

Hydrogen-bonded supramolecular networks of *N,N'*-bis(4-pyridylmethyl)oxalamide and 4,4'-[[oxalylbis(azanediyl)]dimethylene]dipyridinium dinitrate

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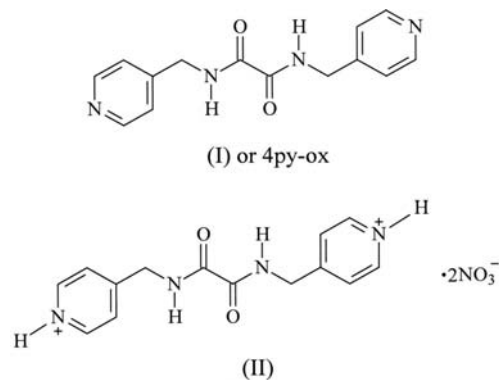
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The molecule of *N,N'*-bis(4-pyridylmethyl)oxalamide, $C_{14}H_{14}N_4O_2$, (I) or 4py-ox, has an inversion center in the middle of the oxalamide group. Adjacent molecules are then linked through intermolecular $N-H\cdots N$ and $C-H\cdots O$ hydrogen bonds, forming an extended supramolecular network. 4,4'-[[Oxalylbis(azanediyl)]dimethylene]dipyridinium dinitrate, $C_{14}H_{16}N_4O_2^{2+}\cdot 2NO_3^-$, (II), contains a diprotonated 4py-ox cation and two nitrate counter-anions. Each nitrate ion is hydrogen bonded to four 4py-ox cations *via* intermolecular $N-H\cdots O$ and $C-H\cdots O$ interactions. Adjacent 4py-ox cations are linked through weak $C-H\cdots O$ hydrogen bonding between an α -pyridinium C atom and an oxalamide O atom, forming a two-dimensional extended supramolecular network.

Comment

Since Jean-Marie Lehn's famous description of supramolecular chemistry (Lehn, 1998), the chemistry of molecular assemblies and intermolecular noncovalent binding interactions (*i.e.* hydrogen bonding, ionic interactions and π - π stacking) have attracted increasing attention in crystal engineering. In particular, hydrogen bonding, which is a powerful organizing force in designing various supramolecules and solid-state architectures (Subramanian & Zaworotko, 1994), is extensively used not only for networking numerous organic and organometallic compounds (Desiraju, 2000), but also for generating interesting supramolecular properties, such as electrical, optical and magnetic (Letard *et al.*, 1998) properties. Pyridyl groups, with effective sites for coordination to transition metal ions, have been used for the construction of supramolecular coordination compounds (Maspoeh *et al.*, 2004; Barnett & Champness, 2003; Carlucci *et al.*, 2003). In addition, organic amides have proved to be very useful in self-assembly through hydrogen bonding, and the assembled products have relevance to biological systems. Thus, di-

pyridylamide ligands have recently been designed and synthesized in crystal engineering; in these compounds, amide–amide hydrogen bonding has been demonstrated to increase supramolecular versatility (Burchell *et al.*, 2004; Muthu *et al.*, 2001, 2002; Nguyen *et al.*, 1998, 2001).



The title compound, (I) or 4py-ox, has been employed successfully in the synthesis of novel metal–organic frameworks (Tzeng *et al.*, 2005, 2006, 2007). We have focused our attention on this organic ligand to obtain a one-dimensional zigzag chain structure with the Co^{2+} ion (Lee & Wang, 2007). In this work, we report a new crystal morphology constructed by 4py-ox, which is a polymorphic crystal of the previous work (Lee & Wang, 2007). The second title compound, (II), was obtained as a by-product in the course of attempts to prepare a coordination polymer by the reaction of $Cd(NO_3)_2\cdot 4H_2O$ and 4py-ox. The molecular structures and the related supramolecular constructions of (I) and (II) are presented in detail and compared with that of the polymorphic crystal in the previous work.

