

# Synthesis, crystal structure and Hirshfeld surface analysis of tetraaquabis(isonicotinamide- $\kappa N^1$ )-cobalt(II) fumarate

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**Keywords:** crystal structure; fumaric acid; isonicotinamide; cobalt(II); Hirshfeld surfaces.

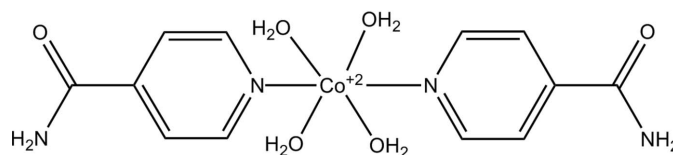
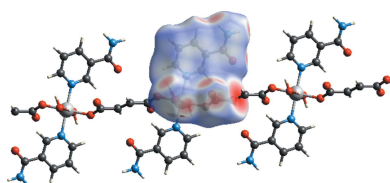
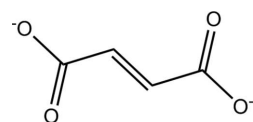
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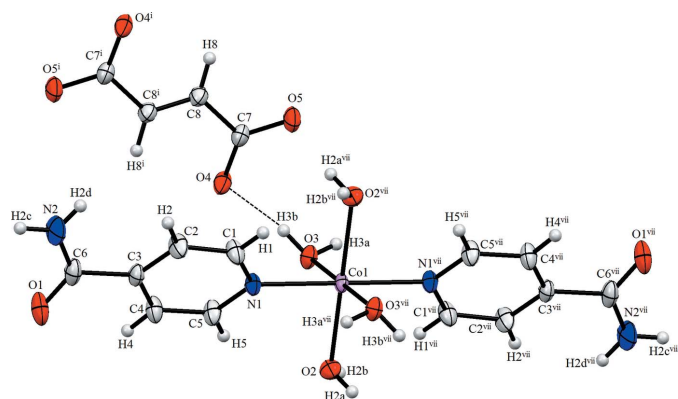
The reaction of cobalt(II) with fumaric acid ( $H_2fum$ ) and isonicotinamide in a basic solution produces the title salt,  $[Co(C_6H_6N_2O)_2(H_2O)_4](C_4H_2O_4)$ . In the complex cation, the  $Co^{II}$  atom, located on an inversion centre, is coordinated by two isonicotinamide and four water molecules in a distorted  $N_2O_4$  octahedral geometry. The fumarate anion is located on another inversion centre and is linked to neighbouring complex cations *via*  $O-H\cdots O$  and  $N-H\cdots O$  hydrogen bonds and weak  $C-H\cdots O$  hydrogen bonds. In the crystal, the complex cations are further linked by  $O-H\cdots O$ ,  $N-H\cdots O$  and weak  $C-H\cdots O$  hydrogen bonds, forming a three-dimensional supramolecular architecture. Hirshfeld surface analyses ( $d_{norm}$  surfaces and two-dimensional fingerprint plots) for the title compound are presented and discussed.

## 1. Chemical context

Metal carboxylates have attracted intense attention because of their interesting framework topologies (Rao *et al.*, 2004). Among metal carboxylates, fumarate dianions (fum) have good conformational freedom and they possess some desirable features such as being versatile ligands because of the four electron-donor oxygen atoms they carry, and their ability to link inorganic moieties (Zheng *et al.*, 2003). Moreover, metal fumarates exhibit interesting structural varieties.



Dicarboxylic acids such as fumaric acid and amides have been particularly useful in creating many supramolecular structures involving isonicotinamide and a variety of carboxylic acid molecules (Vishweshwar *et al.*, 2003; Aakeröy *et al.*, 2002). Dicarboxylic acid ligands are utilized in the synthesis of a wide variety of metal carboxylates. For this reason they have



**Figure 1**  
The molecular structure of the title compound, showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (vii)  $-x + 1, -y + 1, -z + 2$ .]

