Acta Cryst. (1995). C**51**, 206–207

trans-[Co(salen)(py)$_2$][BPh$_4$]

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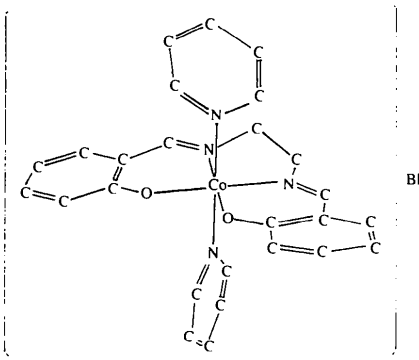
(*Received* 28 *April* 1994; *accepted* 5 *September* 1994)

Abstract

In the *trans*-{2,2′-[1,2-ethanediylbis(nitrilomethylidyne)]diphenolato-*O*,*O*′}bis(pyridine-*N*)cobalt(III) cation of the title compound, $[Co(C_{16}H_{14}N_2O_2)(C_5H_5N)_2]C_{24}H_{20}B$, the Co atom displays a tetragonally distorted octahedral coordination geometry with axial Co—N(py) (py = pyridine) bond lengths of 1.975 (3) and 1.987 (3) Å, rather longer than the equatorial Co—N(salen) distances of 1.880 (3) and 1.896 (4) Å.

Comment

The use of Fe^{II} complexes with N- and O-atom donor ligands for optical storage and optical filters has been investigated by Gutlich & Hauser (1989, and references therein). Since the Fe^{II} complexes are always air-sensitive, we chose to study Co^{III} systems with the same d^6 electronic configuration as Fe^{II}. Here we report the structure of *trans*-[Co(salen)(py)$_2$][BPh$_4$], (I).



(I)

X-ray characterization of the complex shows that the Co^{III} ion is in a pseudo-octahedral environment. The dihedral angle between the salen phenyl rings is 15.9°. The Co—N(salen) and Co—O(salen) bond lengths are almost equal, but are shorter than the Co—N(py) distances. Even longer Co—N(py) bond lengths are found in [Co(CH=CH$_2$)(salen)(py)], where py is *trans* to the strong σ-donor vinyl ligand (Calligaris, Nardin & Randaccio, 1972).

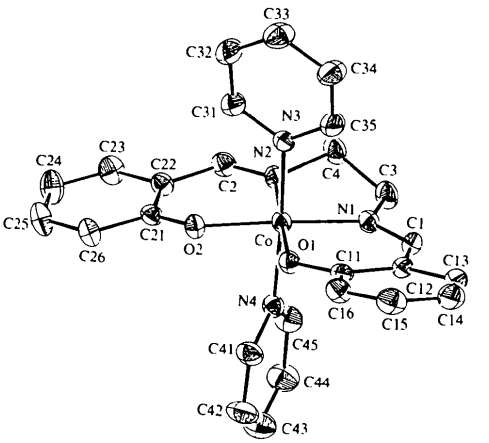


Fig. 1. Cation structure showing 30% probability displacement ellipsoids. H atoms are omitted for clarity.

Experimental

Synthesis of (I) was carried out by reacting $CoCl_2.6H_2O$, pyridine and H_2salen (molar ratio 1:1:2) in absolute alcohol, followed by the addition of an aqueous solution of $NaBPh_4$. Single crystals were formed by slowly diffusing petroleum into an acetone solution of the compound for a few days.

Crystal data

$[Co(C_{16}H_{14}N_2O_2)(C_5H_5N)_2]C_{24}H_{20}B$
M_r = 802.67
Monoclinic
$P2_1/c$
a = 16.74 (1) Å
b = 13.570 (4) Å
c = 19.65 (2) Å
β = 113.22 (9)°
V = 4102 (5) Å^3
Z = 4
D_x = 1.30 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 13.99–14.74°
μ = 0.460 mm^{-1}
T = 296 K
Prism
0.45 × 0.27 × 0.22 mm
Dark brown

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
T_{min} = 0.952, T_{max} = 1.000
7806 measured reflections
7563 independent reflections
4912 observed reflections [$I \geq 3\sigma(I)$]
R_{int} = 0.00469
θ_{max} = 25°
$h = -19 \rightarrow 0$
$k = 0 \rightarrow 16$
$l = -23 \rightarrow 23$
3 standard reflections
frequency: 60 min
intensity decay: 4%

