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Diaqua(2,9-dimethyl-1,10-phenanthroline-κ^2N,N')(3-hydroxybenzoato-κ^2O,O')cobalt(II) nitrate

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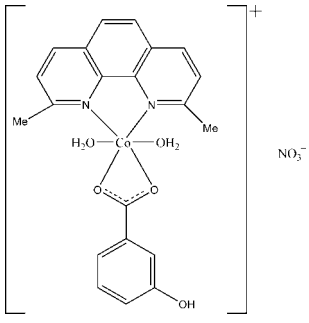
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.005 Å; disorder in main residue; R factor = 0.032; wR factor = 0.102; data-to-parameter ratio = 12.8.

In the symmetric unit of the title compound, $[Co(C_7H_5O_3)(C_{14}H_{12}N_2)(H_2O)_2]NO_3$, the Co^{2+} cation is coordinated by a bidentate 2,9-dimethyl-1,10-phenanthroline (dmphen) ligand, a bidentate 3-hydroxybenzoate anion and two water molecules in a distorted octahedral environment. The 3-hydroxybenzoate ligand, Co atom and nitrate anion are situated on a crystallographic twofold rotation axis. The OH group of the benzoate anion is disordered over two symmetry-related positions with site-occupancy factors of 0.5. An extensive series of O—H···O hydrogen bonds, involving water molecules and 3-hydroxybenzoate and nitrate anions, and weak C—H···O hydrogen bonds lead to a supramolecular network structure.

Related literature

The structure of a closely related isomorphous complex has been reported by Xuan & Zhao (2007).



Experimental

Crystal data

$[Co(C_7H_5O_3)(C_{14}H_{12}N_2)(H_2O)_2]NO_3$
M_r = 501.33
Monoclinic, $C2/c$
a = 10.9405 (14) Å
b = 28.750 (4) Å
c = 7.967 (1) Å
β = 119.142 (1)°
V = 2188.7 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.84 mm^{-1}
T = 298 (2) K
0.49 × 0.40 × 0.37 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
T_{min} = 0.67, T_{max} = 0.73
8035 measured reflections
2040 independent reflections
1878 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.102
S = 1.02
2040 reflections
159 parameters
33 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.50 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}

Table 1
Selected bond lengths (Å).

Co1—O3	2.0706 (17)	Co1—O1	2.1993 (16)
Co1—N1	2.1363 (19)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H1W···O1^{i}	0.82	1.99	2.772 (3)	160
O2—H2···O4^{i}	0.82	2.10	2.688 (7)	128
O3—H2W···O5	0.83	1.97	2.765 (2)	159
C1—H1C···O1^{ii}	0.96	2.47	3.242 (4)	137
C7—H7···O2^{iii}	0.93	2.58	3.418 (8)	150

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BG2125).

References

Bruker (1997). *SMART*, *SAINT*, *SADABS* and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Xuan, X. & Zhao, P. (2007). *Acta Cryst.* E**63**, m2856.

supplementary materials

Acta Cryst. (2007). E**63**, m3009 [**doi:10.1107/S1600536807057509**]

Diaqua(2,9-dimethyl-1,10-phenanthroline-κ^2N,N')(3-hydroxybenzoato-κ^2O,O')cobalt(II) nitrate

X. Xuan and P. Zhao

Comment

We have recently reported the structure of diaqua(3-hydroxy-benzoato-κ^2O,O')(2,9-dimethyl-1,10-phenanthroline-κ^2N,N')nickel(II) nitrate (Xuan *et al.* 2007). We report herein the isomorphous cobalt analogue,$Co(C_7H_5O_3)(C_{14}H_{12}N_2)(H_2O)_2]\cdot NO_3$, (I).

