233 (7) | 1.18 (3) | 0.26 (3)* |
| C8   | 0.594 (3) | 0.287 (11) | 1.23 (2) | 0.26 (3)* |
| C10  | 0.5516 (10) | 0.485 (9) | 1.077 (11) | 0.26 (3)* |
| C11  | 0.8397 (9) | 0.301 (2) | 0.895 (13) | 0.026 (13)* |
| O12  | 0.8581 (8) | 0.108 (3) | 0.890 (6) | 0.026 (13)* |
| O13  | 0.9031 (7) | 0.446 (2) | 0.938 (3) | 0.026 (13)* |
| H2   | 0.58666 | 0.79555 | 0.81088 | 0.3419* |
| H4   | 0.75003 | 0.66882 | 0.67401 | 0.3419* |
| H7   | 0.72054 | 0.07982 | 1.31427 | 0.3419* |
| H9   | 0.54982 | 0.17404 | 1.38976 | 0.3419* |
| O16  | 0.9611 (9) | 0.8112 (12) | 0.471 (3) | 0.0500* |
| H17  | 0.89031 | 0.81057 | 0.42272 | 0.0650* |
| Co14 | 1.00000 | 0.00000 | 1.00000 | 0.018 (3)* |
| Co15 | 1.00000 | 0.50000 | 0.50000 | 0.018 (3)* |

Geometric parameters (Å, °)

|      | C1—C3 | O12—C11 | O12—Co14 | C1—C10 | O12—C11 | O12—Co14 |
|------|-------|---------|----------|--------|---------|----------|
| C1   | 1.399 (18) | 1.232 (10) | 2.105 (9) | 1.272 (11) | 2.098 (8) |
| C3   | 1.427 (15) | 1.272 (11) | 2.098 (8) | 1.212 (8) | 2.028 (8) |
| C5   | 1.389 (7) | 0.992 (13) | 2.098 (8) | 2.028 (8) | 2.098 (8) |
| C6   | 1.385 (8) | 0.992 (13) | 2.098 (8) | 2.028 (8) | 2.098 (8) |
| C7   | 1.41 (3) | 2.098 (8) | 2.028 (8) | 2.098 (8) | 2.028 (8) |
| C8   | 1.41 (3) | 2.098 (8) | 2.028 (8) | 2.098 (8) | 2.028 (8) |
| C9   | 1.447 (15) | 2.121 (8) | 2.028 (8) | 2.098 (8) | 2.028 (8) |
| C10  | 1.427 (15) | 2.121 (8) | 2.028 (8) | 2.098 (8) | 2.028 (8) |
| C10  | 1.447 (15) | 2.121 (8) | 2.028 (8) | 2.098 (8) | 2.028 (8) |
| C11  | 1.503 (8) | 2.028 (8) | 2.098 (8) | 2.028 (8) | 2.098 (8) |
| C12  | 1.232 (10) | 2.028 (8) | 2.098 (8) | 2.028 (8) | 2.098 (8) |
| C13  | 1.272 (11) | 2.028 (8) | 2.098 (8) | 2.028 (8) | 2.098 (8) |

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supporting information

| Bond         | Distance (Å) |
|--------------|--------------|
| C5—C6—C8    | 120.5 (9)    |
| C6—C8—C10   | 120.9 (10)   |

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

(Co_DFT)

Crystal data

\[\text{C}_{39}\text{H}_{16}\text{Co}_{2}\text{O}_{6}\]

\(M_r = 392.09\)

Triclinic, \(P\bar{1}\)

\(a = 14.20000\) Å  
\(b = 6.23720\) Å  
\(c = 3.46100\) Å

\(\alpha = 91.80^\circ\)

\(\beta = 99.44^\circ\)

\(\gamma = 89.98^\circ\)

\(V = 302.23\) Å³

\(Z = 1\)

Data collection

\(h = \rightarrow\)

\(k = \rightarrow\)

\(l = \rightarrow\)

