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Imidazolium *trans*-bis(iminodiacetato- κ^3O,N,O')cobaltate(III)

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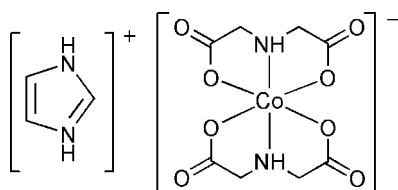
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 Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(C-C) = 0.004$ Å; R factor = 0.029; wR factor = 0.079; data-to-parameter ratio = 13.5.

In the title compound, $(C_3H_5N_2)[Co(C_4H_5NO_4)_2]$, the cation and anion are located on a twofold rotation axis and inversion center, respectively. Intermolecular $N-H \cdots O$ hydrogen bonds link the cations and anions into layers parallel to the ab plane. The crystal packing also exhibits weak $C-H \cdots O$ hydrogen bonds, including bifurcated hydrogen bonds, and $C=O \cdots \pi$ interactions.

Related literature

For hydrogen bonds in related compounds containing imidazolium, see: Allen (2002); Chattopadhyay *et al.* (1995); Gao *et al.* (2009); Hsu & Schlemper (1980); Rissanen & Pursiainen (2000). Bifurcated hydrogen bonds were discussed by Jeffrey *et al.* (1985). For graph-set notation, see: Bernstein *et al.* (1995).



Experimental

Crystal data

 $(C_3H_5N_2)[Co(C_4H_5NO_4)_2]$
 $M_r = 390.20$

 Orthorhombic, *Pcca*
 $a = 16.889$ (3) Å

 $b = 5.2906$ (10) Å

 $c = 16.901$ (3) Å

 $V = 1510.2$ (5) Å³
 $Z = 4$

 Mo $K\alpha$ radiation

 $\mu = 1.19$ mm⁻¹
 $T = 298$ K

 $0.20 \times 0.20 \times 0.20$ mm

Data collection

Bruker SMART CCD area-detector diffractometer

 Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)

 $T_{\min} = 0.783$, $T_{\max} = 0.797$

6218 measured reflections

1495 independent reflections

 1299 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.079$
 $S = 1.08$

1495 reflections

111 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.35$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.27$ e Å⁻³
Table 1

Hydrogen-bond geometry (Å, °).

 $Cg1$ is the centroid of the imidazolium ring.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1 \cdots O3^i$	0.79	2.12	2.880 (2)	161
$N2-H2 \cdots O2^{ii}$	0.86	1.95	2.775 (3)	162
$C3-H3B \cdots O2^{iii}$	0.97	2.43	3.338 (3)	156
$C5-H5 \cdots O4^i$	0.93	2.36	3.117 (4)	138
$C5-H5 \cdots O4^{iv}$	0.93	2.36	3.117 (4)	138
$C1-O2 \cdots Cg1^v$	1.23 (1)	3.54 (1)	3.953 (2)	0?

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL/PC* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL/PC*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2551).

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
 Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
 Bruker (2000). *SMART* and *SAINTE*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Chattopadhyay, S. K., Mak, T. C. W., Luo, B., Thompson, L. K., Rana, A. & Ghosh, S. (1995). *Polyhedron*, **14**, 3661–3667.
 Gao, X.-L., Lu, L.-P. & Zhu, M.-L. (2009). *Acta Cryst.* **C65**, o123–o127.
 Hsu, B. & Schlemper, E. O. (1980). *Acta Cryst.* **B36**, 3017–3023.
 Jeffrey, G. A., Maluszynska, H. & Mitra, J. (1985). *Int. J. Biol. Macromol.* **7**, 336–348.
 Rissanen, K. & Pursiainen, J. (2000). *New J. Chem.* **24**, 47–52.
 Sheldrick, G. M. (2000). *SADABS*. University of Göttingen, Germany.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

supplementary materials

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Imidazolium *trans*-bis(iminodiacetato- κ^3O,N,O')cobaltate(III)

X.-L. Gao, L.-P. Lu and M.-L. Zhu

Comment

In continuation of our study of weak C—H \cdots O and C=O \cdots π interactions in the building of three-dimensional structures (Gao *et al.*, 2009), we present here the crystal structure of the title 1:1 adduct, (I).