The asymmetric unit of the title compound is composed of one half of the Co^{II} complex cation and one half of the non-coordinated nitrate anion: a twofold rotation axis passes through the central Co^{II} atom, N atom and one O atom of the nitrate anion. The metal is in a distorted octahedral environment, being six-coordinated by two N atoms from the dmphen ligand and two O atoms from the carboxyl group of the 3-hydroxy-benzoate anion, defining the equatorial plane, and two O atoms from two water molecules in the apical position (Table 1). The OH group on the 3-hydroxybenzoate ligand is disordered over two symmetry-related positions with equal site occupancy.

The crystal structure is stabilized by a network of O—H···O and C—H···O hydrogen bonds (Table 2 and Figure 2). The former interactions link molecules into two-dimensional networks parallel to (010) while the latter ones join them along the [010] direction generating a three-dimensional framework.

Experimental

To a solution of 2,9-dimethyl-1,10-phenanthroline ($C_{14}H_{12}N_2\cdot 0.5H_2O$, 0.1096 g, 0.5 mmol), 3-hydroxy-benzoate (0.1382 g, 1 mmol) and sodium hydroxide (0.03820 g, 1 mmol) in ethanol/water (*v*:*v*=1:1, 20 ml) was added a solution of $Co(NO_3)_2\cdot 6H_2O$ (0.1458 g, 0.5 mmol) in distilled water (10 ml). The resulting solution was stirred for 5 h at 323 K and then a pink precipitate was filtered. Brown single crystals of (I) were obtained by slow evaporation of the filtrate over two weeks.

Refinement

The OH group of the benzoate anion is disordered over two symmetry-related positions with equal occupancy. The carbon-bound H atoms were placed in calculated positions and were included in the refinement in the riding model approximation, with d(C—H) = 0.93 Å, U_{iso}=1.2U_{eq}(C) for aromatic and 0.96 Å, U_{iso} = 1.5U_{eq}(C) for CH_3 atoms. The hydroxyl H atoms were placed in calculated positions (O—H =0.82 Å) and refined with free torsion angles to fit the electron density; water H atoms were found in a difference Fourier and allowed to ride. For all O—H's, U_{iso}(H) = 1.5 U_{eq}(O).

Figures

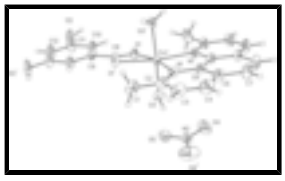

Fig. 1. The structure of (I), with atom labels and 30% probability displacement ellipsoids for non-H atoms. Symmetry code: (A) 1 − *x*, *y*, 3/2 − *z* for the cation; 1 − *x*, *y*, 1/2 − *z* for the anion.

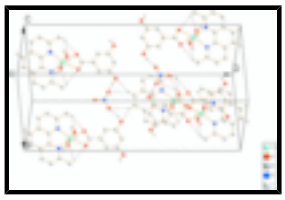

Fig. 2. Packing diagram of (I), viewed down [001], showing hydrogen bonds as dashed lines.

Diaqua(2,9-dimethyl-1,10-phenanthroline-κ^2*N*,*N*')(3-hydroxybenzoato- κ^2*O*,*O*')cobalt(II) nitrate

Crystal data

$[Co(C_7H_5O_3)(C_{14}H_{12}N_2)(H_2O)_2]NO_3$	F_{000} = 1032
M_r = 501.33	D_x = 1.518 Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 5273 reflections
a = 10.9405 (14) Å	θ = 2.3–28.0º
b = 28.750 (4) Å	μ = 0.84 mm^{-1}
c = 7.9670 (10) Å	*T* = 298 (2) K
β = 119.142 (1)º	Block, brown
V = 2188.7 (5) Å^3	0.49 × 0.40 × 0.37 mm
Z = 4	

Data collection

Bruker SMART CCD area-detector diffractometer	2040 independent reflections
Radiation source: fine-focus sealed tube	1878 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.023
T = 298(2) K	θ_{max} = 25.5º
φ and ω scans	θ_{min} = 2.3º
Absorption correction: multi-scan (SADABS; Bruker, 1997)	*h* = −13→13
T_{min} = 0.67, T_{max} = 0.73	*k* = −34→34
8035 measured reflections	*l* = −9→9