The crystal structure of 4py-ox is shown in Fig. 1, and selected bond lengths and angles are listed in Table 1. No obvious differences in the $C-O$, $C-N$ and $C-C$ bond lengths are found compared with those of the two independent molecules of the other polymorph (Lee & Wang, 2007). In this study, 4py-ox has a crystallographic inversion center in the middle of the oxalamide group, and one-half of the molecule is independent. Therefore, the two pyridyl rings separated by the oxalamide linkage in the molecule are parallel to each other. The central oxalamide group is planar. The $C2-C3-C6-N2$ torsion angle is $53.55(18)^\circ$, which is between the corre-

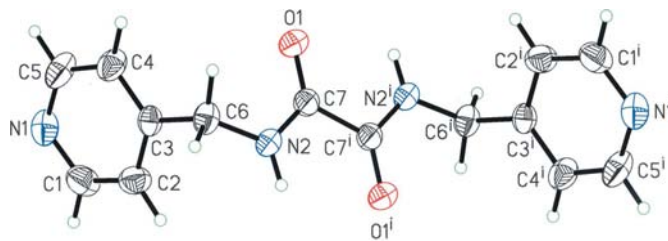
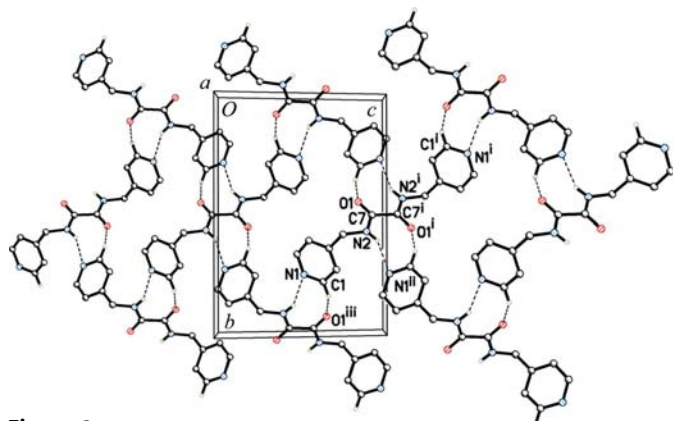
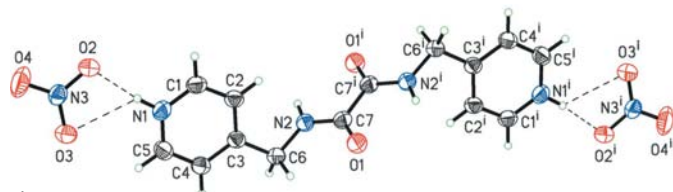


Figure 1

The molecular structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $-x + 1, -y + 1, -z + 2$.]


Figure 2

A packing diagram for (I), viewed along the *a* axis. Dashed lines represent hydrogen bonds. [Symmetry codes: (i) $-x + 1, -y + 1, -z + 2$; (ii) $x + 1, -y + \frac{3}{2}, z + \frac{1}{2}$; (iii) $-x, y + \frac{1}{2}, -z + \frac{3}{2}$.]