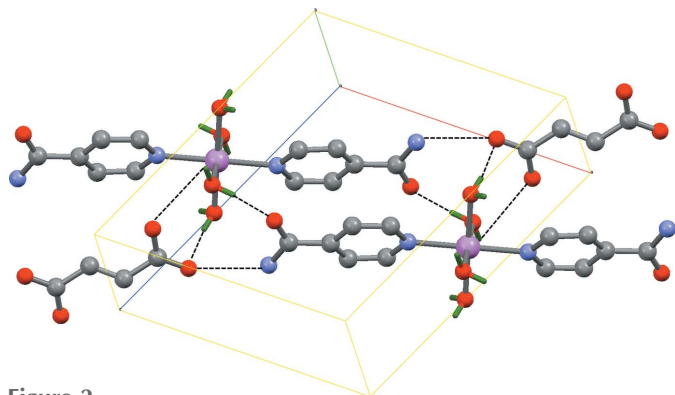
been investigated extensively, both experimentally and computationally. We describe herein the synthesis, structural features and Hirshfeld surface analysis of the title salt.

## 2. Structural commentary

The molecular structure of the title compound is illustrated in Fig. 1. The  $\text{Co}^{\text{II}}$  cation and midpoint of the  $\text{C}=\text{C}$  bond of the fumarate anion are each located on an inversion centre. In the complex cation, the  $\text{Co}^{\text{II}}$  atom is coordinated to two isonicotinamide ligands and four water molecules in a distorted  $\text{N}_2\text{O}_4$  octahedral geometry. The fumarate anion interacts with neighboring complex cations *via*  $\text{O}-\text{H}\cdots\text{O}$  and  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds and weak  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds (Table 1).

## 3. Supramolecular features

In the crystal, the fumarate anions and complex cations are linked by  $\text{O}-\text{H}\cdots\text{O}$ ,  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds; the complex cations also interact with each other through  $\text{O}-\text{H}\cdots\text{O}$ ,  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds, forming a three-dimensional supramolecular architecture (Table 1, Fig. 2).



**Figure 2**  
Packing of the title compound in the unit cell. Dashed lines indicate hydrogen bonds.

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

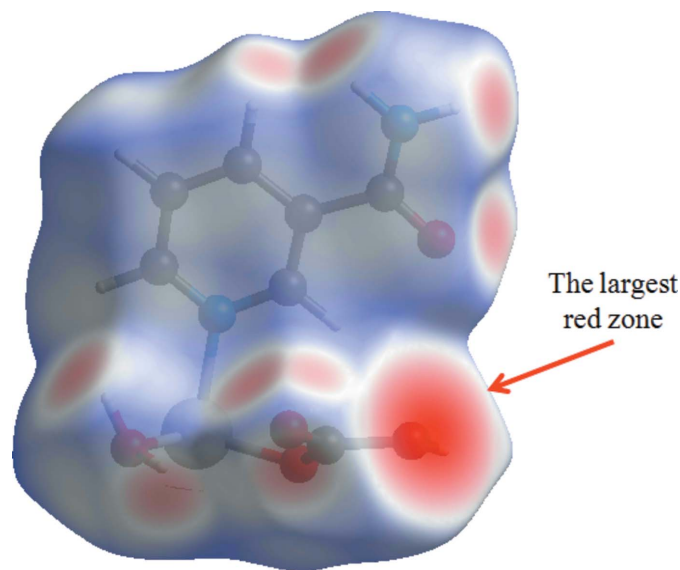
$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O}2-\text{H}2\text{A}\cdots\text{O}5^{\text{i}}$	0.86	1.96	2.814 (2)	171
$\text{O}2-\text{H}2\text{B}\cdots\text{O}4^{\text{ii}}$	0.86	1.88	2.7165 (19)	165
$\text{O}3-\text{H}3\text{A}\cdots\text{O}1^{\text{iii}}$	0.86	1.95	2.792 (2)	168
$\text{O}3-\text{H}3\text{B}\cdots\text{O}4$	0.86	1.82	2.6652 (19)	172
$\text{N}2-\text{H}2\text{C}\cdots\text{O}5^{\text{iv}}$	0.86	2.13	2.955 (2)	160
$\text{N}2-\text{H}2\text{D}\cdots\text{O}1^{\text{v}}$	0.86	2.47	3.288 (3)	159
$\text{C}1-\text{H}1\cdots\text{O}4^{\text{vi}}$	0.93	2.41	3.322 (2)	168
$\text{C}2-\text{H}2\cdots\text{O}1^{\text{v}}$	0.93	2.30	3.225 (3)	173

Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $x, -y + \frac{3}{2}, z - \frac{1}{2}$ ; (iii)  $x + 1, y, z$ ; (iv)  $x - 1, y, z$ ; (v)  $-x, y - \frac{1}{2}, -z + \frac{3}{2}$ ; (vi)  $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$ .

