Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

cyclo-Tetrakis[*μ*-*N*-(2-hydroxybenzoyl)-*N*′-(2-hydroxy-3-methoxybenzylidene)-hydrazinate(2−)]tetracobalt(II) *N*,*N*-dimethylformamide tetrasolvate

Yu-Xiang Gao,* Li-Bin Wang and Yan-Ling Niu

Department of Chemistry, Tonghua Teachers' College, Tonghua 134002, People's Republic of China
Correspondence e-mail: yxgao_tonghua@yahoo.com.cn

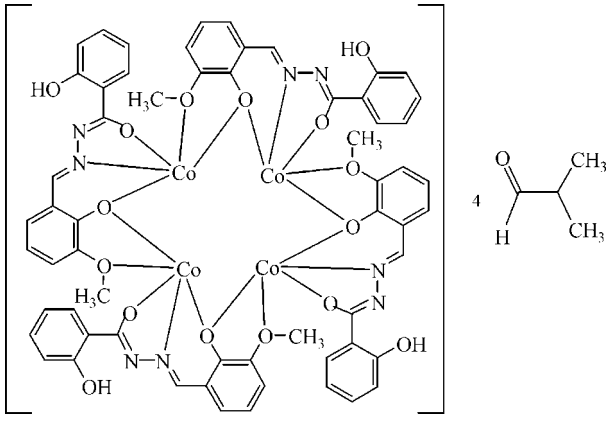
Received 14 June 2007; accepted 8 July 2007

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.008 Å; R factor = 0.041; wR factor = 0.136; data-to-parameter ratio = 13.3.

The title compound, $[Co_4(C_{15}H_{12}N_2O_4)_4]\cdot 4C_3H_7NO$, contains *N*-(2-hydroxybenzoyl)-*N*-(2-hydroxy-3-methoxybenzylidene)-hydrazine anions and Co^{II} cations linked into tetrameric complexes about positions of $\overline{4}$ point symmetry. Each Co^{II} cation is pentacoordinated and adopts a distorted square-based pyramidal geometry. There is one O—H···N hydrogen bond [O···N = 2.595 (6) Å].

Related literature

One motivation to study hydrazine and its analogues is to understand better the mechanism of enzymes containing vitamin B6. For related literature, see: Maghler *et al.* (1982); Rath *et al.* (1997, 1998).



Experimental

Crystal data

$[Co_4(C_{15}H_{12}N_2O_4)_4]\cdot 4C_3H_7NO$
M_r = 1665.17
Tetragonal, $I4_1/a$
a = 23.996 (2) Å
c = 13.1605 (10) Å
V = 7578.0 (11) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.94 mm^{-1}
T = 298 (2) K
0.10 × 0.10 × 0.10 mm

Data collection

Bruker APEX II CCD diffractometer
Absorption correction: none
18342 measured reflections
3308 independent reflections
2180 reflections with $I > 2\sigma(I)$
R_{int} = 0.060

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.136
S = 1.00
3308 reflections
249 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

Table 1
Selected bond lengths (Å).

Co1—N2	1.970 (3)	Co1—O4^{i}	2.039 (3)
Co1—O4	1.941 (3)	Co1—O3^{i}	2.270 (3)
Co1—O5	1.927 (3)	Co1—O4^{ii}	2.686 (3)

Symmetry codes: (i) $y-\frac{1}{4}, -x+\frac{5}{4}, -z+\frac{9}{4}$; (ii) $-x+1, -y+\frac{3}{2}, z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O6—H6A···N3	0.82	1.89	2.595 (6)	143

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 1999); 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, 1999); software used to prepare material for publication: *SHELXTL*.

The authors thank the NSFC (grant No. 20501017) and Tonghua Teachers' College.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BI2200).