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites

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

$wR(F^2) = 0.102$

$S = 1.02$

2040 reflections

159 parameters

33 restraints

Primary atom site location: structure-invariant direct methods

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0659P)^2 + 2.1796P]$ where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.50$ e Å^{-3}

$\Delta\rho_{min} = -0.39$ e Å^{-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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Co1	0.5000	0.294272 (13)	0.7500	0.03386 (17)	
O1	0.39631 (16)	0.22788 (5)	0.7385 (2)	0.0405 (4)	
O2	0.3140 (5)	0.05502 (14)	0.7959 (10)	0.0861 (17)	0.50
H2	0.2760	0.0705	0.8442	0.129*	0.50
O3	0.38785 (18)	0.29149 (5)	0.4529 (2)	0.0451 (4)	
H1W	0.3041	0.2893	0.4180	0.068*	
H2W	0.4025	0.3083	0.3795	0.068*	
O4	0.4231 (3)	0.39849 (12)	0.2935 (4)	0.1120 (11)	
O5	0.5000	0.33543 (12)	0.2500	0.0923 (12)	
N1	0.6166 (2)	0.35148 (7)	0.7293 (3)	0.0416 (4)	
N2	0.5000	0.37833 (10)	0.2500	0.0461 (6)	
C1	0.7857 (3)	0.30542 (11)	0.6842 (6)	0.0720 (9)	
H1A	0.8586	0.2953	0.8074	0.108*	
H1B	0.8228	0.3089	0.5978	0.108*	
H1C	0.7119	0.2828	0.6337	0.108*	
C2	0.7295 (3)	0.35093 (10)	0.7058 (4)	0.0528 (6)	
C3	0.7935 (3)	0.39298 (12)	0.6971 (5)	0.0717 (9)	
H3A	0.8724	0.3920	0.6817	0.086*	
C4	0.7413 (4)	0.43432 (12)	0.7110 (5)	0.0786 (10)	
H4	0.7846	0.4617	0.7062	0.094*	
C5	0.6219 (4)	0.43603 (10)	0.7327 (4)	0.0647 (8)	
C6	0.5623 (3)	0.39312 (8)	0.7410 (3)	0.0465 (6)	
C7	0.5582 (5)	0.47851 (10)	0.7418 (6)	0.0882 (12)	