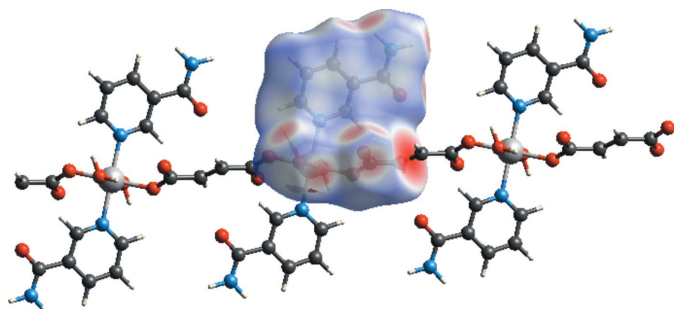
## 4. Hirshfeld surface analysis

*Crystal Explorer 17.5* (Turner *et al.*, 2017) was used to analyse the interactions in the crystal and fingerprint plots mapped over  $d_{\text{norm}}$  (Figs. 3 and 4) were generated. The contact distances to the closest atom inside ( $d_i$ ) and outside ( $d_e$ ) of the Hirshfeld surface are used to analyse the intermolecular interactions *via* the mapping of  $d_{\text{norm}}$ . The molecular Hirshfeld surfaces were obtained using a standard (high) surface resolution with the three-dimensional  $d_{\text{norm}}$  surfaces mapped over a fixed colour scale of  $-1.227$  (red) to  $1.279$  (blue). Many studies on Hirshfeld surfaces can be found in the literature (see, for example, Şen *et al.*, 2018; Yaman *et al.*, 2018).

In a  $d_{\text{norm}}$  surface, any intermolecular interactions will appear as red spots. The red spots indicate the regions of donor–acceptor interactions. There are many red spots in the  $d_{\text{norm}}$  surface (Fig. 3), which are usually on the O-acceptor atoms involved in the interactions listed in Table 1. Strong hydrogen-bond interactions, such as  $\text{O}-\text{H}\cdots\text{O}$ , are seen as a bright-red areas on the Hirshfeld surfaces (Şen *et al.*, 2017).



**Figure 3**  
The Hirshfeld surface of the title compound mapped with  $d_{\text{norm}}$ . The red spots indicate the regions of the donor–acceptor interactions.

