Unusual coordination mode of tetradentate Schiff base cobalt(III) complexes

Anish Cyriac,[a] Jong Yeob Jeon,[a] Jobi Kodiyan Varghese,[a] Ji Hae Park,[a] Soo Young Choi,[b] Young Keun Chung,[b] and Bun Yeoul Lee[a]*

[a]Department of Molecular Science and Technology, Ajou University, Suwon, 443-749, South Korea;
[b]Department of Chemistry, Seoul National University, Silimdong Gwanak-gu, Seoul 151-747 Korea

Supporting Information

General Remarks. CH_2Cl_2, CD_2Cl_2 and $CDCl_3$ were dried by stirring over CaH_2, and they were subsequently vacuum-transferred to reservoirs. THF-d_8 was dried over KH and filtered. The dmso-d_6 was dried over molecular sieves 3A. The ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Varian Mercury Plus 400. Elemental analyses were carried out at the Analytical Center, Kyunghee University.

X-ray Crystallography. Single crystal diffraction data were measured by an Bruker-Nonius CCD single-crystal X-ray diffractometer at room temperature (293K) using graphite-monochromated MoKα radiation (λ = 0.71073 Å). Preliminary orientation matrices and unit cell parameters were obtained from the peaks of the first 10 frames and then refined using the whole data set. Frames were integrated and corrected for Lorentz and polarization effects using DENZO. The structure was solved by direct or patterson methods using SHELXS-97 and refined by full-matrix least-squares with SHELXL-97. All non-hydrogen atoms were refined anisotropically. Some of hydrogen atoms were found during refinement. Crystallographic parameters for (Me-salcy)Co(OAc)·2(HOAc), (Me-salcy)Co(κ^2-OAc), (Me-salcy)Co(κ^2-NO_3), (Me-salen)Co(OAc)(H_2O) and (Me-sal-*cis*-cy)Co(II) are summarized in Table S1 and S2.

Table S1. Crystallographic parameters for (Me-salcy)Co(OAc)·2(HOAc), (Me-salcy)Co(κ^2-OAc) and (Me-salcy)Co(κ^2-NO_3)

	(Me-salcy)Co(OAc)·2(HOAc)	(Me-salcy) Co(κ^2-OAc)	(Me-salcy) Co(κ^2-NO_3)
Formula	$C_{30}H_{39}Co\ N_2O_8$	$C_{26}H_{31}Co\ N_2O_4 \cdot CH_2Cl_2$	$C_{24}H_{28}Co\ N_3O_5$
Fw	614.56	579.38	497.42
a, Å	11.6690(6)	11.0257(4)	12.1174(9)
b, Å	17.5399(13)	12.2862(4)	10.9880(8)
c, Å	16.0611(11)	12.3223(4)	17.4499(11)
α, deg	90	82.506(2)	90
β, deg	110.763(4)	65.358(2)	95.855(4)
γ, deg	90	66.712(2)	90
V, Å^3	3073.8(3)	1392.42(8)	2311.3(3)
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	P 2_1/c	P -1	P 2_1/c
D(calc),mg m^{-3}	1.328	1.382	1.430
Z	4	2	4
μ, mm^{-1}	0.609	0.843	0.783
No. of data collected	9388	9154	9108
No. of unique data [R(int)]	5539(0.0335)	6350 (0.0242)	5274 (0.0762)
No. of variables	381	330	302
Final R indices (I>2σ(I))	R_1 = 0.0650, wR_2 = 0.1623	R_1 = 0.0575, wR_2 = 0.1499	R_1 = 0.0606, wR_2 = 0.0977
R indices (all data)	R_1 = 0.0957, wR_2 = 0.1813	R_1 = 0.0796, wR_2 = 0.1651	R_1 = 0.1566, wR_2 = 0.1216
Goodness of fit	1.038	1.029	0.966

Table S2. Crystallographic parameters for (Me-salen)Co(OAc)(H_2O) and (Me-sal-*cis*-cy)Co(II)