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.003$
$R = 0.048$	$\Delta\rho_{max} = 0.27$ e Å^{-3}
$wR = 0.056$	$\Delta\rho_{min} = -0.25$ e Å^{-3}
$S = 1.17$	Extinction correction: none
4728 reflections	Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)
523 parameters	
Only H-atom U's refined	
$w = 1/\sigma^2(\|F_o\|)$	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
Co	0.30242 (3)	0.41913 (4)	0.24672 (3)	2.62 (2)
O(1)	0.4070 (1)	0.4136 (2)	0.2318 (1)	3.0 (1)
O(2)	0.3645 (1)	0.3547 (2)	0.3370 (1)	3.0 (1)
N(1)	0.2379 (2)	0.4771 (2)	0.1533 (2)	3.0 (1)
N(2)	0.2001 (2)	0.4329 (2)	0.2638 (2)	3.1 (1)
C(1)	0.2669 (3)	0.4999 (3)	0.1036 (2)	3.3 (2)
C(2)	0.1851 (2)	0.3963 (3)	0.3181 (2)	3.7 (2)
C(3)	0.1448 (3)	0.4935 (3)	0.1379 (2)	4.0 (2)
C(4)	0.1378 (3)	0.5022 (3)	0.2118 (2)	4.4 (2)
C(11)	0.4215 (2)	0.4548 (3)	0.1769 (2)	3.1 (1)
C(12)	0.3553 (2)	0.4934 (3)	0.1120 (2)	3.0 (1)
C(13)	0.3775 (3)	0.5362 (3)	0.0569 (2)	3.9 (2)
C(14)	0.4623 (3)	0.5430 (3)	0.0641 (3)	4.7 (2)
C(15)	0.5273 (3)	0.5056 (3)	0.1282 (3)	4.7 (2)
C(16)	0.5076 (3)	0.4620 (3)	0.1826 (2)	3.7 (2)
C(21)	0.3294 (2)	0.3155 (3)	0.3798 (2)	3.0 (1)
C(22)	0.2437 (2)	0.3338 (3)	0.3747 (2)	3.2 (2)
C(23)	0.2155 (3)	0.2936 (3)	0.4274 (3)	4.3 (2)
C(24)	0.2687 (3)	0.2344 (4)	0.4832 (3)	5.0 (2)
C(25)	0.3517 (3)	0.2139 (3)	0.4871 (3)	4.9 (2)
C(26)	0.3818 (3)	0.2532 (3)	0.4376 (2)	3.9 (2)
N(3)	0.3438 (2)	0.5484 (2)	0.2955 (2)	3.0 (1)
C(31)	0.3659 (3)	0.5592 (3)	0.3680 (2)	4.0 (2)
C(32)	0.4052 (3)	0.6428 (3)	0.4067 (2)	4.7 (2)
C(33)	0.4240 (3)	0.7187 (3)	0.3700 (3)	5.1 (2)
C(34)	0.4010 (4)	0.7095 (3)	0.2951 (3)	5.6 (2)
C(35)	0.3611 (3)	0.6245 (3)	0.2601 (2)	4.8 (2)
N(4)	0.2720 (2)	0.2858 (2)	0.2041 (2)	3.1 (1)
C(41)	0.3371 (3)	0.2242 (3)	0.2096 (2)	4.3 (2)
C(42)	0.3235 (3)	0.1304 (3)	0.1814 (3)	5.4 (2)
C(43)	0.2397 (4)	0.0961 (4)	0.1463 (3)	5.8 (3)
C(44)	0.1731 (3)	0.1574 (4)	0.1408 (3)	5.3 (2)
C(45)	0.1912 (3)	0.2502 (3)	0.1712 (2)	4.3 (2)
B	0.8438 (3)	0.2122 (3)	1.0254 (3)	2.7 (2)
C(51)	0.8873 (2)	0.2413 (3)	0.9657 (2)	2.8 (1)
C(52)	0.9723 (2)	0.2774 (3)	0.9923 (3)	3.6 (2)
C(53)	1.0155 (3)	0.2998 (3)	0.9463 (3)	4.3 (2)
C(54)	0.9743 (3)	0.2848 (3)	0.8712 (3)	4.5 (2)
C(55)	0.8911 (3)	0.2490 (3)	0.8426 (2)	4.1 (2)
C(56)	0.8483 (2)	0.2282 (3)	0.8891 (2)	3.3 (2)
C(61)	0.7480 (2)	0.1594 (3)	0.9827 (2)	2.8 (1)
C(62)	0.6791 (2)	0.2137 (3)	0.9312 (2)	3.7 (2)
C(63)	0.5969 (3)	0.1731 (4)	0.8933 (2)	4.3 (2)
C(64)	0.5804 (3)	0.0766 (4)	0.9047 (2)	4.5 (2)
C(65)	0.6458 (3)	0.0216 (3)	0.9551 (2)	3.9 (2)
C(66)	0.7280 (2)	0.0625 (3)	0.9934 (2)	3.3 (2)
C(71)	0.8301 (2)	0.3097 (3)	1.0693 (2)	2.8 (1)
C(72)	0.7770 (3)	0.3032 (3)	1.1098 (2)	3.6 (2)
C(73)	0.7600 (3)	0.3831 (3)	1.1461 (2)	4.3 (2)
C(74)	0.7947 (3)	0.4738 (3)	1.1438 (2)	4.6 (2)
C(75)	0.8488 (3)	0.4830 (3)	1.1067 (2)	4.4 (2)
C(76)	0.8665 (3)	0.4026 (3)	1.0708 (2)	3.5 (2)
C(81)	0.9127 (2)	0.1348 (3)	1.0838 (2)	2.6 (1)
C(82)	0.9529 (2)	0.1485 (3)	1.1603 (2)	3.4 (2)
C(83)	1.0108 (3)	0.0795 (3)	1.2062 (2)	3.9 (2)
C(84)	1.0300 (3)	−0.0055 (3)	1.1790 (2)	3.8 (2)
C(85)	0.9923 (2)	−0.0218 (3)	1.1030 (2)	3.5 (2)
C(86)	0.9354 (2)	0.0480 (3)	1.0572 (2)	3.1 (1)

