

fac-Tris(pyridine-2-carboxylato- κ^2 N,O)-cobalt(III)

Irina A. Golenia,^a Alexander N. Boyko,^a Natalia V. Kotova,^a Matti Haukka^b and Valentina A. Kalibabchuk^{c*}

^aDepartment of Chemistry, Kiev National Taras Shevchenko University, Volodymyrska Street 64, 01601 Kiev, Ukraine, ^bDepartment of Chemistry, University of Joensuu, PO Box 111, FI-80101 Joensuu, Finland, and ^cDepartment of General Chemistry, O. O. Bohomolets National Medical University, Shevchenko Boulevard 13, 01601 Kiev, Ukraine

Correspondence e-mail: kalibabchuk@ukr.net

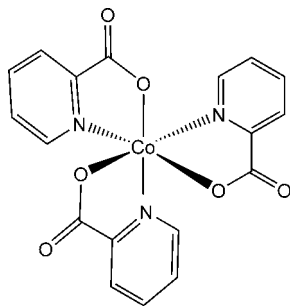
Received 11 October 2011; accepted 19 October 2011

Key indicators: single-crystal X-ray study; $T = 120$ K; mean $\sigma(\text{C}-\text{C}) = 0.017$ Å; R factor = 0.068; wR factor = 0.197; data-to-parameter ratio = 11.4.

In the title compound, $[\text{Co}(\text{C}_6\text{H}_4\text{NO}_2)_3]$, the Co^{III} ion lies on a threefold rotation axis and is in a distorted octahedral environment defined by three N and three O donor atoms from three *fac*-disposed pyridine-2-carboxylate ligands. The ligands are coordinated in a chelate fashion, forming three five-membered rings. In the crystal, translationally related complex molecules are organized into columns along $[001]$ via $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds.

Related literature

For the use of hydroxamate ligands in the synthesis of polynuclear compounds, see: Dobosz *et al.* (1999); Fritsky *et al.* (1998); Sachse *et al.* (2008). For hydrolytic destruction of hydroxamate ligands upon complex formation, see: Świątek-Kozłowska *et al.* (2000). For related structures, see: Fritsky *et al.* (2001); Fu & Wang (2005); Kovbasyuk *et al.* (2004); Krämer & Fritsky (2000); Mokhir *et al.* (2002); Moroz *et al.* (2010); Pelizzi & Pelizzi (1981); Sliva *et al.* (1997); Wörl, Fritsky *et al.* (2005); Wörl, Pritzkow *et al.* (2005). For the synthesis of pyridine-2-hydroxamic acid, see: Hynes (1970).



Experimental

Crystal data

$[\text{Co}(\text{C}_6\text{H}_4\text{NO}_2)_3]$
 $M_r = 425.24$
 Hexagonal, $P6$
 $a = 12.8617$ (12) Å
 $c = 6.2122$ (9) Å
 $V = 890.0$ (2) Å³

$Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 1.01$ mm⁻¹
 $T = 120$ K
 $0.23 \times 0.08 \times 0.03$ mm

Data collection

Nonius KappaCCD diffractometer
 Absorption correction: multi-scan
 (DENZO/SCALEPACK;
 Otwinowski & Minor, 1997)
 $T_{\text{min}} = 0.800$, $T_{\text{max}} = 0.970$

5635 measured reflections
 978 independent reflections
 893 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.043$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.068$
 $wR(F^2) = 0.197$
 $S = 1.16$
 978 reflections
 86 parameters
 1 restraint

H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 1.05$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.59$ e Å⁻³
 Absolute structure: Flack (1983),
 400 Friedel pairs
 Flack parameter: -0.02 (7)

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C3}-\text{H3}\cdots\text{O2}^i$	0.95	2.60	3.212 (14)	123

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

Data collection: COLLECT (Nonius, 1998); cell refinement: DENZO/SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO/SCALEPACK; program(s) used to solve structure: SIR2004 (Burla *et al.*, 2005); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: DIAMOND (Brandenburg, 1999); software used to prepare material for publication: SHELXL97.