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

| Atom | \(x\)   | \(y\)   | \(z\)   | \(B_{iso}/B_{eq}\) |
|------|---------|---------|---------|---------------------|
| C1   | 0.61569 | 0.62016 | 0.89476 |                     |
| C3   | 0.70973 | 0.56535 | 0.88026 |                     |
| C5   | 0.74057 | 0.35498 | 0.94939 |                     |
| C6   | 0.67601 | 0.20338 | 1.04253 |                     |
| C8   | 0.58279 | 0.26043 | 1.06503 |                     |
| C10  | 0.54978 | 0.47000 | 0.98891 |                     |
| C11  | 0.84012 | 0.29062 | 0.92724 |                     |
| O12  | 0.85873 | 0.09206 | 0.91494 |                     |
| O13  | 0.90299 | 0.44077 | 0.92824 |                     |
| H2   | 0.59361 | 0.78413 | 0.83081 |                     |
| H4   | 0.76000 | 0.68483 | 0.81104 |                     |
| H7   | 0.70119 | 0.04101 | 1.10392 |                     |
| H9   | 0.53543 | 0.13971 | 1.15004 |                     |
| O16  | 0.95981 | -0.19591 | 0.47462 |                     |
| H17  | 0.89031 | -0.18943 | 0.42272 |                     |
| Co14 | 1.00000 | 0.00000 | 1.00000 |                     |
| Co15 | 1.00000 | 0.50000 | 0.50000 |                     |

Poly[(\(\mu_4\)-4,4′-biphenyldicarboxylato)di-\(\mu\)-hydroxido-dinickel] (Ni_X)

Crystal data

\([\text{Ni(C14H8O4)}_{0.5}(\text{OH})]\]

\(M_r = 391.63\)

Triclinic, \(P\bar{1}\)

Hall symbol: -P 1

\(a = 15.0 (11)\) Å  
\(b = 6.04 (12)\) Å  
\(c = 4.04 (9)\) Å  
\(\alpha = 82.7 (2)^\circ\)

\(\beta = 72.3 (8)^\circ\)

\(\gamma = 82 (2)^\circ\)

\(V = 345 (2)\) Å³

\(Z = 1\)

\(D_\text{M} = 1.883\) Mg m⁻³

\(K\alpha\) radiation, \(\lambda = 1.54059, 1.54445\) Å

\(T = 300\) K

flat_sheet, 16 × 16 mm

Acta Cryst. (2022). E78, 1066-1071  sup-3
Data collection

PANalytical X′Pert
diffractometer
Specimen mounting: Si zero-background cell
with well

Data collection mode: reflection
Scan method: step
2θ_{min} = 4.008°, 2θ_{max} = 99.998°, 2θ_{step} = 0.017°

Refinement

Least-squares matrix: full
R_p = 0.042
R_wp = 0.059
R_exp = 0.011
R(F^2) = 0.09176
5745 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 5.186, -8.449, 5.755, 3.463, 0.000,
0.021,
47 parameters
30 restraints
H-atom parameters not defined?
(Δ/σ)_{max} = 4.433
Background function: Background function:
"chebyschev-l" function with 6 terms:
6.12(5)e3, -3.68(4)e3, 8.6(4)e2, 83(31),
-134(21), 50(21),
Preferred orientation correction: March-Dollase
correction coef. = 1.000 axis = [0, 0, 1]

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

|          | x      | y      | z      | U_{iso} / U_{eq} |
|----------|--------|--------|--------|------------------|
| C1       | 0.620  | 0.56   | -0.23  | 0.02             |
| C3       | 0.707  | 0.51   | -0.21  | 0.02             |
| C5       | 0.7272 | 0.38   | 0.07   | 0.02             |
| C6       | 0.653  | 0.30   | 0.34   | 0.02             |
| C8       | 0.568  | 0.322  | 0.32   | 0.02             |
| C10      | 0.546  | 0.46   | 0.02   | 0.02             |
| C11      | 0.8370 | 0.350  | 0.074  | 0.2200           |
| O12      | 0.873  | 0.147  | 0.13   | 0.2200           |
| O13      | 0.897  | 0.50   | -0.066 | 0.2200           |
| H2       | 0.6036 | 0.6836 | -0.44499 | 0.0500       |
| H4       | 0.7670 | 0.58056| -0.43809 | 0.0500       |
| H7       | 0.66673| 0.210111| 0.58822 | 0.0500       |
| H9       | 0.51034| 0.233993| 0.52487 | 0.0500       |
| Ni14     | 1.00000| 0.00000| 0.00000 | 0.018 (14)     |
| O16      | 1.00 (2)| -0.179 (4) | 0.43 (2) | 0.1000       |
| H17      | 0.93829| -0.17184| 0.50234 | 0.1300       |
| Ni15     | 1.00000| 0.50000| -0.50000| 0.018 (14)     |