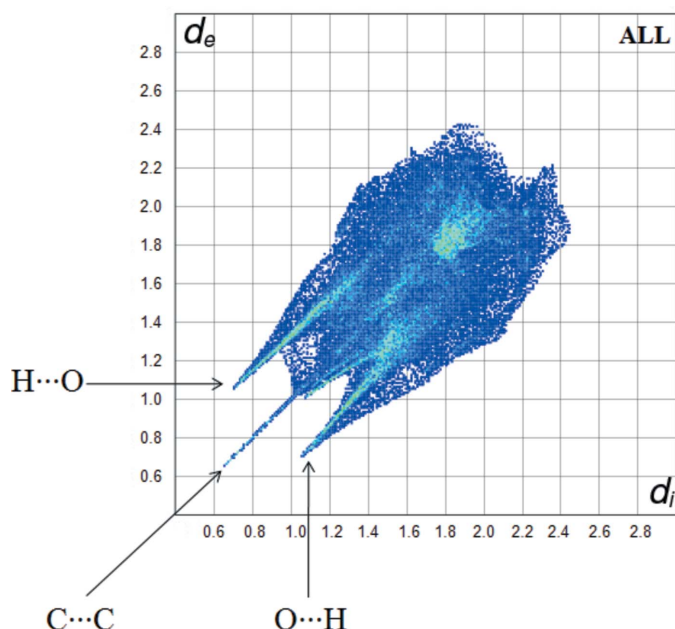


**Figure 4**  
 $d_{\text{norm}}$  mapped on the Hirshfeld surfaces for the title structure.

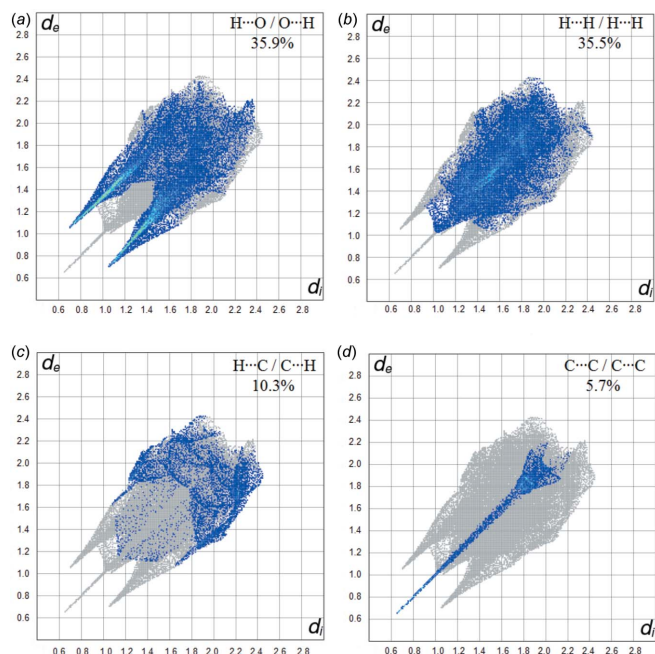
The fingerprint plot for the title complex is presented in Fig. 5. The  $\text{H}\cdots\text{H}$  interactions appear in the middle of the scattered points in the two-dimensional fingerprint plots with an overall contribution to the Hirshfeld surface of 35.5% (Fig. 6*b*). The contribution from the  $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$  contacts, corresponding to  $\text{C}-\text{H}\cdots\text{O}$ ,  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{O}-\text{H}\cdots\text{O}$  interactions, is represented by a pair of sharp spikes characteristic of a strong hydrogen-bond interaction (35.9%) (Fig. 6*a*). The  $\text{C}\cdots\text{C}/\text{C}\cdots\text{C}$  contacts have a sharp spike between the  $\text{O}\cdots\text{H}$  and  $\text{H}\cdots\text{O}$  spikes (5.7%) (Fig. 6*d*). The contribution of the other intermolecular contacts to the Hirshfeld surfaces is  $\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$  (10.3%) (Fig. 6*c*).

## 5. Database survey

A search of the Cambridge Structural Database for fumaric acid and isonicotinamide revealed the presence of seven structures: isonicotinohyrazide nicotinamide fumaric acid (Aitipamula *et al.*, 2013), *catena*-poly[[aquabis[*N*-(pyridin-3-yl)isonicotinamide- $\kappa\text{N}^1$ ]]copper(II)]-( $\mu_2$ -fumarato- $\kappa\text{O},\text{O}'$ )-



**Figure 5**  
 A fingerprint plot of the title complex.



**Figure 6**  
 (a)  $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$ , (b)  $\text{H}\cdots\text{H}/\text{H}\cdots\text{H}$ , (c)  $\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$  and (d)  $\text{C}\cdots\text{C}/\text{C}\cdots\text{C}$  contacts in the title complex, showing the percentages of contacts contributing to the total Hirshfeld surface area.

(Qiblawi & LaDuca, 2012), bis(isonicotinamide) fumaric acid (Aakeröy *et al.*, 2002), *catena*-[bis( $\mu_2$ -fumarato)bis( $\mu_2$ -3-pyridylisonicotinamide)dizinc(II)] (Uebler *et al.*, 2013) and *catena*-[bis( $\mu$ -but-2-enedioato)bis( $\mu$ -pyridine-4-carbohydrazide)dizinc(II)] (Naskar *et al.*, 2017). In these compounds, the  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds have  $\text{H}\cdots\text{O}$  distances ranging from 2.56 to 3.59 Å and  $\text{C}\cdots\text{O}$  distances ranging from 3.27 to 3.96 Å. The  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds have  $\text{H}\cdots\text{O}$  distances ranging from 1.86 to 2.33 Å and  $\text{N}\cdots\text{O}$  distances ranging from 2.82 to 3.15 Å.

