



# Structures of dicobalt and dinickel 4,4'-biphenyldicarboxylate dihydroxide, $M_2(O_2CC_6H_4C_6H_4CO_2)(OH)_2$ , $M = Co$ and $Ni$ , and diammonium 4,4'-biphenyldicarboxylate from powder diffraction data

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The triclinic structures of poly[( $\mu_4$ -4,4'-biphenyldicarboxylato)di- $\mu$ -hydroxido-dicobalt],  $[Co_2(C_{14}H_8O_4)(OH)_2]_n$ , and poly[( $\mu_4$ -4,4'-biphenyldicarboxylato)di- $\mu$ -hydroxido-dinickel],  $[Ni_2(C_{14}H_8O_4)(OH)_2]_n$ , were established using laboratory X-ray powder diffraction data. These structures, as well as that of poly[( $\mu_4$ -4,4'-biphenyldicarboxylato)di- $\mu$ -hydroxido-dimanganese],  $[Mn_2(C_{14}H_8O_4)(OH)_2]_n$ , were optimized using density functional techniques. The structure of diammonium 4,4'-biphenyldicarboxylate,  $2NH_4^+ \cdot C_{14}H_8O_4^{2-}$ , was also solved using laboratory powder data. The Mn and Co compounds are isostructural: the octahedral  $MO_6$  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  $(NH_4)_2BPDC$  consists of alternating layers of BPDC and ammonium ions lying parallel to the  $ab$  plane. Each hydrogen atom of the ammonium ions in  $(NH_4)_2BPDC$  participates in a strong  $N-H \cdots O$  hydrogen bond.

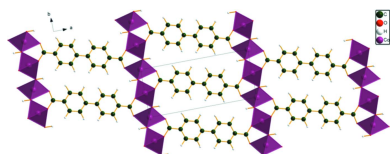
## 1. Chemical context

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,  $C_{14}H_8O_4^{2-}$ ) 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- $Co_3O_4$ . 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  $Co_2BPDC(OH)_2$  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).

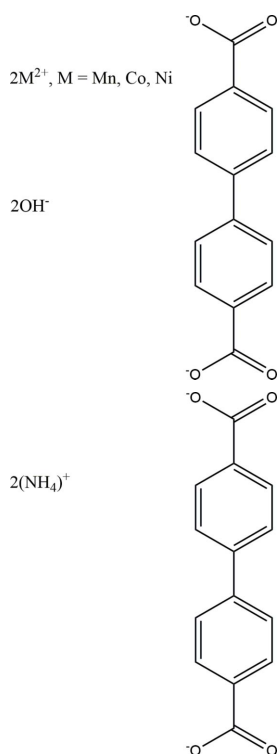
Most syntheses involving BPDC use  $H_2BPDC$  and a base. We prepared diammonium 4,4'-biphenyldicarboxylate as an



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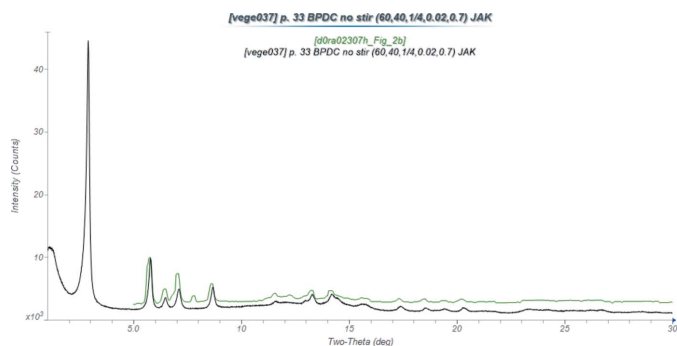
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alternative (and more soluble) reagent, characterized its crystal structure, and used it to prepare  $\text{Ni}_2\text{BPDC}(\text{OH})_2$ .



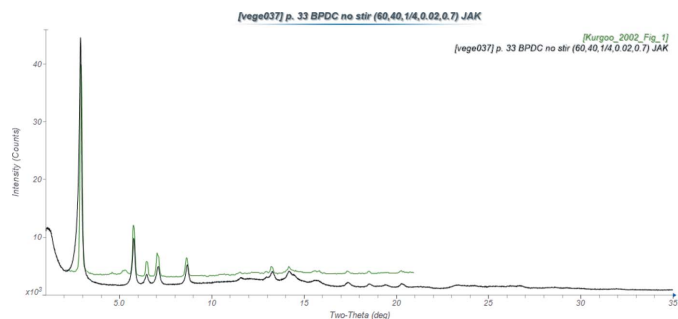
## 2. Structural commentary

The X-ray powder patterns show that the  $M_2\text{BPDC}(\text{OH})_2$  phases for  $M = \text{Mn, Co, Ni}$  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  $M = \text{Mn, Co, Ni}$ , 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



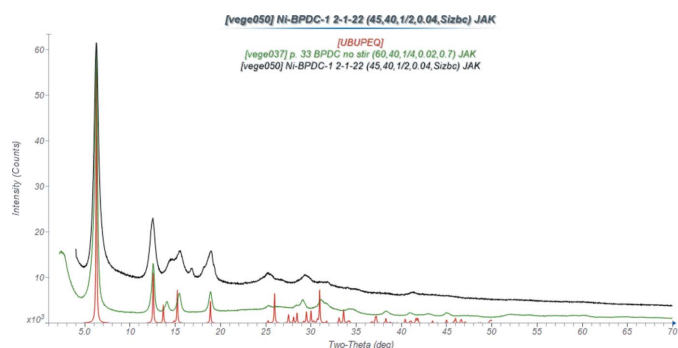
**Figure 1**

Comparison of the powder pattern of the  $\text{Co}_2\text{BPDC}(\text{OH})_2$  of this study (black) to that reported by Ipadeola & Ozoemena (2020; green). The literature pattern (measured using  $\text{Cu } K\alpha$  radiation) was digitized using *UN-SCAN-IT* (Silk Scientific, 2013), and converted to  $\text{Mo } K\alpha$  using *JADE Pro* (MDI, 2021). Image generated using *JADE Pro* (MDI, 2021).



