Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Investigation of nitro–nitrito photoisomerization: crystal structures of *trans*-{2,2′-[ethane-1,2-diylbis(nitrilomethylidyne)]diphenolato}(pyridine/4-methylpyridine)nitrocobalt(III)

Shigeru Ohba,[a]* Masanobu Tsuchimoto[b] and Naoki Yamada[c]

[a]Research and Education Center for Natural Sciences, Keio University, 4-1-1 Hiyoshi, Kohoku-ku, Yokohama 223-8521, Japan, [b]Department of Chemistry, Chiba Institute of Technology, Shibazono 2-1-1, Narashino, Chiba 275-0023, Japan, and [c]Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3-14-1, Kohoku-ku, Yokohama 223-8522, Japan. *Correspondence e-mail: ohba@a3.keio.jp

Received 31 October 2018
Accepted 1 November 2018

Edited by W. T. A. Harrison, University of Aberdeen, Scotland

Keywords: crystal structure; nitro-nitrito photoisomerization; reaction cavity.

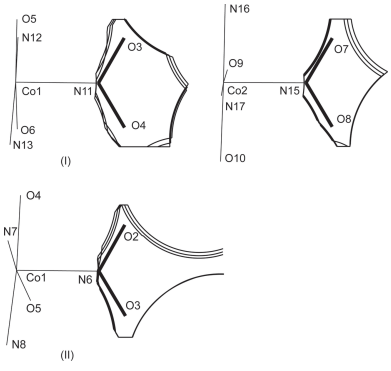
CCDC references: 1876726; 1876725

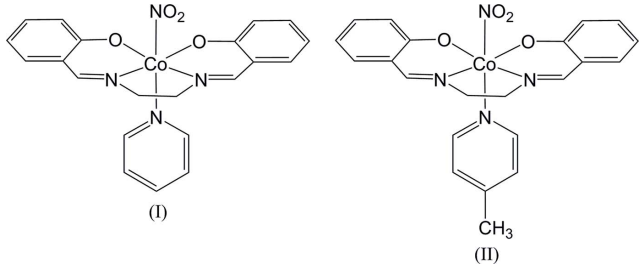
Supporting information: this article has supporting information at journals.iucr.org/e

The reaction cavities of the nitro groups in the title compounds, *trans*-{2,2′-[ethane-1,2-diylbis(nitrilomethylidyne)]diphenolato-κ^4O,N,N',O'}(nitro-κN)(pyridine-κN)cobalt(III), $[Co(C_{16}H_{14}N_2O_2)(NO_2)(C_5H_5N)]$, (I), and *trans*-{2,2′-[ethane-1,2-diylbis(nitrilomethylidyne)]diphenolato-κ^4O,N,N',O'}(4-methylpyridine-κN)(nitro-κN)cobalt(III), $[Co(C_{16}H_{14}N_2O_2)(NO_2)(C_6H_7N)]$, (II), have been investigated to reveal that the intermolecular C_{Me}—H···O(nitro) contacts in (II) are unfeasible for the nitro–nitrito photochemical linkage isomerization process. In (I), there are two independent complexes showing similar conformations, and the central five-membered chelate ring of the tetradentate salen ligand adopts the same absolute configuration. This is the result of pseudo-spontaneous resolution, since the configuration of the five-membered chelate ring may frequently be reversed in solution. In the crystals of (I) and (II), the molecules are linked into three-dimensional networks by C—H···O hydrogen bonds.

1. Chemical context

The nitrite ion is an ambidentate ligand, which shows linkage isomerism. In a Co^{III} complex, nitro (N-bonded) coordination is thermodynamically more stable than the nitrito (O-bonded) form, but nitro-nitrito linkage isomerization may occur in the solid state by irradiation with visible or UV light (Balzani *et al.*, 1968; Coppens *et al.*, 2002). The crystal structures of *trans*-$[Co(en)_2(NO_2)(NCS)]NCS$ (Ohba, Tsuchimoto & Kurachi, 2018) and *trans*-$[Co(acac)_2(NO_2)(\text{pyridine derivative})]$ (Ohba, Tsuchimoto & Miyazaki, 2018) indicated that a certain geometry of the intermolecular N/C—H···O contacts restricts the photoisomerization. In the present study, we investigated another type of nitrocobalt complex, *trans*-[Co(salen)(NO_2)-(*X*-py)], where H_2salen is *N*,*N*′-bis(salicylidene)-1,2-ethanediamine, and *X*-py is pyridine in (I) or 4-methylpyridine in (II).





OPEN ACCESS

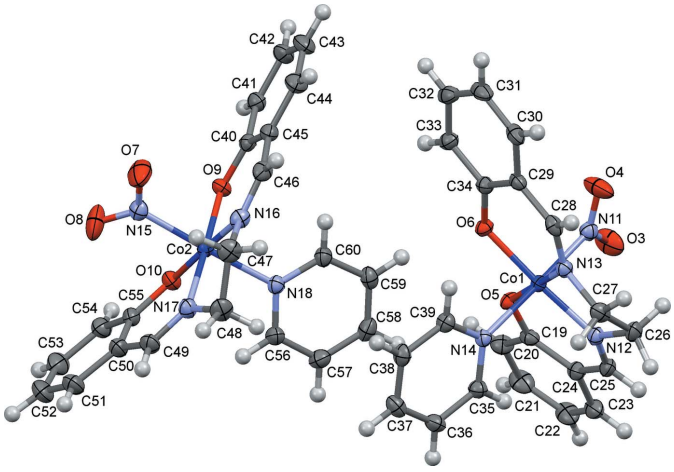


Figure 1
The molecular structure of (I), showing displacement ellipsoids at the 30% probability level.

When the KBr disk of the py complex (I) was irradiated for 30 min with a Xe lamp, the colour changed from brown to reddish brown, and the IR spectrum showed an increase in intensity of the absorption peak in the region of 1040–1060 cm^{-1} (see figure in the supporting information), which corresponds to the symmetric N—O stretching mode of the nitrito form (Heyns & De Waal, 1989). The colour and IR spectrum reverted to those before irradiation on standing at room temperature for 2 h. On the other hand, the 4-Me-py complex (II) was photo-stable and did not show any change in the colour or IR spectrum upon irradiation. The crystal structures of (I) and (II) were determined to investigate the steric circumstances of the nitro ligand.

The photo-reactivities of nitrocobalt complexes in the solid state depend not only on the steric conditions but also on the electronic effects of the co-existing ligands (Miyoshi *et al.*, 1983). The change of the IR spectrum of (I) upon irradiation was less apparent and it disappeared much more quickly after irradiation than that of *trans*-[Co(acac)$_2$(NO$_2$)(py)] (Ohba, Tsuchimoto& Miyazaki, 2018), indicating that salen^{2-} is not as suitable as acac$^-$ for stabilization of the nitrito form.

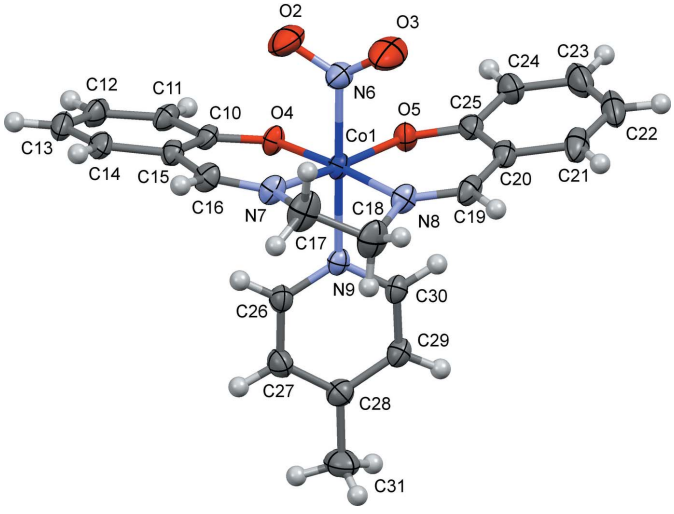


Figure 2
The molecular structure of (II), showing displacement ellipsoids at the 30% probability level.

Table 1
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
C25—H25···O3^{i}	0.93	2.48	3.341 (5)	154
C38—H38···O9^{ii}	0.93	2.39	3.280 (5)	160
C48—H48B···O8^{ii}	0.97	2.48	3.285 (7)	140
C54—H54···O7^{iii}	0.93	2.54	3.291 (7)	138
C59—H59···O6	0.93	2.38	3.213 (5)	149

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

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

D—H···A	D—H	H···A	D···A	D—H···A
C16—H16···O2^{i}	0.93	2.58	3.358 (6)	141
C31—H31B···O2^{ii}	0.96	2.51	3.429 (7)	159
C31—H31C···O3^{iii}	0.96	2.55	3.483 (7)	164

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

2. Structural commentary

The molecular structures of (I) and (II) are shown in Figs. 1 and 2, respectively. In (I), there are two independent complex molecules, which have similar conformations, the five-membered chelate ring of salen being *gauche* with a λ form. The chirality of the crystal structure indicates that the crystals are pseudo-racemic conglomerates, because the configuration of the chelate ring may frequently switch from λ to δ, and *vice versa*, in solution. The Co—N(nitro) bond lengths are 1.944 (4) and 1.950 (3) Å in (I) and 1.916 (4) Å in (II). In each case, the coordination geometry around the Co atom is a distorted octahedron with the N(nitro) and N(py) atoms at the *trans* positions.

3. Supramolecular features

The crystal structures of (I) and (II) are shown in Figs. 3 and 4, respectively. In both (I) and (II), the molecules are connected by C—H···O hydrogen bonds (Tables 1 and 2), forming a three-dimensional network. There are π–π interactions between the pyridine rings in (I) (see Figs. 1 and 3), the distance between the centroids being 3.82 (1) Å with a dihedral angle of 15.74 (8)°. The shortest contact between the rings is C39···C59 of 3.351 (6) Å.