## 6. Synthesis and crystallization

An aqueous solution of fumaric acid (26 mmol, 3 g) in water was added to a solution of NaOH (52 mmol, 2.07 g) while stirring. A solution of  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$  (25 mmol, 6.19 g) in water was added. The reaction mixture was stirred for an hour at room temperature. The pink mixture was filtered and left to dry. The pink crystals (0.88 mmol, 0.20 g) were dissolved in water and added to an aqueous solution of isonicotinamide (1.75 mmol, 0.21 g). The resulting suspension was filtered and allowed to crystallize for five weeks at room temperature yielding orange block-shaped crystals suitable for X-ray diffraction analysis.

## 7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The N-bound and C-bound

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	[Co(C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ](C <sub>4</sub> H <sub>2</sub> O <sub>4</sub> )
<i>M</i> <sub>r</sub>	489.30
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.6914 (10), 10.0106 (11), 11.3811 (12)
β (°)	113.416 (3)
<i>V</i> (Å <sup>3</sup> )	1013.22 (19)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm <sup>-1</sup> )	0.91
Crystal size (mm)	0.25 × 0.19 × 0.16
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Analytical ( <i>X-RED32</i> ; Stoe & Cie, 2002)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.394, 0.746
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	19963, 1962, 1830
<i>R</i> <sub>int</sub>	0.032
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.617
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.032, 0.077, 1.14
No. of reflections	1962
No. of parameters	144
H-atom treatment	H-atom parameters constrained
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.35, -0.35

Computer programs: *APEX2* and *SAINT* (Bruker, 2007), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2016* (Sheldrick, 2015b), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

hydrogen atoms were positioned geometrically and treated as riding: N–H = 0.86 Å and C–H = 0.93 Å with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C,N). Water H atoms were found in a difference-Fourier map, restrained with O–H = 0.85 Å and refined with *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(O).

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## References

- Aakeröy, C. B., Beatty, A. M. & Helfrich, B. A. (2002). *J. Am. Chem. Soc.* **124**, 14425–14432.
- Aitipamula, S., Wong, A. B. H., Chow, P. S. & Tan, R. B. H. (2013). *CrystEngComm*, **15**, 5877–5887.
- Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Naskar, K., Dey, A., Dutta, B., Ahmed, F., Sen, C., Mir, M. H., Roy, P. P. & Sinha, C. (2017). *Cryst. Growth Des.* **17**, 3267–3276.
- Qiblawi, S. H. & LaDuca, R. L. (2012). *Acta Cryst.* **E68**, m1514.
- Rao, C. N. R., Natarajan, S. & Vaidhyanathan, R. (2004). *Angew. Chem. Int. Ed.* **43**, 1466–1496.
- Şen, F., Çapan, İ., Dincer, M. & Cukurovali, A. (2018). *J. Mol. Struct.* **1155**, 278–287.
- Şen, F., Kansiz, S. & Uçar, İ. (2017). *Acta Cryst.* **C73**, 517–524.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Stoe & Cie (2002). *X-RED32*. Stoe & Cie, Darmstadt, Germany.
- Turner, M. J., MacKinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). *Crystal Explorer*. University of Western Australia.
- Uebler, J. W., Wilson, J. A. & LaDuca, R. L. (2013). *CrystEngComm*, **15**, 1586–1596.
- Vishweshwar, P., Nangia, A. & Lynch, V. M. (2003). *CrystEngComm*, **5**, 164–168.
- Yaman, M., Almarhoon, Z. M., Çakmak, Ş., Kütük, H., Meral, G. & Dege, N. (2018). *Acta Cryst.* **E74**, 41–44.
- Zheng, Y.-Q., Sun, J. & Lin, J.-L. (2003). *J. Mol. Struct.* **650**, 49–56.