In (I) (Fig. 1), the cation and anion are located on a two-fold rotation axis and inversion center, respectively. Strong N2—H \cdots O2ⁱⁱ hydrogen bonds (Table 1) link imidazolium and *trans*-bis(iminodiacetato-N,*O,O'*)cobalt(III) with the direction of (1 $\bar{2}$ 0) to form one-dimensional chains (Fig. 2) with graph-set notation C₂²(13). These chains further assemble to other *trans*-bis(iminodiacetato-N,*O,O'*)cobalt(III) anions in two-dimensional structures on (001) plane via C5—H \cdots O4^{vi}, C5—H \cdots O4^{viii} and C3^{viii}—H \cdots O2^{iv} (Table 1) hydrogen bonds, as shown in Fig. 2. Further, the layers assemble to a three-dimensional structure by strong N1—H \cdots Oⁱ hydrogen bond and weak C1=O2 \cdots π (centroid of imidazolium ring) interaction (Table 1). Imidazolium has three donors, two N—H and one C—H, the latter forming a non-conventional bifurcated hydrogen bond between imidazolium C5—H and carboxylate groups O4H and O4F from *trans*-bis(iminodiacetato-N,*O,O'*)cobalt(III). Interestingly, this type of hydrogen bond in imidazolium compounds was found in a search of the Cambridge Structural Database (CSD version 5.30; Allen, 2002). Among the 200 hits for imidazolium compounds, there are only seven compounds having the similar bifurcated hydrogen bonds (C—H from imidazolium), namely, imidazolium hydrogen maleate (Hsu & Schlemper, 1980), benzo-18-crown-6 imidazolium clathrate perchlorate (Rissanen & Pursiainen, 2000), bis(imidazolium) bis(oxalato-*O,O'*)copper(II) (Chattopadhyay *et al.*, 1995). Their distances of H \cdots O are in the range of 2.10 to 2.49 Å. However, analysis in sum of three angles about H atom are all less than 360° in the seven compounds, which indicated that these weak hydrogen bonds are not of characters of bifurcated hydrogen bonds from H-bond classification (Jeffrey *et al.*, 1985).

Experimental

Chemicals were readily available from commercial sources and were used as received without further purification. To a 10 ml of solution containing imidazole (0.14 g, 2 mmol) in a flask with constant stirring, added dropwise Co(CH₃COO)₂.3H₂O (0.23 g, 1 mmol) in 5 ml of aqueous solution and 5 ml aqueous solution containing iminodiacetic acid (0.27 g, 2 mmol) was added dropwise. The mixture was stirred for 3 h, and then filtered. The dark-red filtrate was left to stand at room temperature, and after three weeks, dark-red crystals of the title compound were formed.

Refinement

H atoms attached to C atoms of (I) were placed in geometrically idealized positions and refined with $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{C})$. H atoms attached to N1 and N2 in (I) were located from difference Fourier maps, with fixed bond lengths, and refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$.

Figures

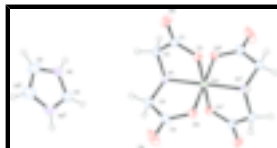


Fig. 1. View of (I) with displacement ellipsoids drawn at the 30% probability level and atomic numbering [symmetry codes: (i) $-x, -y, -z$; (ii) $1/2 - x, -1 - y, z$].

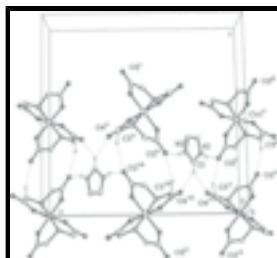


Fig. 2. A portion of the crystal packing showing hydrogen-bonding patterns with graph-set notations $R_3^2(9)$, $R_3^2(9)$ and $R_2^2(12)$, respectively. Dotted lines denote hydrogen bonds. H atoms non-involved in hydrogen-bonding omitted for clarity. [Symmetry codes: (i) $1/2 - x, 1 - y, z$; (ii) $-x, -1 + y, 1/2 - z$; (iii) $x, 1 - y, 1/2 + z$; (iv) $1/2 + x, 2 - y, 1/2 - z$; (v) $1/2 - x, y, 1/2 + z$; (vi) $x, -1 + y, z$; (vii) $-x, 1 - y, -z$; (viii) $1/2 - x, 2 - y, z$; (ix) $1/2 + x, y, -z$].