Slices of the reaction cavities around the NO_2^- group near its plane in (I) and (II) are compared in Fig. 5, where the radii of neighboring atoms are assumed to be 1.0 Å greater than the corresponding van der Waals radii (Bondi, 1964) except for Co, its radius being set to 1.90 Å. The shape of the cavity in the nitro plane is mainly defined by the C—H···O(nitro) contacts, which are shown in Figs. 6 and 7. In (I), the cavity of O3—N11—O4 is wide enough to rotate in the original plane to

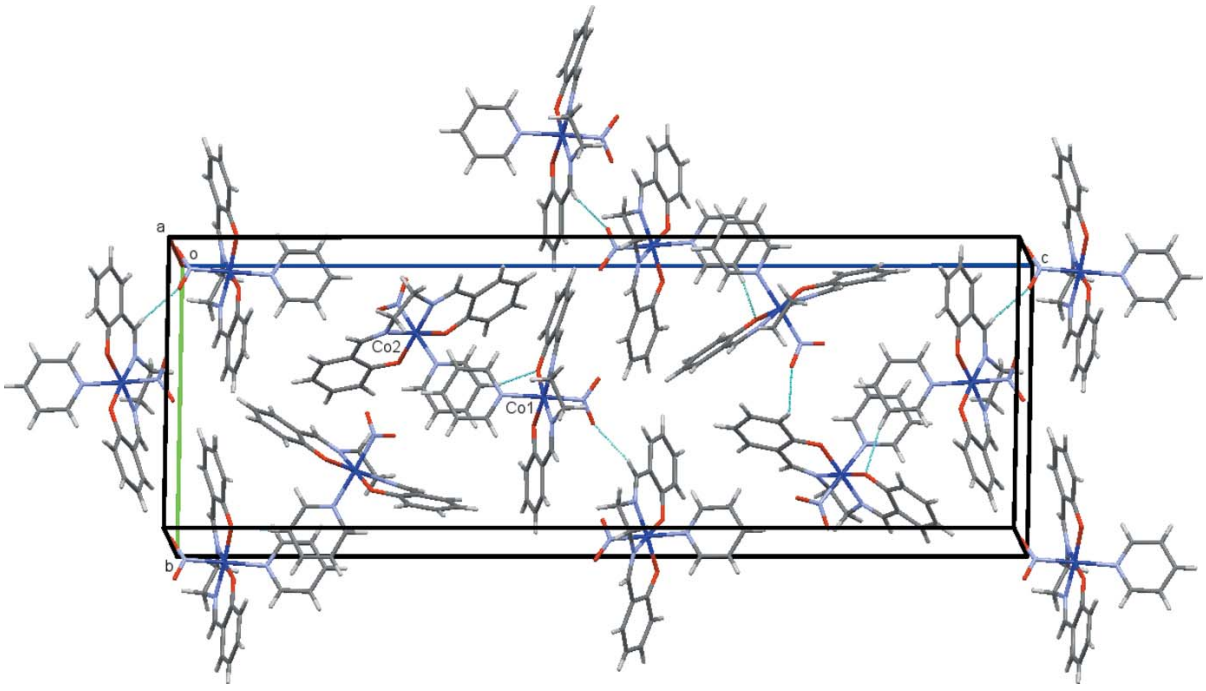


Figure 3
The crystal structure of (I), projected along *a*. The C—H···O hydrogen bonds are shown as blue dashed lines.

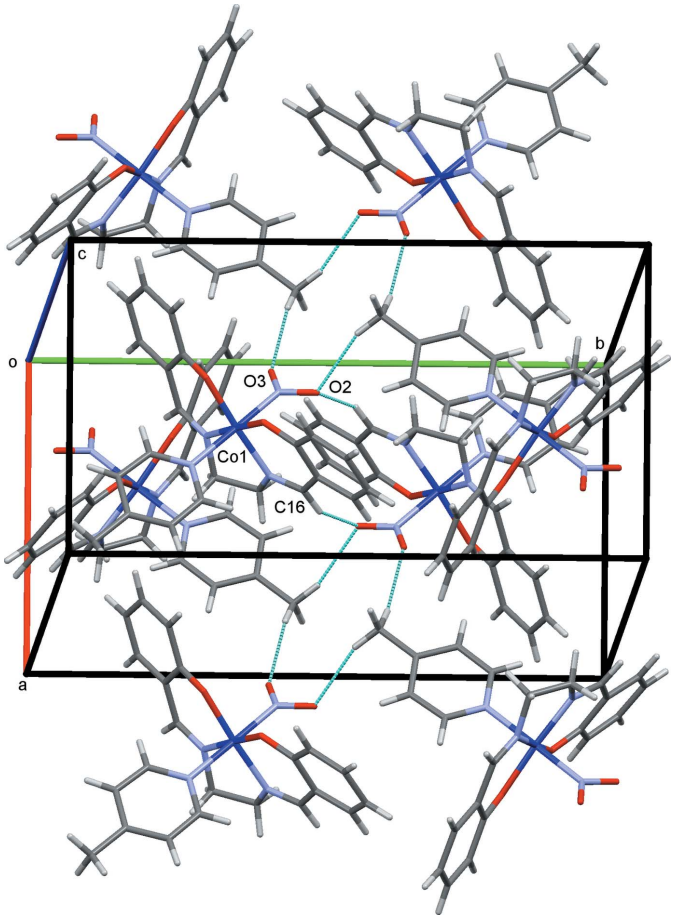


Figure 4
The crystal structure of (II), projected along *c*. The C—H···O hydrogen bonds are shown as blue dashed lines.

achieve the N,O-bidentate transition state toward the nitrito form, in accord with the observed photo-activity of (I). In (II), the cavity of O2—N6—O3 has a tail, which is connected to that of the symmetry-related one, as seen in Fig. 7. These nitro groups are connected *via* C_{Me}—H···O hydrogen bonds to form an $R_4^4(12)$ ring, there being a narrow void around the center of the ring. The photo-stability of (II) suggests that the

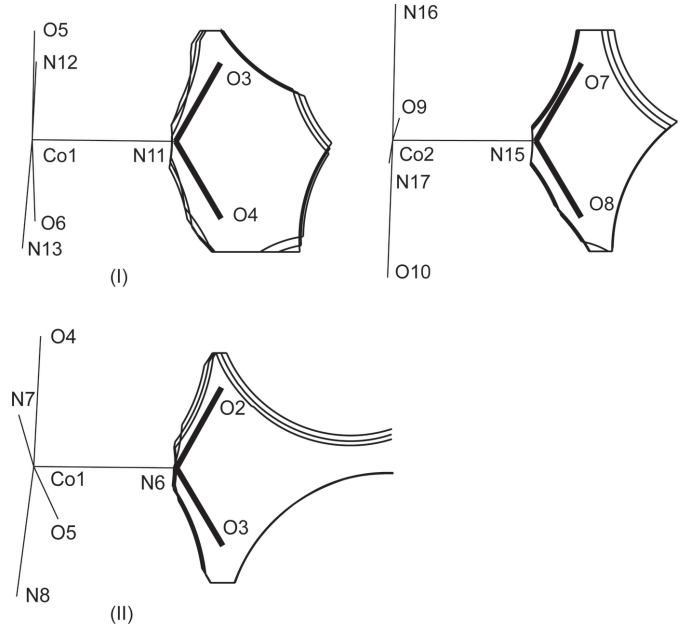


Figure 5
Comparison of the slices of the cavity around the nitro group within 0.1 Å from the plane in (I) and (II).

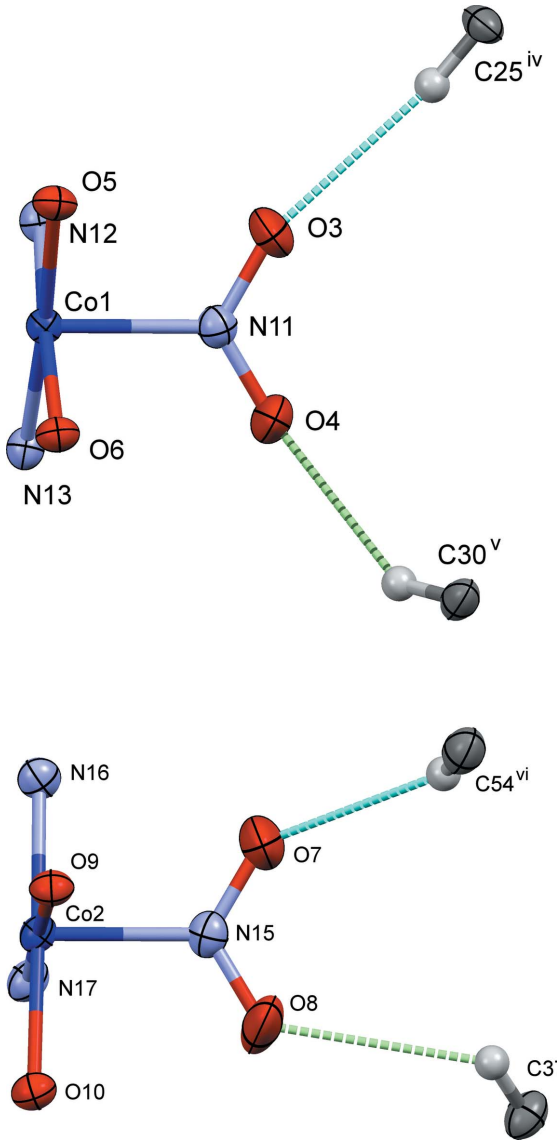


Figure 6
The steric circumstances of the nitro groups in (I). Only parts of the complex are shown for clarity. The C—H···O hydrogen bonds are shown as blue dashed lines. The green dashed lines indicate other O···H contacts shorter than 2.8 Å, O4···H30^{v} = 2.77 Å and O8···H37^{vii} = 2.66 Å. Symmetry codes: (i) $x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$; (ii) $x+1, y, z$; (iii) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $x-\frac{1}{2}, -y+\frac{3}{2}, -z+1$; (v) $x-\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (vi) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$;; (vii) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$.

rotation of the NO_2^- group in its plane will be blocked by the C—H···O hydrogen bonds. The steric condition of O7—N15—O8 in (I) is similar to that in (II), suggesting that the photoreaction in (I) mainly occurs at the Co1 complex site.

