

## Hydrogen-bonded supramolecule of *N,N'*-bis(4-pyridylmethyl)oxalamide and a zigzag chain structure of *catena*-poly[[[dichloridocobalt(II)]- $\mu$ -*N,N'*-bis(4-pyridylmethyl)oxalamide- $\kappa^2 N^4:N^4'$ ] hemihydrate]

Gene-Hsiang Lee and Hsin-Ta Wang\*

 Institute of Organic and Polymeric Materials, National Taipei University of Technology, Taipei, Taiwan  
 Correspondence e-mail: htwang@ntut.edu.tw

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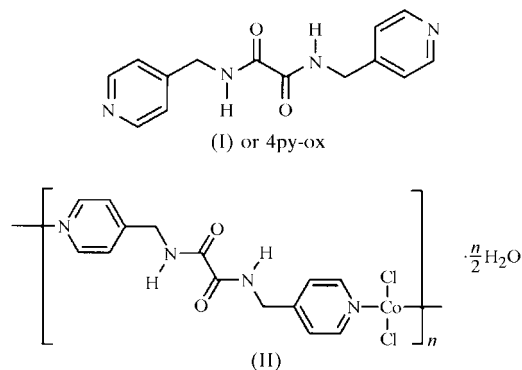
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*N,N'*-Bis(4-pyridylmethyl)oxalamide, C<sub>14</sub>H<sub>14</sub>N<sub>4</sub>O<sub>2</sub>, exists as a dimer which is extended into a two-dimensional network with other dimers through pyridine–amide hydrogen bonds. The crystal structure of the title coordination polymer, {[CoCl<sub>2</sub>(C<sub>14</sub>H<sub>14</sub>N<sub>4</sub>O<sub>2</sub>)]·0.5H<sub>2</sub>O}<sub>n</sub>, features a one-dimensional zigzag chain, in which the cobalt ion sits at a twofold symmetry position and adopts a tetrahedral geometry, and the bridging ligand lies on an inversion center and connects to Co<sup>II</sup> ions in a bis-monodentate mode. Furthermore, two interwoven chains create a cavity of *ca* 8.6 × 8.6 Å, which produces a three-dimensional channel. Water molecules are held in the channel by hydrogen bonds.

### Comment

The coordination-bond and hydrogen-bond approaches have recently been recognized as very powerful and versatile strategies in supramolecular design and materials synthesis (Janiak, 2003; Nguyen *et al.*, 2001). Pyridyl groups, with effective sites for coordination to transition metal ions, have been used for the construction of supramolecular coordination compounds (Maspoth *et al.*, 2004; Barnett & Champness, 2003; Carlucci *et al.*, 2003). In addition, organic amides have been proved to be very useful in self-assembly through hydrogen bonding, and the assembled products have relevance to biological systems. Thus, dipyridylamide ligands have recently been designed and synthesized in crystal engineering; in these compounds, the amide–amide hydrogen bonding has been demonstrated to increase supramolecular versatility (Burchell *et al.*, 2004; Muthu *et al.*, 2001, 2002; Nguyen *et al.*, 1998). In the present paper, the *N,N'*-bis(4-pyridylmethyl)oxalamide (4py-ox) ligand has been chosen to construct a supramolecular coordination compound, and the single-crystal X-ray structures of 4py-ox, (I), and its Co complex, (II), are reported.

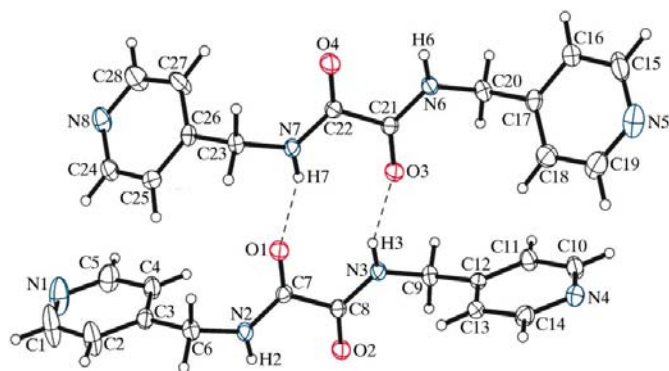
The crystal structure of 4py-ox is presented in Fig. 1, and selected bond lengths and angles are listed in Table 1. There are two crystallographically independent molecules, which



form a dimer through amide–amide hydrogen bonds, with *Z* = 8 in the unit cell. In the crystal structure of 4py-ox, the two pyridine rings in each molecule are separated by an oxalamide linkage, and the terminal (pyridyl) N···N separations are 13.075 (2) and 12.951 (2) Å. The two pyridine rings in a molecule are almost parallel to each other, with dihedral angles of 4.9 (1) and 6.6 (1)°, respectively. The central oxalamide group is planar and nearly perpendicular to the pyridine rings.