Figure 3

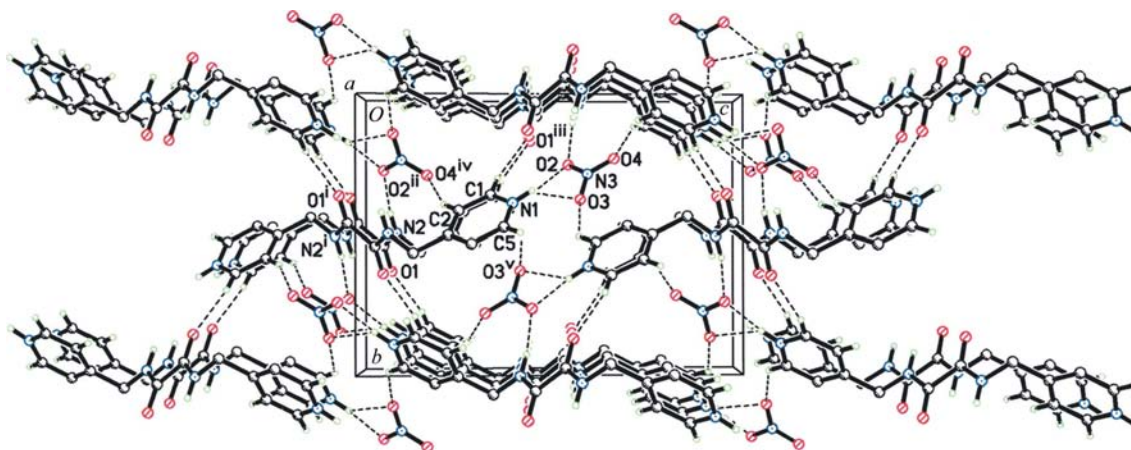
The molecular structure of (II), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines represent hydrogen bonds. [Symmetry code: (i) $-x + 1, -y + 1, -z$.]

sponding values for the two independent molecules of the other polymorph [30.1 (3) and 32.9 (3)° for one of the independent molecules, and 75.9 (2) and 80.8 (2)° for the other; Lee & Wang, 2007]. The terminal (pyridyl) N···N separation of 12.199 (2) Å is slightly shorter than those of the other polymorph [13.075 (2) and 12.951 (2) Å; Lee & Wang, 2007].

The two-dimensional array of 4py-ox molecules in (I) is presented in Fig. 2, showing a two-dimensional sheet-like supramolecular network formed through intermolecular

hydrogen bonds. Details of the hydrogen-bonding geometry are given in Table 2. Two types of intermolecular hydrogen bonds are observed in the unit cell. One is between the N atom of the oxalamide group and the pyridyl N atom of a neighboring molecule [$N2 \cdots N1^{ii} = 3.006$ (2) Å; symmetry code: (ii) $x + 1, -y + \frac{3}{2}, z + \frac{1}{2}$], and the other is between the O atom of the oxalamide group and the α -pyridyl C atom of a neighboring molecule [$C1 \cdots O1^{iii} = 3.254$ (2) Å; symmetry code: (iii) $-x, y + \frac{1}{2}, -z + \frac{3}{2}$]. The 4py-ox molecules are then interlinked *via* four sets of combined N—H···N and C—H···O hydrogen bonds to form a two-dimensional supramolecular architecture. It is interesting to note that this two-dimensional array is different from that of the other polymorph (Lee & Wang, 2007), in which dimers of 4py-ox molecules, formed *via* a pair of N—H···O hydrogen bonds [$N \cdots O = 2.916$ (2) and 2.888 (2) Å], act as the basic building units and are then interlinked *via* four sets of N—H···N hydrogen bonds [$N \cdots N = 2.903$ (2) and 2.930 (2) Å] between the N atoms of the oxalamide group and the pyridyl N atoms of neighboring dimers to form the two-dimensional supramolecular network.

Slow diffusion of $Cd(NO_3)_2 \cdot 4H_2O$ into a solution of 4py-ox resulted in colorless crystals of the unexpected composition $[H_2(4py-ox)](NO_3)_2$, (II). The diprotonation of 4py-ox has also been observed in $[H_2(4,4'-bipy)](NO_3)_2$ (where 4,4'-bipy is 4,4'-bipyridine; Felloni *et al.*, 2002; Iyere *et al.*, 2003) and $[H_2(bpe)](NO_3)_2$ [where bpe is 1,2-bis(4-pyridyl)ethene; Felloni *et al.*, 2002; Yan, 2006]. The molecular structure of (II) contains diprotonated 4py-ox and nitrate counter-ions, as shown in Fig. 3. There is an inversion center in the middle of the oxalamide group and the asymmetric unit contains one-half of an $[H_2(4py-ox)]^{2+}$ cation and one nitrate anion. Bond lengths and angles (Table 3) are comparable with those of (I). Similar to (I), the central oxalamide group is planar. The dihedral angle between the pyridinium ring and the oxalamide group is 103.9 (1)°, which is slightly smaller than the corresponding angle in (I) [104.9 (1)°]. The C2—C3—C6—N2 torsion angle is 23.3 (3)°, which is less than that observed in (I), although both are comparable with those of one molecule


