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Aqua[bis(salicylidene)ethylenediaminato]-(isobutyl)cobalt(III)

HUILAN CHEN,^a DEYAN HAN,^a HONG YAN,^a WENXIA TANG,^a YAO YANG^b AND WENJUAN YANG^b

^aDepartment of Chemistry and Coordination State Key Laboratory, Nanjing University, Nanjing 210008, People's Republic of China, and ^bCentre of Material Analysis, Nanjing University, Nanjing 210008, People's Republic of China

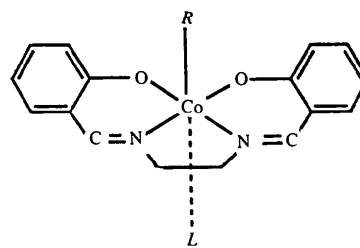
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Abstract

The title B₁₂ model compound, aqua{2,2'-[1,2-ethanediybis(nitrilomethylidene)]diphenolato-*N,N',O,O'*}(isobutyl)cobalt(III), [Co(C₄H₉)(C₁₆H₁₄N₂O₂)(H₂O)], has distorted octahedral stereochemistry around the Co^{III} ion. The equatorial salen ligand displays a 'stepped' conformation, which is the preferred conformation in penta- and hexacoordinate organocobalt-salen complexes. The axial Co—C bond length is close to that of coenzyme B₁₂ and in accordance with those of other B₁₂ models, but the difference in the axial Co—O bond length as well as the deviation from the ideal tetrahedral value of the Co—C—C angle are due to the *trans* influence of the axial isobutyl group, which has stronger σ -donor power.

Comment

The title compound, (1), was studied as a coenzyme B₁₂ model compound (Halpern, 1982).



(1) $R = i\text{Bu}$, $L = \text{H}_2\text{O}$

The X-ray analysis of (1) showed that the crystal consists of discrete molecules with distorted octahedral stereochemistry (Fig. 1). The salen ligand, coordinated to the Co^{III} ion *via* its two N and two O atoms, is in the equatorial plane, the atoms of which are coplanar to within ± 0.014 Å. One isobutyl group and one H₂O molecule occupy the two axial positions. The Co^{III} ion lies above the N₂O₂ mean plane by 0.078 Å, towards the isobutyl group. The isobutyl group is oriented with respect to the equatorial salen plane in such a way that it lies above and towards the plane through O1, N1, C1, C12, C16 and C11. As a result, the O1—Co—C5 and N1—Co—C5 angles are slightly larger than the O2—Co—C5 and N2—Co—C5 angles. The Co(salen) unit is significantly distorted from planarity, with an asymmetric 'stepped' conformation ($\alpha \neq \gamma$), while the ethylenediamine bridge assumes an asymmetric half-chair conformation,

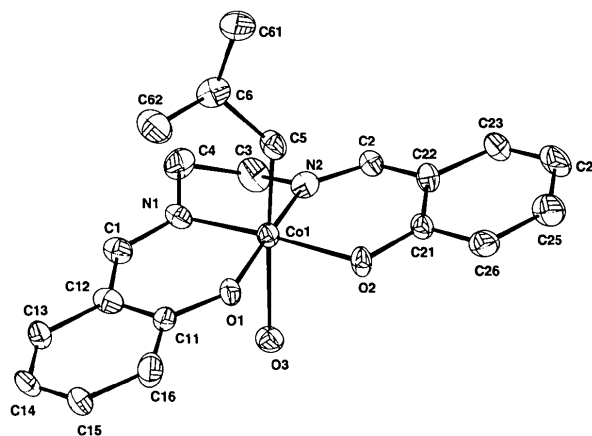


Fig. 1. A displacement ellipsoid (50% probability) plot of the title complex, with H atoms omitted for clarity.