Table 2. *Selected geometric parameters* (Å, °)

Co—N(2)	1.880 (3)	C(3)—C(4)	1.506 (6)
Co—O(2)	1.881 (3)	N(3)—C(31)	1.333 (5)
Co—O(1)	1.887 (3)	N(3)—C(35)	1.339 (5)
Co—N(1)	1.896 (4)	C(31)—C(32)	1.379 (6)
Co—N(4)	1.975 (3)	C(32)—C(33)	1.364 (6)
Co—N(3)	1.987 (3)	C(33)—C(34)	1.372 (6)
O(1)—C(11)	1.319 (4)	C(34)—C(35)	1.375 (6)
O(2)—C(21)	1.314 (4)	N(4)—C(45)	1.338 (5)
N(1)—C(1)	1.287 (5)	N(4)—C(41)	1.342 (5)
N(1)—C(3)	1.482 (5)	C(41)—C(42)	1.371 (6)
N(2)—C(2)	1.287 (5)	C(42)—C(43)	1.387 (7)
N(2)—C(4)	1.475 (5)	C(43)—C(44)	1.360 (7)
C(1)—C(12)	1.425 (5)	C(44)—C(45)	1.376 (6)
C(2)—C(22)	1.434 (5)		
N(2)—Co—O(2)	94.7 (1)	N(1)—C(1)—C(12)	125.5 (4)
N(2)—Co—O(1)	176.3 (1)	N(2)—C(2)—C(22)	125.0 (4)
N(2)—Co—N(1)	85.5 (2)	N(1)—C(3)—C(4)	106.9 (3)
N(2)—Co—N(4)	93.8 (1)	N(2)—C(4)—C(3)	108.4 (3)
N(2)—Co—N(3)	89.7 (1)	O(1)—C(11)—C(16)	118.6 (4)
O(2)—Co—O(1)	85.8 (1)	O(1)—C(11)—C(12)	124.0 (3)
O(2)—Co—N(1)	176.8 (1)	C(31)—N(3)—C(35)	116.4 (4)
O(2)—Co—N(4)	85.9 (1)	C(31)—N(3)—Co	120.7 (3)
O(2)—Co—N(3)	89.9 (1)	C(35)—N(3)—Co	122.4 (3)
O(1)—Co—N(1)	94.3 (1)	N(3)—C(31)—C(32)	123.5 (4)
O(1)—Co—N(4)	89.8 (1)	C(33)—C(32)—C(31)	119.3 (4)
O(1)—Co—N(3)	86.7 (1)	C(32)—C(33)—C(34)	118.2 (4)
N(1)—Co—N(4)	90.9 (1)	C(33)—C(34)—C(35)	119.3 (4)
N(1)—Co—N(3)	93.3 (1)	N(3)—C(35)—C(34)	123.4 (4)
N(4)—Co—N(3)	174.7 (1)	C(45)—N(4)—C(41)	116.6 (3)
C(11)—O(1)—Co	126.3 (2)	C(45)—N(4)—Co	125.3 (3)
C(21)—O(2)—Co	124.9 (2)	C(41)—N(4)—Co	118.1 (3)
C(1)—N(1)—C(3)	119.3 (3)	N(4)—C(41)—C(42)	123.0 (4)
C(1)—N(1)—Co	126.4 (3)	C(41)—C(42)—C(43)	119.4 (4)
C(3)—N(1)—Co	114.2 (3)	C(44)—C(43)—C(42)	118.3 (4)
C(2)—N(2)—C(4)	120.3 (3)	C(43)—C(44)—C(45)	119.4 (4)
C(2)—N(2)—Co	126.8 (3)	N(4)—C(45)—C(44)	123.3 (4)
C(4)—N(2)—Co	112.6 (3)		

All non-H atoms were located by direct methods and difference Fourier synthesis. The structure was refined on F by full-matrix least-squares techniques. All calculations were performed using *TEXSAN* (Molecular Structure Corporation, 1987) on a MicroVAX 3100 computer.

This work is supported by grants from the State Science and Technology Commission and The National Nature Science Foundation of China.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, least-squares-planes data and complete geometry have been deposited with the IUCr (Reference: MU1116). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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