The two-dimensional structure of 4py-ox is shown in Fig. 2 and the related hydrogen-bonding geometries are tabulated in Table 2. Besides two amide–amide hydrogen bonds (N3···O3 and N7···O1) binding the two independent molecules into a dimer, two intermolecular hydrogen bonds exist between the oxalamide part of the dimer and the pyridyl N atom of the neighboring dimer (Table 2). Dimers are further linked to form a two-dimensional supramolecular structure.

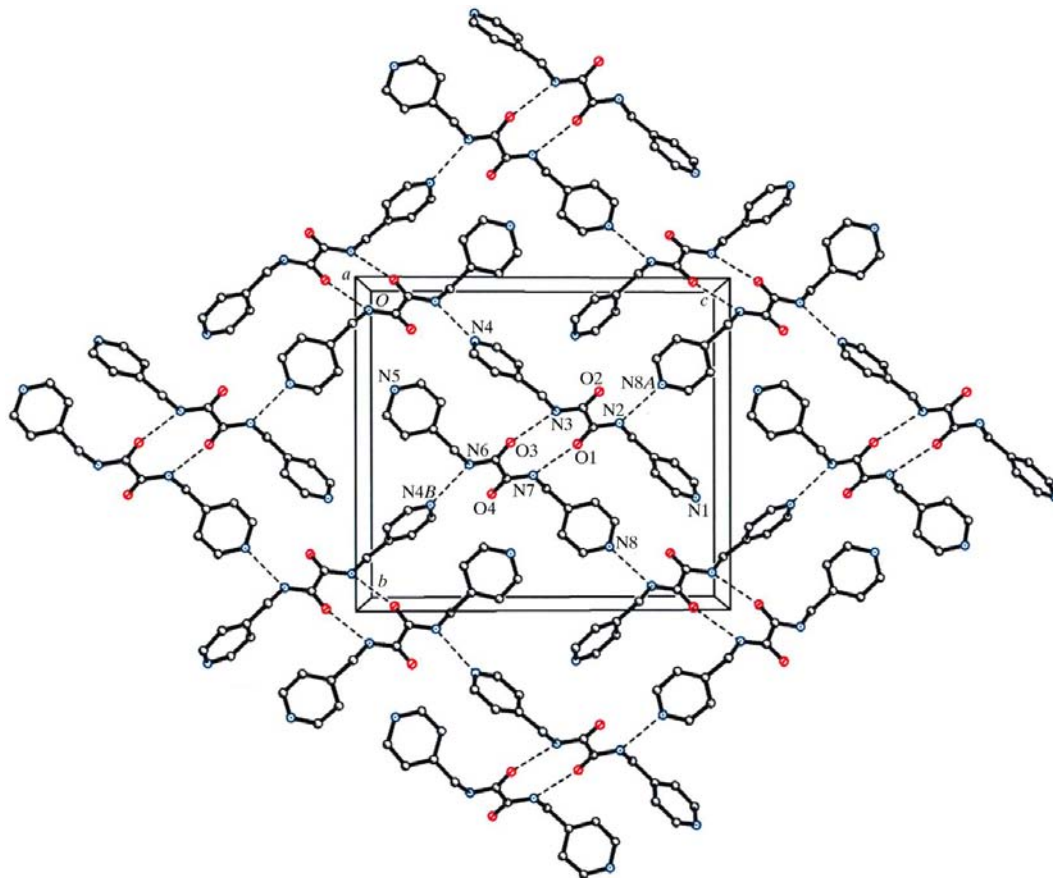
The one-dimensional zigzag chain structure of compound (II), {[CoCl<sub>2</sub>{ $\mu$ -2(4py-ox)}]}·0.5H<sub>2</sub>O}<sub>n</sub>, is shown in Fig. 3. The structure consists of a distorted tetrahedral Co<sup>II</sup> center coordinating to two Cl atoms and two pyridyl N atoms of two 4py-ox ligands [Co1–Cl1 = 2.2420 (11) Å and Co1–N1 = 2.028 (3) Å]. The Co<sup>II</sup> atom sits on a twofold symmetry position, and has an occupancy of 0.5. The symmetry operation



**Figure 1**  
The molecular structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines represent the hydrogen bonding.