The bond lengths between the Co^{III} ion and the salen ligand donor atoms are in agreement with the values found in other hexacoordinate organocobalt(III)-salen complexes. The bond lengths and angles of the equatorial salen ligand as well as the axial C—Co—O(H₂O)

angles are also comparable with those previously reported (Calligaris, Minichelli, Nardin & Randaccio, 1971). The Co—C bond length is in the range reported for organocobalt B₁₂ model compounds (1.9–2.0 Å) and close to the value reported for 5'-deoxyadenosylcobalamin [2.00 (1) Å; Savage, Lindley, Finney & Timmins, 1987]. The axial Co—O bond length is a little longer than that in [(CH₃COCH₂)Co(salen)(CH₃OH)] [2.202 (9) Å; Cesari, Neri, Perego, Perrotti & Zazzetta, 1970]. This difference may be ascribed to the different *trans* influences of the axial substituents and is in accordance with the strong σ -donor power of the isobutyl group. On the other hand, the Co—O bond in (1) is slightly shorter than that in [(C₂H₅)Co(salen)]₂ [2.342 (9) Å], which has a weak secondary Co—O coordination bridging the two halves of the dimer (Calligaris, Nardin & Randaccio, 1972).

The axial Co—C—C angle in (1) is found to be 126.9 (8)°, which is very close to the Co—C—C angle in B₁₂ coenzyme (*R* = 5'-deoxyadenosyl in scheme above) [124.0 (5)°; Savage, Lindley, Finney & Timmins, 1987]; they are both much larger than the expected value of 109.5°. Furthermore, a surprisingly large Co—C—C bond angle of 130 (4)° is also observed in an alkylcobaloxime compound with *R* = CH₂C(CH₃)₃ (Randaccio, Bresiani-Pahor, Toscano & Marzilli, 1981). These are presumably a result of the steric interaction of the bulky *R* group with the equatorial moiety. Generally, steric and electronic effects have to be taken into account in order to explain the large distortion of the axial alkyl and equatorial ligands in Schiff base B₁₂ models.

Experimental

The title complex was synthesized according to the method of Schrauzer, Sibert & Windgassen (1968) and slowly crystallized as purple brick-shaped crystals from methanol/water solution.

Crystal data

[Co(C₄H₉)(C₁₆H₁₄N₂O₂)-
(H₂O)]

M_r = 400.37

Monoclinic

*P*2₁

a = 11.378 (2) Å

b = 7.124 (1) Å

c = 11.585 (2) Å

β = 101.7 (8)°

V = 919 (3) Å³

Z = 2

D_x = 1.446 Mg m⁻³

D_m not measured

Data collection

Enraf–Nonius CAD-4
diffractometer

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25
reflections

θ = 10–12°

μ = 0.946 mm⁻¹

T = 293 K

Oblong

0.3 × 0.2 × 0.2 mm

Dark red

1461 observed reflections
[*I* > 3σ(*I*)]

ω -2 θ scans

Absorption correction:

empirical *via* ψ scan

(North, Phillips &

Mathews, 1968)

T_{min} = 0.67, *T_{max}* = 0.83

1855 measured reflections

1673 independent reflections

R_{int} = 0.019

θ_{max} = 25°

h = 0 → 13

k = 0 → 8

l = -13 → 13

3 standard reflections

frequency: 60 min

intensity decay: 10%

Refinement

Refinement on *F*

R = 0.053

wR = 0.067

S = 1.24

1461 reflections

315 parameters

H-atom parameters not
refined

w = 1/ σ^2 (*F*)

(Δ/σ)_{max} = 0.15

$\Delta\rho_{\text{max}}$ = 0.221 e Å⁻³

$\Delta\rho_{\text{min}}$ = -0.073 e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables*
for *X-ray Crystallography*
(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

