Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Bis{2-[2-(hydroxymethyl)phenyliminomethyl]-phenolato}cobalt(III) nitrate monohydrate

Masahiro Muto, Natsumi Nakagawa, Masayuki Koikawa* and Tadashi Tokii

Department of Chemistry and Applied Chemistry, Faculty of Science and Engineering, Saga University, Honjo 1, Saga 840-8502, Japan

Correspondence e-mail: koikawa@cc.saga-u.ac.jp

Received 22 October 2006
Accepted 25 November 2006

Key indicators

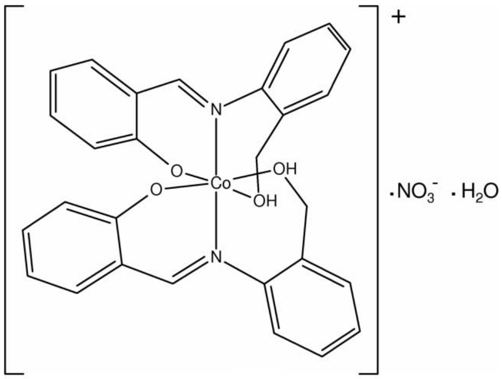
Single-crystal X-ray study
T = 303 K
Mean σ(C–C) = 0.004 Å
R factor = 0.036
wR factor = 0.096
Data-to-parameter ratio = 15.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $[Co(C_{14}H_{12}NO_2)_2]NO_3 \cdot H_2O$, is the first structurally characterized mononuclear complex of the monoanionic tridentate *N*-(2-hydroxymethylphenyl)salycylideneiminate ligand. The Co atom has an octahedral environment formed by two ligands with meridional coordination.

Comment

Tridentate ligands containing hydroxyl groups at both peripheral positions of the ligand framework form various kinds of polynuclear complexes as a result of the ability of the hydroxyl groups to act as good bridging atoms (Oshio *et al.*, 2005). We are interested in the syntheses of such metal complexes with the *N*-(2-hydroxymethylphenyl)salycylideneimine ligand, H_2L, derived from salicylaldehyde and 2-aminobenzyl alcohol. Recently, we reported that this ligand proved to be useful for syntheses of complexes with a defective double-cubane tetranuclear metal core, such as Ni^{II}_4 or $Ni^{II}_2Mn^{III}_2$ systems (Koikawa *et al.*, 2005). While attempting to prepare polynuclear cobalt complexes, we obtained single crystals of the title compound, $[Co(HL)_2]NO_3 \cdot H_2O$, (I). Here we report the results of its X-ray diffraction study, the first structural study of a mononuclear complex with the tridentate monoanionic HL^- ligand.



(I)

The structure of (I) is shown in Fig. 1. The complex cation has a meridional octahedral coordination and shows approximate C_2 symmetry with a pseudo-twofold axis passing through the mid-points of the O1$\cdots$O3 and O2$\cdots$O4 vectors. The Co^{III} atom has an octahedral N_2O_4 environment and lies at the intersection of the O1$\cdots$O2, O3$\cdots$O4 and N1$\cdots$N2 axes. The Co1—O1 and Co1—O3 distances, involving protonated O atoms, are *ca* 0.1 Å longer than the Co1—O2 and Co1—O4 bonds, involving deprotonated phenolate O atoms (Table 1). A similar coordination feature was also observed in the Ni^{II}_4 complex $[Ni_2Cl(L)(HL)]_2$ (Koikawa *et al.*, 2005).