4. Database survey

There is no entry for *trans*-[Co(salen)(NO_2)(*X*-py)] in the Cambridge Structural Database (CSD Version 5.39; Groom *et al.*, 2016), although the structures of related compounds have been published, for example *trans*-[Co(salen)(py)$_2$][BPh_4^-] (Shi *et al.*, 1995) and *trans*-[Co(salen)(4-Cl-py)$_2$][ClO_4^-]·CH_3OH (Zhang, 2010).

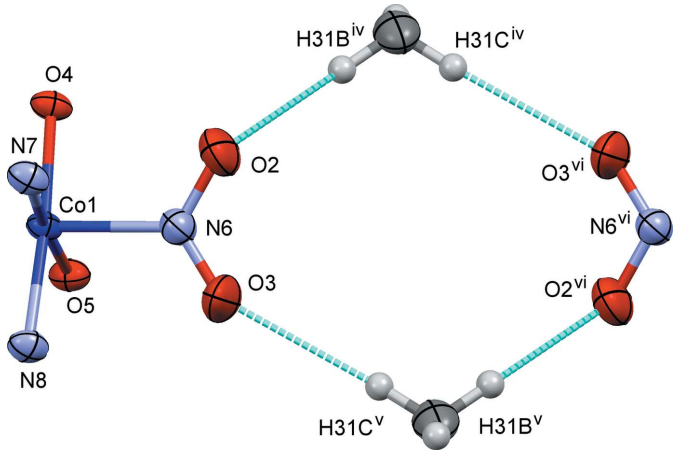


Figure 7
The steric circumstance of the nitro group in (II). Only parts of the complex are shown for clarity. The C—H···O hydrogen bonds are shown as blue dashed lines. Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (iii) $x+1, -y+\frac{1}{2}, z+\frac{1}{2}$; (iv) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$; (v) $x-1, -y+\frac{1}{2}, z-\frac{1}{2}$; (vi) $-x, 1-y, 1-z$.

5. Synthesis and crystallization

Cobalt(II) acetate tetrahydrate, sodium nitrite, H_2salen, and pyridine/4-methylpyridine (molar ratio 1:1:1:1) were reacted in methanol. Air was bubbled through the solution at 328 K for 1 h to precipitate the title compound. Brown needles of (I) and (II) were grown from a dimethyl sulfoxide solution and an *N, N′*-dimethylformamide solution, respectively, by diffusion of diethyl ether vapour.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The H atoms bound to C were positioned geometrically, the methyl H atoms being introduced by an HFIX 137 command. They were refined as riding, with C—H = 0.93–0.97 Å, and U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(C_{Me}). (I): Since the *c* axis is longer than 40 Å, the overlapping of reflections was avoided in the intensity measurement by a longer sample-to-detector distance than the usual. (II): Six reflections showing poor agreement were omitted from the final refinement.

Acknowledgements

The authors thank Dr Takashi Nemoto, Kyoto University, for making the program *CAVITY* available to the public.

References

Balzani, V., Ballardini, R., Sabbatini, N. & Moggi, L. (1968). *Inorg. Chem.* **7**, 1398–1404.
Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Bruker (2016). *APEX3*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Coppens, P., Novozhilova, I. & Kovalevsky, A. (2002). *Chem. Rev.* **102**, 861–883.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.

Table 3
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$[Co(C_{16}H_{14}N_2O_2)(NO_2)(C_5H_5N)]$	$[Co(C_{16}H_{14}N_2O_2)(NO_2)(C_6H_7N)]$
M_r	450.33	464.36
Crystal system, space group	Orthorhombic, $P2_12_12_1$	Monoclinic, $P2_1/c$
Temperature (K)	302	301
a, b, c (Å)	6.924 (2), 14.007 (3), 40.339 (8)	9.7430 (4), 18.0136 (6), 12.8488 (5)
α, β, γ (°)	90, 90, 90	90, 106.476 (1), 90
V (Å^3)	3912.3 (16)	2162.45 (14)
Z	8	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.91	0.83
Crystal size (mm)	0.29 × 0.06 × 0.04	0.30 × 0.10 × 0.07
Data collection		
Diffractometer	Bruker D8 VENTURE	Bruker D8 VENTURE
Absorption correction	Integration (*SADABS*; Bruker, 2016)	Integration (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.841, 0.965	0.847, 0.952
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	52512, 9036, 6955	23719, 5114, 3793
R_{int}	0.057	0.034
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.656	0.659
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.034, 0.081, 1.11	0.055, 0.192, 1.08
No. of reflections	9036	5114
No. of parameters	541	281
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.41, −0.38	1.25, −0.61
Absolute structure	Flack x determined using 2597 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)	–
Absolute structure parameter	−0.010 (6)	–

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *Mercury* (Macrae *et al.*, 2008), *CAVITY* (Ohashi *et al.*, 1981), *SHELXL2014* (Sheldrick, 2015*b*) and *publCIF* (Westrip, 2010).

Heyns, A. M. & de Waal, D. (1989). *Spectrochim. Acta A*, **45**, 905–909.
Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
Miyoshi, K., Katoda, N. & Yoneda, H. (1983). *Inorg. Chem.* **22**, 1839–1843.
Ohashi, Y., Yanagi, K., Kurihara, T., Sasada, Y. & Ohgo, Y. (1981). *J. Am. Chem. Soc.* **103**, 5805–5812.
Ohba, S., Tsuchimoto, M. & Kurachi, S. (2018). *Acta Cryst.* E**74**, 1526–1531.
Ohba, S., Tsuchimoto, M. & Miyazaki, H. (2018). *Acta Cryst.* E**74**, 1637–1642.
Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* B**69**, 249–259.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Shi, X.-H., You, X.-Z., Li, C., Song, B.-L., Li, T.-H. & Huang, X.-Y. (1995). *Acta Cryst.* C**51**, 206–207.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Zhang, D. (2010). *Acta Cryst.* E**66**, m1633.

supporting information

Acta Cryst. (2018). E**74**, 1759-1763 [https://doi.org/10.1107/S2056989018015487]

Investigation of nitro–nitrito photoisomerization: crystal structures of *trans*-{2,2′-[ethane-1,2-diylbis(nitrilomethylidyne)]diphenolato}(pyridine/4-methylpyridine)nitrocobalt(III)

Shigeru Ohba, Masanobu Tsuchimoto and Naoki Yamada

Computing details

For both structures, data collection: *APEX3* (Bruker, 2016); cell refinement: *SAINT* (Bruker, 2016); data reduction: *SAINT* (Bruker, 2016); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2008) and *CAVITY* (Ohashi *et al.*, 1981); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015b) and *publCIF* (Westrip, 2010).

trans-{2,2′-[Ethane-1,2-diylbis(nitrilomethylidyne)]diphenolato-κ^4O,N,N',O'}(nitro-κN)(pyridine-κN)cobalt(III) (I)

Crystal data

$[Co(C_{16}H_{14}N_2O_2)(NO_2)(C_5H_5N)]$
M_r = 450.33
Orthorhombic, $P2_12_12_1$
a = 6.924 (2) Å
b = 14.007 (3) Å
c = 40.339 (8) Å
V = 3912.3 (16) Å^3
Z = 8
$F(000)$ = 1856
D_x = 1.529 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9904 reflections
θ = 2.5–26.4°
μ = 0.91 mm^{-1}
T = 302 K
Needle, brown
0.29 × 0.06 × 0.04 mm

Data collection

Bruker D8 VENTURE diffractometer
φ and ω scans
Absorption correction: integration (SADABS; Bruker, 2016)
T_{min} = 0.841, T_{max} = 0.965
52512 measured reflections
9036 independent reflections
6955 reflections with $I > 2\sigma(I)$
R_{int} = 0.057
θ_{max} = 27.8°, θ_{min} = 2.1°
h = −9→9
k = −18→18
l = −52→52

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.081
S = 1.11
9036 reflections
541 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0226P)^2 + 1.3354P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ e Å^{-3}
Absolute structure: Flack *x* determined using 2597 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: −0.010 (6)

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.85121 (8)	0.53498 (3)	0.44179 (2)	0.02769 (12)
Co2	0.35957 (8)	0.26710 (4)	0.28219 (2)	0.03077 (13)
O3	0.6714 (6)	0.6081 (3)	0.49733 (8)	0.0730 (12)
O4	0.7526 (7)	0.4641 (3)	0.50386 (8)	0.0762 (12)
O5	0.6418 (4)	0.61244 (17)	0.42729 (6)	0.0339 (6)
O6	0.6913 (4)	0.42812 (18)	0.43168 (6)	0.0330 (7)
O7	0.2938 (7)	0.0765 (3)	0.26808 (10)	0.0924 (16)
O8	0.1576 (7)	0.1673 (3)	0.23428 (10)	0.0816 (13)
O9	0.1581 (4)	0.24890 (18)	0.31341 (6)	0.0352 (6)
O10	0.1888 (4)	0.3519 (2)	0.25961 (6)	0.0384 (7)
N11	0.7471 (5)	0.5353 (3)	0.48670 (8)	0.0372 (8)
N12	1.0111 (5)	0.6392 (2)	0.45445 (8)	0.0340 (8)
N13	1.0645 (5)	0.4574 (3)	0.45381 (7)	0.0327 (8)
N14	0.9458 (5)	0.5370 (2)	0.39372 (7)	0.0311 (7)
N15	0.2570 (5)	0.1572 (3)	0.25859 (9)	0.0396 (8)
N16	0.5391 (5)	0.1846 (3)	0.30391 (9)	0.0389 (9)
N17	0.5586 (5)	0.2833 (3)	0.25025 (8)	0.0392 (9)
N18	0.4514 (5)	0.3825 (2)	0.30847 (8)	0.0352 (8)
C19	0.6357 (7)	0.7062 (3)	0.42854 (9)	0.0347 (9)
C20	0.4657 (7)	0.7517 (3)	0.41647 (10)	0.0453 (11)
H20	0.3664	0.7149	0.4076	0.054*
C21	0.4467 (9)	0.8500 (3)	0.41780 (12)	0.0565 (14)
H21	0.3331	0.8783	0.4104	0.068*
C22	0.5943 (9)	0.9073 (3)	0.43004 (12)	0.0588 (15)
H22	0.5790	0.9732	0.4307	0.071*
C23	0.7612 (8)	0.8667 (3)	0.44100 (11)	0.0485 (12)
H23	0.8601	0.9057	0.4488	0.058*
C24	0.7873 (6)	0.7656 (3)	0.44078 (10)	0.0370 (10)
C25	0.9653 (7)	0.7287 (3)	0.45369 (9)	0.0396 (10)
H25	1.0541	0.7722	0.4621	0.048*
C26	1.1903 (6)	0.6075 (3)	0.47122 (10)	0.0426 (11)
H26A	1.1685	0.6010	0.4949	0.051*
H26B	1.2927	0.6537	0.4678	0.051*
C27	1.2453 (6)	0.5121 (3)	0.45626 (11)	0.0420 (11)