**Figure 2**

Comparison of the powder pattern of the  $\text{Co}_2\text{BPDC}(\text{OH})_2$  of this study (black) to that reported by Kurmoo & Kumagai (2002; green). The literature pattern (measured using  $\text{Cu } K\alpha$  radiation) was digitized using *UN-SCAN-IT* (Silk Scientific, 2013), and converted to  $\text{Mo } K\alpha$  using *JADE Pro* (MDI, 2021). Image generated using *JADE Pro* (MDI, 2021).



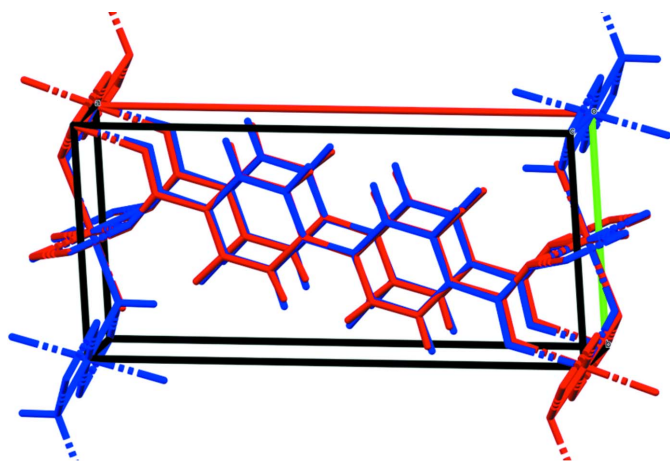
**Figure 3**

Powder patterns of  $\text{Mn}_2\text{BPDC}(\text{OH})_2$  (calculated from CSD entry UBUPEQ; red) to the experimental patterns of  $\text{Co}_2\text{BPDC}(\text{OH})_2$  (green) and  $\text{Ni}_2\text{BPDC}(\text{OH})_2$  (black). The patterns were converted to  $\text{Cu } K\alpha$  using *JADE Pro* (MDI, 2021). Image generated using *JADE Pro* (MDI, 2021).

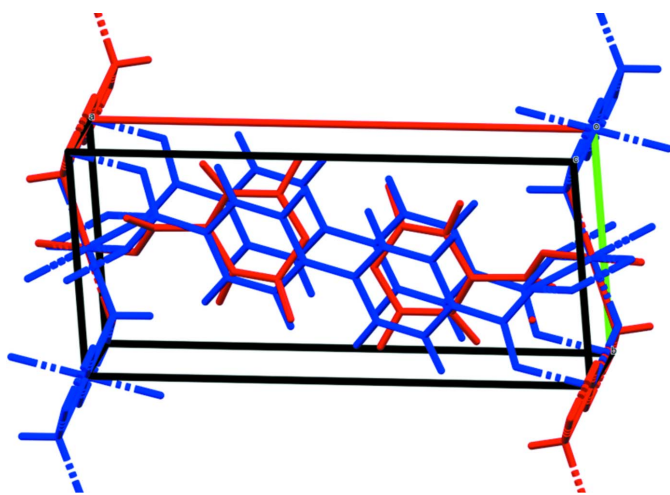
alternate coordination of the Ni cations. Sorting out these details is not supported by the relatively poor diffraction data on the Ni compound. This discussion concentrates on the DFT-optimized structures.

All of the bond distances, angles, and torsion angles in the BPDC anions fall within the normal ranges indicated by a *Mercury Mogul Geometry check* (Macrae *et al.*, 2020). The  $\text{O}12-\text{C}11-\text{C}5-\text{C}6$  torsion angles (which represent the twist of the carboxylate group out of the phenyl ring plane) of  $-13.1$ ,  $-14.1$ , and  $-6.6^\circ$  for Mn, Co, and Ni, respectively, represent increases of conformational energy of approximately  $1 \text{ kcal mol}^{-1}$  (Kaduk *et al.*, 1999). These small increases can be easily overcome by energy gains in coordination to the metal ions. The  $\text{C}8-\text{C}10-\text{C}10-\text{C}1$  torsion angles of  $0.6$ ,  $0.6$ , and  $0.1^\circ$  indicate that the BPDC ligands are essentially planar. The approximate Miller planes of the benzene rings of the BPDC moieties are (238), (225) and (259) for Mn, Co, and Ni, respectively.