Financial support from the State Fund for Fundamental Research of Ukraine (grant No. F40.3/041) and the Swedish Institute (Visby Program) is gratefully acknowledged.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2479).

References

- Brandenburg, K. (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G. & Spagna, R. (2005). *J. Appl. Cryst.* **38**, 381–388.
- Dobosz, A., Dudarenko, N. M., Fritsky, I. O., Głowiak, T., Karaczyn, A., Kozłowski, H., Sliva, T. Yu. & Świątek-Kozłowska, J. (1999). *J. Chem. Soc. Dalton Trans.* pp. 743–749.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Fritsky, I. O., Kozłowski, H., Sadler, P. J., Yefetova, O. P., Świątek-Kozłowska, J., Kalibabchuk, V. A. & Głowiak, T. (1998). *J. Chem. Soc. Dalton Trans.* pp. 3269–3274.
- Fritsky, I. O., Ott, R., Pritzkow, H. & Krämer, R. (2001). *Chem. Eur. J.* **7**, 1221–1231.
- Fu, A.-Y. & Wang, D.-Q. (2005). *Acta Cryst.* **E61**, m481–m482.
- Hynes, J. B. (1970). *J. Med. Chem.* **13**, 1235–1237.
- Kovbasyuk, L., Pritzkow, H., Krämer, R. & Fritsky, I. O. (2004). *Chem. Commun.* pp. 880–881.

- Krämer, R. & Fritsky, I. O. (2000). *Eur. J. Org. Chem.* pp. 3505–3510.
- Mokhir, A. A., Gumienna-Kontecka, E. S., Świętek-Kozłowska, J., Petkova, E. G., Fritsky, I. O., Jerzykiewicz, L., Kapshuk, A. A. & Sliva, T. Yu. (2002). *Inorg. Chim. Acta*, **329**, 113–121.
- Moroz, Y. S., Szyrweil, L., Demeshko, S., Kozłowski, H., Meyer, F. & Fritsky, I. O. (2010). *Inorg. Chem.* **49**, 4750–4752.
- Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Pelizzi, C. & Pelizzi, G. (1981). *Transition Met. Chem.* **6**, 315–316.
- Sachse, A., Penkova, L., Noel, G., Dechert, S., Varzatskii, O. A., Fritsky, I. O. & Meyer, F. (2008). *Synthesis*, **5**, 800–806.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sliva, T. Yu., Kowalik-Jankowska, T., Amirkhanov, V. M., Głowiak, T., Onindo, C. O., Fritsky, I. O. & Kozłowski, H. (1997). *J. Inorg. Biochem.* **65**, 287–294.
- Świętek-Kozłowska, J., Fritsky, I. O., Dobosz, A., Karaczyn, A., Dudarenko, N. M., Sliva, T. Yu., Gumienna-Kontecka, E. & Jerzykiewicz, L. (2000). *J. Chem. Soc. Dalton Trans.* pp. 4064–4068.
- Wörl, S., Fritsky, I. O., Hellwinkel, D., Pritzkow, H. & Krämer, R. (2005). *Eur. J. Inorg. Chem.* pp. 759–765.
- Wörl, S., Pritzkow, H., Fritsky, I. O. & Krämer, R. (2005). *Dalton Trans.* pp. 27–29.

supplementary materials

Acta Cryst. (2011). E67, m1596-m1597 [doi:10.1107/S1600536811043303]

***fac*-Tris(pyridine-2-carboxylato- κ^2 N,O)cobalt(III)**

I. A. Golenia, A. N. Boyko, N. V. Kotova, M. Haukka and V. A. Kalibabchuk

Comment

Hydroxamic groups and their derivatives are often used in syntheses of polynuclear metal complexes (Dobosz *et al.*, 1999; Fritsky *et al.*, 1998; Sachse *et al.*, 2008). However, functionalized hydroxamate ligands having additional donor functions often undergo hydrolytic destruction when complex formation with 3d-metal ions takes place (Dobosz *et al.*, 1999; Świątek-Kozłowska *et al.*, 2000). As a result, a carboxylic group is formed. The title compound was obtained as a result of hydrolytic decomposition of pyridine-2-hydroxamic acid during the reaction of complex formation with cobalt(II) perchlorate.