H27A	1.3024	0.5208	0.4345	0.050*
H27B	1.3374	0.4792	0.4703	0.050*
C28	1.0614 (7)	0.3662 (3)	0.45981 (9)	0.0369 (10)
H28	1.1759	0.3376	0.4666	0.044*
C29	0.8932 (7)	0.3063 (3)	0.45665 (9)	0.0350 (10)
C30	0.9070 (8)	0.2098 (3)	0.46782 (10)	0.0443 (12)
H30	1.0224	0.1879	0.4768	0.053*
C31	0.7526 (9)	0.1493 (3)	0.46547 (11)	0.0524 (13)
H31	0.7620	0.0871	0.4734	0.063*
C32	0.5809 (8)	0.1813 (3)	0.45115 (11)	0.0497 (13)
H32	0.4763	0.1399	0.4495	0.060*
C33	0.5639 (7)	0.2740 (3)	0.43937 (10)	0.0398 (10)
H33	0.4500	0.2931	0.4291	0.048*
C34	0.7180 (6)	0.3401 (3)	0.44278 (10)	0.0333 (9)
C35	0.9600 (6)	0.6196 (3)	0.37649 (10)	0.0377 (10)
H35	0.9483	0.6771	0.3878	0.045*
C36	0.9910 (7)	0.6218 (3)	0.34278 (10)	0.0438 (11)
H36	0.9996	0.6801	0.3318	0.053*
C37	1.0094 (6)	0.5382 (4)	0.32536 (10)	0.0452 (11)
H37	1.0270	0.5387	0.3025	0.054*
C38	1.0009 (6)	0.4531 (3)	0.34269 (10)	0.0407 (10)
H38	1.0163	0.3952	0.3317	0.049*
C39	0.9692 (6)	0.4549 (3)	0.37652 (10)	0.0357 (9)
H39	0.9638	0.3973	0.3879	0.043*
C40	0.1643 (7)	0.1934 (3)	0.33973 (9)	0.0341 (9)
C41	0.0003 (7)	0.1897 (3)	0.36051 (10)	0.0413 (11)
H41	−0.1075	0.2262	0.3552	0.050*
C42	−0.0040 (9)	0.1333 (4)	0.38859 (11)	0.0534 (13)
H42	−0.1152	0.1314	0.4015	0.064*
C43	0.1563 (9)	0.0792 (3)	0.39774 (11)	0.0581 (13)
H43	0.1535	0.0421	0.4169	0.070*
C44	0.3176 (8)	0.0815 (3)	0.37825 (11)	0.0523 (13)
H44	0.4237	0.0445	0.3841	0.063*
C45	0.3277 (7)	0.1381 (3)	0.34951 (9)	0.0381 (10)
C46	0.5049 (7)	0.1355 (3)	0.33027 (11)	0.0430 (11)
H46	0.6021	0.0948	0.3376	0.052*
C47	0.7144 (6)	0.1661 (4)	0.28403 (12)	0.0505 (12)
H47A	0.6959	0.1102	0.2702	0.061*
H47B	0.8242	0.1549	0.2985	0.061*
C48	0.7488 (6)	0.2536 (4)	0.26278 (12)	0.0524 (13)
H48A	0.8067	0.3042	0.2758	0.063*
H48B	0.8346	0.2384	0.2445	0.063*
C49	0.5353 (7)	0.3142 (3)	0.22032 (10)	0.0455 (11)
H49	0.6417	0.3122	0.2062	0.055*
C50	0.3591 (8)	0.3512 (3)	0.20717 (10)	0.0451 (10)
C51	0.3481 (9)	0.3711 (4)	0.17269 (11)	0.0595 (13)
H51	0.4541	0.3577	0.1593	0.071*
C52	0.1864 (9)	0.4093 (4)	0.15869 (12)	0.0676 (17)

H52	0.1793	0.4184	0.1359	0.081*
C53	0.0304 (9)	0.4347 (4)	0.17923 (13)	0.0624 (15)
H53	−0.0773	0.4642	0.1701	0.075*
C54	0.0354 (7)	0.4162 (3)	0.21282 (11)	0.0495 (12)
H54	−0.0684	0.4343	0.2260	0.059*
C55	0.1962 (6)	0.3703 (3)	0.22745 (10)	0.0386 (11)
C56	0.4742 (6)	0.4679 (3)	0.29333 (10)	0.0412 (10)
H56	0.4693	0.4706	0.2703	0.049*
C57	0.5047 (7)	0.5513 (3)	0.31087 (11)	0.0487 (12)
H57	0.5201	0.6088	0.2997	0.058*
C58	0.5122 (7)	0.5488 (4)	0.34477 (11)	0.0479 (12)
H58	0.5288	0.6046	0.3569	0.058*
C59	0.4945 (6)	0.4619 (4)	0.36050 (10)	0.0434 (11)
H59	0.5031	0.4579	0.3835	0.052*
C60	0.4639 (6)	0.3808 (3)	0.34170 (10)	0.0401 (10)
H60	0.4515	0.3225	0.3525	0.048*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0270 (3)	0.0279 (3)	0.0282 (2)	−0.0004 (3)	−0.0004 (2)	−0.0005 (2)
Co2	0.0271 (3)	0.0352 (3)	0.0299 (3)	−0.0001 (3)	0.0000 (2)	−0.0016 (2)
O3	0.099 (3)	0.061 (2)	0.058 (2)	0.027 (2)	0.031 (2)	−0.0067 (17)
O4	0.124 (3)	0.055 (2)	0.0490 (19)	0.014 (2)	0.032 (2)	0.0148 (18)
O5	0.0319 (15)	0.0253 (13)	0.0445 (15)	0.0007 (14)	−0.0021 (14)	−0.0007 (11)
O6	0.0332 (17)	0.0265 (14)	0.0394 (15)	−0.0010 (12)	−0.0037 (12)	0.0017 (11)
O7	0.143 (4)	0.044 (2)	0.090 (3)	−0.018 (3)	−0.041 (3)	0.001 (2)
O8	0.087 (3)	0.071 (2)	0.087 (3)	0.013 (3)	−0.047 (3)	−0.034 (2)
O9	0.0356 (15)	0.0402 (16)	0.0299 (13)	0.0024 (15)	0.0034 (13)	0.0058 (12)
O10	0.0383 (18)	0.0445 (16)	0.0324 (14)	0.0029 (14)	−0.0005 (12)	0.0024 (13)
N11	0.0356 (19)	0.0391 (19)	0.0368 (18)	−0.0019 (19)	0.0010 (15)	−0.0020 (17)
N12	0.0295 (19)	0.039 (2)	0.0335 (17)	−0.0033 (16)	−0.0021 (15)	−0.0028 (15)
N13	0.0288 (18)	0.0395 (19)	0.0299 (16)	−0.0015 (16)	−0.0009 (14)	0.0012 (16)
N14	0.0311 (18)	0.0334 (18)	0.0289 (15)	−0.0008 (16)	−0.0019 (14)	−0.0001 (15)
N15	0.035 (2)	0.043 (2)	0.040 (2)	0.0008 (18)	0.0034 (17)	−0.0072 (18)
N16	0.030 (2)	0.040 (2)	0.046 (2)	0.0021 (17)	0.0002 (16)	0.0003 (17)
N17	0.032 (2)	0.050 (2)	0.0354 (18)	−0.0015 (18)	−0.0003 (16)	−0.0023 (17)
N18	0.0326 (19)	0.040 (2)	0.0334 (18)	−0.0018 (17)	−0.0033 (15)	0.0005 (15)
C19	0.043 (2)	0.030 (2)	0.0306 (19)	0.003 (2)	0.009 (2)	0.0021 (15)
C20	0.046 (3)	0.038 (3)	0.052 (3)	0.007 (2)	0.002 (2)	0.006 (2)
C21	0.074 (4)	0.040 (3)	0.055 (3)	0.023 (3)	0.002 (3)	0.005 (2)
C22	0.095 (5)	0.030 (2)	0.051 (3)	0.013 (3)	0.000 (3)	0.000 (2)
C23	0.074 (3)	0.033 (2)	0.039 (2)	−0.004 (2)	0.004 (2)	−0.004 (2)
C24	0.050 (3)	0.029 (2)	0.032 (2)	0.001 (2)	0.0057 (19)	−0.0049 (18)
C25	0.047 (3)	0.037 (2)	0.035 (2)	−0.013 (2)	0.0022 (19)	−0.0079 (19)
C26	0.035 (3)	0.054 (3)	0.038 (2)	−0.010 (2)	−0.0066 (19)	−0.002 (2)
C27	0.028 (2)	0.055 (3)	0.043 (2)	0.001 (2)	−0.0018 (19)	0.009 (2)
C28	0.038 (2)	0.042 (3)	0.031 (2)	0.012 (2)	−0.0025 (18)	−0.0004 (18)