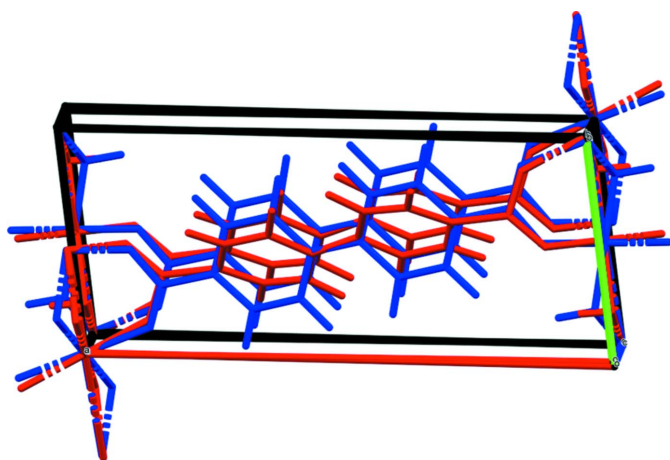
Unlike the metal complexes, in diammonium BPDC, the aromatic rings are nearly perpendicular ( $\text{C}2-\text{C}4-\text{C}11-\text{C}14 = 85.7^\circ$ ). One carboxylate group lies nearly in the ring plane ( $\text{O}25-\text{C}21-\text{C}12-\text{C}15 = 4.6^\circ$ ), while the other ( $\text{O}24-\text{C}22-\text{C}6-\text{C}3 = 85.6^\circ$ ) is nearly perpendicular to its ring. The r.m.s. Cartesian displacement of the non-H atoms in the BPDC anion is  $0.384 \text{ \AA}$  (Fig. 7).



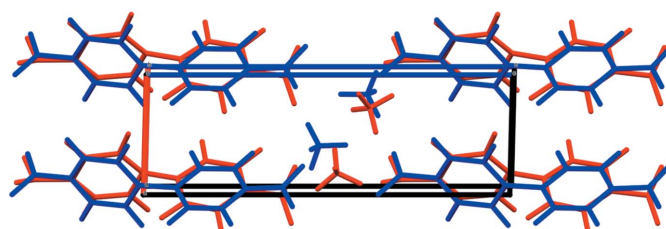
**Figure 4**  
Comparison of the Rietveld-refined (red) and VASP-optimized (blue) structures of  $\text{Mn}_2(\text{BPDC})(\text{OH})_2$ . The r.m.s. Cartesian displacement is 0.133 Å. Image generated using *Mercury* (Macrae *et al.*, 2020).



**Figure 5**  
Comparison of the Rietveld-refined (red) and VASP-optimized (blue) structures of  $\text{Co}_2(\text{BPDC})(\text{OH})_2$ . The r.m.s. Cartesian displacement is 0.264 Å. Image generated using *Mercury* (Macrae *et al.*, 2020).



**Figure 6**  
Comparison of the Rietveld-refined (red) and VASP-optimized (blue) structures of  $\text{Ni}_2(\text{BPDC})(\text{OH})_2$ . The r.m.s. Cartesian displacement is 0.563 Å. Image generated using *Mercury* (Macrae *et al.*, 2020).



**Figure 7**  
Comparison of the Rietveld-refined (red) and VASP-optimized (blue) structures of  $(\text{NH}_4)_2(\text{BPDC})$ . The r.m.s. Cartesian displacement is 0.384 Å. Image generated using *Mercury* (Macrae *et al.*, 2020).

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  $M\text{—O}$  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.

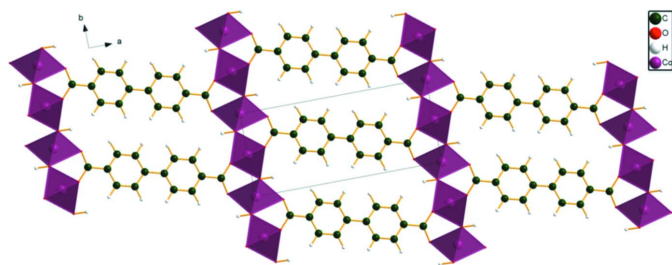
A uniaxial microstrain model (100 as the unique axis) was used to model the peak profiles. The axial and equatorial microstrains for Co are  $7.4 \times 10^4$  and  $5.6 \times 10^4$  ppm, while those for Ni show a greater difference, at  $1.1 \times 10^5$  and  $1.5 \times 10^4$  ppm, respectively. 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.

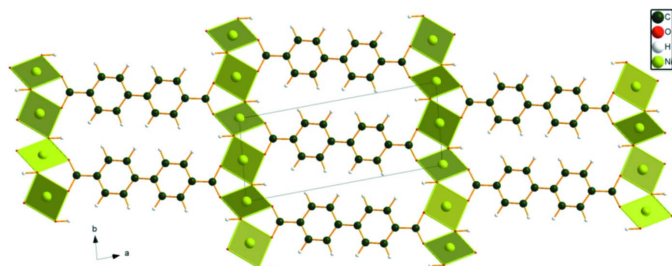
### 3. Supramolecular features

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  $M15$ .

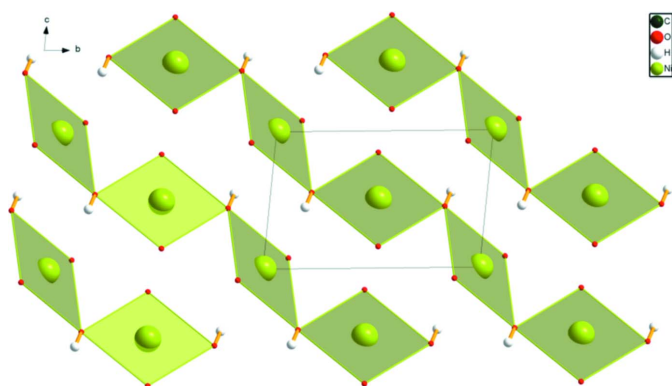




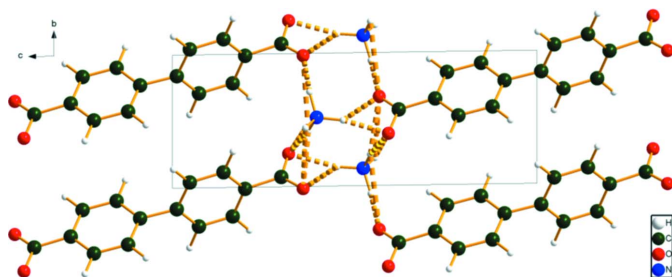
**Figure 8**  
Crystal structure of  $\text{Co}_2(\text{BPDC})(\text{OH})_2$ , viewed down the  $c$ -axis. Image generated using *DIAMOND* (Crystal Impact, 2022).