	(Me-salen)Co(OAc)(H_2O)	(Me-sal-*cis*-cy)Co(II)
Formula	$C_{45}\ H_{59}\ Cl_2\ Co_2\ N_4\ O_{11.50}$	$C_{24}H_{28}Co\ N_2O_2$
Fw	1028.72	435.41
a, Å	11.9561(9)	13.5058(4)
b, Å	15.1436(11)	8.7766(4)
c, Å	15.2435(8)	18.0814(7)
α, deg	92.675(4)	90
β, deg	92.569(4)	96.924(2)
γ, deg	110.492(3)	90
V, Å^3	2577.0(3)	2127.65(14)
Crystal system	Triclinic	Monoclinic
Space group	P -1	P 2_1/n
D(calc),mg m^{-3}	1.326	1.359
Z	2	4
μ, mm^{-1}	0.805	0.829
No. of data collected	15632	7867
No. of unique data [R(int)]	10799 (0.0997)	4861 (0.0265)
No. of variables	605	266
Final R indices (I>2σ(I))	R_1 = 0.1130, wR_2 = 0.2840	R_1 = 0.0391, wR_2 = 0.0872
R indices (all data)	R_1 = 0.2889, wR_2 = 0.3760	R_1 = 0.0618, wR_2 = 0.0956
Goodness of fit	1.015	1.030

(Me-salen)(H)$_2$. 3,5-Dimethyl-2-hydroxybenzaldehyde was prepared according to the reported method.[1] 3,5-Dimethyl-2-hydroxybenzaldehyde (1.00 g, 6.66 mmol) was weighed into a 50 mL round bottom flask inside a glove box, and then ethylenediamine (200 mg, 3.33 mmol) and methylene chloride (10 mL) were added. The reaction mixture was stirred overnight at room temperature. The solution was filtered through Celite and solvent was removed under reduced pressure. Yellow solid was obtained in quantitative yield which was pure enough to use without further purification. IR (KBr): 3453 (OH), 1632 (C=N) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 13.23 (br, s, 2H, OH), 8.29 (s, 2H, N=CH), 7.01 (s, 2H), 7.87 (s, 2H), 3.92 (s, 4H, N-CH_2), 2.27 (s, 12H, CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 166.45, 156.87, 134.31, 129.06, 127.02, 125.44, 117.51, 59.96 (N-CH), 20.52, 15.69 ppm. Anal. Calc. ($C_{20}H_{24}N_2O_2$): C, 74.04; H, 7.46; N, 8.64 %. Found: C, 74.16; H, 7.50; N, 8.73 %.

(Me-sal-*cis*-cy)(H)$_2$. This compound was prepared by the same procedure as that of (Me-salen)(H)$_2$, using *cis*-1,2-diaminocyclohexane instead of ethylenediamine. Yellow solid was obtained in quantitative yield which was pure enough to use without further purification. IR (KBr): 3475 (OH), 1637 (C=N) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 13.42 (s, 2H, OH), 8.28 (s, 2H, N=CH), 6.99 (s, 2H), 6.88 (s, 2H), 3.58 (m, 2H, N-CH), 2.26 (s, 6H, CH_3), 2.23 (s, 6H, CH_3), 1.93 (br, 4H, CH_2), 1.76 (m, 2H, CH_2) 1.59 (m, 2H, CH_2) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 164.14, 157.12, 134.16, 129.09, 126.83, 125.49, 117.76, 69.70, 30.86, 22.84, 20.55, 15.72 ppm. Anal. Calc. ($C_{24}H_{30}N_2O_2$): C, 76.16; H, 7.99; N, 7.40 %. Found: C, 75.85; H, 7.97; N, 7.49 %.