C29	0.048 (3)	0.034 (2)	0.0234 (18)	0.003 (2)	0.0027 (18)	0.0009 (16)
C30	0.068 (4)	0.035 (2)	0.030 (2)	0.011 (2)	−0.004 (2)	0.0010 (18)
C31	0.094 (4)	0.028 (2)	0.036 (2)	0.000 (3)	0.008 (3)	0.0025 (19)
C32	0.072 (4)	0.033 (2)	0.044 (3)	−0.013 (2)	0.016 (2)	−0.007 (2)
C33	0.043 (2)	0.035 (2)	0.041 (2)	−0.006 (2)	0.007 (2)	−0.004 (2)
C34	0.039 (2)	0.030 (2)	0.0306 (19)	0.0006 (18)	0.0044 (18)	−0.0008 (18)
C35	0.042 (3)	0.035 (2)	0.037 (2)	−0.001 (2)	0.0011 (19)	0.0017 (19)
C36	0.047 (3)	0.047 (3)	0.037 (2)	−0.003 (2)	0.005 (2)	0.010 (2)
C37	0.042 (3)	0.061 (3)	0.033 (2)	0.008 (3)	0.0024 (19)	0.005 (2)
C38	0.040 (3)	0.044 (3)	0.038 (2)	0.004 (2)	0.0013 (19)	−0.012 (2)
C39	0.034 (2)	0.034 (2)	0.039 (2)	0.003 (2)	0.0006 (18)	−0.0036 (19)
C40	0.040 (3)	0.029 (2)	0.033 (2)	−0.004 (2)	0.004 (2)	−0.0044 (16)
C41	0.047 (3)	0.042 (3)	0.035 (2)	−0.004 (2)	0.005 (2)	−0.0027 (19)
C42	0.067 (4)	0.058 (3)	0.034 (2)	−0.014 (3)	0.013 (2)	−0.001 (2)
C43	0.082 (4)	0.057 (3)	0.035 (2)	−0.007 (3)	−0.003 (3)	0.014 (2)
C44	0.062 (4)	0.047 (3)	0.048 (3)	0.002 (3)	−0.006 (3)	0.011 (2)
C45	0.045 (3)	0.035 (2)	0.034 (2)	−0.004 (2)	−0.003 (2)	0.0020 (17)
C46	0.041 (3)	0.037 (2)	0.052 (3)	0.002 (2)	−0.011 (2)	0.005 (2)
C47	0.032 (2)	0.061 (3)	0.059 (3)	0.011 (2)	0.002 (2)	0.002 (3)
C48	0.027 (2)	0.075 (4)	0.055 (3)	−0.002 (3)	0.005 (2)	−0.001 (3)
C49	0.041 (3)	0.061 (3)	0.035 (2)	−0.008 (2)	0.007 (2)	−0.001 (2)
C50	0.044 (3)	0.056 (3)	0.036 (2)	−0.009 (3)	−0.001 (2)	0.003 (2)
C51	0.063 (3)	0.078 (4)	0.038 (2)	−0.015 (3)	0.005 (3)	0.008 (2)
C52	0.085 (5)	0.077 (4)	0.041 (3)	−0.015 (3)	−0.012 (3)	0.017 (3)
C53	0.068 (4)	0.063 (4)	0.056 (3)	−0.004 (3)	−0.021 (3)	0.019 (3)
C54	0.050 (3)	0.051 (3)	0.047 (3)	−0.005 (2)	−0.009 (2)	0.011 (2)
C55	0.043 (3)	0.040 (2)	0.032 (2)	−0.007 (2)	−0.0061 (18)	0.0035 (18)
C56	0.045 (3)	0.041 (2)	0.037 (2)	−0.009 (2)	0.0022 (19)	0.000 (2)
C57	0.049 (3)	0.041 (3)	0.056 (3)	−0.010 (2)	0.002 (2)	0.002 (2)
C58	0.040 (3)	0.051 (3)	0.053 (3)	−0.005 (2)	−0.003 (2)	−0.017 (2)
C59	0.038 (3)	0.057 (3)	0.035 (2)	0.002 (2)	−0.0058 (19)	−0.005 (2)
C60	0.039 (3)	0.045 (3)	0.036 (2)	−0.002 (2)	−0.0060 (19)	−0.001 (2)

Geometric parameters (Å, º)

Co1—N13	1.896 (3)	C30—H30	0.9300
Co1—N12	1.901 (3)	C31—C32	1.396 (7)
Co1—O5	1.903 (3)	C31—H31	0.9300
Co1—O6	1.906 (3)	C32—C33	1.389 (6)
Co1—N11	1.950 (3)	C32—H32	0.9300
Co1—N14	2.047 (3)	C33—C34	1.419 (6)
Co2—O9	1.897 (3)	C33—H33	0.9300
Co2—N17	1.900 (4)	C35—C36	1.377 (6)
Co2—O10	1.908 (3)	C35—H35	0.9300
Co2—N16	1.910 (4)	C36—C37	1.372 (6)
Co2—N15	1.944 (4)	C36—H36	0.9300
Co2—N18	2.035 (3)	C37—C38	1.384 (6)
O3—N11	1.224 (5)	C37—H37	0.9300

O4—N11	1.215 (4)	C38—C39	1.382 (5)
O5—C19	1.315 (4)	C38—H38	0.9300
O6—C34	1.325 (4)	C39—H39	0.9300
O7—N15	1.220 (5)	C40—C41	1.412 (6)
O8—N15	1.206 (5)	C40—C45	1.427 (6)
O9—C40	1.316 (4)	C41—C42	1.382 (6)
O10—C55	1.324 (5)	C41—H41	0.9300
N12—C25	1.295 (5)	C42—C43	1.394 (7)
N12—C26	1.481 (5)	C42—H42	0.9300
N13—C28	1.300 (5)	C43—C44	1.366 (7)
N13—C27	1.471 (5)	C43—H43	0.9300
N14—C39	1.353 (5)	C44—C45	1.407 (6)
N14—C35	1.353 (5)	C44—H44	0.9300
N16—C46	1.289 (5)	C45—C46	1.452 (6)
N16—C47	1.477 (5)	C46—H46	0.9300
N17—C49	1.293 (5)	C47—C48	1.514 (7)
N17—C48	1.471 (6)	C47—H47A	0.9700
N18—C60	1.343 (5)	C47—H47B	0.9700
N18—C56	1.352 (5)	C48—H48A	0.9700
C19—C20	1.424 (6)	C48—H48B	0.9700
C19—C24	1.428 (6)	C49—C50	1.427 (6)
C20—C21	1.385 (6)	C49—H49	0.9300
C20—H20	0.9300	C50—C55	1.419 (6)
C21—C22	1.389 (8)	C50—C51	1.421 (6)
C21—H21	0.9300	C51—C52	1.363 (7)
C22—C23	1.362 (7)	C51—H51	0.9300
C22—H22	0.9300	C52—C53	1.407 (8)
C23—C24	1.428 (6)	C52—H52	0.9300
C23—H23	0.9300	C53—C54	1.380 (7)
C24—C25	1.434 (6)	C53—H53	0.9300
C25—H25	0.9300	C54—C55	1.415 (6)
C26—C27	1.515 (6)	C54—H54	0.9300
C26—H26A	0.9700	C56—C57	1.382 (6)
C26—H26B	0.9700	C56—H56	0.9300
C27—H27A	0.9700	C57—C58	1.369 (6)
C27—H27B	0.9700	C57—H57	0.9300
C28—C29	1.441 (6)	C58—C59	1.378 (6)
C28—H28	0.9300	C58—H58	0.9300
C29—C34	1.417 (6)	C59—C60	1.382 (6)
C29—C30	1.428 (5)	C59—H59	0.9300
C30—C31	1.368 (7)	C60—H60	0.9300
N13—Co1—N12	85.27 (15)	C31—C30—H30	119.6
N13—Co1—O5	176.89 (12)	C29—C30—H30	119.6
N12—Co1—O5	95.08 (13)	C30—C31—C32	119.7 (4)
N13—Co1—O6	93.28 (13)	C30—C31—H31	120.2
N12—Co1—O6	176.70 (12)	C32—C31—H31	120.2
O5—Co1—O6	86.52 (12)	C33—C32—C31	121.0 (5)

N13—Co1—N11	92.96 (14)	C33—C32—H32	119.5
N12—Co1—N11	87.92 (14)	C31—C32—H32	119.5
O5—Co1—N11	90.14 (14)	C32—C33—C34	120.9 (4)
O6—Co1—N11	89.20 (13)	C32—C33—H33	119.6
N13—Co1—N14	90.07 (13)	C34—C33—H33	119.6
N12—Co1—N14	93.29 (14)	O6—C34—C29	124.3 (4)
O5—Co1—N14	86.83 (12)	O6—C34—C33	118.0 (4)
O6—Co1—N14	89.67 (13)	C29—C34—C33	117.7 (4)
N11—Co1—N14	176.83 (14)	N14—C35—C36	122.6 (4)
O9—Co2—N17	178.70 (14)	N14—C35—H35	118.7
O9—Co2—O10	86.83 (12)	C36—C35—H35	118.7
N17—Co2—O10	92.95 (14)	C37—C36—C35	120.0 (4)
O9—Co2—N16	95.33 (13)	C37—C36—H36	120.0
N17—Co2—N16	84.91 (16)	C35—C36—H36	120.0
O10—Co2—N16	177.68 (15)	C36—C37—C38	118.2 (4)
O9—Co2—N15	87.13 (14)	C36—C37—H37	120.9
N17—Co2—N15	91.59 (15)	C38—C37—H37	120.9
O10—Co2—N15	91.87 (15)	C39—C38—C37	119.3 (4)
N16—Co2—N15	89.08 (16)	C39—C38—H38	120.4
O9—Co2—N18	89.46 (13)	C37—C38—H38	120.4
N17—Co2—N18	91.81 (15)	N14—C39—C38	122.8 (4)
O10—Co2—N18	87.00 (13)	N14—C39—H39	118.6
N16—Co2—N18	92.18 (15)	C38—C39—H39	118.6
N15—Co2—N18	176.46 (15)	O9—C40—C41	118.3 (4)
C19—O5—Co1	125.6 (3)	O9—C40—C45	124.7 (4)
C34—O6—Co1	125.3 (3)	C41—C40—C45	117.0 (4)
C40—O9—Co2	126.2 (3)	C42—C41—C40	121.7 (5)
C55—O10—Co2	124.4 (3)	C42—C41—H41	119.2
O4—N11—O3	119.9 (3)	C40—C41—H41	119.2
O4—N11—Co1	121.0 (3)	C41—C42—C43	120.7 (5)
O3—N11—Co1	119.1 (3)	C41—C42—H42	119.6
C25—N12—C26	120.4 (4)	C43—C42—H42	119.6
C25—N12—Co1	126.5 (3)	C44—C43—C42	119.1 (4)
C26—N12—Co1	112.4 (3)	C44—C43—H43	120.5
C28—N13—C27	120.9 (4)	C42—C43—H43	120.5
C28—N13—Co1	126.7 (3)	C43—C44—C45	121.9 (5)
C27—N13—Co1	112.4 (3)	C43—C44—H44	119.1
C39—N14—C35	117.0 (3)	C45—C44—H44	119.1
C39—N14—Co1	120.8 (3)	C44—C45—C40	119.6 (4)
C35—N14—Co1	121.5 (3)	C44—C45—C46	117.9 (4)
O8—N15—O7	118.9 (4)	C40—C45—C46	122.4 (4)
O8—N15—Co2	120.9 (3)	N16—C46—C45	125.6 (4)
O7—N15—Co2	120.2 (3)	N16—C46—H46	117.2
C46—N16—C47	120.3 (4)	C45—C46—H46	117.2
C46—N16—Co2	125.6 (3)	N16—C47—C48	107.1 (4)
C47—N16—Co2	113.1 (3)	N16—C47—H47A	110.3
C49—N17—C48	121.8 (4)	C48—C47—H47A	110.3
C49—N17—Co2	125.6 (3)	N16—C47—H47B	110.3