**Figure 9**  
Crystal structure of  $\text{Ni}_2(\text{BPDC})(\text{OH})_2$ , viewed down the  $c$ -axis. Image generated using *DIAMOND* (Crystal Impact, 2022).



**Figure 10**  
View of the discontinuous layers in  $\text{Ni}_2(\text{BPDC})(\text{OH})_2$  down the  $a$ -axis. Image generated using *DIAMOND* (Crystal Impact, 2022).



**Figure 11**  
Crystal structure of  $(\text{NH}_4)_2(\text{BPDC})$ , viewed down the  $a$ -axis. Image generated using *DIAMOND* (Crystal Impact, 2022). The hydrogen bonds are illustrated by heavy dashed lines.

**Table 1**  
Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N27}-\text{H29}\cdots\text{O25}^{\text{i}}$	1.05	1.88	2.907	167
$\text{N27}-\text{H30}\cdots\text{O26}^{\text{ii}}$	1.04	1.95	2.979	172
$\text{N27}-\text{H31}\cdots\text{O24}^{\text{iii}}$	1.06	1.62	2.650	162
$\text{N27}-\text{H32}\cdots\text{O26}^{\text{iv}}$	1.04	1.90	2.942	174
$\text{N28}-\text{H33}\cdots\text{O23}^{\text{v}}$	1.06	1.62	2.655	164
$\text{N28}-\text{H34}\cdots\text{O26}^{\text{ii}}$	1.04	2.00	3.007	164
$\text{N28}-\text{H35}\cdots\text{O25}^{\text{i}}$	1.04	1.88	2.904	169
$\text{N28}-\text{H36}\cdots\text{O25}$	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)  $x, y-1, z$ .

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  $\text{O16}$  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).  $\text{Ni14}$  is square planar, with *trans* carboxylate  $\text{O12}$  atoms and two *trans* hydroxyl groups.  $\text{Ni15}$  is also square planar, with *trans* hydroxyl  $\text{O16}$  and carboxylate  $\text{O13}$  atoms. Atom  $\text{O12}$  is bonded to  $\text{Ni14}$  (same), and  $\text{O13}$  is bonded to  $\text{Ni15}$  (different). Each carboxyl group bridges two metal atoms (not three), and the hydroxyl group  $\text{O16}$  bridges one  $\text{Ni14}$  and one  $\text{Ni15}$ . Both Ni ions share hydroxyl corners to form chains lying parallel to the  $[01\bar{1}]$  axis. The result is layers, but not connected (Fig. 10).

The structure of  $(\text{NH}_4)_2\text{BPDC}$  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  $(\text{NH}_4)_2\text{BPDC}$  participates in a strong  $\text{N}-\text{H}\cdots\text{O}$  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  $\text{Co}_2\text{BPDC}(\text{OH})_2$  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  $\text{Mn}_2\text{BPDC}(\text{OH})_2$ , 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 triethylamine and  $\sim 60$  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  $(\text{NH}_4)_2\text{BPDC}$ .

## 6. Refinement

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

The powder pattern of  $(\text{NH}_4)_2\text{BPDC}$  was indexed using *DOCVOL14* (Louër & Boulton, 2014). All attempts to solve and refine the structure in space group  $P\bar{1}$  were unsuccessful,

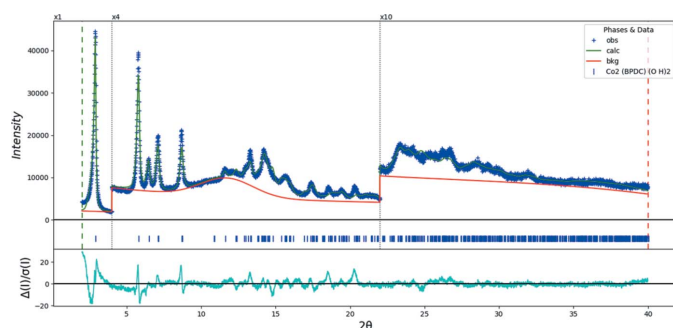


Figure 13

The Rietveld plot for the refinement of  $\text{Co}_2\text{BPDC}(\text{OH})_2$ . 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  $4\times$  for  $2\theta > 4.0^\circ$ , and by a factor of  $10\times$  for  $2\theta > 22.0^\circ$ .

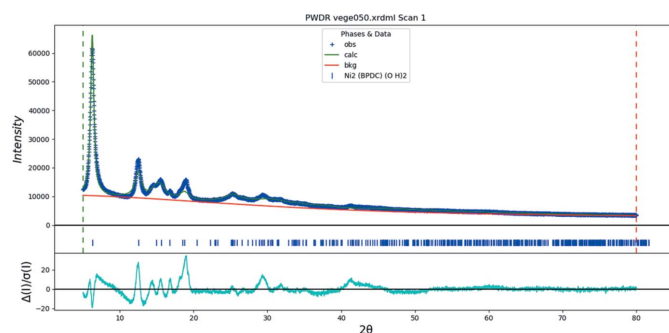


Figure 14

The Rietveld plot for the refinement of  $\text{Ni}_2\text{BPDC}(\text{OH})_2$ . 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.