Imidazolium *trans*-bis(iminodiacetato- κ^3O,N,O')cobaltate(III)

Crystal data

(C₃H₅N₂)[Co(C₄H₅NO₄)₂]

$M_r = 390.20$

Orthorhombic, *Pcca*

Hall symbol: $-P\ 2a\ 2ac$

$a = 16.889\ (3)\ \text{\AA}$

$b = 5.2906\ (10)\ \text{\AA}$

$c = 16.901\ (3)\ \text{\AA}$

$V = 1510.2\ (5)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 800$

$D_x = 1.716\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 2958 reflections

$\theta = 2.4\text{--}27.0^\circ$

$\mu = 1.19\ \text{mm}^{-1}$

$T = 298\ \text{K}$

Block, red

$0.20 \times 0.20 \times 0.20\ \text{mm}$

Data collection

Bruker SMART CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 298\ \text{K}$

ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 2000)

$T_{\min} = 0.783$, $T_{\max} = 0.797$

6218 measured reflections

1495 independent reflections

1299 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.025$

$\theta_{\max} = 26.0^\circ$

$\theta_{\min} = 2.4^\circ$

$h = -19 \rightarrow 20$

$k = -6 \rightarrow 4$

$l = -18 \rightarrow 20$

Refinement

Refinement on F^2

Secondary atom site location: difference Fourier map

Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.029$$

$$wR(F^2) = 0.079$$

$$S = 1.08$$

1495 reflections

111 parameters

Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0405P)^2 + 0.6086P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

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

$$\Delta\rho_{\max} = 0.35 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.27 \text{ e } \text{\AA}^{-3}$$

Extinction correction: none

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.0000	1.0000	0.0000	0.02108 (14)
O1	-0.06498 (8)	1.0888 (2)	0.08656 (8)	0.0305 (3)
O2	-0.10143 (10)	0.9556 (3)	0.20572 (10)	0.0502 (5)
O3	0.07296 (7)	1.2495 (2)	0.03073 (9)	0.0306 (3)
O4	0.17666 (11)	1.3151 (3)	0.10704 (14)	0.0775 (7)
N1	0.05329 (8)	0.7739 (3)	0.07205 (9)	0.0240 (3)
H1	0.0644	0.6440	0.0521	0.029*
C1	-0.06105 (12)	0.9354 (4)	0.14545 (12)	0.0319 (4)
C2	-0.00355 (11)	0.7182 (4)	0.13637 (12)	0.0315 (5)
H2A	0.0249	0.6926	0.1856	0.038*
H2B	-0.0324	0.5644	0.1242	0.038*
C3	0.12727 (11)	0.8972 (4)	0.09931 (13)	0.0327 (4)
H3A	0.1724	0.8161	0.0744	0.039*
H3B	0.1324	0.8764	0.1561	0.039*
C4	0.12754 (12)	1.1751 (4)	0.07933 (13)	0.0369 (5)
N2	0.20741 (11)	0.3528 (4)	0.31139 (13)	0.0526 (5)
H2	0.1749	0.2389	0.2952	0.063*
C5	0.2500	0.5000	0.2661 (2)	0.0461 (9)
H5	0.2500	0.5000	0.2110	0.055*
C6	0.22287 (19)	0.4090 (8)	0.38741 (18)	0.0811 (11)
H6	0.1999	0.3346	0.4317	0.097*