H7	0.5979	0.5067	0.7362	0.106*
C8	0.5000	0.20572 (10)	0.7500	0.0358 (7)
C9	0.5000	0.15334 (11)	0.7500	0.0415 (7)
C10	0.3986 (3)	0.12923 (9)	0.7701 (4)	0.0521 (6)
H10	0.3304	0.1454	0.7840	0.063*
C11	0.3985 (3)	0.08081 (10)	0.7696 (5)	0.0672 (8)
C12	0.5000	0.05691 (14)	0.7500	0.0799 (15)
H12	0.5000	0.0246	0.7500	0.096*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0271 (2)	0.0265 (2)	0.0455 (3)	0.000	0.01572 (19)	0.000
O1	0.0319 (8)	0.0312 (8)	0.0581 (10)	0.0011 (6)	0.0218 (7)	0.0000 (7)
O2	0.080 (3)	0.036 (2)	0.176 (6)	−0.006 (2)	0.088 (4)	0.004 (3)
O3	0.0371 (9)	0.0482 (10)	0.0452 (9)	−0.0074 (7)	0.0162 (7)	0.0025 (7)
O4	0.105 (2)	0.146 (3)	0.0908 (18)	0.065 (2)	0.0517 (16)	0.0036 (17)
O5	0.167 (4)	0.0530 (17)	0.086 (2)	0.000	0.084 (2)	0.000
N1	0.0362 (10)	0.0363 (10)	0.0437 (10)	−0.0056 (8)	0.0127 (8)	0.0036 (8)
N2	0.0463 (15)	0.0445 (15)	0.0519 (16)	0.000	0.0273 (13)	0.000
C1	0.0526 (17)	0.0655 (18)	0.114 (3)	0.0096 (14)	0.0531 (19)	0.0277 (18)
C2	0.0387 (13)	0.0547 (15)	0.0579 (15)	−0.0092 (11)	0.0180 (11)	0.0106 (12)
C3	0.0554 (17)	0.073 (2)	0.083 (2)	−0.0241 (15)	0.0304 (16)	0.0104 (16)
C4	0.087 (2)	0.0552 (19)	0.088 (2)	−0.0352 (17)	0.039 (2)	−0.0023 (16)
C5	0.088 (2)	0.0371 (14)	0.0630 (17)	−0.0181 (14)	0.0315 (16)	−0.0035 (12)
C6	0.0547 (14)	0.0333 (12)	0.0405 (12)	−0.0067 (10)	0.0146 (11)	0.0000 (9)
C7	0.137 (4)	0.0310 (14)	0.101 (3)	−0.0160 (16)	0.061 (3)	−0.0025 (15)
C8	0.0318 (16)	0.0290 (15)	0.0423 (16)	0.000	0.0147 (13)	0.000
C9	0.0371 (16)	0.0296 (16)	0.0519 (18)	0.000	0.0171 (14)	0.000
C10	0.0468 (14)	0.0344 (12)	0.0782 (18)	0.0014 (10)	0.0328 (13)	0.0044 (11)
C11	0.0629 (18)	0.0359 (14)	0.110 (2)	−0.0060 (12)	0.0478 (18)	0.0052 (14)
C12	0.083 (3)	0.0279 (18)	0.140 (5)	0.000	0.063 (3)	0.000

Geometric parameters (Å, °)

Co1—O3	2.0706 (17)	C1—H1C	0.9600
Co1—O3^{i}	2.0706 (17)	C2—C3	1.415 (4)
Co1—N1^{i}	2.1361 (19)	C3—C4	1.346 (5)
Co1—N1	2.1363 (19)	C3—H3A	0.9300
Co1—O1	2.1993 (16)	C4—C5	1.400 (5)
Co1—O1^{i}	2.1993 (16)	C4—H4	0.9300
O1—C8	1.265 (2)	C5—C6	1.412 (4)
O2—C11	1.280 (5)	C5—C7	1.425 (5)
O2—H2	0.8200	C6—C6^{i}	1.439 (6)
O3—H1W	0.8200	C7—C7^{i}	1.341 (9)
O3—H2W	0.8313	C7—H7	0.9300
O4—N2	1.204 (3)	C8—C9	1.506 (4)