C48—N17—Co2	112.5 (3)	C48—C47—H47B	110.3
C60—N18—C56	117.3 (4)	H47A—C47—H47B	108.5
C60—N18—Co2	121.7 (3)	N17—C48—C47	106.4 (4)
C56—N18—Co2	120.3 (3)	N17—C48—H48A	110.4
O5—C19—C20	117.4 (4)	C47—C48—H48A	110.4
O5—C19—C24	124.9 (4)	N17—C48—H48B	110.4
C20—C19—C24	117.7 (4)	C47—C48—H48B	110.4
C21—C20—C19	120.7 (5)	H48A—C48—H48B	108.6
C21—C20—H20	119.7	N17—C49—C50	125.1 (4)
C19—C20—H20	119.7	N17—C49—H49	117.5
C20—C21—C22	121.2 (5)	C50—C49—H49	117.5
C20—C21—H21	119.4	C55—C50—C51	119.0 (5)
C22—C21—H21	119.4	C55—C50—C49	122.3 (3)
C23—C22—C21	119.9 (4)	C51—C50—C49	118.7 (5)
C23—C22—H22	120.0	C52—C51—C50	121.8 (5)
C21—C22—H22	120.0	C52—C51—H51	119.1
C22—C23—C24	121.3 (5)	C50—C51—H51	119.1
C22—C23—H23	119.4	C51—C52—C53	119.0 (5)
C24—C23—H23	119.4	C51—C52—H52	120.5
C19—C24—C23	119.2 (4)	C53—C52—H52	120.5
C19—C24—C25	123.2 (4)	C54—C53—C52	120.8 (5)
C23—C24—C25	117.6 (4)	C54—C53—H53	119.6
N12—C25—C24	124.6 (4)	C52—C53—H53	119.6
N12—C25—H25	117.7	C53—C54—C55	121.0 (5)
C24—C25—H25	117.7	C53—C54—H54	119.5
N12—C26—C27	107.0 (3)	C55—C54—H54	119.5
N12—C26—H26A	110.3	O10—C55—C54	117.8 (4)
C27—C26—H26A	110.3	O10—C55—C50	124.0 (4)
N12—C26—H26B	110.3	C54—C55—C50	118.1 (4)
C27—C26—H26B	110.3	N18—C56—C57	122.3 (4)
H26A—C26—H26B	108.6	N18—C56—H56	118.8
N13—C27—C26	105.8 (3)	C57—C56—H56	118.8
N13—C27—H27A	110.6	C58—C57—C56	119.7 (4)
C26—C27—H27A	110.6	C58—C57—H57	120.2
N13—C27—H27B	110.6	C56—C57—H57	120.2
C26—C27—H27B	110.6	C57—C58—C59	118.6 (4)
H27A—C27—H27B	108.7	C57—C58—H58	120.7
N13—C28—C29	124.6 (4)	C59—C58—H58	120.7
N13—C28—H28	117.7	C58—C59—C60	119.1 (4)
C29—C28—H28	117.7	C58—C59—H59	120.4
C34—C29—C30	119.9 (4)	C60—C59—H59	120.4
C34—C29—C28	122.2 (4)	N18—C60—C59	122.9 (4)
C30—C29—C28	118.0 (4)	N18—C60—H60	118.6
C31—C30—C29	120.9 (5)	C59—C60—H60	118.6
O10—Co2—O9—C40	179.8 (3)	N14—C35—C36—C37	−0.2 (7)
N16—Co2—O9—C40	−1.0 (3)	C35—C36—C37—C38	−1.7 (7)
N15—Co2—O9—C40	87.8 (3)	C36—C37—C38—C39	1.7 (7)

N18—Co2—O9—C40	−93.1 (3)	C35—N14—C39—C38	−1.8 (6)
N12—Co1—N13—C28	162.7 (3)	Co1—N14—C39—C38	168.8 (3)
O6—Co1—N13—C28	−14.4 (3)	C37—C38—C39—N14	0.0 (7)
N11—Co1—N13—C28	75.0 (3)	Co2—O9—C40—C41	179.2 (3)
N14—Co1—N13—C28	−104.0 (3)	Co2—O9—C40—C45	1.1 (5)
N12—Co1—N13—C27	−16.8 (3)	O9—C40—C41—C42	−179.9 (4)
O6—Co1—N13—C27	166.1 (3)	C45—C40—C41—C42	−1.6 (6)
N11—Co1—N13—C27	−104.5 (3)	C40—C41—C42—C43	1.3 (7)
N14—Co1—N13—C27	76.5 (3)	C41—C42—C43—C44	−1.0 (8)
Co1—O5—C19—C20	−180.0 (3)	C42—C43—C44—C45	1.1 (8)
Co1—O5—C19—C24	0.6 (5)	C43—C44—C45—C40	−1.5 (7)
O5—C19—C20—C21	178.3 (4)	C43—C44—C45—C46	−179.7 (4)
C24—C19—C20—C21	−2.3 (6)	O9—C40—C45—C44	179.9 (4)
C19—C20—C21—C22	1.8 (7)	C41—C40—C45—C44	1.7 (6)
C20—C21—C22—C23	0.0 (7)	O9—C40—C45—C46	−2.0 (6)
C21—C22—C23—C24	−1.2 (7)	C41—C40—C45—C46	179.8 (4)
O5—C19—C24—C23	−179.4 (4)	C47—N16—C46—C45	−171.7 (4)
C20—C19—C24—C23	1.1 (6)	Co2—N16—C46—C45	−4.0 (6)
O5—C19—C24—C25	−0.8 (6)	C44—C45—C46—N16	−178.2 (4)
C20—C19—C24—C25	179.8 (4)	C40—C45—C46—N16	3.7 (7)
C22—C23—C24—C19	0.6 (6)	C46—N16—C47—C48	−160.9 (4)
C22—C23—C24—C25	−178.2 (4)	Co2—N16—C47—C48	29.9 (4)
C26—N12—C25—C24	−174.1 (4)	C49—N17—C48—C47	−140.7 (4)
Co1—N12—C25—C24	−4.6 (6)	Co2—N17—C48—C47	37.5 (5)
C19—C24—C25—N12	2.9 (6)	N16—C47—C48—N17	−41.9 (5)
C23—C24—C25—N12	−178.4 (4)	C48—N17—C49—C50	−174.9 (4)
C25—N12—C26—C27	−157.0 (4)	Co2—N17—C49—C50	7.1 (7)
Co1—N12—C26—C27	32.1 (4)	N17—C49—C50—C55	9.1 (8)
C28—N13—C27—C26	−141.8 (4)	N17—C49—C50—C51	−172.0 (4)
Co1—N13—C27—C26	37.8 (4)	C55—C50—C51—C52	1.0 (7)
N12—C26—C27—N13	−43.5 (4)	C49—C50—C51—C52	−177.9 (5)
C27—N13—C28—C29	−177.2 (4)	C50—C51—C52—C53	3.7 (8)
Co1—N13—C28—C29	3.3 (6)	C51—C52—C53—C54	−3.8 (8)
N13—C28—C29—C34	7.6 (6)	C52—C53—C54—C55	−0.8 (8)
N13—C28—C29—C30	−172.8 (4)	Co2—O10—C55—C54	165.5 (3)
C34—C29—C30—C31	−0.3 (6)	Co2—O10—C55—C50	−17.9 (6)
C28—C29—C30—C31	−179.9 (4)	C53—C54—C55—O10	−177.8 (4)
C29—C30—C31—C32	1.8 (6)	C53—C54—C55—C50	5.4 (7)
C30—C31—C32—C33	−0.3 (7)	C51—C50—C55—O10	178.0 (4)
C31—C32—C33—C34	−2.6 (6)	C49—C50—C55—O10	−3.2 (7)
Co1—O6—C34—C29	−16.9 (5)	C51—C50—C55—C54	−5.5 (6)
Co1—O6—C34—C33	165.7 (3)	C49—C50—C55—C54	173.4 (4)
C30—C29—C34—O6	−179.8 (4)	C60—N18—C56—C57	−1.6 (6)
C28—C29—C34—O6	−0.3 (6)	Co2—N18—C56—C57	169.0 (4)
C30—C29—C34—C33	−2.5 (6)	N18—C56—C57—C58	−0.1 (7)
C28—C29—C34—C33	177.1 (3)	C56—C57—C58—C59	1.9 (7)
C32—C33—C34—O6	−178.5 (4)	C57—C58—C59—C60	−2.0 (7)
C32—C33—C34—C29	3.9 (6)	C56—N18—C60—C59	1.4 (6)