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0249 (2)	0.0181 (2)	0.0202 (2)	0.00274 (13)	-0.00159 (13)	-0.00175 (12)
O1	0.0359 (7)	0.0297 (7)	0.0259 (7)	0.0101 (6)	0.0047 (6)	-0.0001 (6)
O2	0.0550 (10)	0.0629 (11)	0.0325 (9)	0.0263 (8)	0.0165 (8)	0.0112 (8)
O3	0.0323 (7)	0.0210 (6)	0.0385 (8)	-0.0005 (5)	-0.0086 (6)	-0.0013 (6)
O4	0.0655 (12)	0.0340 (9)	0.1330 (19)	-0.0079 (9)	-0.0602 (12)	-0.0013 (10)
N1	0.0288 (8)	0.0187 (7)	0.0246 (8)	0.0051 (6)	-0.0019 (6)	-0.0030 (6)
C1	0.0334 (10)	0.0351 (10)	0.0271 (11)	0.0056 (9)	0.0021 (9)	0.0002 (8)
C2	0.0376 (11)	0.0297 (10)	0.0273 (11)	0.0068 (8)	0.0025 (8)	0.0064 (8)
C3	0.0301 (10)	0.0306 (10)	0.0374 (11)	0.0032 (8)	-0.0084 (9)	-0.0001 (9)
C4	0.0345 (10)	0.0269 (10)	0.0492 (13)	0.0013 (8)	-0.0115 (9)	-0.0061 (9)
N2	0.0418 (11)	0.0547 (13)	0.0613 (14)	-0.0206 (10)	-0.0043 (10)	-0.0035 (10)
C5	0.0403 (19)	0.057 (2)	0.041 (2)	-0.0004 (15)	0.000	0.000
C6	0.074 (2)	0.122 (3)	0.0467 (18)	-0.048 (2)	0.0007 (15)	0.0132 (18)

Geometric parameters (\AA , $^\circ$)

Co1—O3 ⁱ	1.8790 (12)	C1—C2	1.512 (3)
Co1—O3	1.8790 (12)	C2—H2A	0.9700
Co1—O1	1.8882 (13)	C2—H2B	0.9700
Co1—O1 ⁱ	1.8882 (13)	C3—C4	1.508 (3)
Co1—N1 ⁱ	1.9299 (14)	C3—H3A	0.9700
Co1—N1	1.9299 (14)	C3—H3B	0.9700
O1—C1	1.286 (2)	N2—C5	1.308 (3)
O2—C1	1.230 (2)	N2—C6	1.344 (4)
O3—C4	1.296 (2)	N2—H2	0.8599
O4—C4	1.207 (3)	C5—N2 ⁱⁱ	1.308 (3)
N1—C2	1.480 (2)	C5—H5	0.9300
N1—C3	1.483 (2)	C6—C6 ⁱⁱ	1.329 (6)
N1—H1	0.7879	C6—H6	0.9300
O3 ⁱ —Co1—O3	180.00 (9)	O1—C1—C2	115.72 (17)
O3 ⁱ —Co1—O1	90.44 (6)	N1—C2—C1	109.88 (16)
O3—Co1—O1	89.56 (6)	N1—C2—H2A	109.7
O3 ⁱ —Co1—O1 ⁱ	89.56 (6)	C1—C2—H2A	109.7
O3—Co1—O1 ⁱ	90.44 (6)	N1—C2—H2B	109.7
O1—Co1—O1 ⁱ	180.0	C1—C2—H2B	109.7
O3 ⁱ —Co1—N1 ⁱ	87.43 (6)	H2A—C2—H2B	108.2
O3—Co1—N1 ⁱ	92.57 (6)	N1—C3—C4	111.22 (15)
O1—Co1—N1 ⁱ	93.65 (6)	N1—C3—H3A	109.4
O1 ⁱ —Co1—N1 ⁱ	86.35 (6)	C4—C3—H3A	109.4
O3 ⁱ —Co1—N1	92.57 (6)	N1—C3—H3B	109.4
O3—Co1—N1	87.43 (6)	C4—C3—H3B	109.4
O1—Co1—N1	86.35 (6)	H3A—C3—H3B	108.0