(Me-salcy)Co(OAc)·2(HOAc). (Me-salcy)(H)$_2$ was prepared according to the reported method.[2] To a flask containing (Me-salcy)(H)$_2$ (830 mg, 2.19 mmol) and Co(OAc)$_2$ (388 mg, 2.19 mmol), methylene chloride (8 mL) was added. After stirring for 20 min, glacial acetic acid (660 mg, 11.0 mmol) in methylene chloride (2 mL) was added and the resulting solution was stirred under O_2 atmosphere for 12 hours. Solvent was removed by vacuum. After dissolving the residue in methylene chloride again, pentane was layered to diffuse slowly. Crystals were deposited in 2 days. ^{1}H NMR (CD_2Cl_2): δ 13.01 (br, 2H, OH), 7.45 (s, 2H, N=CH), 7.16 (s, 2H), 7.10 (s, 2H), 4.01 (br, 2H, N-CH), 2.93 (br, 2H, CH_2), 2.62 (s, 6H, CH_3), 2.43 (s, 6H,

CH_3), 2.07 (br, 2H, CH_2), 1.99 (br, 2H, CH_2), 1.77 (s, 9H, acetate-CH_3), 1.61 (br, 2H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 180.32 (CO), 163.29, 158.33, 136.45, 131.92, 131.19, 125.93, 119.71, 70.90 (N-CH), 30.14 (CH_2), 25.07 (CH_2), 22.41 (acetate-CH_3), 20.03 (CH_3), 17.01 (CH_3). Anal. Calc. ($C_{30}H_{39}CoN_2O_8$): C, 58.63; H, 6.40; N, 4.56 %. Found: C, 58.39; H, 6.34; N, 4.33 %.

(Me-salcy)Co(κ^2-OAc). Two more successive crystallization of (Me-salcy)Co(OAc)·2(HOAc) gave the crystals of (Me-salcy)Co(κ^2-OAc). When **(**Me-salcy)Co(OAc)·2(HOAc) was triturated in diethyl ether for several hours, (Me-salcy)Co(κ^2-OAc) was isolated as powder. ^1H NMR (CD_2Cl_2): δ 7.43 (s, 1H, N=CH), 7.29 (s, 1H, N=CH), 7.12 (s, 1H), 7.02 (s, 1H), 6.90 (s, 1H), 6.80 (s, 1H), 4.23 (br, 1H, N-CH), 3.16 (br, 1H, N-CH), 2.72 (br, 2H, CH_2), 2.50 (s, 3H, CH_3), 2.29 (br, s, 3H, CH_3), 2.25 (br, s, 3H, CH_3), 1.99 (br, 5H, CH_3 and CH_2), 1.68 (s, 3H, acetate-CH_3), 1.58 (br, 4H, CH_2) ppm. ^1H NMR (THF-d_8): δ 7.54 (s, 1H, N=CH), 7.30 (s, 1H, N=CH), 6.99 (s, 1H), 6.94 (s, 1H), 6.74 (s, 1H), 6.70 (s, 1H), 4.10 (br, 1H, N-CH), 2.97 (br, 1H, N-CH), 2.74 (br, 1H, CH_2), 2.67 (br, 1H, CH_2), 2.44 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 2.16 (s, 3H, CH_3), 1.97 (s, 3H, CH_3),1.93 (br, 2H, CH_2), 1.85 (br, 2H, CH_2), 1.53 (s, 3H, acetate-CH_3), 1.44 (br, 2H, CH_2) ppm. In dmso-d_6, two sets of signals were observed in 1:0.09 ratio. Data for the major set: δ 7.78 (s, 1H, N=CH), 7.74 (s, 1H, N=CH), 7.10 (s, 1H), 7.07 (s, 1H), 7.03 (s, 1H), 7.00 (s, 1H), 3.77 (br, 1H, N-CH), 3.53 (br, 1H, N-CH), 2.95 (br, 2H, CH_2), 2.53 (s, 3H, CH_3), 2.49 (s, 3H, CH_3), 2.19 (s, 6H, CH_3), 1.96 (br, 2H, CH_2), 1.79 (br 2H, CH_2), 1.58 (s, 3H, acetate-CH_3), 1.51 (br, 2H, CH_2) ppm. Data for the minor set: δ 7.91 (s, 2H, N=CH), 7.22 (s, 2H), 7.14 (s, 2H), 3.56 (br, 2H, N-CH), 2.58 (s, 6H, CH_3), 2.24 (s, 6H, CH_3), 2.19 (s, 3H, acetate-CH_3), 2.00-1.50 (br, 8H, CH_2) ppm. Anal. Calc. ($C_{26}H_{31}CoN_2O_4$): C, 63.15; H, 6.32; N, 5.67 %. Found: C, 63.02; H, 6.28; N, 5.72 %.