O5—N2	1.233 (4)	C9—C10^{i}	1.382 (3)
N1—C2	1.337 (3)	C9—C10	1.382 (3)
N1—C6	1.360 (3)	C10—C11	1.392 (4)
C1—C2	1.490 (4)	C10—H10	0.9300
C1—H1A	0.9600	C11—C12	1.378 (4)
C1—H1B	0.9600	C12—H12	0.9300
O3—Co1—O3^{i}	175.57 (9)	N1—C2—C1	119.2 (2)
O3—Co1—N1^{i}	94.26 (7)	C3—C2—C1	120.2 (3)
O3^{i}—Co1—N1^{i}	89.15 (7)	C4—C3—C2	120.7 (3)
O3—Co1—N1	89.15 (7)	C4—C3—H3A	119.6
O3^{i}—Co1—N1	94.27 (7)	C2—C3—H3A	119.6
N1^{i}—Co1—N1	79.32 (11)	C3—C4—C5	120.0 (3)
O3—Co1—O1	84.97 (6)	C3—C4—H4	120.0
O3^{i}—Co1—O1	91.18 (6)	C5—C4—H4	120.0
N1^{i}—Co1—O1	110.87 (7)	C4—C5—C6	117.1 (3)
N1—Co1—O1	168.55 (7)	C4—C5—C7	123.1 (3)
O3—Co1—O1^{i}	91.18 (6)	C6—C5—C7	119.9 (3)
O3^{i}—Co1—O1^{i}	84.96 (6)	N1—C6—C5	122.6 (3)
N1^{i}—Co1—O1^{i}	168.55 (7)	N1—C6—C6^{i}	118.26 (14)
N1—Co1—O1^{i}	110.87 (7)	C5—C6—C6^{i}	119.10 (19)
O1—Co1—O1^{i}	59.57 (8)	C7^{i}—C7—C5	121.0 (2)
C8—O1—Co1	90.46 (14)	C7^{i}—C7—H7	119.5
C11—O2—H2	109.5	C5—C7—H7	119.5
Co1—O3—H1W	109.4	O1^{i}—C8—O1	119.5 (3)
Co1—O3—H2W	124.9	O1^{i}—C8—C9	120.25 (13)
H1W—O3—H2W	111.9	O1—C8—C9	120.25 (13)
C2—N1—C6	119.0 (2)	C10^{i}—C9—C10	119.8 (3)
C2—N1—Co1	128.97 (18)	C10^{i}—C9—C8	120.10 (16)
C6—N1—Co1	112.06 (16)	C10—C9—C8	120.10 (16)
O4—N2—O4^{ii}	122.4 (5)	C9—C10—C11	120.1 (3)
O4—N2—O5	118.8 (2)	C9—C10—H10	120.0
O4^{ii}—N2—O5	118.8 (2)	C11—C10—H10	120.0
C2—C1—H1A	109.5	O2—C11—C12	114.6 (3)
C2—C1—H1B	109.5	O2—C11—C10	125.4 (3)
H1A—C1—H1B	109.5	C12—C11—C10	119.9 (3)
C2—C1—H1C	109.5	C11^{i}—C12—C11	120.2 (4)
H1A—C1—H1C	109.5	C11^{i}—C12—H12	119.9
H1B—C1—H1C	109.5	C11—C12—H12	119.9
N1—C2—C3	120.6 (3)		
O3—Co1—O1—C8	94.35 (9)	C3—C4—C5—C7	−177.8 (3)
O3^{i}—Co1—O1—C8	−83.46 (9)	C2—N1—C6—C5	−1.1 (4)
N1^{i}—Co1—O1—C8	−173.00 (8)	Co1—N1—C6—C5	179.4 (2)
N1—Co1—O1—C8	35.0 (4)	C2—N1—C6—C6^{i}	177.7 (3)

O1^{i}—Co1—O1—C8	0.0	Co1—N1—C6—C6^{i}	−1.8 (3)
O3—Co1—N1—C2	−84.2 (2)	C4—C5—C6—N1	0.2 (4)
O3^{i}—Co1—N1—C2	92.9 (2)	C7—C5—C6—N1	178.7 (3)
N1^{i}—Co1—N1—C2	−178.7 (3)	C4—C5—C6—C6^{i}	−178.6 (3)
O1—Co1—N1—C2	−25.3 (4)	C7—C5—C6—C6^{i}	−0.1 (5)
O1^{i}—Co1—N1—C2	6.7 (2)	C4—C5—C7—C7^{i}	178.4 (5)
O3—Co1—N1—C6	95.12 (16)	C6—C5—C7—C7^{i}	0.0 (7)
O3^{i}—Co1—N1—C6	−87.70 (16)	Co1—O1—C8—O1^{i}	0.0
N1^{i}—Co1—N1—C6	0.62 (12)	Co1—O1—C8—C9	180.0
O1—Co1—N1—C6	154.1 (3)	O1^{i}—C8—C9—C10^{i}	−10.93 (16)
O1^{i}—Co1—N1—C6	−173.93 (15)	O1—C8—C9—C10^{i}	169.07 (16)
C6—N1—C2—C3	1.3 (4)	O1^{i}—C8—C9—C10	169.07 (16)
Co1—N1—C2—C3	−179.4 (2)	O1—C8—C9—C10	−10.93 (16)
C6—N1—C2—C1	−177.4 (3)	C10^{i}—C9—C10—C11	−0.2 (2)
Co1—N1—C2—C1	2.0 (4)	C8—C9—C10—C11	179.8 (2)
N1—C2—C3—C4	−0.5 (5)	C9—C10—C11—O2	176.6 (5)
C1—C2—C3—C4	178.1 (3)	C9—C10—C11—C12	0.3 (5)
C2—C3—C4—C5	−0.5 (5)	O2—C11—C12—C11^{i}	−176.8 (5)
C3—C4—C5—C6	0.7 (5)	C10—C11—C12—C11^{i}	−0.2 (2)