References

Bruker (1999). *SAINT* and *SHELXTL* (Version 5.10). Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2004). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.
Maghler, H. R., Cordes, E. H., Dawes, H. M., Waters, J. M. & Waters, T. N. (1982). *Inorg. Chim. Acta*, **66**, 2930–2936.
Rath, S. P., Mondal, S. & Chakravorty, A. (1997). *Inorg. Chim. Acta*, **263**, 247–253.
Rath, S. P., Rajak, K. K. & Mondal, S. (1998). *J. Chem. Soc. Dalton Trans.* pp. 2097–2109.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

  doi:10.1107/S1600536807033338

supplementary materials

Acta Cryst. (2007). E**63**, m2128 [**doi:10.1107/S1600536807033338**]

cyclo-Tetrakis[μ-*N*-(2-hydroxybenzoyl)-*N*'-(2-hydroxy-3-methoxybenzylidene)hydrazinate(2-)]tetracobalt(II) *N*,*N*-dimethylformamide tetrasolvate

Y.-X. Gao, L.-B. Wang and Y.-L. Niu

Comment

Owing to their biological activity and chemical/industrial versatility, metal-hydrazine complexes have received considerable attention. For instance, Schiff base hydrazine and its analogues have been well studied in order to understand better the mechanism of enzymes containing vitamin B6 (Maghler *et al.*, 1982; Rath *et al.*, 1997; Rath *et al.*, 1998)

Herein, we report the structure of the title compound, $[Co_4(C_{15}H_{12}N_2O_4)_4]\cdot 4C_3H_7NO$. As shown in Fig. 1, the asymmetric unit comprises one *N*-(2-hydroxy-benzoyl)-*N*-(2-hydroxy-3-methoxo-benzoylidene)hydrazine anion and one Co^{II} cation. These are linked into tetrameric complexes about positions of $\bar{4}$ point symmetry. Each Co^{II} cation adopts a distorted 6-coordinate geometry through one N and three O atoms lying in the equatorial plane, with the Co1—O3 bond lying to one side of this plane and the longer Co1—O4 bond lying on the opposite side.

Experimental

All chemicals were used as purchased from Shanghai Sci & Tec Co. Ltd. A solution of cobalt(II) acetate (0.5 mmol) and *N*-(2-hydroxy-benzoyl)-*N*-(2-hydroxy-3-methoxo-benzoylidene)hydrazine (0.5 mmol) in DMF (10 ml) was refluxed for 2 h then filtered. Red crystals were obtained after a few days standing at room temperature with a yield of 25%. Elemental analysis calculated: C 51.89, H 4.56, N 10.09%; found: C 51.82, H 4.60, N 10.01%.

Refinement

H atoms were placed geometrically and refined as riding with C—H = 0.93, N—H = 0.86 and O—H = 0.82 Å, and with U_{iso}(H) = 1.2U_{eq}(C/N) or 1.5U_{eq}(O).

Figures

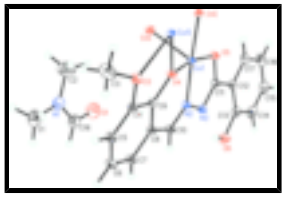


Fig. 1. The asymmetric unit of the title compound, showing displacement ellipsoids at 50% probability for non-H atoms. Atoms labeled with the subscript I are generated by the symmetry operator $y - 1/4, -x + 5/4, -z + 9/4$.

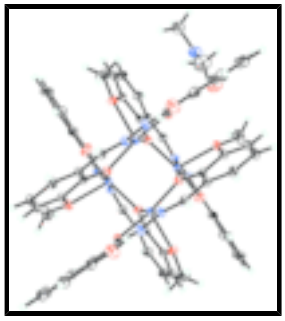


Fig. 2. Tetrameric complex formed about the position of $\bar{4}$ point symmetry.

cyclo-Tetrakis[μ-_N_-(2-hydroxybenzoyl)-_N_'-(2-hydroxy-3-\ methoxybenzylidene)hydrazinate(2-)]tetracobalt(II)} _N_,_N_-dimethylformamide tetrasolvate

Crystal data

$[Co_4(C_{15}H_{12}N_2O_4)_4]\cdot 4C_3H_7NO$	$Z = 4$
$M_r = 1665.17$	$F_{000} = 3440$
Tetragonal, $I4_1/a$	$D_x = 1.460$ Mg m^{-3}
Hall symbol: -I 4ad	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 23.996$ (2) Å	Cell parameters from 3308 reflections
$b = 23.996$ (2) Å	$\theta = 1.7$–25.0º
$c = 13.1605$ (10) Å	$\mu = 0.94$ mm^{-1}
$\alpha = 90$º	$T = 298$ (2) K
$\beta = 90$º	Cube, red
$\gamma = 90$º	0.10 × 0.10 × 0.10 mm
$V = 7578.0$ (11) Å^3	