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  $\chi^2$ . The  $U_{\text{iso}}$  parameters were grouped by chemical similarity: given the complex, low-symmetry structures and poor data quality, these values should be treated with caution. The  $U_{\text{iso}}$  for the H atoms were fixed at  $1.3 \times U_{\text{iso}}$  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  $\mu\text{-R}$  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-

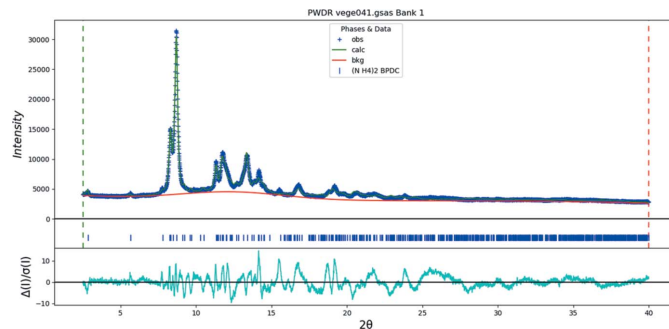


Figure 15

The Rietveld plot for the refinement of  $(\text{NH}_4)_2\text{BPDC}(\text{OH})_2$ . 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.

**Table 2**  
Experimental details.

	Co <sub>2</sub> (O <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> C <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> )(OH) <sub>2</sub>	Ni <sub>2</sub> (O <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> C <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> )(OH) <sub>2</sub>	(NH <sub>4</sub> ) <sub>2</sub> BPDC
Crystal data			
Chemical formula	[Co(C <sub>14</sub> H <sub>8</sub> O <sub>4</sub> ) <sub>0.5</sub> (OH)]	[Ni(C <sub>14</sub> H <sub>8</sub> O <sub>4</sub> ) <sub>0.5</sub> (OH)]	2NH <sub>4</sub> <sup>+</sup> ·C <sub>14</sub> H <sub>8</sub> O <sub>4</sub> <sup>2-</sup>
<i>M<sub>r</sub></i>	392.09	391.63	276.29
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> 1
Temperature (K)	300	300	300
<i>a</i> , <i>b</i> , <i>c</i> (Å)	14.16 (5), 6.269 (3), 3.323 (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)
<i>V</i> (Å <sup>3</sup> )	291.6 (2)	345 (2)	351.43 (17)
<i>Z</i>	1	1	1
Radiation type	<i>K</i> $\alpha$ <sub>1,2</sub> , $\lambda$ = 0.70932, 0.71361 Å	<i>K</i> $\alpha$ <sub>1,2</sub> , $\lambda$ = 1.54059, 1.54445 Å	<i>K</i> $\alpha$ <sub>1,2</sub> , $\lambda$ = 0.70932, 0.71361 Å
Specimen shape, size (mm)	Cylinder, 12 × 0.7	Flat sheet, 16 × 16	Cylinder, 12 × 0.7
Data collection			
Diffraction	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
2 $\theta$ values (°)	2 $\theta$ <sub>min</sub> = 1.002 2 $\theta$ <sub>max</sub> = 49.991, 2 $\theta$ <sub>step</sub> = 0.008	2 $\theta$ <sub>min</sub> = 4.008 2 $\theta$ <sub>max</sub> = 99.998, 2 $\theta$ <sub>step</sub> = 0.017	2 $\theta$ <sub>min</sub> = 1.008 2 $\theta$ <sub>max</sub> = 49.982, 2 $\theta$ <sub>step</sub> = 0.008
Refinement			
<i>R</i> factors and goodness of fit	<i>R<sub>p</sub></i> = 0.065, <i>R<sub>wp</sub></i> = 0.092, <i>R<sub>exp</sub></i> = 0.022, <i>R</i> ( <i>F</i> <sup>2</sup> ) = 0.11340, $\chi^2$ = 21.977	<i>R<sub>p</sub></i> = 0.042, <i>R<sub>wp</sub></i> = 0.059, <i>R<sub>exp</sub></i> = 0.011, <i>R</i> ( <i>F</i> <sup>2</sup> ) = 0.09176, $\chi^2$ = 30.426	<i>R<sub>p</sub></i> = 0.033, <i>R<sub>wp</sub></i> = 0.043, <i>R<sub>exp</sub></i> = 0.015, <i>R</i> ( <i>F</i> <sup>2</sup> ) = 0.09394, $\chi^2$ = 14.055
No. of parameters	49	47	93
No. of restraints	64	30	55
( $\Delta$ / $\sigma$ ) <sub>max</sub>	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 LDSA+U approach, and *U<sub>J</sub>* = 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<sup>-1</sup> leading to a 1 × 3 × 4 mesh.

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## supporting information

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## Structures of dicobalt and dinickel 4,4'-biphenyldicarboxylate dihydroxide, $M_2(O_2CC_6H_4C_6H_4CO_2)(OH)_2$ , $M = Co$ and $Ni$ , and diammonium 4,4'-biphenyldicarboxylate from powder diffraction data

Joshua D. Vegetable and James A. Kaduk

### 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[( $\mu_4$ -4,4'-biphenyldicarboxylato)di- $\mu$ -hydroxido-dicobalt] (Co\_X)

### Crystal data

[Co(C<sub>14</sub>H<sub>8</sub>O<sub>4</sub>)<sub>0.5</sub>(OH)]