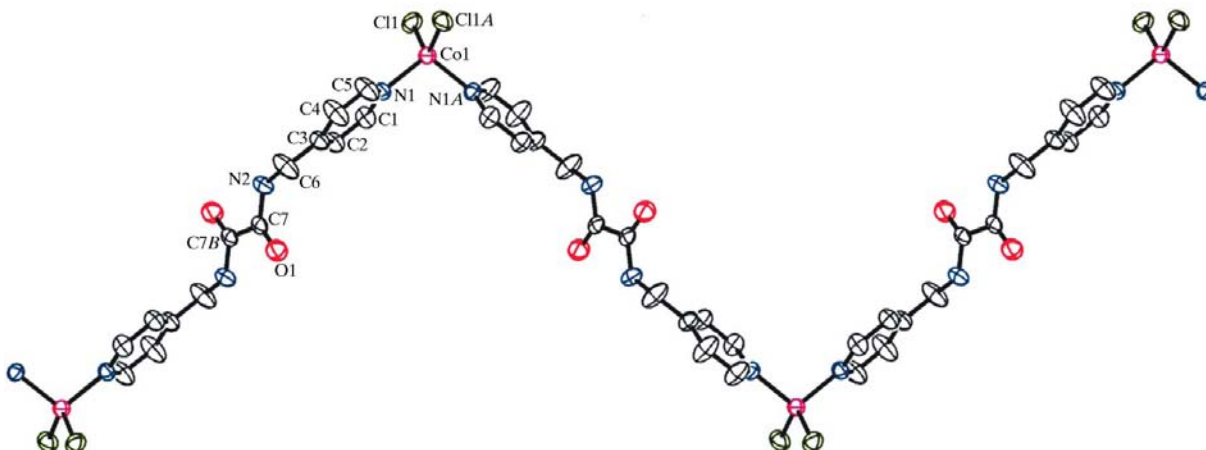
$(\frac{1}{2} - x, 1 - y, z)$  was used to generate another chloride and 4py-ox ligand. Each 4py-ox ligand has an inversion center in the middle of the C7—C7<sup>iv</sup> bond [symmetry code: (iv)  $1 - x, 2 - y, 2 - z$ ], where the symmetry operation was applied to

generate the other half of the ligand. By using one Cl atom and half of the ligand in the asymmetric unit, we obtain (II) with four Co atoms, eight Cl atoms and four complete ligands in the unit cell. Selected bond lengths and angles are listed in Table 3.



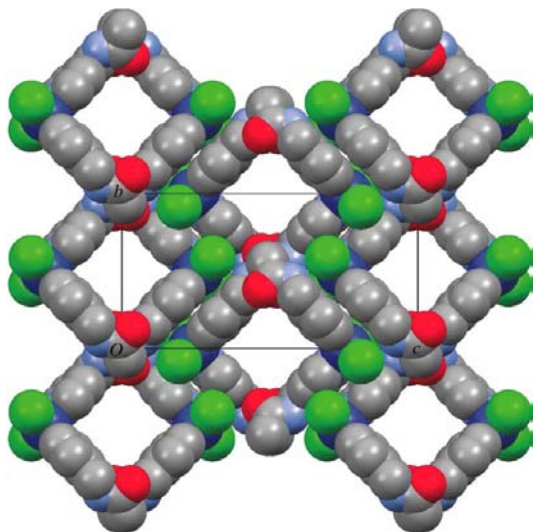
**Figure 2**

The two-dimensional network of (I) formed *via* hydrogen bonds, viewed along the *a* axis. Dashed lines represent the hydrogen bonding. Atoms labeled with the suffixes *A* and *B* are at the symmetry positions  $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$  and  $(\frac{1}{2} - x, -\frac{1}{2} + y, \frac{3}{2} - z)$ , respectively.



**Figure 3**

The zigzag chain structure of (II), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. Atoms labeled with the suffixes *A* and *B* are at the symmetry positions  $(\frac{1}{2} - x, 1 - y, z)$  and  $(1 - x, 2 - y, 2 - z)$ , respectively.