C39—N14—C35—C36	1.9 (6)	Co2—N18—C60—C59	−169.0 (3)
Co1—N14—C35—C36	−168.7 (3)	C58—C59—C60—N18	0.4 (7)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C25—H25···O3^{i}	0.93	2.48	3.341 (5)	154
C38—H38···O9^{ii}	0.93	2.39	3.280 (5)	160
C48—H48*B*···O8^{ii}	0.97	2.48	3.285 (7)	140
C54—H54···O7^{iii}	0.93	2.54	3.291 (7)	138
C59—H59···O6	0.93	2.38	3.213 (5)	149

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

trans-{2,2′-[Ethane-1,2-diylbis(nitrilomethylidyne)]diphenolato-κ^4O,N,N',O'}(4-methylpyridine-κN)(nitro-κN)cobalt(III) (II)

Crystal data

$[Co(C_{16}H_{14}N_2O_2)(NO_2)(C_6H_7N)]$
M_r = 464.36
Monoclinic, $P2_1/c$
a = 9.7430 (4) Å
b = 18.0136 (6) Å
c = 12.8488 (5) Å
β = 106.476 (1)°
V = 2162.45 (14) Å^3
Z = 4
$F(000)$ = 960
D_x = 1.426 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9569 reflections
θ = 2.5–27.9°
μ = 0.83 mm^{-1}
T = 301 K
Needle, brown
0.30 × 0.10 × 0.07 mm

Data collection

Bruker D8 VENTURE diffractometer
φ and ω scans
Absorption correction: integration (SADABS; Bruker, 2016)
T_{min} = 0.847, T_{max} = 0.952
23719 measured reflections
5114 independent reflections
3793 reflections with $I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 27.9°, θ_{min} = 2.0°
h = −11→12
k = −23→23
l = −16→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.192
S = 1.08
5114 reflections
281 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0929P)^2 + 3.2082P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.61 e Å^{-3}

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.43909 (5)	0.31776 (2)	0.59728 (3)	0.03638 (18)
O2	0.3197 (5)	0.4571 (2)	0.5824 (3)	0.0871 (12)
O3	0.2071 (5)	0.3868 (2)	0.4603 (4)	0.1114 (17)
O4	0.4759 (3)	0.35464 (13)	0.74031 (19)	0.0418 (6)
O5	0.2919 (3)	0.26205 (15)	0.6288 (2)	0.0468 (6)
N6	0.3024 (4)	0.39475 (19)	0.5412 (3)	0.0518 (8)
N7	0.5772 (4)	0.37838 (17)	0.5612 (2)	0.0454 (7)
N8	0.4123 (4)	0.27543 (18)	0.4586 (2)	0.0452 (7)
N9	0.5822 (3)	0.23582 (16)	0.6577 (2)	0.0383 (6)
C10	0.5620 (4)	0.40889 (18)	0.7823 (3)	0.0400 (8)
C11	0.5769 (4)	0.4281 (2)	0.8917 (3)	0.0458 (9)
H11	0.5257	0.4019	0.9308	0.055*
C12	0.6657 (5)	0.4847 (2)	0.9408 (3)	0.0558 (10)
H12	0.6746	0.4956	1.0132	0.067*
C13	0.7428 (5)	0.5262 (2)	0.8859 (4)	0.0580 (11)
H13	0.8014	0.5650	0.9201	0.070*
C14	0.7303 (5)	0.5087 (2)	0.7802 (4)	0.0522 (10)
H14	0.7808	0.5367	0.7424	0.063*
C15	0.6436 (4)	0.44982 (19)	0.7263 (3)	0.0418 (8)
C16	0.6455 (5)	0.4327 (2)	0.6194 (3)	0.0478 (9)
H16	0.7003	0.4630	0.5882	0.057*
C17	0.5788 (7)	0.3687 (3)	0.4473 (4)	0.0743 (15)
H17A	0.5174	0.4053	0.4015	0.089*
H17B	0.6752	0.3752	0.4416	0.089*
C18	0.5273 (7)	0.2937 (3)	0.4122 (4)	0.0723 (14)
H18A	0.4929	0.2918	0.3336	0.087*
H18B	0.6048	0.2583	0.4362	0.087*
C19	0.3099 (5)	0.2321 (2)	0.4085 (3)	0.0511 (10)
H19	0.3095	0.2150	0.3401	0.061*
C20	0.1964 (4)	0.2085 (2)	0.4515 (3)	0.0482 (9)
C21	0.0852 (6)	0.1644 (3)	0.3846 (4)	0.0669 (14)
H21	0.0896	0.1506	0.3159	0.080*
C22	−0.0288 (6)	0.1418 (3)	0.4196 (5)	0.0764 (16)
H22	−0.1002	0.1124	0.3752	0.092*
C23	−0.0370 (5)	0.1626 (3)	0.5200 (5)	0.0748 (15)
H23	−0.1159	0.1484	0.5425	0.090*
C24	0.0683 (5)	0.2037 (3)	0.5877 (5)	0.0647 (12)
H24	0.0605	0.2168	0.6558	0.078*
C25	0.1902 (4)	0.2270 (2)	0.5558 (3)	0.0475 (9)

C26	0.7169 (4)	0.2496 (2)	0.7154 (3)	0.0467 (9)
H26	0.7466	0.2988	0.7266	0.056*
C27	0.8141 (5)	0.1943 (2)	0.7592 (4)	0.0535 (10)
H27	0.9066	0.2068	0.7992	0.064*
C28	0.7751 (5)	0.1207 (2)	0.7443 (3)	0.0512 (9)
C29	0.6333 (4)	0.1068 (2)	0.6881 (3)	0.0474 (9)
H29	0.5996	0.0583	0.6790	0.057*
C30	0.5427 (4)	0.1645 (2)	0.6460 (3)	0.0434 (8)
H30	0.4489	0.1534	0.6072	0.052*
C31	0.8785 (6)	0.0589 (3)	0.7867 (5)	0.0770 (15)
H31A	0.9135	0.0400	0.7292	0.116*
H31B	0.8310	0.0199	0.8139	0.116*
H31C	0.9572	0.0772	0.8442	0.116*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0462 (3)	0.0347 (3)	0.0287 (3)	−0.00394 (18)	0.0115 (2)	−0.00221 (16)
O2	0.108 (3)	0.0533 (19)	0.093 (3)	0.023 (2)	0.017 (2)	−0.0042 (19)
O3	0.115 (4)	0.087 (3)	0.094 (3)	0.044 (3)	−0.033 (3)	−0.008 (2)
O4	0.0575 (16)	0.0381 (13)	0.0329 (11)	−0.0110 (11)	0.0176 (11)	−0.0052 (10)
O5	0.0464 (15)	0.0498 (15)	0.0444 (14)	−0.0112 (12)	0.0133 (12)	−0.0081 (11)
N6	0.059 (2)	0.0461 (18)	0.0486 (18)	0.0042 (15)	0.0132 (16)	−0.0021 (14)
N7	0.062 (2)	0.0422 (16)	0.0365 (15)	−0.0051 (14)	0.0220 (14)	−0.0011 (12)
N8	0.060 (2)	0.0472 (17)	0.0300 (14)	−0.0024 (15)	0.0151 (13)	−0.0021 (12)
N9	0.0462 (17)	0.0395 (15)	0.0306 (13)	−0.0046 (12)	0.0131 (12)	−0.0060 (11)
C10	0.051 (2)	0.0279 (15)	0.0373 (17)	0.0030 (14)	0.0066 (15)	−0.0005 (12)
C11	0.061 (2)	0.0393 (18)	0.0354 (17)	0.0030 (16)	0.0102 (16)	−0.0036 (14)
C12	0.068 (3)	0.050 (2)	0.043 (2)	0.005 (2)	0.0054 (19)	−0.0155 (17)
C13	0.059 (3)	0.040 (2)	0.063 (3)	−0.0035 (18)	−0.002 (2)	−0.0124 (18)
C14	0.051 (2)	0.0339 (18)	0.067 (3)	−0.0048 (16)	0.0082 (19)	−0.0005 (17)
C15	0.048 (2)	0.0313 (16)	0.0429 (18)	−0.0022 (14)	0.0082 (15)	0.0007 (14)
C16	0.060 (2)	0.0386 (18)	0.050 (2)	−0.0051 (17)	0.0229 (18)	0.0058 (16)
C17	0.114 (4)	0.073 (3)	0.051 (2)	−0.023 (3)	0.048 (3)	−0.009 (2)
C18	0.097 (4)	0.081 (3)	0.049 (2)	−0.016 (3)	0.036 (3)	−0.020 (2)
C19	0.071 (3)	0.0423 (19)	0.0305 (16)	0.0027 (18)	−0.0010 (17)	−0.0048 (14)
C20	0.051 (2)	0.0380 (18)	0.0448 (19)	−0.0009 (16)	−0.0049 (17)	0.0030 (15)
C21	0.077 (3)	0.045 (2)	0.054 (2)	−0.004 (2)	−0.020 (2)	0.0030 (19)
C22	0.062 (3)	0.053 (3)	0.089 (4)	−0.016 (2)	−0.020 (3)	0.010 (3)
C23	0.051 (3)	0.066 (3)	0.099 (4)	−0.017 (2)	0.007 (3)	0.005 (3)
C24	0.050 (3)	0.057 (3)	0.086 (3)	−0.009 (2)	0.018 (2)	−0.004 (2)
C25	0.043 (2)	0.0383 (18)	0.056 (2)	−0.0010 (15)	0.0057 (17)	−0.0003 (16)
C26	0.046 (2)	0.0418 (19)	0.052 (2)	−0.0082 (16)	0.0138 (17)	−0.0057 (16)
C27	0.043 (2)	0.055 (2)	0.061 (3)	−0.0071 (18)	0.0127 (19)	−0.0006 (19)
C28	0.055 (2)	0.048 (2)	0.051 (2)	0.0003 (18)	0.0162 (18)	0.0015 (17)
C29	0.058 (2)	0.0370 (18)	0.0455 (19)	−0.0040 (16)	0.0125 (17)	−0.0018 (15)
C30	0.050 (2)	0.0414 (18)	0.0364 (17)	−0.0061 (16)	0.0086 (15)	−0.0040 (14)
C31	0.060 (3)	0.065 (3)	0.104 (4)	0.014 (2)	0.019 (3)	0.014 (3)