## supporting information

*Acta Cryst.* (2018). E74, 217-220 [https://doi.org/10.1107/S205698901800107X]

## Synthesis, crystal structure and Hirshfeld surface analysis of tetraaquabis-(isonicotinamide- $\kappa N^1$ )cobalt(II) fumarate

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### Computing details

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINTE* (Bruker, 2007); data reduction: *SAINTE* (Bruker, 2007); program(s) used to solve structure: *SHELXT2014* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

### Tetraaquabis(isonicotinamide- $\kappa N^1$ )cobalt(II) fumarate

#### Crystal data

$[\text{Co}(\text{C}_6\text{H}_6\text{N}_2\text{O})_2(\text{H}_2\text{O})_4](\text{C}_4\text{H}_2\text{O}_4)$

$M_r = 489.30$

Monoclinic,  $P2_1/c$

$a = 9.6914$  (10) Å

$b = 10.0106$  (11) Å

$c = 11.3811$  (12) Å

$\beta = 113.416$  (3)°

$V = 1013.22$  (19) Å<sup>3</sup>

$Z = 2$

$F(000) = 506$

$D_x = 1.604$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 9553 reflections

$\theta = 3.1\text{--}28.3^\circ$

$\mu = 0.91$  mm<sup>-1</sup>

$T = 296$  K

Block, orange

$0.25 \times 0.19 \times 0.16$  mm

#### Data collection

Bruker APEXII CCD  
diffractometer

$\varphi$  and  $\omega$  scans

Absorption correction: analytical  
(X-RED32; Stoe & Cie, 2002)

$T_{\min} = 0.394$ ,  $T_{\max} = 0.746$

19963 measured reflections

1962 independent reflections

1830 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

$\theta_{\max} = 26.0^\circ$ ,  $\theta_{\min} = 3.1^\circ$

$h = -11 \rightarrow 11$

$k = -12 \rightarrow 12$

$l = -14 \rightarrow 13$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.077$

$S = 1.14$

1962 reflections

144 parameters

0 restraints

Hydrogen site location: mixed

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0211P)^2 + 1.1735P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.35$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.35$  e Å<sup>-3</sup>

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.500000	0.500000	0.500000	0.01658 (12)
O3	0.60307 (15)	0.65750 (13)	0.62150 (13)	0.0237 (3)
H3A	0.696404	0.660264	0.635017	0.035*
H3B	0.594575	0.646860	0.692916	0.035*
O2	0.39661 (15)	0.64187 (13)	0.35319 (13)	0.0240 (3)
H2A	0.368923	0.604165	0.279836	0.036*
H2B	0.458953	0.704445	0.358200	0.036*
O4	0.55105 (17)	0.63859 (14)	0.83392 (14)	0.0283 (3)
O1	-0.09235 (17)	0.70328 (16)	0.68073 (17)	0.0365 (4)
O5	0.72605 (18)	0.48025 (16)	0.88934 (16)	0.0356 (4)
N1	0.31337 (18)	0.52596 (16)	0.55744 (16)	0.0208 (3)
C7	0.6189 (2)	0.54056 (19)	0.90123 (18)	0.0221 (4)
C3	0.1007 (2)	0.5713 (2)	0.66124 (18)	0.0216 (4)
C8	0.5656 (2)	0.48648 (19)	0.99864 (19)	0.0239 (4)
H8	0.629871	0.429951	1.061428	0.029*
N2	-0.0347 (3)	0.5112 (2)	0.7922 (2)	0.0491 (6)
H2C	-0.102155	0.523521	0.822413	0.059*
H2D	0.020826	0.440936	0.812861	0.059*
C4	0.1453 (2)	0.6727 (2)	0.6015 (2)	0.0268 (4)
H4	0.103978	0.757665	0.594549	0.032*
C2	0.1627 (2)	0.4464 (2)	0.6655 (2)	0.0297 (5)
H2	0.134441	0.375248	0.703564	0.036*
C6	-0.0163 (2)	0.6003 (2)	0.7141 (2)	0.0279 (4)
C5	0.2516 (2)	0.64642 (19)	0.5523 (2)	0.0263 (4)
H5	0.281757	0.715892	0.513627	0.032*
C1	0.2671 (2)	0.4283 (2)	0.6126 (2)	0.0275 (4)
H1	0.307396	0.343382	0.615691	0.033*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Co1	0.01724 (19)	0.01624 (19)	0.0214 (2)	-0.00028 (12)	0.01310 (14)	0.00056 (13)
O3	0.0239 (7)	0.0251 (7)	0.0276 (7)	-0.0036 (6)	0.0162 (6)	-0.0033 (6)
O2	0.0259 (7)	0.0220 (7)	0.0258 (7)	-0.0015 (5)	0.0121 (6)	0.0031 (5)
O4	0.0421 (8)	0.0219 (7)	0.0319 (7)	0.0059 (6)	0.0264 (7)	0.0046 (6)
O1	0.0332 (8)	0.0303 (8)	0.0602 (11)	-0.0001 (7)	0.0334 (8)	-0.0075 (7)
O5	0.0354 (8)	0.0430 (9)	0.0409 (9)	0.0129 (7)	0.0284 (7)	0.0091 (7)
N1	0.0207 (8)	0.0199 (8)	0.0274 (8)	-0.0003 (6)	0.0154 (7)	-0.0003 (6)
C7	0.0262 (9)	0.0217 (9)	0.0234 (9)	-0.0018 (8)	0.0151 (8)	-0.0023 (8)