Figure 4

A packing diagram for (II), viewed along the *a* axis. Dashed lines represent hydrogen bonds. [Symmetry codes: (i) $-x + 1, -y + 1, -z$; (ii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (iii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (iv) $x - 1, -y + \frac{1}{2}, z - \frac{1}{2}$; (v) $-x + 3, -y + 1, -z + 1$.]

(N1/C14) in the previously reported polymorph of (I) [30.1 (3) and 32.9 (3)°, respectively; Lee & Wang, 2007].

In (II), there is a bifurcated hydrogen bond. One is between the nitrate anion and the N1—H1 group of the pyridinium ring of the [H₂(4py-ox)]²⁺ cation, with N1···O2 = 2.701 (3) Å and N1···O3 = 3.089 (3) Å. These results are similar to those found in [H₂(4,4'-bipy)](NO₃)₂ reported earlier [N1···O2 = 2.668 (2) Å and N1···O3 = 3.148 (2) Å; Iyere *et al.*, 2003]. The amide N—H group also forms a hydrogen bond with an O atom of a nitrate anion [N2···O2ⁱⁱ = 2.943 (2) Å; symmetry code: (ii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$].

The supramolecular aggregation of (II) in the packing (Fig. 4) is more complicated than that in (I). Each nitrate ion is hydrogen bonded to four cations *via* three N—H···O contacts [N1···O2 = 2.701 (3) Å, N1···O3 = 3.089 (3) Å and N2···O2ⁱⁱ = 2.943 (2) Å] and two C—H···O interactions [C2···O4^{iv} = 3.180 (3) Å and C5···O3^v = 3.160 (3) Å; symmetry codes: (iv) $x - 1, -y + \frac{1}{2}, z - \frac{1}{2}$; (v) $-x + 3, -y + 1, -z + 1$]. Such coordination of each nitrate ion by four cations was also observed in the structure of [H₂(4,4'-bipy)](NO₃)₂ (Iyere *et al.*, 2003). Furthermore, adjacent cations are linked *via* weak C—H···O hydrogen bonding [C1···O1ⁱⁱⁱ = 3.159 (3) Å; symmetry code: (iii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$] between the α -pyridinium C atoms and the oxalamide O atoms, forming an extended two-dimensional supramolecular network. Details of the hydrogen-bonding geometry are given in Table 4.

Experimental

N,N'-Bis(pyridin-4-ylmethyl)oxalamide was prepared from 4-(aminomethyl)pyridine and diethyl oxalate, according to the method of Nguyen *et al.* (1998). Single crystals of (I) were obtained by the DMF/ether diffusion method. For the preparation of (II), a methanol solution (5 ml) of Cd(NO₃)₂·4H₂O (1 mmol) was mixed with a methanol solution (5 ml) of 4py-ox (3 mmol). Slow diffusion with ether resulted in large colorless crystals of (II).

Compound (I)

Crystal data

C ₁₄ H ₁₄ N ₄ O ₂	$V = 650.99 (4) \text{ \AA}^3$
$M_r = 270.29$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 4.7578 (2) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$b = 13.8845 (4) \text{ \AA}$	$T = 150 \text{ K}$
$c = 10.1331 (3) \text{ \AA}$	$0.30 \times 0.25 \times 0.15 \text{ mm}$
$\beta = 103.465 (2)^\circ$	