(Me-salen)Co(OAc)(H_2O). This complex can be prepared by the same procedure as that of (Me-salcy)Co(OAc)·2(HOAc) using (Me-salen)$(H)_2$. Removal of solvent gave (Me-salcy)Co(OAc)·2(HOAc). (550 mg, 95%). Repeated recrystallization twice times by layer-diffusion in methylene chloride/pentane gave (Me-salen)Co(OAc)·(HOAc), of which composition was inferred from the integration value in the ^1H NMR

spectrum. Repeated recrystallization five times yielded (Me-salen)Co(OAc)(H_2O), of which structure was proved by the X-ray crystallography. Data for (Me-salen)Co(OAc)·HOAc: ^{1}H NMR (CD_2Cl_2), δ 7.39 (s, 2H, N=CH), 7.11 (s, 2H), 7.05 (s, 2H), 4.38 (br, 4H, N-CH), 2.56 (s, 6H, CH_3), 2.50 (s, 6H, CH_3), 1.78 (s, 6H, acetate-CH_3) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 180-184 (br, CO), 166.65, 158.60, 135.88, 132.25, 129.73, 126.27, 121.11, 59.73 (N-CH), 23-27 (acetate-CH_3), 19.75 (CH_3), 16.99 (CH_3) ppm. Anal. Calc. ($C_{24}H_{29}CoN_2O_6$): C, 57.60; H, 5.84; N, 5.60 %. Found: C, 57.39; H, 5.82; N, 5.71 %. In the ^{1}H NMR spectrum in dmso-d_6, two sets of signals were observed in 1:0.39 ratio. Data for the major set: δ 8.01 (s, 2H, N=CH), 7.03 and 6.97 (s, 4H), 4.21 (AA'BB', 2H, N-CH), 4.05 (AA'BB', 2H, N-CH), 2.52 (s, 6H, CH_3), 2.20 (s, 6H, CH_3), 1.51 (s, 3H, acetate-CH_3) ppm. Data for the minor set: δ 8.01 (s, 2H, N=CH), 7.16 (s, 2H), 7.10 (s, 2H), 4.16 (s, 4H, N-CH_2), 2.60 (s, 6H, CH_3), 2.26 (s, 6H, CH_3), 1.51 (s, 3H, acetate-CH_3) ppm.

(Me-sal-*cis*-cy)Co(OAc)·2(HOAc). This complex can be prepared by the same procedure as that of (Me-salcy)Co(OAc)·2(HOAc) using (Me-sal-*cis*-cy)$(H)_2$. Yield was 93%. ^{1}H NMR (CD_2Cl_2): δ 13.60 (br, 2H, OH), 7.41(s, 2H), 7.28 (s, 2H), 6.17 (br, 2H, N=CH), 4.94 (br, 2H, N-CH), 3.32 (br, 6H, CH_3), 2.96 (s, 6H, CH_3), 2.12 (br, 4H, CH_2), 1.72 (s, 9H, acetate-CH_3), 1.66 (br, 2H, CH_2), 1.60 (br, 2H, CH_2) ppm. Anal. Calc. ($C_{30}H_{39}CoN_2O_8$): C, 58.63; H, 6.40; N, 4.56 %. Found: C, 58.31; H, 6.36; N, 4.61 %.