C3	0.0178 (9)	0.0268 (10)	0.0247 (9)	-0.0017 (7)	0.0134 (7)	-0.0023 (8)
C8	0.0282 (10)	0.0240 (10)	0.0243 (10)	0.0033 (8)	0.0155 (8)	0.0037 (7)
N2	0.0411 (12)	0.0675 (15)	0.0591 (14)	0.0163 (11)	0.0416 (11)	0.0225 (11)
C4	0.0285 (10)	0.0182 (9)	0.0425 (12)	0.0012 (8)	0.0234 (9)	-0.0016 (8)
C2	0.0303 (10)	0.0270 (10)	0.0428 (12)	0.0024 (9)	0.0261 (10)	0.0110 (9)
C6	0.0208 (9)	0.0359 (12)	0.0330 (11)	-0.0056 (9)	0.0170 (8)	-0.0089 (9)
C5	0.0300 (10)	0.0191 (9)	0.0397 (11)	-0.0005 (8)	0.0245 (9)	0.0032 (8)
C1	0.0274 (10)	0.0204 (10)	0.0432 (12)	0.0039 (8)	0.0229 (9)	0.0058 (8)

*Geometric parameters (Å, °)*

Co1—O3 <sup>i</sup>	2.0731 (13)	C7—C8	1.498 (3)
Co1—O3	2.0731 (13)	C3—C2	1.380 (3)
Co1—O2 <sup>i</sup>	2.1171 (13)	C3—C4	1.383 (3)
Co1—O2	2.1171 (13)	C3—C6	1.509 (3)
Co1—N1	2.1694 (16)	C8—C8 <sup>ii</sup>	1.313 (4)
Co1—N1 <sup>i</sup>	2.1694 (16)	C8—H8	0.9300
O3—H3A	0.8556	N2—C6	1.320 (3)
O3—H3B	0.8555	N2—H2C	0.8600
O2—H2A	0.8564	N2—H2D	0.8600
O2—H2B	0.8564	C4—C5	1.380 (3)
O4—C7	1.258 (2)	C4—H4	0.9300
O1—C6	1.236 (3)	C2—C1	1.379 (3)
O5—C7	1.254 (2)	C2—H2	0.9300
N1—C1	1.332 (3)	C5—H5	0.9300
N1—C5	1.337 (2)	C1—H1	0.9300
O3 <sup>i</sup> —Co1—O3	180.0	O4—C7—C8	118.86 (17)
O3 <sup>i</sup> —Co1—O2 <sup>i</sup>	88.15 (6)	C2—C3—C4	117.75 (17)
O3—Co1—O2 <sup>i</sup>	91.85 (6)	C2—C3—C6	123.14 (18)
O3 <sup>i</sup> —Co1—O2	91.85 (6)	C4—C3—C6	119.07 (18)
O3—Co1—O2	88.15 (6)	C8 <sup>ii</sup> —C8—C7	124.4 (2)
O2 <sup>i</sup> —Co1—O2	180.0	C8 <sup>ii</sup> —C8—H8	117.8
O3 <sup>i</sup> —Co1—N1	93.08 (6)	C7—C8—H8	117.8
O3—Co1—N1	86.92 (6)	C6—N2—H2C	120.0
O2 <sup>i</sup> —Co1—N1	91.85 (6)	C6—N2—H2D	120.0
O2—Co1—N1	88.15 (6)	H2C—N2—H2D	120.0
O3 <sup>i</sup> —Co1—N1 <sup>i</sup>	86.92 (6)	C5—C4—C3	119.29 (18)
O3—Co1—N1 <sup>i</sup>	93.08 (6)	C5—C4—H4	120.4
O2 <sup>i</sup> —Co1—N1 <sup>i</sup>	88.14 (6)	C3—C4—H4	120.4
O2—Co1—N1 <sup>i</sup>	91.85 (6)	C1—C2—C3	119.26 (18)
N1—Co1—N1 <sup>i</sup>	180.0	C1—C2—H2	120.4
Co1—O3—H3A	109.8	C3—C2—H2	120.4
Co1—O3—H3B	109.6	O1—C6—N2	123.2 (2)
H3A—O3—H3B	109.1	O1—C6—C3	119.28 (19)
Co1—O2—H2A	109.9	N2—C6—C3	117.5 (2)
Co1—O2—H2B	109.8	N1—C5—C4	123.21 (18)
H2A—O2—H2B	109.1	N1—C5—H5	118.4