Geometric parameters (Å, º)

Co1—O5	1.886 (3)	C17—H17A	0.9700
Co1—N8	1.887 (3)	C17—H17B	0.9700
Co1—O4	1.890 (2)	C18—H18A	0.9700
Co1—N7	1.891 (3)	C18—H18B	0.9700
Co1—N6	1.916 (4)	C19—C20	1.433 (6)
Co1—N9	2.027 (3)	C19—H19	0.9300
O2—N6	1.233 (5)	C20—C25	1.399 (6)
O3—N6	1.190 (5)	C20—C21	1.419 (6)
O4—C10	1.301 (4)	C21—C22	1.373 (8)
O5—C25	1.317 (4)	C21—H21	0.9300
N7—C16	1.295 (5)	C22—C23	1.367 (8)
N7—C17	1.478 (5)	C22—H22	0.9300
N8—C19	1.287 (5)	C23—C24	1.360 (7)
N8—C18	1.449 (6)	C23—H23	0.9300
N9—C26	1.335 (5)	C24—C25	1.426 (6)
N9—C30	1.338 (5)	C24—H24	0.9300
C10—C11	1.414 (5)	C26—C27	1.380 (6)
C10—C15	1.421 (5)	C26—H26	0.9300
C11—C12	1.371 (6)	C27—C28	1.378 (6)
C11—H11	0.9300	C27—H27	0.9300
C12—C13	1.387 (7)	C28—C29	1.388 (6)
C12—H12	0.9300	C28—C31	1.496 (6)
C13—C14	1.366 (6)	C29—C30	1.371 (6)
C13—H13	0.9300	C29—H29	0.9300
C14—C15	1.410 (5)	C30—H30	0.9300
C14—H14	0.9300	C31—H31A	0.9600
C15—C16	1.412 (5)	C31—H31B	0.9600
C16—H16	0.9300	C31—H31C	0.9600
C17—C18	1.465 (7)		

O5—Co1—N8	94.47 (13)	N7—C17—H17A	110.0
O5—Co1—O4	85.66 (11)	C18—C17—H17B	110.0
N8—Co1—O4	175.79 (13)	N7—C17—H17B	110.0
O5—Co1—N7	176.15 (13)	H17A—C17—H17B	108.4
N8—Co1—N7	85.35 (14)	N8—C18—C17	108.7 (4)
O4—Co1—N7	94.80 (12)	N8—C18—H18A	110.0
O5—Co1—N6	88.63 (14)	C17—C18—H18A	110.0
N8—Co1—N6	92.44 (15)	N8—C18—H18B	110.0
O4—Co1—N6	91.77 (13)	C17—C18—H18B	110.0
N7—Co1—N6	87.54 (15)	H18A—C18—H18B	108.3
O5—Co1—N9	90.72 (12)	N8—C19—C20	124.1 (3)
N8—Co1—N9	87.88 (13)	N8—C19—H19	117.9
O4—Co1—N9	87.91 (11)	C20—C19—H19	117.9
N7—Co1—N9	93.11 (13)	C25—C20—C21	118.8 (4)
N6—Co1—N9	179.30 (14)	C25—C20—C19	123.1 (3)
C10—O4—Co1	126.1 (2)	C21—C20—C19	118.2 (4)

C25—O5—Co1	124.5 (3)	C22—C21—C20	121.1 (5)
O3—N6—O2	117.5 (4)	C22—C21—H21	119.4
O3—N6—Co1	121.9 (3)	C20—C21—H21	119.4
O2—N6—Co1	120.2 (3)	C23—C22—C21	119.8 (5)
C16—N7—C17	120.9 (3)	C23—C22—H22	120.1
C16—N7—Co1	125.4 (3)	C21—C22—H22	120.1
C17—N7—Co1	112.5 (3)	C24—C23—C22	121.1 (5)
C19—N8—C18	120.8 (3)	C24—C23—H23	119.4
C19—N8—Co1	126.7 (3)	C22—C23—H23	119.4
C18—N8—Co1	112.4 (3)	C23—C24—C25	121.0 (5)
C26—N9—C30	116.6 (3)	C23—C24—H24	119.5
C26—N9—Co1	122.6 (2)	C25—C24—H24	119.5
C30—N9—Co1	120.8 (3)	O5—C25—C20	124.7 (4)
O4—C10—C11	117.9 (3)	O5—C25—C24	117.2 (4)
O4—C10—C15	124.6 (3)	C20—C25—C24	118.1 (4)
C11—C10—C15	117.6 (3)	N9—C26—C27	123.0 (4)
C12—C11—C10	120.9 (4)	N9—C26—H26	118.5
C12—C11—H11	119.6	C27—C26—H26	118.5
C10—C11—H11	119.6	C28—C27—C26	120.5 (4)
C11—C12—C13	121.9 (4)	C28—C27—H27	119.7
C11—C12—H12	119.0	C26—C27—H27	119.7
C13—C12—H12	119.0	C27—C28—C29	116.1 (4)
C14—C13—C12	118.3 (4)	C27—C28—C31	122.4 (4)
C14—C13—H13	120.9	C29—C28—C31	121.6 (4)
C12—C13—H13	120.9	C30—C29—C28	120.3 (4)
C13—C14—C15	122.3 (4)	C30—C29—H29	119.9
C13—C14—H14	118.9	C28—C29—H29	119.9
C15—C14—H14	118.9	N9—C30—C29	123.4 (4)
C14—C15—C16	118.1 (4)	N9—C30—H30	118.3
C14—C15—C10	119.0 (3)	C29—C30—H30	118.3
C16—C15—C10	122.9 (3)	C28—C31—H31A	109.5
N7—C16—C15	125.5 (3)	C28—C31—H31B	109.5
N7—C16—H16	117.3	H31A—C31—H31B	109.5
C15—C16—H16	117.3	C28—C31—H31C	109.5
C18—C17—N7	108.4 (4)	H31A—C31—H31C	109.5
C18—C17—H17A	110.0	H31B—C31—H31C	109.5

O5—Co1—O4—C10	−170.8 (3)	C17—N7—C16—C15	175.7 (4)
N7—Co1—O4—C10	5.4 (3)	Co1—N7—C16—C15	9.2 (6)
N6—Co1—O4—C10	−82.3 (3)	C14—C15—C16—N7	176.7 (4)
N9—Co1—O4—C10	98.3 (3)	C10—C15—C16—N7	−1.3 (6)
N8—Co1—O5—C25	−17.1 (3)	C16—N7—C17—C18	165.0 (5)
O4—Co1—O5—C25	167.1 (3)	Co1—N7—C17—C18	−26.9 (6)
N6—Co1—O5—C25	75.3 (3)	C19—N8—C18—C17	149.1 (4)
N9—Co1—O5—C25	−105.0 (3)	Co1—N8—C18—C17	−33.8 (6)
N8—Co1—N7—C16	174.4 (4)	N7—C17—C18—N8	38.1 (6)
O4—Co1—N7—C16	−9.8 (4)	C18—N8—C19—C20	176.8 (4)
N6—Co1—N7—C16	81.8 (4)	Co1—N8—C19—C20	0.1 (6)

N9—Co1—N7—C16	−98.0 (3)	N8—C19—C20—C25	−3.8 (6)
N8—Co1—N7—C17	6.9 (3)	N8—C19—C20—C21	176.0 (4)
O4—Co1—N7—C17	−177.3 (3)	C25—C20—C21—C22	1.8 (6)
N6—Co1—N7—C17	−85.7 (3)	C19—C20—C21—C22	−178.1 (4)
N9—Co1—N7—C17	94.5 (3)	C20—C21—C22—C23	0.8 (7)
O5—Co1—N8—C19	8.3 (3)	C21—C22—C23—C24	−1.9 (8)
N7—Co1—N8—C19	−167.8 (4)	C22—C23—C24—C25	0.5 (8)
N6—Co1—N8—C19	−80.5 (3)	Co1—O5—C25—C20	18.4 (5)
N9—Co1—N8—C19	98.9 (3)	Co1—O5—C25—C24	−164.4 (3)
O5—Co1—N8—C18	−168.7 (3)	C21—C20—C25—O5	174.0 (4)
N7—Co1—N8—C18	15.2 (3)	C19—C20—C25—O5	−6.1 (6)
N6—Co1—N8—C18	102.5 (4)	C21—C20—C25—C24	−3.1 (6)
N9—Co1—N8—C18	−78.1 (3)	C19—C20—C25—C24	176.7 (4)
Co1—O4—C10—C11	−179.3 (3)	C23—C24—C25—O5	−175.3 (4)
Co1—O4—C10—C15	0.0 (5)	C23—C24—C25—C20	2.1 (7)
O4—C10—C11—C12	−179.9 (4)	C30—N9—C26—C27	1.8 (6)
C15—C10—C11—C12	0.8 (6)	Co1—N9—C26—C27	178.3 (3)
C10—C11—C12—C13	1.0 (6)	N9—C26—C27—C28	0.3 (7)
C11—C12—C13—C14	−1.0 (7)	C26—C27—C28—C29	−2.9 (6)
C12—C13—C14—C15	−0.7 (6)	C26—C27—C28—C31	177.6 (4)
C13—C14—C15—C16	−175.6 (4)	C27—C28—C29—C30	3.4 (6)
C13—C14—C15—C10	2.4 (6)	C31—C28—C29—C30	−177.0 (4)
O4—C10—C15—C14	178.4 (3)	C26—N9—C30—C29	−1.2 (5)
C11—C10—C15—C14	−2.4 (5)	Co1—N9—C30—C29	−177.8 (3)
O4—C10—C15—C16	−3.7 (6)	C28—C29—C30—N9	−1.5 (6)
C11—C10—C15—C16	175.6 (4)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C16—H16···O2^{i}	0.93	2.58	3.358 (6)	141
C31—H31*B*···O2^{ii}	0.96	2.51	3.429 (7)	159
C31—H31*C*···O3^{iii}	0.96	2.55	3.483 (7)	164

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