**Figure 4**  
The extended framework of (II), showing the channel structure with dimensions of *ca* 8.6 × 8.6 Å.

Interestingly, a square cavity with a cross-section dimension of *ca* 8.6 × 8.6 Å is created from two interwoven chains, and a channel along the *a* axis is produced (Fig. 4). The void is 23.1% of the volume, as calculated by *PLATON* (Spek, 2003) upon removal of the solvent. Both the cavity dimension and the void volume are slightly greater than those in the complex [ZnCl<sub>2</sub>(4py-ox)<sub>2</sub>] (8.5 × 8.5 Å and 22.1%; Tzeng *et al.*, 2005). Each repeat unit of complex (II) contains one-half of a solvent water molecule as a guest molecule. The guest molecules are intercalated into these channels and one of the H atoms is bonded to the carbonyl O atom of a neighboring oxalamide unit (O2···O1), as detailed in Table 4.

The crystal structure of (II) also reveals three sets of intermolecular hydrogen bonds (geometric parameters and symmetry codes are given in Table 4). The C2—H2B···O1<sup>iv</sup> distance falls in the middle of the range of published values [2.22 (3)–2.62 (2) Å; Steiner, 1996] and the C6—H6B···Cl1<sup>v</sup> distance is equal to a previously reported value [2.64 (1) Å; Steiner, 1998].

### Experimental

All solvents (analytical grade) were used without further purification and the metal salt (CoCl<sub>2</sub>) was commercially available. *N,N'*-Bis(4-pyridylmethyl)oxalamide was prepared from 4-(aminomethyl)pyridine and diethyl oxalate according to the method described by Nguyen *et al.* (1998), and single crystals were obtained by DMF/diethyl ether diffusion. The metal-organic complex was obtained by mixing CoCl<sub>2</sub> (13.0 mg, 0.1 mmol) and 4py-ox (27.0 mg, 0.1 mmol) in methanol (5 ml). The mixture was placed in a 23 ml Teflon-lined stainless steel autoclave and heated at 423 K for 48 h. The mixture was then cooled to room temperature at a rate of 5 K h<sup>-1</sup>. Blue crystals were collected in 68% yield. Analysis calculated for C<sub>14</sub>H<sub>15</sub>Cl<sub>2</sub>CoN<sub>4</sub>O<sub>2.5</sub>: C 41.00, H 3.70, N 13.70%; found: C 41.03, H 3.66, N 13.67%.

### Compound (I)

#### Crystal data

C <sub>14</sub> H <sub>14</sub> N <sub>4</sub> O <sub>2</sub>	<i>V</i> = 2615.0 (2) Å <sup>3</sup>
<i>M<sub>r</sub></i> = 270.29	<i>Z</i> = 8
Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>	Mo <i>K</i> α radiation
<i>a</i> = 9.5188 (4) Å	<i>μ</i> = 0.10 mm <sup>-1</sup>
<i>b</i> = 15.4474 (7) Å	<i>T</i> = 150 (2) K
<i>c</i> = 17.8238 (8) Å	0.32 × 0.22 × 0.15 mm
<i>β</i> = 93.833 (1)°	

#### Data collection

Bruker SMART APEX CCD area-detector diffractometer	25256 measured reflections
Absorption correction: multi-scan ( <i>SADABS</i> ; Sheldrick, 2000a)	6006 independent reflections
<i>T<sub>min</sub></i> = 0.970, <i>T<sub>max</sub></i> = 0.986	4530 reflections with <i>I</i> > 2σ( <i>I</i> )
	<i>R<sub>int</sub></i> = 0.044

#### Refinement

<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )] = 0.060	361 parameters
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.143	H-atom parameters constrained
<i>S</i> = 1.13	Δ <i>ρ</i> <sub>max</sub> = 0.34 e Å <sup>-3</sup>
6006 reflections	Δ <i>ρ</i> <sub>min</sub> = -0.25 e Å <sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °) for (I).