$M_r = 392.09$

Triclinic,  $P\bar{1}$

Hall symbol: -P 1

$a = 14.16$  (5) Å

$b = 6.269$  (3) Å

$c = 3.323$  (4) Å

$\alpha = 91.43$  (2)°

$\beta = 98.46$  (7)°

$\gamma = 90.0$  (3)°

$V = 291.6$  (2) Å<sup>3</sup>

$Z = 1$

$D_x = 2.233$  Mg m<sup>-3</sup>

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

$T = 300$  K

cylinder,  $12 \times 0.7$  mm

### Data collection

PANalytical Empyrean  
diffractometer

Specimen mounting: glass capillary

Data collection mode: transmission

Scan method: step

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

### Refinement

Least-squares matrix: full

$R_p = 0.065$

$R_{wp} = 0.092$

$R_{\text{exp}} = 0.022$

$R(F^2) = 0.11340$

5864 data points

Profile function: Finger-Cox-Jephcoat function

parameters U, V, W, X, Y, SH/L: peak

variance(Gauss) =  $U \tan(\text{Th})^2 + V \tan(\text{Th}) + W$ :

peak HW(Lorentz) =  $X / \cos(\text{Th}) + Y \tan(\text{Th})$ ;

SH/L = S/L + H/L U, V, W in (centideg)<sup>2</sup>, X & Y

in centideg 30.816, 10.768, 0.000, 1.935, 0.000,

0.033,

49 parameters

H-atom parameters not defined?

$(\Delta/\sigma)_{\max} = 2.587$

Background function: Background function:

"chebyshev-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 ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
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 ( $\text{\AA}$ ,  $^\circ$ )

C1—C3	1.399 (18)	O12—C11	1.232 (10)
C1—C10	1.427 (15)	O12—Co14	2.105 (9)
C3—C1	1.399 (18)	O13—C11	1.272 (11)
C3—C5	1.389 (7)	O16—H17	0.992 (13)
C5—C3	1.389 (7)	O16—Co14 <sup>ii</sup>	2.098 (8)
C5—C6	1.385 (8)	O16—Co14 <sup>iii</sup>	2.121 (8)
C5—C11	1.503 (8)	O16—Co15	2.028 (8)
C6—C5	1.385 (8)	H17—O16	0.992 (13)
C6—C8	1.41 (3)	Co14—O12	2.105 (9)
C8—C6	1.41 (3)	Co14—O12 <sup>iv</sup>	2.105 (9)
C8—C10	1.447 (15)	Co14—O16 <sup>v</sup>	2.121 (8)
C10—C1	1.427 (15)	Co14—O16 <sup>vi</sup>	2.098 (8)
C10—C8	1.447 (15)	Co14—O16 <sup>vii</sup>	2.098 (8)
C10—C10 <sup>i</sup>	1.489 (5)	Co14—O16 <sup>viii</sup>	2.121 (8)
C11—C5	1.503 (8)	Co15—O16	2.028 (8)
C11—O12	1.232 (10)	Co15—O16 <sup>viii</sup>	2.028 (8)
C11—O13	1.272 (11)		
C3—C1—C10	121.0 (6)	C1—C10—C8	116.0 (9)
C1—C3—C5	121.4 (5)	C1—C10—C10 <sup>i</sup>	114 (5)
C3—C5—C6	119.5 (5)	C8—C10—C10 <sup>i</sup>	124 (6)
C3—C5—C11	119.9 (5)	C5—C11—O12	117.3 (8)
C6—C5—C11	120.5 (6)	C5—C11—O13	117.1 (8)



C5—C6—C8	120.5 (9)	O12—C11—O13	123.6 (10)
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)  $x, y-1, z+1$ ; (vi)  $x, y-1, z$ ; (vii)  $-x+2, -y+1, -z+2$ ; (viii)  $-x+2, -y+1, -z+1$ .

(Co\_DFT)

Crystal data

$C_{14}H_{10}Co_2O_6$	$\alpha = 91.80^\circ$
$M_r = 392.09$	$\beta = 99.44^\circ$
Triclinic, $P\bar{1}$	$\gamma = 89.98^\circ$
$a = 14.20000 \text{ \AA}$	$V = 302.23 \text{ \AA}^3$
$b = 6.23720 \text{ \AA}$	$Z = 1$
$c = 3.46100 \text{ \AA}$	

Data collection

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$B_{iso}^*/B_{eq}$
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

$[Ni(C_{14}H_8O_4)_{0.5}(OH)]$	$\beta = 72.3 (8)^\circ$
$M_r = 391.63$	$\gamma = 82 (2)^\circ$
Triclinic, $P\bar{1}$	$V = 345 (2) \text{ \AA}^3$
Hall symbol: -P 1	$Z = 1$
$a = 15.0 (11) \text{ \AA}$	$D_x = 1.883 \text{ Mg m}^{-3}$
$b = 6.04 (12) \text{ \AA}$	$K\alpha_{1,2}$ radiation, $\lambda = 1.54059, 1.54445 \text{ \AA}$
$c = 4.04 (9) \text{ \AA}$	$T = 300 \text{ K}$
$\alpha = 82.7 (2)^\circ$	flat_sheet, $16 \times 16 \text{ mm}$

Data collection

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

Data collection mode: reflection  
Scan method: step  
 $2\theta_{\min} = 4.008^\circ$ ,  $2\theta_{\max} = 99.998^\circ$ ,  $2\theta_{\text{step}} = 0.017^\circ$

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) =  $U \tan(\text{Th})^2 + V \tan(\text{Th}) + W$ ;  
peak HW(Lorentz) =  $X / \cos(\text{Th}) + Y \tan(\text{Th})$ ;  
SH/L = S/L+H/L U, V, W in (centideg)<sup>2</sup>, 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?  
 $(\Delta/\sigma)_{\max} = 4.433$   
Background function: Background function:  
"chebyshev-1" 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 ( $\text{\AA}^2$ )