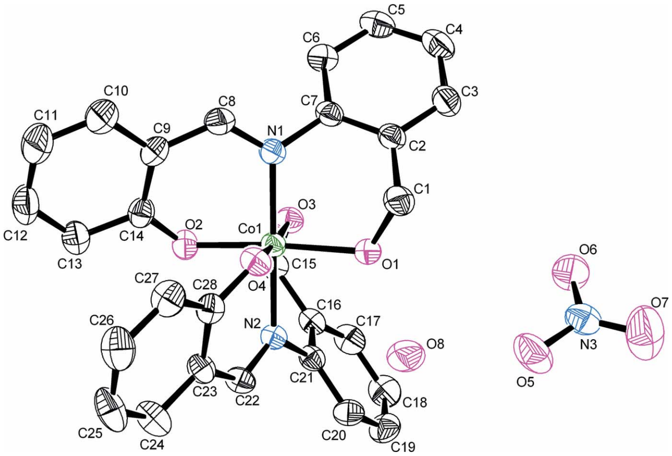


Figure 1
The asymmetric unit of the title complex, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

Each of the four independent ‘active’ H atoms in the structure participates in hydrogen bonding. The hydrogen bonds link the cationic complexes, nitrate anions and water molecules into infinite chains running along the *a* axis (Fig. 2, Table 2).

Experimental

The ligand, H_2L, was prepared by the method reported by Jezowska-Trzebiatowska *et al.* (1988). The title compound was synthesized as follows: a solution of cobalt(II) nitrate hexahydrate (0.146 g, 0.5 mmol) and a solution of H_2L (0.227 g, 1.0 mmol) in 5 and 10 ml of methanol, respectively, were mixed and stirred for 10 min; triethylamine (*ca* 2 mmol, 0.2 g) was then added to the mixture with continuing stirring. After 10 min, a 30% hydrogen peroxide solution (10 ml) was added dropwise over the course of 10 min. The solution was filtered and allowed to stand. After a few weeks, dark-brown crystals were obtained and collected by suction filtration. Yield 29%. Analysis found: C 56.71, H 4.48, N 7.11%, Co 10.98%; calculated for $C_{28}H_{26}CoN_3O_8$: C 56.86, H 4.43, N 7.11, Co 9.96%. Crystals of (I), suitable for single-crystal X-ray diffraction study, were selected directly from the sample as prepared, although those crystals showed slight efflorescence.

Crystal data

$[Co(C_{14}H_{12}NO_2)_2]NO_3 \cdot H_2O$
$M_r = 591.46$
Triclinic, $P\bar{1}$
$a = 9.5409$ (18) Å
$b = 12.257$ (3) Å
$c = 13.477$ (4) Å
$\alpha = 115.68$ (2)°
$\beta = 97.30$ (2)°
$\gamma = 106.18$ (2)°
$V = 1307.0$ (7) Å^3
$Z = 2$
$D_x = 1.503$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.71$ mm^{-1}
$T = 303.1$ K
Prism, dark brown
$0.50 \times 0.50 \times 0.40$ mm

Data collection

Rigaku AFC-5S diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.716$, $T_{max} = 0.751$
6286 measured reflections
6009 independent reflections
4269 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$
$\theta_{max} = 27.5°$
3 standard reflections every 150 reflections intensity decay: 18.8%

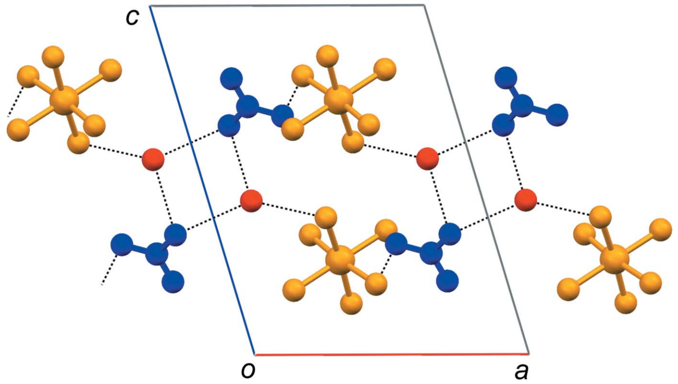


Figure 2
A fragment of the hydrogen-bonded chain in the crystal structure of (I), viewed down the *b* axis of the unit cell. Only the coordination node of the complex is shown (in orange); water molecules and nitrate anions are shown in red and blue, respectively. Hydrogen bonds are represented as dashed lines; H atoms have been omitted.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.096$
$S = 1.03$
6009 reflections
379 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.04P)^2 + 0.3547P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0079 (9)

Table 1
Selected geometric parameters (Å, °).