In the title compound, the Co^{III} ion lies on a threefold rotation axis and is in a distorted octahedral environment of three N and three O donor atoms from three pyridine-2-carboxylate ligands (Fig. 1). Unlike in the case of earlier reported tris(pyridine-2-carboxylato)cobalt(III) monohydrate, in which the realization of *mer*-isomer is observed, in the title complex three pyridine-2-carboxylate ligands are disposed in a *fac*-fashion (Fu & Wang, 2005; Pelizzi & Pelizzi, 1981). The ligands are coordinated in a chelate mode, forming three five-membered rings. The Co—N and Co—O bond lengths are consistent with the values typically quoted for the octahedral cobalt(III) complexes with N,O-mixed donor ligands (Mokhir *et al.*, 2002; Sliva *et al.*, 1997). The C—O bond lengths in the deprotonated carboxylate groups of the ligands differ significantly [1.232 (14) and 1.339 (15) Å], which is typical for monodentately coordinated carboxylates (Wörl, Fritsky *et al.*, 2005; Wörl, Pritzkow *et al.*, 2005). The C—C and C—N bond lengths in the pyridine rings are normal for 2-substituted pyridine derivatives (Fritsky *et al.*, 2001; Kovbasyuk *et al.*, 2004; Krämer & Fritsky, 2000; Moroz *et al.*, 2010).

In the crystal, the translational complex molecules are organized into columns along the *c* axis (Fig. 2). The neighboring molecules are united by C—H \cdots O hydrogen bonds (Table 1).

Experimental

Cobalt(II) perchlorate hexahydrate (0.0365 g, 0.1 mmol) was dissolved in water (3 ml) and mixed with a solution of pyridine-2-hydroxamic acid (0.0414 g, 0.3 mmol) (Hynes, 1970) in methanol (3 ml). The resulting clear red solution was set aside for crystallization by slow diffusion of diethyl ether into the formed solution. The pink crystals formed in 5–7 days were filtered off, washed with diethyl ether and air-dried (yield: 83%).

Refinement

The final structure refinement was performed by using a twin law (-1 -1 0 0 1 0 0 0 -1) with the final BASF parameter refining to 0.80178. H atoms were positioned geometrically and refined as riding atoms, with C—H = 0.95 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Figures

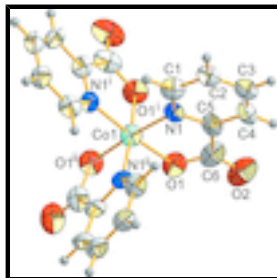


Fig. 1. The molecular structure of the title compound. Displacement ellipsoids are shown at the 50% probability level. [Symmetry codes: (i) $-x+y, 1-x, z$; (ii) $1-y, 1+x-y, z$.]

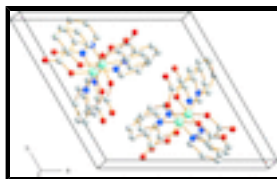


Fig. 2. A packing diagram of the title compound. H atoms have been omitted for clarity.

fac-Tris(pyridine-2-carboxylato- κ^2N,O)cobalt(III)

Crystal data

$[\text{Co}(\text{C}_6\text{H}_4\text{NO}_2)_3]$

$M_r = 425.24$

Hexagonal, $P6$

Hall symbol: $P\ 6$

$a = 12.8617\ (12)\ \text{\AA}$

$c = 6.2122\ (9)\ \text{\AA}$

$V = 890.0\ (2)\ \text{\AA}^3$

$Z = 2$

$F(000) = 432$

$D_x = 1.587\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 713 reflections