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.620 (3)	0.56 (4)	-0.23 (3)	0.02 (4)*
C3	0.707 (2)	0.51 (2)	-0.21 (3)	0.02 (4)*
C5	0.7272 (18)	0.38 (2)	0.07 (2)	0.02 (4)*
C6	0.653 (4)	0.30 (3)	0.34 (3)	0.02 (4)*
C8	0.568 (2)	0.322 (18)	0.32 (2)	0.02 (4)*
C10	0.546 (3)	0.46 (3)	0.02 (4)	0.02 (4)*
C11	0.8370 (16)	0.350 (15)	0.074 (19)	0.2200*
O12	0.873 (4)	0.147 (19)	0.13 (5)	0.2200*
O13	0.897 (4)	0.50 (2)	-0.066 (13)	0.2200*
H2	0.60369	0.68368	-0.44499	0.0500*
H4	0.76708	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 ( $\text{\AA}$ ,  $^\circ$ )

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 <sup>ii</sup>	1.942 (14)
C6—C5	1.404 (16)	Ni14—O16	1.927 (19)
C6—C8	1.31 (2)	Ni14—O16 <sup>ii</sup>	1.927 (19)
C8—C6	1.31 (2)	O16—Ni14	1.927 (19)
C8—C10	1.46 (2)	O16—Ni15 <sup>ii</sup>	1.919 (13)
C10—C1	1.39 (3)	Ni15—O13	1.953 (12)
C10—C8	1.46 (2)	Ni15—O13 <sup>iii</sup>	1.953 (12)
C10—C10 <sup>i</sup>	1.464 (8)	Ni15—O16 <sup>iv</sup>	1.919 (13)
C11—C5	1.642 (12)	Ni15—O16 <sup>ii</sup>	1.919 (13)
C11—O12	1.297 (10)		
C3—C1—C10	122 (2)	C1—C10—C8	117.5 (18)
C1—C3—C5	120.8 (6)	C1—C10—C10 <sup>i</sup>	114 (5)
C3—C5—C6	119.0 (9)	C8—C10—C10 <sup>i</sup>	128 (8)
C5—C6—C8	120.9 (19)	O12—C11—O13	115.7 (12)
C6—C8—C10	119.7 (8)		

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\_DFT)

##### Crystal data

$C_{14}H_{10}Ni_2O_6$

$M_r = 391.63$

Triclinic,  $P\bar{1}$

$a = 15.10000 \text{ \AA}$

$b = 6.05000 \text{ \AA}$

$c = 4.02000 \text{ \AA}$

$\alpha = 81.57^\circ$

$\beta = 71.90^\circ$

$\gamma = 81.90^\circ$

$V = 343.52 \text{ \AA}^3$

$Z = 1$

##### Data collection

$h = \rightarrow$

$k = \rightarrow$

$l = \rightarrow$

##### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

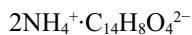
	$x$	$y$	$z$	$B_{\text{iso}}^*/B_{\text{eq}}$
C1	0.61147	0.63610	-0.07671	
C3	0.70313	0.58310	-0.06941	
C5	0.73667	0.36292	0.03127	
C6	0.67329	0.19956	0.14026	
C8	0.58130	0.25374	0.13082	
C10	0.54811	0.47197	0.01398	
C11	0.83907	0.31116	-0.01437	
O12	0.87153	0.11194	0.07915	
O13	0.88625	0.47867	-0.15724	
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

## (UBUPEQ\_DFT)

*Crystal data*Triclinic, *P1* $a = 14.20370 \text{ \AA}$  $b = 6.47851 \text{ \AA}$  $c = 3.45320 \text{ \AA}$  $\alpha = 90.09^\circ$  $\beta = 96.84^\circ$  $\gamma = 91.71^\circ$  $V = 315.35 \text{ \AA}^3$  $Z = 2$ *Data collection* $h = \rightarrow$  $l = \rightarrow$  $k = \rightarrow$ *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{iso}}^*/B_{\text{eq}}$
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 (NH4\_X)***Crystal data* $M_r = 276.29$ Triclinic, *P1*Hall symbol: *P 1* $a = 4.6770 (6) \text{ \AA}$  $b = 5.2306 (14) \text{ \AA}$  $c = 14.387 (6) \text{ \AA}$  $\alpha = 90.57 (7)^\circ$  $\beta = 91.41 (4)^\circ$  $\gamma = 92.775 (11)^\circ$  $V = 351.43 (17) \text{ \AA}^3$  $Z = 1$  $D_x = 1.306 \text{ Mg m}^{-3}$  $K\alpha_{1,2}$  radiation,  $\lambda = 0.70932, 0.71361 \text{ \AA}$  $T = 300 \text{ K}$ cylinder,  $12 \times 0.7 \text{ mm}$



Data collection

PANalytical Empyrean  
diffractometer  
Specimen mounting: glass capillary

Data collection mode: transmission  
Scan method: step  
 $2\theta_{\min} = 1.008^\circ$ ,  $2\theta_{\max} = 49.982^\circ$ ,  $2\theta_{\text{step}} = 0.008^\circ$

Refinement

Least-squares matrix: full  
 $R_p = 0.033$   
 $R_{wp} = 0.043$   
 $R_{\text{exp}} = 0.015$   
 $R(F^2) = 0.09394$   
5862 data points  
Profile function: Finger-Cox-Jephcoat function  
parameters U, V, W, X, Y, SH/L: peak  
variance(Gauss) =  $U \tan(\text{Th})^2 + V \tan(\text{Th}) + W$ :  
peak HW(Lorentz) =  $X / \cos(\text{Th}) + Y \tan(\text{Th})$ ;  
SH/L = S/L+H/L U, V, W in (centideg)<sup>2</sup>, 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?