Data collection

Nonius KappaCCD area-detector diffractometer	7355 measured reflections
Absorption correction: multi-scan (SORTAV; Blessing, 1995)	1485 independent reflections
$T_{\min} = 0.972, T_{\max} = 0.986$	868 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.043$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$	91 parameters
$wR(F^2) = 0.101$	H-atom parameters constrained
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.14 \text{ e \AA}^{-3}$
1485 reflections	$\Delta\rho_{\text{min}} = -0.19 \text{ e \AA}^{-3}$

Compound (II)

Crystal data

C ₁₄ H ₁₆ N ₄ O ₂ ·2NO ₃ ⁻	$V = 852.72 (14) \text{ \AA}^3$
$M_r = 396.33$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 5.3668 (5) \text{ \AA}$	$\mu = 0.13 \text{ mm}^{-1}$
$b = 10.7271 (10) \text{ \AA}$	$T = 150 \text{ K}$
$c = 14.8628 (14) \text{ \AA}$	$0.50 \times 0.22 \times 0.01 \text{ mm}$
$\beta = 94.746 (2)^\circ$	

Data collection

Nonius KappaCCD area-detector diffractometer	7829 measured reflections
Absorption correction: multi-scan (SORTAV; Blessing, 1995)	1931 independent reflections
$T_{\min} = 0.939, T_{\max} = 0.999$	1293 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.066$

Table 1

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

O1—C7	1.2280 (16)	N2—C6	1.4511 (17)
N2—C7	1.3301 (18)	C7—C7 ⁱ	1.532 (3)
C7—N2—C6	121.09 (12)	O1—C7—C7 ⁱ	121.76 (17)
N2—C6—C3	113.31 (12)	N2—C7—C7 ⁱ	113.59 (16)
O1—C7—N2	124.65 (13)		

Symmetry code: (i) $-x + 1, -y + 1, -z + 2$.

Table 2

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2···N1 ⁱⁱ	0.88	2.20	3.006 (2)	152
C1—H1···O1 ⁱⁱⁱ	0.95	2.53	3.254 (2)	133

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

Table 3

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

O1—C7	1.222 (2)	N3—O4	1.230 (3)
N2—C7	1.331 (3)	N3—O3	1.234 (2)
N2—C6	1.449 (3)	N3—O2	1.272 (2)
C7—C7 ⁱ	1.539 (4)		
C7—N2—C6	121.47 (17)	N2—C7—C7 ⁱ	113.2 (2)
N2—C6—C3	113.94 (17)	O4—N3—O3	121.8 (2)
O1—C7—N2	125.80 (19)	O4—N3—O2	119.46 (19)
O1—C7—C7 ⁱ	121.0 (2)	O3—N3—O2	118.67 (17)

Symmetry code: (i) $-x + 1, -y + 1, -z$.

Table 4

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1···O2	0.89 (3)	1.82 (3)	2.701 (3)	173 (3)
N1—H1···O3	0.89 (3)	2.46 (3)	3.089 (3)	128 (2)
N2—H2···O2 ⁱⁱ	0.88	2.09	2.943 (2)	162
C1—H1A···O1 ⁱⁱⁱ	0.95	2.27	3.159 (3)	156
C2—H2A···O4 ^{iv}	0.95	2.29	3.180 (3)	156
C5—H5···O3 ^v	0.95	2.43	3.160 (3)	134

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

Refinement

$$R[F^2 > 2\sigma(F^2)] = 0.052$$

$$wR(F^2) = 0.140$$

$$S = 1.04$$

1931 reflections

132 parameters

H atoms treated by a mixture of independent and constrained refinement

$$\Delta\rho_{\max} = 0.22 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -0.34 \text{ e } \text{Å}^{-3}$$

The pyridinium H atom of (II) was located in a difference Fourier map and refined isotropically. Other H atoms attached to C and N atoms were positioned geometrically and refined using a riding model, with C–H = 0.95–0.99 Å and N–H = 0.88 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$ for both (I) and (II).

For both compounds, data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: UK3019). Services for accessing these data are described at the back of the journal.

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