Data collection

Bruker APEXII CCD diffractometer	2180 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.060$
Monochromator: graphite	$\theta_{max} = 25.0$º
$T = 298(2)$ K	$\theta_{min} = 1.7$º
φ and ω scans	$h = -28\rightarrow25$
Absorption correction: none	$k = -26\rightarrow28$
18342 measured reflections	$l = -15\rightarrow15$
3308 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.041$	H-atom parameters constrained
$wR(F^2) = 0.136$	$w = 1/[\sigma^2(F_o^2) + (0.0641P)^2 + 15.4281P]$

	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} < 0.001$
3308 reflections	$\Delta\rho_{max} = 0.36$ e Å^{-3}
249 parameters	$\Delta\rho_{min} = -0.27$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	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}
Co1	0.48657 (2)	0.81667 (2)	1.03441 (3)	0.0390 (2)
C13	0.5884 (2)	0.8962 (2)	0.7148 (4)	0.0729 (14)
C14	0.6317 (3)	0.9226 (3)	0.6646 (6)	0.099 (2)
H14	0.6337	0.9224	0.5940	0.118*
C15	0.6710 (3)	0.9486 (3)	0.7205 (7)	0.105 (2)
H15	0.7005	0.9660	0.6873	0.126*
C16	0.6689 (2)	0.9502 (2)	0.8288 (7)	0.098 (2)
H16	0.6961	0.9694	0.8651	0.117*
C17	0.6263 (2)	0.9231 (2)	0.8797 (5)	0.0736 (14)
H17	0.6248	0.9235	0.9503	0.088*
C12	0.58614 (19)	0.89558 (18)	0.8248 (4)	0.0572 (11)
C11	0.54300 (18)	0.86555 (17)	0.8812 (3)	0.0516 (10)
C10	0.42641 (18)	0.79092 (18)	0.8447 (3)	0.0547 (11)
H10	0.4223	0.7953	0.7749	0.066*
C8	0.38607 (17)	0.75893 (18)	0.8983 (3)	0.0517 (10)
C7	0.3406 (2)	0.7401 (2)	0.8402 (4)	0.0681 (13)
H7	0.3380	0.7495	0.7717	0.082*
C6	0.3005 (2)	0.7085 (2)	0.8840 (4)	0.0723 (14)
H6	0.2702	0.6966	0.8458	0.087*
C5	0.3047 (2)	0.6933 (2)	0.9878 (4)	0.0668 (13)
H5	0.2767	0.6717	1.0168	0.080*
C4	0.34892 (18)	0.70962 (18)	1.0463 (3)	0.0528 (10)
C9	0.39024 (17)	0.74385 (17)	1.0048 (3)	0.0478 (10)
C3	0.3125 (3)	0.6763 (3)	1.2083 (5)	0.125 (3)
H3A	0.2843	0.7046	1.2079	0.188*
H3B	0.3249	0.6701	1.2767	0.188*