Geometric parameters (Å, °)

| C1—C3   | 1.31 (2) | C11—O13 | 1.311 (16) |
| C1—C10  | 1.39 (3) | O12—C11 | 1.297 (10) |
| C3—C1   | 1.31 (2) | O12—Ni14| 1.942 (14) |
| C3—C5   | 1.396 (9)| O13—C11 | 1.311 (16) |
C5—C3 1.396 (9)  O13—Ni15 1.953 (12)
C5—C6 1.404 (16)  Ni14—O12 1.942 (14)
C5—C11 1.642 (12)  Ni14—O12\textsuperscript{ii} 1.942 (14)
C6—C5 1.404 (16)  Ni14—O16 1.927 (19)
C6—C8 1.31 (2)  Ni14—O16\textsuperscript{i} 1.927 (19)
C8—C6 1.31 (2)  O16—Ni14 1.927 (19)
C8—C10 1.46 (2)  O16—Ni15\textsuperscript{ii} 1.919 (13)
C10—C1 1.39 (3)  Ni15—O13 1.953 (12)
C10—C8 1.46 (2)  Ni15—O13\textsuperscript{iii} 1.953 (12)
C10—C10\textsuperscript{i} 1.464 (8)  Ni15—O16\textsuperscript{iv} 1.919 (13)
C11—C5 1.642 (12)  Ni15—O16\textsuperscript{i} 1.919 (13)
C11—O12 1.297 (10)

Symmetry codes: (i) −x+1, −y+1, −z; (ii) −x+2, −y, −z; (iii) −x+2, −y+1, −z−1; (iv) x, y+1, z−1.

(Ni\textsubscript{DFT})

Crystal data

| C\textsubscript{14}H\textsubscript{10}Ni\textsubscript{2}O\textsubscript{6} | Mr = 391.63 |
|---------------------------|------------|
| Triclinic, P\textsubscript{1} | a = 81.57\textdegree |
| a = 15.1000 Å | b = 6.05000 Å |
| b = 4.02000 Å | c = 343.52 Å |

Data collection

| h = | l = |
|-----|-----|

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å\textsuperscript{2})

| x  | y   | z   | B\textsubscript{iso}\textsuperscript{+}/B\textsubscript{eq} |
|----|-----|-----|------------------|
| C1 | 0.61147 | 0.63610 | −0.07671 |
| C3 | 0.70313 | 0.58310 | −0.06941 |
| C5 | 0.73667 | 0.36292 | 0.03127 |
| C6 | 0.67329 | 0.19956 | 0.14026 |
| C8 | 0.58130 | 0.25374 | 0.13082 |
| C10| 0.54811 | 0.47197 | 0.01398 |
| C11| 0.83907 | 0.31116 | −0.01437 |
| O12| 0.87153 | 0.11944 | 0.07915 |
| O13| 0.88625 | 0.47867 | −0.15724 |
| H2 | 0.58988 | 0.80914 | −0.16146 |
| H4 | 0.75109 | 0.71275 | −0.14925 |
| H7 | 0.69710 | 0.02821 | 0.22559 |
| H9 | 0.53478 | 0.12063 | 0.21394 |
Ni14  1.00000  0.00000  0.00000
O16   0.96416  −0.18943  0.44560
H17   0.89673  −0.16684  0.55127
Ni15  1.00000  0.50000  −0.50000

Crystal data
C\textsubscript{14}H\textsubscript{10}Mn\textsubscript{2}O\textsubscript{6}  \quad \alpha = 90.09^\circ
Triclinic, \textit{P}\textit{1}
\quad \beta = 96.84^\circ
a = 14.20370 Å  \quad \gamma = 91.71^\circ
b = 6.47851 Å  \quad V = 315.35 Å\textsuperscript{3}
c = 3.45320 Å  \quad Z = 2