$\theta = 3.2\text{--}24.5^\circ$

$\mu = 1.01\ \text{mm}^{-1}$

$T = 120\ \text{K}$

Block, pink

$0.23 \times 0.08 \times 0.03\ \text{mm}$

Data collection

Nonius KappaCCD
diffractometer

Radiation source: fine-focus sealed tube
horizontally mounted graphite crystal

Detector resolution: $9\ \text{pixels mm}^{-1}$

φ and ω scans with κ offset

Absorption correction: multi-scan
(*DENZO/SCALEPACK*; Otwinowski & Minor, 1997)

$T_{\min} = 0.800, T_{\max} = 0.970$

5635 measured reflections

978 independent reflections

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

$R_{\text{int}} = 0.043$

$\theta_{\max} = 25.0^\circ, \theta_{\min} = 3.2^\circ$

$h = -15 \rightarrow 15$

$k = -15 \rightarrow 15$

$l = -7 \rightarrow 7$

Refinement

Refinement on F^2

Secondary atom site location: difference Fourier map

Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.068$$

$$wR(F^2) = 0.197$$

$$S = 1.16$$

978 reflections

86 parameters

1 restraint

Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.1316P)^2 + 0.9442P]$$

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

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

$$\Delta\rho_{\max} = 1.05 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.59 \text{ e } \text{\AA}^{-3}$$

Absolute structure: Flack (1983), 400 Friedel pairs

$$\text{Flack parameter: } -0.02 (7)$$

Special details

Experimental. The final structural refinement was performed by using the twin law -1 -1 0 0 1 0 0 0 -1 with the final BASF parameter refining to 0.80178.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.3333	0.6667	0.3408 (2)	0.0379 (5)
O1	0.4550 (7)	0.7860 (7)	0.5147 (11)	0.0514 (18)
O2	0.6490 (9)	0.8907 (8)	0.5627 (16)	0.083 (3)
N1	0.4619 (6)	0.6785 (6)	0.1705 (12)	0.0332 (15)
C1	0.4622 (10)	0.6303 (9)	-0.0009 (17)	0.051 (2)
H1	0.3875	0.5756	-0.0656	0.061*
C2	0.5687 (9)	0.6533 (9)	-0.1037 (17)	0.050 (2)
H2	0.5659	0.6145	-0.2355	0.061*
C3	0.6747 (10)	0.7308 (9)	-0.0138 (18)	0.052 (2)
H3	0.7483	0.7480	-0.0795	0.062*
C4	0.6729 (9)	0.7796 (9)	0.159 (2)	0.052 (3)
H4	0.7469	0.8358	0.2241	0.062*
C5	0.5690 (8)	0.7548 (9)	0.2577 (18)	0.048 (2)
C6	0.5660 (11)	0.8159 (9)	0.4512 (18)	0.057 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0513 (7)	0.0513 (7)	0.0111 (8)	0.0256 (3)	0.000	0.000
O1	0.067 (4)	0.066 (4)	0.018 (4)	0.031 (4)	-0.007 (3)	-0.008 (3)
O2	0.105 (7)	0.067 (5)	0.054 (6)	0.027 (4)	-0.036 (5)	0.004 (4)
N1	0.045 (4)	0.047 (4)	0.014 (3)	0.028 (3)	-0.001 (3)	0.007 (3)
C1	0.065 (5)	0.056 (5)	0.034 (5)	0.031 (4)	0.006 (4)	0.008 (4)
C2	0.061 (5)	0.058 (5)	0.041 (6)	0.036 (5)	0.010 (4)	0.006 (4)
C3	0.060 (6)	0.059 (6)	0.046 (6)	0.038 (5)	0.014 (5)	0.016 (5)
C4	0.042 (5)	0.067 (6)	0.055 (7)	0.033 (4)	0.012 (5)	0.023 (6)
C5	0.048 (5)	0.057 (5)	0.042 (6)	0.029 (4)	-0.005 (4)	0.021 (5)

supplementary materials

C6 0.071 (7) 0.052 (6) 0.036 (6) 0.021 (5) -0.027 (6) 0.010 (5)