H3C	0.2973	0.6423	1.1815	0.188*
C18	0.2797 (4)	0.8669 (4)	0.8818 (8)	0.121 (2)
H2	0.2621	0.8535	0.8238	0.41 (11)*
N1	0.2578 (3)	0.8534 (3)	0.9732 (5)	0.124 (2)
N3	0.50473 (15)	0.84230 (15)	0.8251 (3)	0.0571 (9)
N2	0.46821 (15)	0.81391 (14)	0.8886 (3)	0.0526 (9)
O1	0.3210 (3)	0.8956 (3)	0.8710 (5)	0.174 (3)
O6	0.55073 (19)	0.87083 (19)	0.6544 (3)	0.0981 (13)
H6A	0.5288	0.8530	0.6895	0.147*
O5	0.54502 (12)	0.86371 (12)	0.9823 (2)	0.0579 (8)
O4	0.43272 (11)	0.75891 (12)	1.0661 (2)	0.0503 (7)
O3	0.35778 (12)	0.69341 (13)	1.1480 (2)	0.0643 (8)
C1	0.2100 (4)	0.8200 (4)	0.9791 (7)	0.146 (3)
H1A	0.1977	0.8106	0.9118	0.219*
H1B	0.1810	0.8400	1.0137	0.219*
H1C	0.2184	0.7865	1.0159	0.219*
C2	0.2841 (5)	0.8651 (5)	1.0693 (8)	0.205 (5)
H2A	0.3212	0.8786	1.0578	0.308*
H2B	0.2856	0.8317	1.1092	0.308*
H2C	0.2629	0.8929	1.1048	0.308*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0497 (3)	0.0468 (3)	0.0207 (3)	−0.0024 (2)	−0.0030 (2)	0.0027 (2)
C13	0.079 (3)	0.076 (3)	0.064 (3)	0.009 (3)	0.020 (3)	0.019 (3)
C14	0.104 (5)	0.095 (4)	0.097 (5)	0.007 (4)	0.041 (4)	0.031 (4)
C15	0.086 (5)	0.088 (4)	0.140 (7)	0.001 (4)	0.036 (5)	0.039 (5)
C16	0.069 (4)	0.083 (4)	0.141 (7)	−0.009 (3)	−0.003 (4)	0.032 (4)
C17	0.064 (3)	0.065 (3)	0.092 (4)	−0.003 (3)	0.000 (3)	0.019 (3)
C12	0.060 (3)	0.053 (2)	0.059 (3)	0.006 (2)	0.004 (2)	0.014 (2)
C11	0.060 (3)	0.054 (2)	0.040 (3)	0.006 (2)	0.000 (2)	0.011 (2)
C10	0.064 (3)	0.066 (3)	0.034 (2)	−0.002 (2)	−0.012 (2)	0.005 (2)
C8	0.055 (2)	0.060 (3)	0.040 (2)	−0.004 (2)	−0.006 (2)	0.002 (2)
C7	0.071 (3)	0.088 (3)	0.044 (3)	−0.005 (3)	−0.016 (2)	0.003 (2)
C6	0.065 (3)	0.087 (4)	0.064 (3)	−0.018 (3)	−0.015 (3)	0.001 (3)
C5	0.061 (3)	0.075 (3)	0.064 (3)	−0.014 (2)	−0.004 (2)	0.003 (3)
C4	0.058 (3)	0.060 (3)	0.041 (2)	−0.001 (2)	−0.002 (2)	0.001 (2)
C9	0.050 (2)	0.054 (2)	0.040 (2)	0.0002 (19)	−0.0044 (19)	−0.0029 (18)
C3	0.102 (5)	0.189 (8)	0.085 (5)	−0.056 (5)	0.000 (4)	0.053 (5)
C18	0.107 (6)	0.137 (7)	0.117 (7)	0.011 (5)	0.013 (6)	−0.005 (6)
N1	0.106 (5)	0.167 (6)	0.099 (5)	−0.006 (4)	0.019 (4)	−0.012 (4)
N3	0.063 (2)	0.072 (2)	0.037 (2)	−0.0066 (19)	−0.0005 (17)	0.0081 (18)
N2	0.062 (2)	0.062 (2)	0.0328 (19)	−0.0019 (17)	−0.0020 (17)	0.0070 (16)
O1	0.149 (5)	0.215 (7)	0.157 (6)	−0.027 (5)	0.030 (5)	0.007 (5)
O6	0.122 (3)	0.125 (3)	0.048 (2)	−0.025 (3)	0.013 (2)	0.010 (2)
O5	0.0687 (19)	0.0638 (18)	0.0412 (18)	−0.0062 (15)	−0.0044 (14)	0.0044 (14)
O4	0.0575 (17)	0.0633 (17)	0.0302 (14)	−0.0054 (13)	−0.0032 (13)	0.0038 (13)