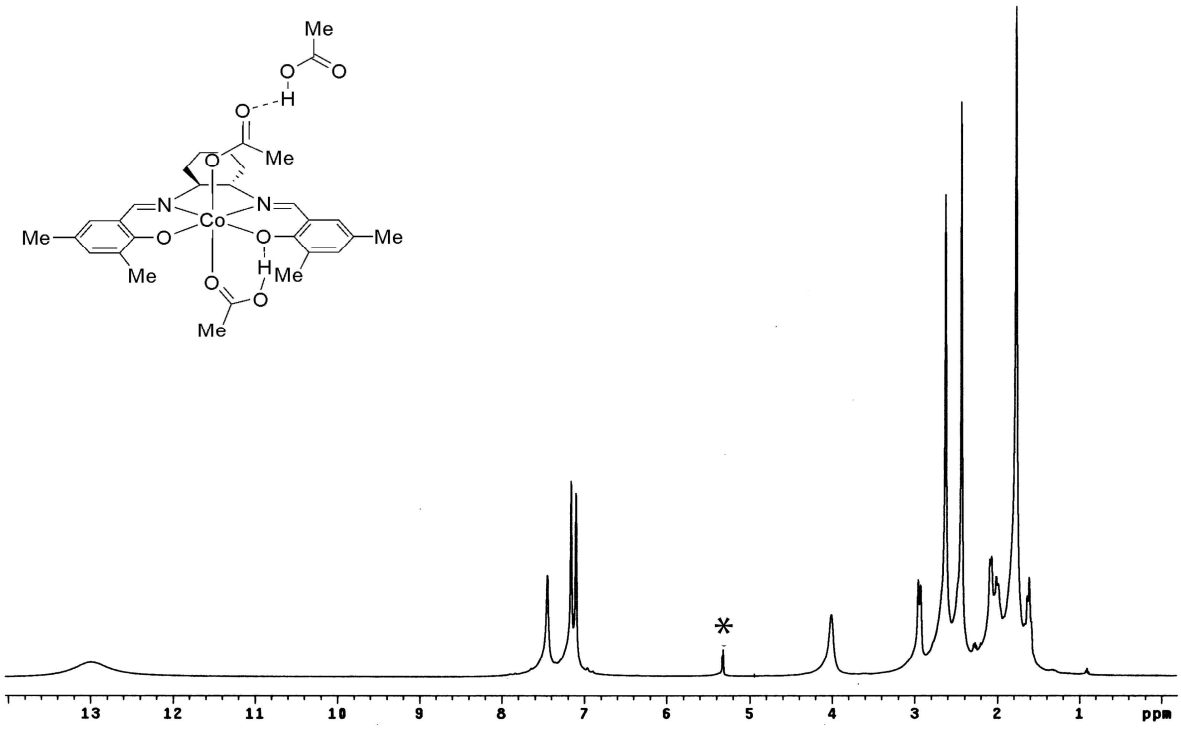
References

[1] P. D. Knight, P. N. O'Shaughnessy, I. J. Munslow, B. S. Kimberley, P. Scott, *J. Organomet. Chem.* **2003**, *683*, 103-113.

[2] P. J. Pospisil, D. H. Carsten, E. N. Jacobsen, *Chem. Eur. J.* **1996**, *2*, 974-980.

< The ^{1}H spectrum of (Me-salcy)Co(OAc)·2(HOAc) in CD_2Cl_2>

Signals marked with "*" and "#" are the deuterated solvent signals and the residual solvent (or water) signals, respectively.