O1 ⁱ —Co1—N1	93.65 (6)	O4—C4—O3	123.3 (2)
N1 ⁱ —Co1—N1	180.00 (7)	O4—C4—C3	120.91 (19)
C1—O1—Co1	114.38 (12)	O3—C4—C3	115.83 (16)
C4—O3—Co1	115.36 (12)	C5—N2—C6	108.8 (2)
C2—N1—C3	113.95 (15)	C5—N2—H2	125.6
C2—N1—Co1	106.52 (11)	C6—N2—H2	125.6
C3—N1—Co1	108.42 (11)	N2 ⁱⁱ —C5—N2	108.3 (3)
C2—N1—H1	107.2	N2 ⁱⁱ —C5—H5	125.9
C3—N1—H1	108.4	N2—C5—H5	125.9
Co1—N1—H1	112.5	C6 ⁱⁱ —C6—N2	107.09 (15)
O2—C1—O1	123.87 (19)	C6 ⁱⁱ —C6—H6	126.5
O2—C1—C2	120.40 (18)	N2—C6—H6	126.5
O3 ⁱ —Co1—O1—C1	77.41 (15)	O1 ⁱ —Co1—N1—C3	80.29 (12)
O3—Co1—O1—C1	-102.59 (15)	Co1—O1—C1—O2	-176.80 (17)
N1 ⁱ —Co1—O1—C1	164.87 (14)	Co1—O1—C1—C2	2.0 (2)
N1—Co1—O1—C1	-15.13 (14)	C3—N1—C2—C1	92.47 (19)
O1—Co1—O3—C4	90.08 (15)	Co1—N1—C2—C1	-27.03 (19)
O1 ⁱ —Co1—O3—C4	-89.92 (15)	O2—C1—C2—N1	-163.64 (19)
N1 ⁱ —Co1—O3—C4	-176.29 (15)	O1—C1—C2—N1	17.5 (3)
N1—Co1—O3—C4	3.71 (15)	C2—N1—C3—C4	-104.50 (19)
O3 ⁱ —Co1—N1—C2	-66.96 (12)	Co1—N1—C3—C4	13.92 (19)
O3—Co1—N1—C2	113.04 (12)	Co1—O3—C4—O4	-176.8 (2)
O1—Co1—N1—C2	23.32 (12)	Co1—O3—C4—C3	3.9 (2)
O1 ⁱ —Co1—N1—C2	-156.68 (12)	N1—C3—C4—O4	168.6 (2)
O3 ⁱ —Co1—N1—C3	170.01 (12)	N1—C3—C4—O3	-12.2 (3)
O3—Co1—N1—C3	-9.99 (12)	C6—N2—C5—N2 ⁱⁱ	0.4 (2)
O1—Co1—N1—C3	-99.71 (12)	C5—N2—C6—C6 ⁱⁱ	-1.2 (5)

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

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1 \cdots O3 ⁱⁱⁱ	0.79	2.12	2.880 (2)	161
N2—H2 \cdots O2 ^{iv}	0.86	1.95	2.775 (3)	162
C3—H3B \cdots O2 ^v	0.97	2.43	3.338 (3)	156
C5—H5 \cdots O4 ⁱⁱⁱ	0.93	2.36	3.117 (4)	138
C5—H5 \cdots O4 ^{vi}	0.93	2.36	3.117 (4)	138
C1—O2 \cdots Cg1 ^{vii}	1.230 (2)	3.54 (1)	3.953 (2)	.

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

Fig. 1

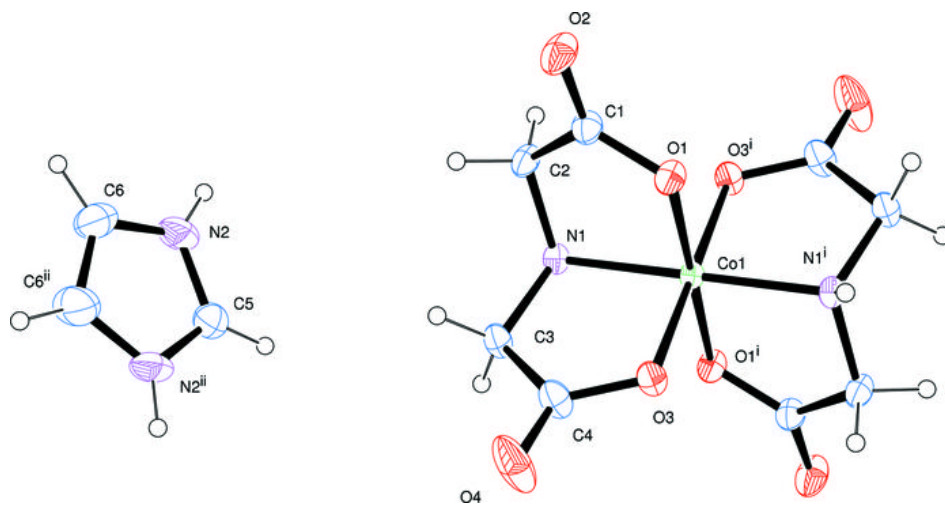


Fig. 2