Data collection
\quad h = \rightarrow
\quad k = \rightarrow
\quad l = \rightarrow

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å\textsuperscript{2})

|      | x      | y      | z      | \(B_{iso}\)/\(B_{eq}\) |
|------|--------|--------|--------|------------------------|
| C1   | 0.62098| 0.61370| 0.92029|                        |
| H1   | 0.60389| 0.77429| 0.86234|                        |
| C2   | 0.71402| 0.55707| 0.91323|                        |
| H2   | 0.76792| 0.67253| 0.85491|                        |
| C3   | 0.73912| 0.35104| 0.97430|                        |
| C4   | 0.66914| 0.20599| 0.05646|                        |
| H3   | 0.68946| 0.04707| 0.11422|                        |
| C5   | 0.57681| 0.26460| 0.07216|                        |
| H4   | 0.52506| 0.14840| 0.14642|                        |
| C6   | 0.54945| 0.46945| 0.99724|                        |
| C7   | 0.83666| 0.28496| 0.94908|                        |
| O1   | 0.85281| 0.09402| 0.92904|                        |
| O2   | 0.90327| 0.42816| 0.95195|                        |
| Mn1  | 1.00000| 0.00000| 0.00000|                        |
| Mn2  | 1.00000| 0.50000| −0.50000|                       |
| O3   | 0.95566| −0.19618| 0.47885|                        |
| H17  | 0.886619| −0.19037| 0.44315|                        |

Diammonium 4,4′-biphenyldicarboxylate (NH\textsubscript{4}_X)

Crystal data
2NH\textsubscript{4}+·C\textsubscript{14}H\textsubscript{8}O\textsubscript{4}2−  \quad \beta = 91.41 (4)^\circ
\(M_r = 276.29\)
Triclinic, \textit{P}\textit{1}
\quad \gamma = 92.775 (11)^\circ
Hall symbol: P 1
\quad \upsilon = 351.43 (17) Å\textsuperscript{3}
\(a = 4.6770 (6)\) Å  \quad Z = 1
\(b = 5.2306 (14)\) Å
\(c = 14.387 (6)\) Å  \quad D_x = 1.306 Mg m\textsuperscript{−3}
\(a = 90.57 (7)^\circ\)
\(K\alpha\textsubscript{1,2}\) radiation, \(\lambda = 0.70932, 0.71361\) Å
\(T = 300\) K
cylinder, 12 × 0.7 mm
Data collection

PANalytical Empyrean
diffractometer
Specimen mounting: glass capillary

Data collection mode: transmission
Scan method: step
2θ min = 1.008°, 2θ max = 49.982°, 2θ step = 0.008°

Refinement

Least-squares matrix: full
R p = 0.033
R w p = 0.043
R exp = 0.015
R(F²) = 0.09394

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)² + 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,
93 parameters
55 restraints
H-atom parameters not defined?