Geometric parameters (Å, °)

Co1—O1 ⁱ	1.889 (7)	C1—C2	1.402 (14)
Co1—O1	1.889 (7)	C1—H1	0.9500
Co1—O1 ⁱⁱ	1.889 (7)	C2—C3	1.344 (16)
Co1—N1 ⁱ	1.904 (7)	C2—H2	0.9500
Co1—N1 ⁱⁱ	1.904 (7)	C3—C4	1.251 (15)
Co1—N1	1.904 (7)	C3—H3	0.9500
O1—C6	1.339 (15)	C4—C5	1.354 (14)
O2—C6	1.232 (14)	C4—H4	0.9500
N1—C1	1.233 (14)	C5—C6	1.447 (15)
N1—C5	1.343 (12)		
O1 ⁱ —Co1—O1	90.6 (3)	N1—C1—C2	122.4 (10)
O1 ⁱ —Co1—O1 ⁱⁱ	90.6 (3)	N1—C1—H1	118.8
O1—Co1—O1 ⁱⁱ	90.6 (3)	C2—C1—H1	118.8
O1 ⁱ —Co1—N1 ⁱ	85.4 (3)	C3—C2—C1	119.3 (10)
O1—Co1—N1 ⁱ	92.1 (2)	C3—C2—H2	120.4
O1 ⁱⁱ —Co1—N1 ⁱ	175.1 (3)	C1—C2—H2	120.4
O1 ⁱ —Co1—N1 ⁱⁱ	92.1 (2)	C4—C3—C2	117.6 (10)
O1—Co1—N1 ⁱⁱ	175.1 (3)	C4—C3—H3	121.2
O1 ⁱⁱ —Co1—N1 ⁱⁱ	85.4 (3)	C2—C3—H3	121.2
N1 ⁱ —Co1—N1 ⁱⁱ	92.1 (3)	C3—C4—C5	122.2 (11)
O1 ⁱ —Co1—N1	175.1 (3)	C3—C4—H4	118.9
O1—Co1—N1	85.4 (3)	C5—C4—H4	118.9
O1 ⁱⁱ —Co1—N1	92.1 (2)	N1—C5—C4	121.4 (11)
N1 ⁱ —Co1—N1	92.1 (3)	N1—C5—C6	115.8 (10)
N1 ⁱⁱ —Co1—N1	92.1 (3)	C4—C5—C6	122.5 (11)
C6—O1—Co1	113.3 (7)	O2—C6—O1	116.2 (13)
C1—N1—C5	117.1 (9)	O2—C6—C5	130.0 (13)
C1—N1—Co1	131.3 (7)	O1—C6—C5	113.8 (10)
C5—N1—Co1	111.5 (7)		
O1 ⁱ —Co1—O1—C6	179.0 (6)	C1—C2—C3—C4	-0.2 (14)
O1 ⁱⁱ —Co1—O1—C6	88.4 (8)	C2—C3—C4—C5	1.2 (15)
N1—Co1—O1—C6	-3.7 (7)	C1—N1—C5—C4	1.3 (13)
O1—Co1—N1—C1	-175.4 (8)	Co1—N1—C5—C4	-177.9 (7)
O1 ⁱⁱ —Co1—N1—C1	94.2 (9)	C1—N1—C5—C6	176.1 (7)
N1 ⁱ —Co1—N1—C1	-83.4 (7)	Co1—N1—C5—C6	-3.1 (8)
N1 ⁱⁱ —Co1—N1—C1	8.8 (8)	C3—C4—C5—N1	-1.8 (14)
O1—Co1—N1—C5	3.7 (6)	C3—C4—C5—C6	-176.3 (8)
O1 ⁱⁱ —Co1—N1—C5	-86.7 (6)	Co1—O1—C6—O2	-177.8 (7)
N1 ⁱ —Co1—N1—C5	95.7 (7)	Co1—O1—C6—C5	2.9 (9)