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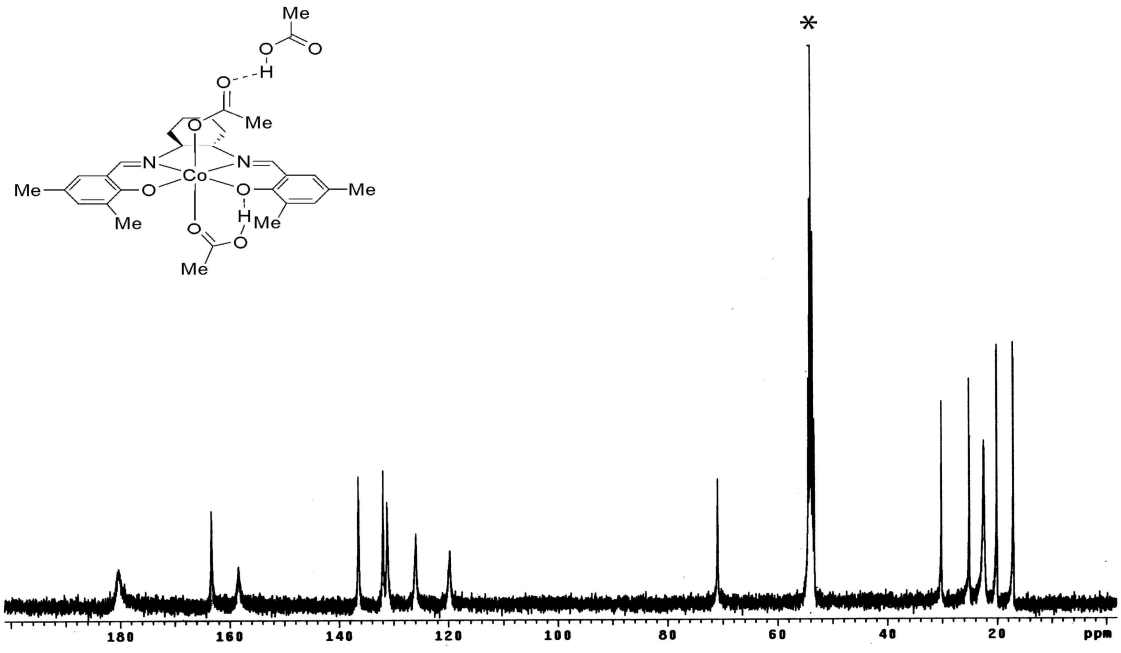

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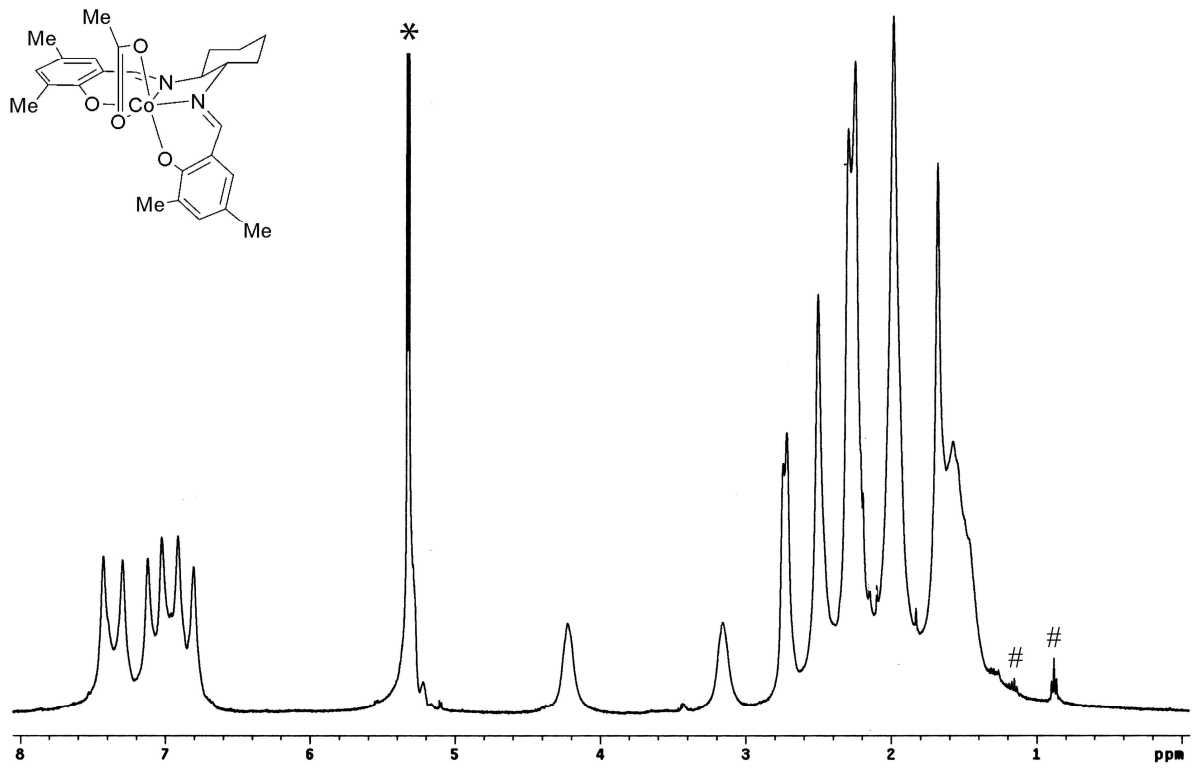