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

|   | x      | y      | z       | U(eq)   |
|---|--------|--------|---------|---------|
| H1| 0.56271| 0.55748| -0.04903| 0.0500* |
| C2| 0.72650| 0.71007| -0.07277| 0.0042* |
| C3| 1.092 (10)| 1.091 (7)| -0.1369 (14)| 0.0042* |
| C4| 0.886 (5)| 0.858 (4)| -0.0073 (7)| 0.0042* |
| C5| 0.759 (8)| 0.741 (7)| -0.1644 (4)| 0.0042* |
| C6| 0.942 (5)| 0.928 (5)| -0.1987 (9)| 0.0042* |
| C7| 1.068 (8)| 1.055 (6)| -0.0421 (13)| 0.0042* |
| H8| 0.63274| 0.60998| -0.21606| 0.0500* |
| H9| 1.19666| 1.18586| 0.00901| 0.0500* |
| H10| 1.23536| 1.25494| -0.16391| 0.0500* |
| C11| 0.935 (5)| 0.754 (5)| 0.0884 (8)| 0.0042* |
| C12| 1.040 (7)| 0.578 (6)| 0.2730 (11)| 0.0042* |
| C13| 0.788 (12)| 0.847 (10)| 0.1638 (15)| 0.0042* |
| C14| 1.140 (8)| 0.571 (9)| 0.1072 (12)| 0.0042* |
| C15| 1.197 (11)| 0.490 (10)| 0.1986 (15)| 0.0042* |
| C16| 0.833 (10)| 0.754 (9)| 0.2538 (12)| 0.0042* |
| H17| 0.62741| 1.00179| 0.15295| 0.0500* |
| H18| 1.26305| 0.48583| 0.04787| 0.0500* |
| H19| 1.37364| 0.35094| 0.21156| 0.0500* |
| H20| 0.69528| 0.82586| 0.31194| 0.0500* |
| C21| 1.076 (7)| 0.480 (7)| 0.3737 (13)| 0.0566* |
| C22| 0.944 (5)| 0.962 (6)| -0.3033 (10)| 0.0566* |
| O23| 0.840 (7)| 0.413 (8)| 0.4081 (17)| 0.0566* |
| O24| 0.969 (10)| 0.758 (7)| -0.3508 (14)| 0.0566* |
| O25| 1.309 (7)| 0.371 (8)| 0.4015 (16)| 0.0566* |
supporting information

| Atom | U1   | U2   | U3   | C1-U1 | C1-U2 | C1-U3 |
|------|------|------|------|-------|-------|-------|
| O26  | 0.762(7) | 1.119(7) | -0.3310(18) | 0.0566* |
| N27  | 0.34475 | 1.28836 | -0.39168 | 0.0500* |
| H29  | 0.36001 | 1.43931 | -0.43695 | 0.0500* |
| H30  | 0.22878 | 1.13756 | -0.42606 | 0.0500* |
| H31  | 0.54682 | 1.23237 | -0.37405 | 0.0500* |
| H32  | 0.24338 | 1.34422 | -0.33265 | 0.0500* |
| N28  | 0.88714 | 0.85588 | -0.47716 | 0.0500* |
| H33  | 0.85037 | 0.66062 | -0.48279 | 0.0500* |
| H34  | 0.69609 | 0.94431 | -0.48449 | 0.0500* |
| H35  | 1.02320 | 0.91738 | -0.52839 | 0.0500* |
| H36  | 0.97893 | 0.90122 | -0.41298 | 0.0500* |

Geometric parameters (Å, °)

| Bond        | Distance   |
|-------------|------------|
| C2—C4       | 1.392 (7)  |
| C2—C5       | 1.342 (6)  |
| C3—C6       | 1.379 (6)  |
| C3—C7       | 1.385 (6)  |
| C4—C2       | 1.392 (7)  |
| C4—C7       | 1.408 (7)  |
| C4—C11      | 1.501 (8)  |
| C5—C2       | 1.342 (6)  |
| C5—C6       | 1.373 (6)  |
| C6—C3       | 1.379 (6)  |
| C6—C5       | 1.373 (6)  |
| C6—C22      | 1.518 (7)  |
| C7—C3       | 1.385 (6)  |
| C7—C4       | 1.408 (7)  |
| C11—C4      | 1.501 (8)  |
| C11—C13     | 1.394 (8)  |
| C11—C14     | 1.410 (7)  |
| C12—C15     | 1.401 (6)  |
| C12—C16     | 1.390 (6)  |
| C12—C21     | 1.550 (7)  |
| C13—C11     | 1.394 (8)  |
| C13—C16     | 1.402 (7)  |
| C14—C11     | 1.410 (7)  |
| C14—C15     | 1.408 (6)  |
| C15—C12     | 1.401 (6)  |
| C15—C14     | 1.408 (6)  |
| C16—C12     | 1.390 (6)  |
| C4—C2—C5    | 121.9 (4)  |
| C6—C3—C7    | 119.9 (3)  |
| C2—C4—C7    | 116.5 (4)  |
| C2—C4—C11   | 119.4 (6)  |
| C7—C4—C11   | 120.9 (6)  |
| C2—C5—C6    | 121.7 (3)  |
C3—C6—C5 118.8 (4) O24—C22—O26 118.2 (8)
C3—C6—C22 123.5 (5) H29—N27—H30 109.483
C5—C6—C22 117.4 (5) H29—N27—H31 109.476
C3—C7—C4 121.0 (4) H30—N27—H31 109.464
C4—C11—C13 120.6 (5) H29—N27—H32 109.459
C4—C11—C14 122.2 (5) H30—N27—H32 109.468
C13—C11—C14 117.1 (4) H31—N27—H32 109.477
C15—C12—C16 117.7 (3) H33—N28—H34 109.48
C15—C12—C21 123.1 (4) H33—N28—H35 109.471
C16—C12—C21 119.1 (4) H34—N28—H35 109.47
C11—C13—C16 121.4 (6) H33—N28—H36 109.475
C11—C14—C15 121.2 (4) H34—N28—H36 109.469
C12—C15—C14 120.8 (4) H35—N28—H36 109.461