N1 ⁱⁱ —Co1—N1—C5	-172.1 (6)	N1—C5—C6—O2	-179.0 (10)
C5—N1—C1—C2	-0.3 (13)	C4—C5—C6—O2	-4.2 (13)
Co1—N1—C1—C2	178.7 (6)	N1—C5—C6—O1	0.2 (9)
N1—C1—C2—C3	-0.2 (14)	C4—C5—C6—O1	174.9 (9)

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

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C3—H3 \cdots O2 ⁱⁱⁱ	0.95	2.60	3.212 (14)	123

Symmetry codes: (iii) $x-y+1, x, z-1$.

Fig. 1

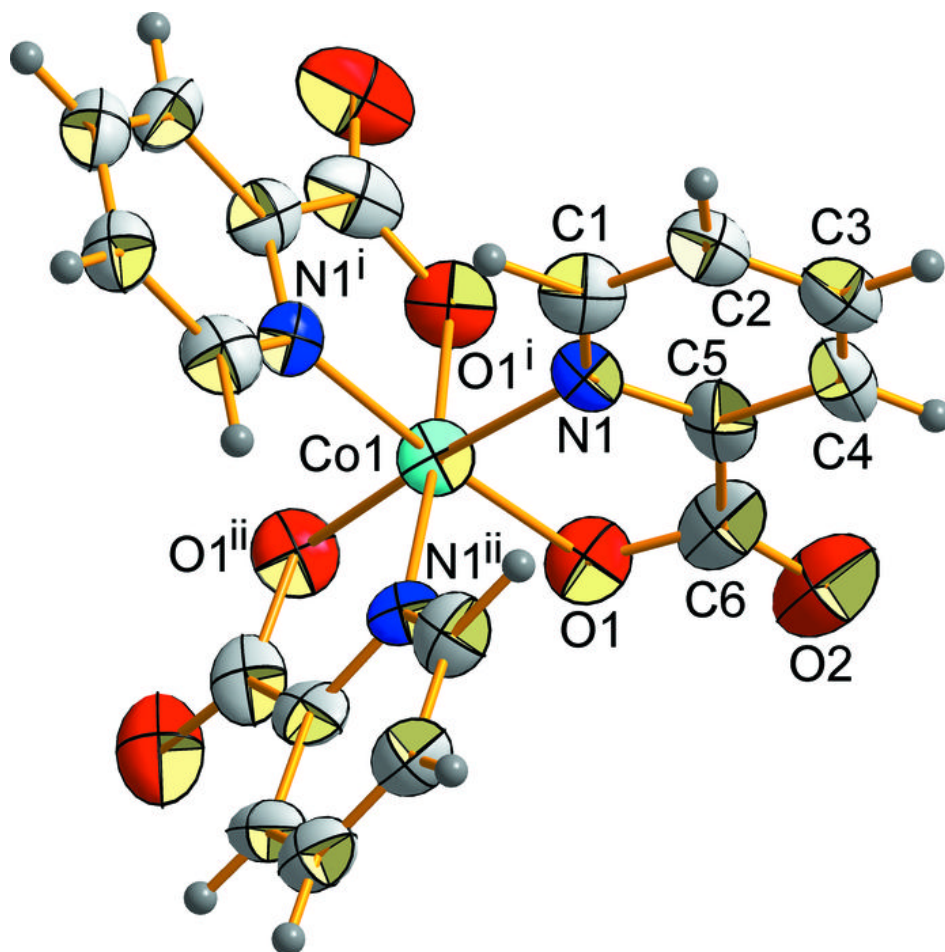


Fig. 2