C1—N1—C5	117.00 (16)	C4—C5—H5	118.4
C1—N1—Co1	122.07 (13)	N1—C1—C2	123.47 (19)
C5—N1—Co1	120.48 (13)	N1—C1—H1	118.3
O5—C7—O4	124.37 (18)	C2—C1—H1	118.3
O5—C7—C8	116.71 (18)		
O5—C7—C8—C8 <sup>ii</sup>	-161.6 (3)	C2—C3—C6—N2	15.6 (3)
O4—C7—C8—C8 <sup>ii</sup>	15.7 (4)	C4—C3—C6—N2	-166.7 (2)
C2—C3—C4—C5	-1.8 (3)	C1—N1—C5—C4	0.4 (3)
C6—C3—C4—C5	-179.59 (19)	Co1—N1—C5—C4	-172.01 (17)
C4—C3—C2—C1	1.1 (3)	C3—C4—C5—N1	1.1 (3)
C6—C3—C2—C1	178.8 (2)	C5—N1—C1—C2	-1.2 (3)
C2—C3—C6—O1	-162.7 (2)	Co1—N1—C1—C2	171.10 (17)
C4—C3—C6—O1	14.9 (3)	C3—C2—C1—N1	0.5 (4)

Symmetry codes: (i)  $-x+1, -y+1, -z+1$ ; (ii)  $-x+1, -y+1, -z+2$ .

#### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2A $\cdots$ O5 <sup>i</sup>	0.86	1.96	2.814 (2)	171
O2—H2B $\cdots$ O4 <sup>iii</sup>	0.86	1.88	2.7165 (19)	165
O3—H3A $\cdots$ O1 <sup>iv</sup>	0.86	1.95	2.792 (2)	168
O3—H3B $\cdots$ O4	0.86	1.82	2.6652 (19)	172
N2—H2C $\cdots$ O5 <sup>v</sup>	0.86	2.13	2.955 (2)	160
N2—H2D $\cdots$ O1 <sup>vi</sup>	0.86	2.47	3.288 (3)	159
C1—H1 $\cdots$ O4 <sup>vii</sup>	0.93	2.41	3.322 (2)	168
C2—H2 $\cdots$ O1 <sup>vi</sup>	0.93	2.30	3.225 (3)	173

Symmetry codes: (i)  $-x+1, -y+1, -z+1$ ; (iii)  $x, -y+3/2, z-1/2$ ; (iv)  $x+1, y, z$ ; (v)  $x-1, y, z$ ; (vi)  $-x, y-1/2, -z+3/2$ ; (vii)  $-x+1, y-1/2, -z+3/2$ .