O3	0.0636 (19)	0.082 (2)	0.0475 (19)	−0.0145 (16)	0.0005 (15)	0.0124 (16)
C1	0.122 (7)	0.136 (7)	0.181 (10)	−0.001 (6)	0.019 (6)	0.009 (6)
C2	0.219 (11)	0.282 (15)	0.115 (8)	−0.050 (11)	0.010 (8)	−0.015 (9)

Geometric parameters (Å, °)

Co1—N2	1.970 (3)	C6—C5	1.417 (7)
Co1—O4	1.941 (3)	C6—H6	0.930
Co1—O5	1.927 (3)	C5—C4	1.369 (6)
Co1—O4^{i}	2.039 (3)	C5—H5	0.930
Co1—O3^{i}	2.270 (3)	C4—C9	1.399 (6)
Co1—O4^{ii}	2.686 (3)	C4—O3	1.409 (5)
C13—O6	1.349 (6)	C9—O4	1.350 (5)
C13—C14	1.385 (8)	C3—O3	1.408 (6)
C13—C12	1.450 (7)	C3—H3A	0.960
C14—C15	1.349 (9)	C3—H3B	0.960
C14—H14	0.930	C3—H3C	0.960
C15—C16	1.427 (10)	C18—O1	1.214 (9)
C15—H15	0.930	C18—N1	1.352 (10)
C16—C17	1.386 (7)	C18—H2	0.930
C16—H16	0.930	N1—C1	1.403 (9)
C17—C12	1.373 (7)	N1—C2	1.441 (11)
C17—H17	0.930	N3—N2	1.390 (5)
C12—C11	1.463 (6)	O6—H6A	0.820
C11—N3	1.304 (5)	O4—Co1^{iii}	2.039 (3)
C11—O5	1.332 (5)	O3—Co1^{iii}	2.270 (3)
C10—N2	1.282 (5)	C1—H1A	0.960
C10—C8	1.423 (6)	C1—H1B	0.960
C10—H10	0.930	C1—H1C	0.960
C8—C7	1.408 (6)	C2—H2A	0.960
C8—C9	1.450 (6)	C2—H2B	0.960
C7—C6	1.354 (7)	C2—H2C	0.960
C7—H7	0.930		
O5—Co1—O4	168.50 (12)	C4—C5—H5	119.2
O5—Co1—N2	80.55 (13)	C6—C5—H5	119.2
O4—Co1—N2	92.10 (13)	C5—C4—C9	119.8 (4)
O5—Co1—O4^{i}	98.51 (12)	C5—C4—O3	124.9 (4)
O4—Co1—O4^{i}	88.43 (11)	C9—C4—O3	115.2 (4)
N2—Co1—O4^{i}	177.24 (13)	O4—C9—C4	117.3 (4)
O5—Co1—O3^{i}	90.22 (12)	O4—C9—C8	124.3 (4)
O4—Co1—O3^{i}	100.50 (12)	C4—C9—C8	118.4 (4)
N2—Co1—O3^{i}	107.87 (13)	O3—C3—H3A	109.5
O4^{i}—Co1—O3^{i}	74.68 (11)	O3—C3—H3B	109.5
O6—C13—C14	115.4 (6)	H3A—C3—H3B	109.5
O6—C13—C12	124.0 (4)	O3—C3—H3C	109.5
C14—C13—C12	120.6 (6)	H3A—C3—H3C	109.5