	$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$			<i>B_{eq}</i>
	<i>x</i>	<i>y</i>	<i>z</i>	
Co	0.63986 (9)	0.128	0.16942 (9)	2.39 (2)
O1	0.6880 (5)	0.318 (1)	0.0744 (5)	3.2 (1)
O2	0.5112 (5)	0.291 (1)	0.1876 (5)	2.9 (1)
O3	0.5225 (6)	0.021 (1)	0.0059 (6)	3.3 (1)
N1	0.7539 (7)	-0.043 (1)	0.1408 (6)	2.8 (2)
N2	0.5871 (7)	-0.066 (1)	0.2533 (7)	2.8 (2)
C1	0.8163 (9)	-0.036 (2)	0.0586 (8)	3.2 (2)
C2	0.5077 (8)	-0.058 (2)	0.3216 (8)	3.3 (2)
C3	0.633 (1)	-0.251 (2)	0.231 (1)	4.1 (2)
C4	0.762 (1)	-0.218 (2)	0.211 (1)	4.1 (2)
C5	0.7373 (8)	0.240 (2)	0.3156 (8)	3.6 (2)
C6	0.868 (1)	0.209 (2)	0.364 (1)	4.0 (2)
C11	0.7580 (8)	0.295 (2)	-0.0020 (8)	3.0 (2)
C12	0.8220 (7)	0.130 (3)	-0.0133 (7)	3.7 (2)
C13	0.8931 (7)	0.125 (3)	-0.1009 (7)	4.6 (2)
C14	0.8987 (9)	0.270 (2)	-0.1738 (8)	5.0 (3)
C15	0.838 (1)	0.425 (2)	-0.1646 (9)	4.6 (3)
C16	0.7669 (9)	0.449 (2)	-0.079 (1)	4.6 (3)
C21	0.4470 (7)	0.272 (1)	0.2714 (7)	2.6 (2)
C22	0.4455 (7)	0.109 (1)	0.3388 (7)	2.8 (2)
C23	0.3712 (8)	0.115 (3)	0.4233 (8)	4.6 (2)
C24	0.3029 (9)	0.261 (2)	0.4395 (9)	5.4 (3)
C25	0.303 (1)	0.418 (2)	0.370 (1)	5.0 (3)
C26	0.3728 (9)	0.429 (2)	0.2869 (9)	3.9 (2)
C61	0.907 (1)	0.281 (3)	0.482 (1)	6.0 (3)
C62	0.946 (1)	0.301 (3)	0.286 (1)	6.4 (4)

Table 2. Selected geometric parameters (Å, °)

Co—N1	1.861 (8)	Co—N2	1.859 (8)
Co—O1	1.892 (7)	Co—O2	1.911 (6)
Co—C5	1.991 (9)	Co—O3	2.218 (6)
O1—C11	1.316 (12)	O2—C21	1.335 (11)
N1—C1	1.301 (13)	N2—C2	1.319 (13)
N1—C4	1.476 (14)	N2—C3	1.464 (14)
C1—C12	1.45 (2)	C2—C22	1.419 (15)
C3—C4	1.55 (2)	C5—C6	1.500 (14)
O1—Co—N1	94.0 (3)	O1—Co—O2	87.3 (3)
O1—Co—N2	176.0 (3)	O1—Co—O3	86.8 (3)
O1—Co—C5	91.9 (4)	O2—Co—N1	174.2 (3)

O2—Co—N2	93.2 (3)	O2—Co—O3	87.8 (3)
O2—Co—C5	88.3 (4)	O3—Co—N1	86.6 (3)
O3—Co—C5	175.9 (4)	O3—Co—N2	89.3 (3)
N1—Co—C5	97.3 (4)	N1—Co—N2	85.2 (4)
N2—Co—C5	92.1 (4)	Co—O1—C11	126.2 (7)
Co—O2—C21	124.5 (6)	Co—N1—C1	127.5 (7)
Co—N1—C4	115.1 (7)	Co—N2—C2	128.0 (7)
Co—N2—C3	114.3 (7)	C2—N2—C3	117.5 (9)
N1—C1—C12	123 (1)	N2—C2—C22	123 (1)
N2—C3—C4	105.9 (9)	N1—C4—C3	104.9 (8)
Co—C5—C6	126.9 (8)	C5—C6—C61	113 (1)
C5—C6—C62	111.0 (9)	C61—C6—C62	108 (1)

Intensity data were corrected for Lorentz and polarization effects, and corrected empirically for absorption. The Co atom was found by direct methods. Several cycles of difference Fourier syntheses revealed all the non-H atoms. Full-matrix least-squares refinement was performed with anisotropic displacement parameters for all non-H atoms. All H atoms were located in a difference Fourier map or calculated theoretically, except for the water H atoms. All calculations were performed on a PDP11/44 computer using the *SDP-Plus* (Frenz, 1985) program package.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1052). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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