(NH4_DFT)

Crystal data

C14H16N2O4  α = 90.7300°
M_r = 276.29  β = 91.3790°
Triclinic, P  γ = 92.7400°
a = 4.6875 Å  V = 352.86 Å³
b = 5.2421 Å  Z = 1
c = 14.3820 Å

Data collection

h = →

k = →
l = →

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

|     | x    | y    | z    | U_iso*/U_eq |
|-----|------|------|------|-------------|
| H1  | 0.59450 | 0.55016 | -0.04709 | 0.0500* |
| C2  | 0.72650 | 0.71007 | -0.07277 | 0.0042* |
| C3  | 1.06402 | 1.11446 | -0.14004 | 0.0042* |
| C4  | 0.92175 | 0.84164 | -0.01188 | 0.0042* |
| C5  | 0.69564 | 0.78221 | -0.16536 | 0.0042* |
| C6  | 0.86113 | 0.98774 | -0.19952 | 0.0042* |
| C7  | 1.09298 | 1.04187 | -0.04764 | 0.0042* |
| H8  | 0.54136 | 0.67676 | -0.21098 | 0.0500* |
| H9  | 1.25407 | 1.13999 | -0.00242 | 0.0500* |
| H10 | 1.20239 | 1.26916 | -0.16643 | 0.0500* |
| C11 | 0.93949 | 0.77658 | 0.08868 | 0.0042* |
| C12 | 0.94951 | 0.64759 | 0.27910 | 0.0042* |
| C13 | 0.78111 | 0.91048 | 0.15313 | 0.0042* |
| C14 | 1.10777 | 0.58142 | 0.12166 | 0.0042* |
| C15 | 1.11387 | 0.51792 | 0.21543 | 0.0042* |
| C16 | 0.78458 | 0.84572 | 0.24662 | 0.0042* |
| H17 | 0.65053 | 1.06440 | 0.12910 | 0.0500* |
| H18 | 1.23568 | 0.47852 | 0.07278 | 0.0500* |
| H19 | 1.24343 | 0.36444 | 0.24034 | 0.0500* |
Hydrogen-bond geometry (Å, °)

| D—H···A     | D—H | H···A | D···A | D—H···A |
|-------------|------|-------|-------|---------|
| N27—H29···O25i | 1.05 | 1.88  | 2.907 | 167     |
| N27—H30···O26ii | 1.04 | 1.95  | 2.979 | 172     |
| N27—H31···O24iii | 1.06 | 1.62  | 2.650 | 162     |
| N27—H32···O26iv | 1.04 | 1.90  | 2.942 | 174     |
| N28—H33···O23v | 1.06 | 1.62  | 2.655 | 164     |
| N28—H34···O26vi | 1.04 | 2.00  | 3.007 | 164     |
| N28—H35···O25i | 1.04 | 1.88  | 2.904 | 169     |
| N28—H36···O25ii | 1.05 | 1.85  | 2.885 | 172     |

Symmetry codes: (i) x−1, y, z; (ii) x, y−1, z+1; (iii) x−1, y, z+1; (iv) x−1, y−1, z+1; (v) x, y−1, z.