Co1—O1	1.951 (2)	Co1—O4	1.8564 (18)
Co1—O2	1.861 (2)	Co1—N1	1.9322 (15)
Co1—O3	1.9516 (19)	Co1—N2	1.9519 (14)
O1—Co1—O2	175.15 (5)	O2—Co1—N2	87.52 (8)
O1—Co1—O3	90.42 (9)	O3—Co1—O4	174.67 (5)
O1—Co1—O4	89.95 (8)	O3—Co1—N1	86.60 (7)
O1—Co1—N1	92.18 (8)	O3—Co1—N2	93.06 (7)
O1—Co1—N2	88.05 (8)	O4—Co1—N1	88.07 (7)
O2—Co1—O3	87.86 (9)	O4—Co1—N2	92.26 (7)
O2—Co1—O4	92.18 (8)	N1—Co1—N2	179.60 (8)
O2—Co1—N1	92.24 (8)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O8	0.82 (3)	1.75 (4)	2.557 (3)	171 (2)
O3—H13···O6^{i}	0.81 (5)	1.91 (5)	2.712 (3)	168 (4)
O8—H25···O5^{ii}	0.90 (2)	2.01 (2)	2.873 (2)	160 (3)
O8—H26···O5	0.92 (2)	1.84 (3)	2.745 (3)	169 (3)

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

It is supposed that the observed large intensity decay was caused by unexpected crystal-surface cracking. In fact, it seemed that the mounted crystal had been opaque slightly after the data collection. H atoms involved in hydrogen bonds were located in difference Fourier maps and refined with an isotropic displacement parameter [O1—

Acta Cryst. (2007). E**63**, m64–m66 Muto *et al.* • $[Co(C_{14}H_{12}NO_2)_2]NO_3 \cdot H_2O$ **m65**

H1 = 0.82 (3) Å, O3—H13 = 0.81 (5) Å]. O—H distances in the water molecule were restrained to ensure a reasonable distance [O8—H25 = 0.90 (2) Å, O8—H26 = 0.92 (2) Å] by applying an O—H DFIX restraint (Sheldrick, 1997) of 0.95 (2) Å. H atoms bound to C atoms were placed at geometrically calculated positions and included in the refinement in a riding-model approximation with the C—H bond distances equal to 0.93 or 0.97 Å. Their isotropic displacement parameters were set to be $1.2U_{eq}$ of the carrier atoms.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *CrystalStructure* (Rigaku/MSC, 2006); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Version 1.076; Farrugia, 1997); software used to prepare material for publication: *CrystalStructure*.

This work was supported by Grants-in-Aid for Science Research (C) (No.15510092).

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Jezowska-Trzebiatowska, B., Lisowski, J., Vogt, A. & Chmielewski, P. (1988). *Polyhedron*, **7**, 337–343.

Koikawa, M., Ohba, M. & Tokii, T. (2005). *Polyhedron*, **24**, 2257–2262.

Molecular Structure Corporation (1991). *MSC/AFC Diffractometer Control Software*. MSC, The Woodlands, Texas, USA.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Oshio, H., Nihei, M., Koizumi, S., Shiga, T., Nojiri, H., Nakano, M., Shirakawa, N. & Akatsu, M. (2005). *J. Am. Chem. Soc.* **127**, 4568–4569.

Rigaku/MSC (2006). *CrystalStructure*. Version 3.8.0. Rigaku/MSC, The Woodlands, Texas, USA.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

m66 Muto *et al.* • $[Co(C_{14}H_{12}NO_2)_2]NO_3·H_2O$ *Acta Cryst.* (2007). E**63**, m64–m66