Symmetry codes: (i) −*x*+1, *y*, −*z*+3/2; (ii) −*x*+1, *y*, −*z*+1/2.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H1W···O1^{iii}	0.82	1.99	2.772 (3)	160
O2—H2···O4^{iii}	0.82	2.10	2.688 (7)	128
O3—H2W···O5	0.83	1.97	2.765 (2)	159
C1—H1C···O1^{i}	0.96	2.47	3.242 (4)	137
C7—H7···O2^{iv}	0.93	2.58	3.418 (8)	150

Symmetry codes: (iii) −*x*+1/2, −*y*+1/2, −*z*+1; (i) −*x*+1, *y*, −*z*+3/2; (iv) *x*+1/2, *y*+1/2, *z*.

Fig. 1

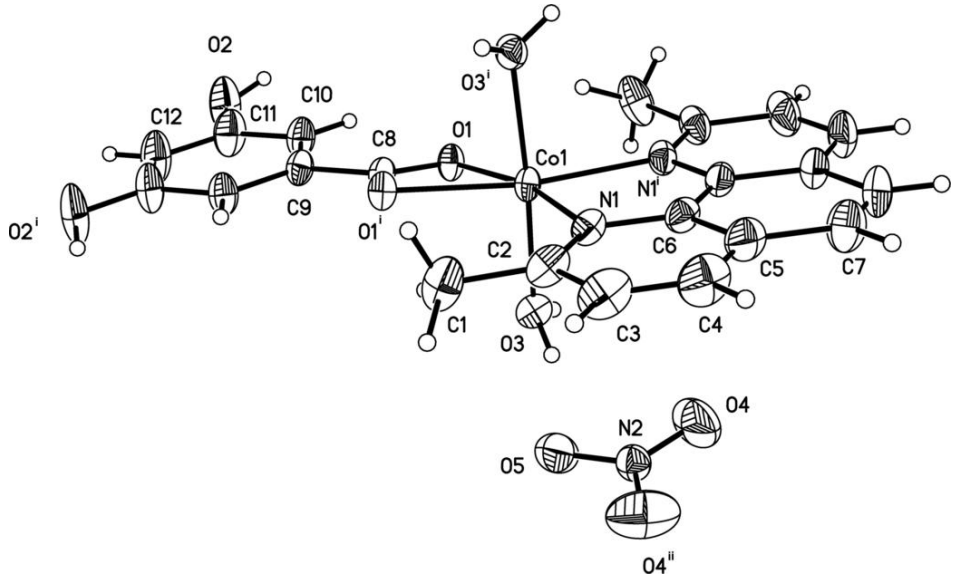
O2
O3i
C12
C11
C10
C8
O1
Co1
N1i
N1
O2i
C9
O1i
C2
C6
C5
C7
C1
O3
C3
C4
O4
N2
O5
O4ii

Fig. 2