C15—C14—C13	118.4 (7)	H3B—C3—H3C	109.5
C15—C14—H14	120.8	O1—C18—N1	123.8 (10)
C13—C14—H14	120.8	O1—C18—H2	118.1
C14—C15—C16	122.3 (6)	N1—C18—H2	118.1
C14—C15—H15	118.9	C18—N1—C1	120.3 (8)
C16—C15—H15	118.9	C18—N1—C2	124.4 (8)
C17—C16—C15	119.7 (6)	C1—N1—C2	114.9 (8)
C17—C16—H16	120.1	C11—N3—N2	108.3 (3)
C15—C16—H16	120.2	C10—N2—N3	115.7 (3)
C12—C17—C16	119.3 (6)	C10—N2—Co1	128.9 (3)
C12—C17—H17	120.3	N3—N2—Co1	115.4 (3)
C16—C17—H17	120.3	C13—O6—H6A	109.5
C17—C12—C13	119.6 (5)	C11—O5—Co1	110.4 (3)
C17—C12—C11	117.8 (5)	C9—O4—Co1	124.4 (3)
C13—C12—C11	122.5 (4)	C9—O4—Co1^{iii}	120.8 (2)
N3—C11—O5	125.3 (4)	Co1—O4—Co1^{iii}	112.99 (13)
N3—C11—C12	115.0 (4)	C4—O3—C3	120.0 (4)
O5—C11—C12	119.8 (4)	C4—O3—Co1^{iii}	111.5 (2)
N2—C10—C8	122.7 (4)	C3—O3—Co1^{iii}	121.9 (3)
N2—C10—H10	118.6	N1—C1—H1A	109.5
C8—C10—H10	118.6	N1—C1—H1B	109.5
C7—C8—C10	115.5 (4)	H1A—C1—H1B	109.5
C7—C8—C9	119.9 (4)	N1—C1—H1C	109.5
C10—C8—C9	124.5 (4)	H1A—C1—H1C	109.5
C6—C7—C8	119.9 (5)	H1B—C1—H1C	109.5
C6—C7—H7	120.1	N1—C2—H2A	109.5
C8—C7—H7	120.1	N1—C2—H2B	109.5
C7—C6—C5	120.4 (4)	H2A—C2—H2B	109.5
C7—C6—H6	119.8	N1—C2—H2C	109.5
C5—C6—H6	119.8	H2A—C2—H2C	109.5
C4—C5—C6	121.5 (4)	H2B—C2—H2C	109.5

Symmetry codes: (i) *y*−1/4, −*x*+5/4, −*z*+9/4; (ii) −*x*+1, −*y*+3/2, *z*; (iii) −*y*+5/4, *x*+1/4, −*z*+9/4.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O6—H6A···N3	0.82	1.89	2.595 (6)	143

Fig. 1

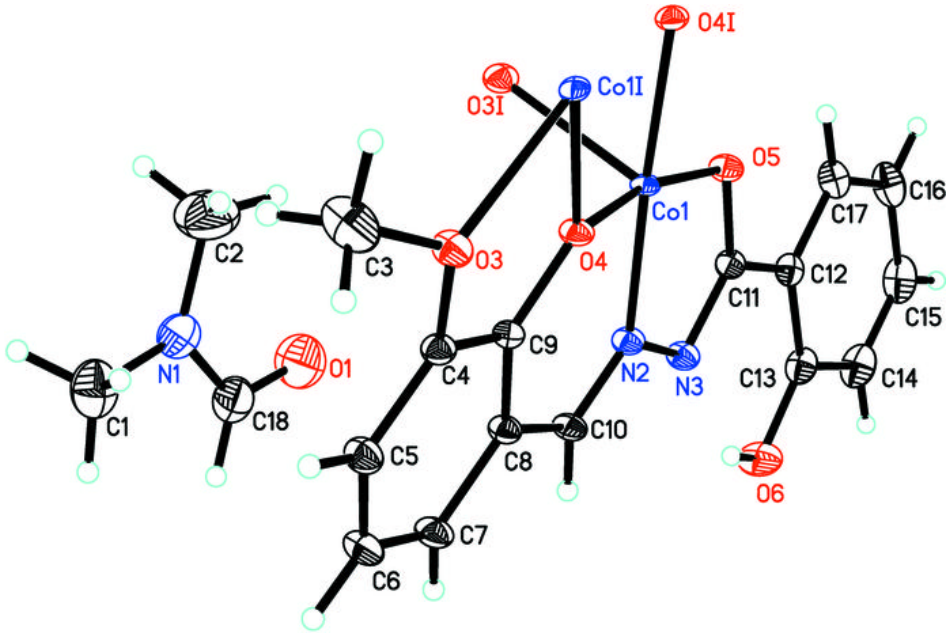

O4I
O3I
Co1I
O5
Co1
C16
C17
C2
C3
O3
O4
C11
C12
C15
N1
O1
C4
C9
N2
N3
C13
C14
C1
C18
C5
C8
C10
O6
C7
C6

Fig. 2