O1—C7	1.227 (2)	O3—C21	1.231 (2)
O2—C8	1.222 (2)	O4—C22	1.225 (2)
N2—C7	1.329 (2)	N6—C21	1.324 (2)
N2—C6	1.449 (2)	N6—C20	1.461 (2)
N3—C8	1.334 (2)	N7—C22	1.328 (2)
N3—C9	1.454 (2)	N7—C23	1.460 (2)
C7—C8	1.541 (2)	C21—C22	1.541 (2)
C7—N2—C6	122.00 (16)	C21—N6—C20	121.95 (16)
C8—N3—C9	122.16 (16)	C22—N7—C23	121.89 (16)
O1—C7—N2	125.71 (17)	O3—C21—N6	125.71 (17)
O1—C7—C8	121.85 (15)	O3—C21—C22	121.29 (15)
N2—C7—C8	112.43 (15)	N6—C21—C22	112.99 (15)
O2—C8—N3	125.71 (17)	O4—C22—N7	125.79 (17)
O2—C8—C7	121.04 (15)	O4—C22—C21	120.70 (15)
N3—C8—C7	113.25 (15)	N7—C22—C21	113.50 (15)

**Table 2**

Hydrogen-bond geometry (Å, °) for (I).

<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>
N2—H2···N8 <sup>i</sup>	0.88	2.08	2.903 (2)	155
N3—H3···O3	0.88	2.09	2.916 (2)	157
N6—H6···N4 <sup>ii</sup>	0.88	2.09	2.930 (2)	158
N7—H7···O1	0.88	2.06	2.888 (2)	156

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

### Compound (II)

#### Crystal data

[CoCl <sub>2</sub> (C <sub>14</sub> H <sub>14</sub> N <sub>4</sub> O <sub>2</sub> )]·0.5H <sub>2</sub> O	<i>V</i> = 1998.38 (11) Å <sup>3</sup>
<i>M<sub>r</sub></i> = 409.13	<i>Z</i> = 4
Orthorhombic, <i>Pnna</i>	Mo <i>K</i> α radiation
<i>a</i> = 7.4566 (2) Å	<i>μ</i> = 1.14 mm <sup>-1</sup>
<i>b</i> = 11.8572 (4) Å	<i>T</i> = 150 (2) K
<i>c</i> = 22.6024 (7) Å	0.30 × 0.15 × 0.15 mm

## Data collection

Bruker SMART APEX CCD area-detector diffractometer  
Absorption correction: multi-scan (SADABS; Sheldrick, 2000a)  
 $T_{\min} = 0.681$ ,  $T_{\max} = 0.852$

11410 measured reflections  
2297 independent reflections  
1627 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.051$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.060$   
 $wR(F^2) = 0.189$   
 $S = 1.19$   
2297 reflections

110 parameters  
H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.82 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.31 \text{ e } \text{\AA}^{-3}$

Table 3

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (II).

Co1—N1	2.028 (3)	O1—C7	1.210 (4)
Co1—N1 <sup>iii</sup>	2.028 (3)	N2—C7	1.341 (4)
Co1—Cl1	2.2422 (11)	N2—C6	1.438 (5)
Co1—Cl1 <sup>iii</sup>	2.2422 (11)	C7—C7 <sup>iv</sup>	1.529 (7)
N1—Co1—N1 <sup>iii</sup>	107.33 (16)	Cl1—Co1—Cl1 <sup>iii</sup>	120.85 (6)
N1—Co1—Cl1	111.20 (9)	C7—N2—C6	122.2 (4)
N1 <sup>iii</sup> —Co1—Cl1	102.90 (9)	O1—C7—N2	125.8 (3)
N1—Co1—Cl1 <sup>iii</sup>	102.90 (9)	O1—C7—C7 <sup>iv</sup>	121.9 (4)
N1 <sup>iii</sup> —Co1—Cl1 <sup>iii</sup>	111.20 (9)	N2—C7—C7 <sup>iv</sup>	112.3 (4)

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

Table 4

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2C $\cdots$ O1	0.85	2.34	3.06 (2)	143
N2—H2A $\cdots$ Cl1 <sup>v</sup>	0.88	2.66	3.435 (3)	147
C2—H2B $\cdots$ O1 <sup>vi</sup>	0.95	2.46	3.403 (5)	169
C6—H6B $\cdots$ Cl1 <sup>iii</sup>	0.99	2.64	3.605 (4)	163

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

In both compounds, H atoms attached to C and N atoms were positioned geometrically and refined using a riding model [ $C-H = 0.95-0.99 \text{ \AA}$ ,  $N-H = 0.88 \text{ \AA}$  and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$ ]. The site-occupancy factor of the solvent molecule in (II) was refined and its value is closed to one-quarter; it was fixed at 0.25 during the final least-squares refinement. H atoms of the solvent molecule were found in a difference Fourier map and constrained at an O—H distance of  $0.85 \text{ \AA}$  [ $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ ].

For both compounds, data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2000b) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3082). Services for accessing these data are described at the back of the journal.

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