$(\Delta/\sigma)_{\max} = 0.723$   
Background function: Background function:  
"chebyshev-1" function with 4 terms:  
3149(17), -491(16), 99(12), -147(15),  
Background peak parameters: pos, int, sig, gam:  
12.38(8), 1.18(6)e6, 1.20(8)e5, 0.100,  
Preferred orientation correction: Simple  
spherical harmonic correction Order = 4  
Coefficients: 0:0:C(2,-2) = 0.79(3); 0:0:C(2,-1)  
= 0.32(7); 0:0:C(2,0) = 0.330(31); 0:0:C(2,1) =  
1.58(9); 0:0:C(2,2) = 0.88(4); 0:0:C(4,-4) =  
0.33(7); 0:0:C(4,-3) = 1.02(5); 0:0:C(4,-2) =  
0.65(6); 0:0:C(4,-1) = -0.39(8); 0:0:C(4,0) =  
-0.79(4); 0:0:C(4,1) = -0.01(9); 0:0:C(4,2) =  
1.10(6); 0:0:C(4,3) = 0.79(8); 0:0:C(4,4) =  
-0.31(7)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
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*

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, °)*

C2—C4	1.392 (7)	C16—C13	1.402 (7)
C2—C5	1.342 (6)	C21—C12	1.550 (7)
C3—C6	1.379 (6)	C21—O23	1.258 (9)
C3—C7	1.385 (6)	C21—O25	1.310 (9)
C4—C2	1.392 (7)	C22—C6	1.518 (7)
C4—C7	1.408 (7)	C22—O24	1.269 (9)
C4—C11	1.501 (8)	C22—O26	1.272 (9)
C5—C2	1.342 (6)	O23—C21	1.258 (9)
C5—C6	1.373 (6)	O24—C22	1.269 (9)
C6—C3	1.379 (6)	O25—C21	1.310 (9)
C6—C5	1.373 (6)	O26—C22	1.272 (9)
C6—C22	1.518 (7)	N27—H29	1.0294
C7—C3	1.385 (6)	N27—H30	1.0294
C7—C4	1.408 (7)	N27—H31	1.0295
C11—C4	1.501 (8)	N27—H32	1.0294
C11—C13	1.394 (8)	H29—N27	1.0294
C11—C14	1.410 (7)	H30—N27	1.0294
C12—C15	1.401 (6)	H31—N27	1.0295
C12—C16	1.390 (6)	H32—N27	1.0294
C12—C21	1.550 (7)	N28—H33	1.0295
C13—C11	1.394 (8)	N28—H34	1.0295
C13—C16	1.402 (7)	N28—H35	1.0294
C14—C11	1.410 (7)	N28—H36	1.0293
C14—C15	1.408 (6)	H33—N28	1.0295
C15—C12	1.401 (6)	H34—N28	1.0295
C15—C14	1.408 (6)	H35—N28	1.0294
C16—C12	1.390 (6)	H36—N28	1.0293
C4—C2—C5	121.9 (4)	C12—C16—C13	121.6 (3)
C6—C3—C7	119.9 (3)	C12—C21—O23	111.9 (7)
C2—C4—C7	116.5 (4)	C12—C21—O25	121.5 (7)
C2—C4—C11	119.4 (6)	O23—C21—O25	119.6 (8)
C7—C4—C11	120.9 (6)	C6—C22—O24	115.6 (7)
C2—C5—C6	121.7 (3)	C6—C22—O26	112.0 (7)

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*C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>*M<sub>r</sub>* = 276.29Triclinic, *P*1*a* = 4.6875 Å*b* = 5.2421 Å*c* = 14.3820 Å $\alpha = 90.7300^\circ$  $\beta = 91.3790^\circ$  $\gamma = 92.7400^\circ$ *V* = 352.86 Å<sup>3</sup>*Z* = 1*Data collection**h* = →*l* = →*k* = →*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>)*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub> <sup>*</sup> / <i>U</i> <sub>eq</sub>
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*

H20	0.65294	0.94638	0.29501	0.0500*
C21	0.93857	0.56900	0.37898	0.0566*
C22	0.83362	1.07341	-0.29872	0.0566*
O23	0.76266	0.66899	0.43252	0.0566*
O24	0.99747	0.98318	-0.35852	0.0566*
O25	1.09802	0.39029	0.40741	0.0566*
O26	0.65872	1.24648	-0.31870	0.0566*
N27	0.16243	0.51693	0.60441	0.0400*
H29	0.16090	0.49359	0.53198	0.0500*
H30	0.33993	0.43870	0.63488	0.0500*
H31	0.13695	0.71068	0.62373	0.0500*
H32	-0.01991	0.41734	0.62701	0.0500*
N28	0.59171	0.12978	0.47646	0.0400*
H33	0.62253	-0.06146	0.45540	0.0500*
H34	0.58472	0.14431	0.54856	0.0500*
H35	0.41516	0.20817	0.44485	0.0500*
H36	0.77650	0.23333	0.45705	0.0500*

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N27—H29...O25 <sup>i</sup>	1.05	1.88	2.907	167
N27—H30...O26 <sup>ii</sup>	1.04	1.95	2.979	172
N27—H31...O24 <sup>iii</sup>	1.06	1.62	2.650	162
N27—H32...O26 <sup>iv</sup>	1.04	1.90	2.942	174
N28—H33...O23 <sup>v</sup>	1.06	1.62	2.655	164
N28—H34...O26 <sup>ii</sup>	1.04	2.00	3.007	164
N28—H35...O25 <sup>i</sup>	1.04	1.88	2.904	169
N28—H36...O25	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)  $x, y-1, z$ .