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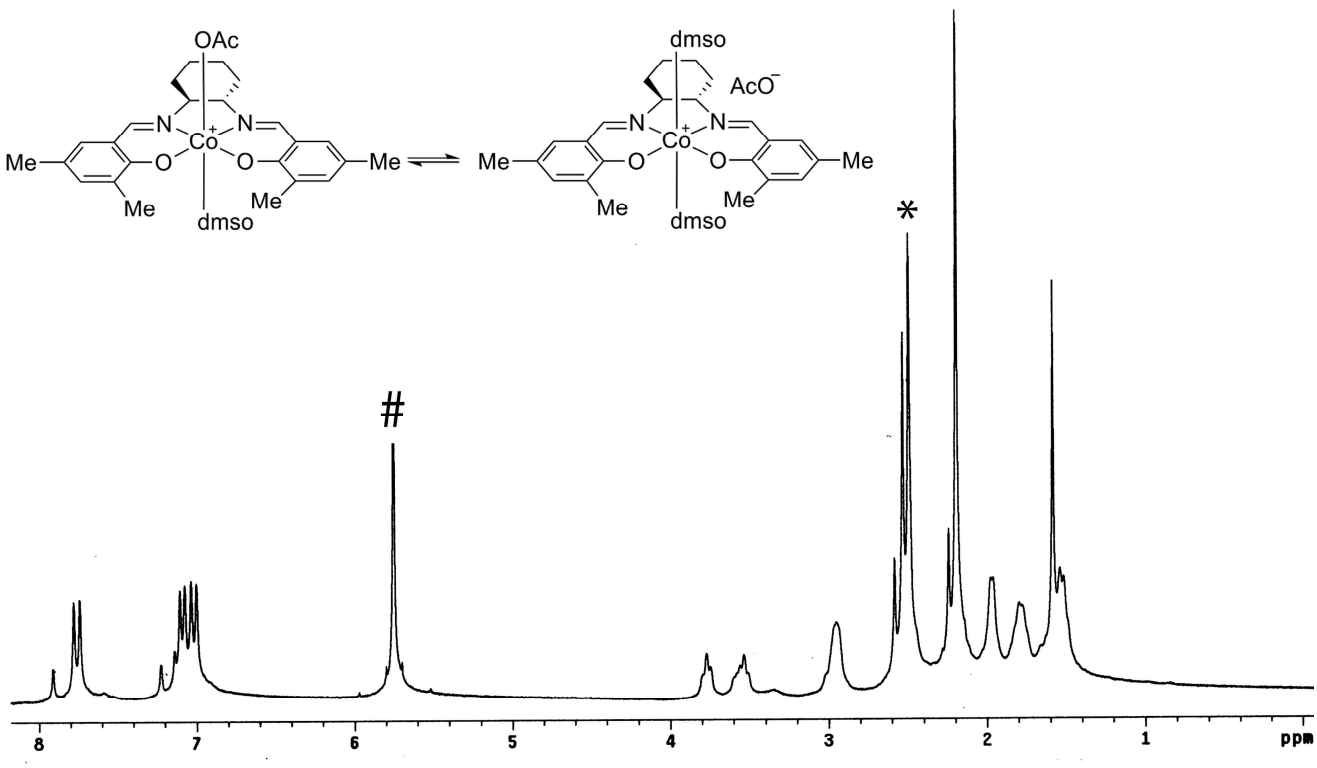

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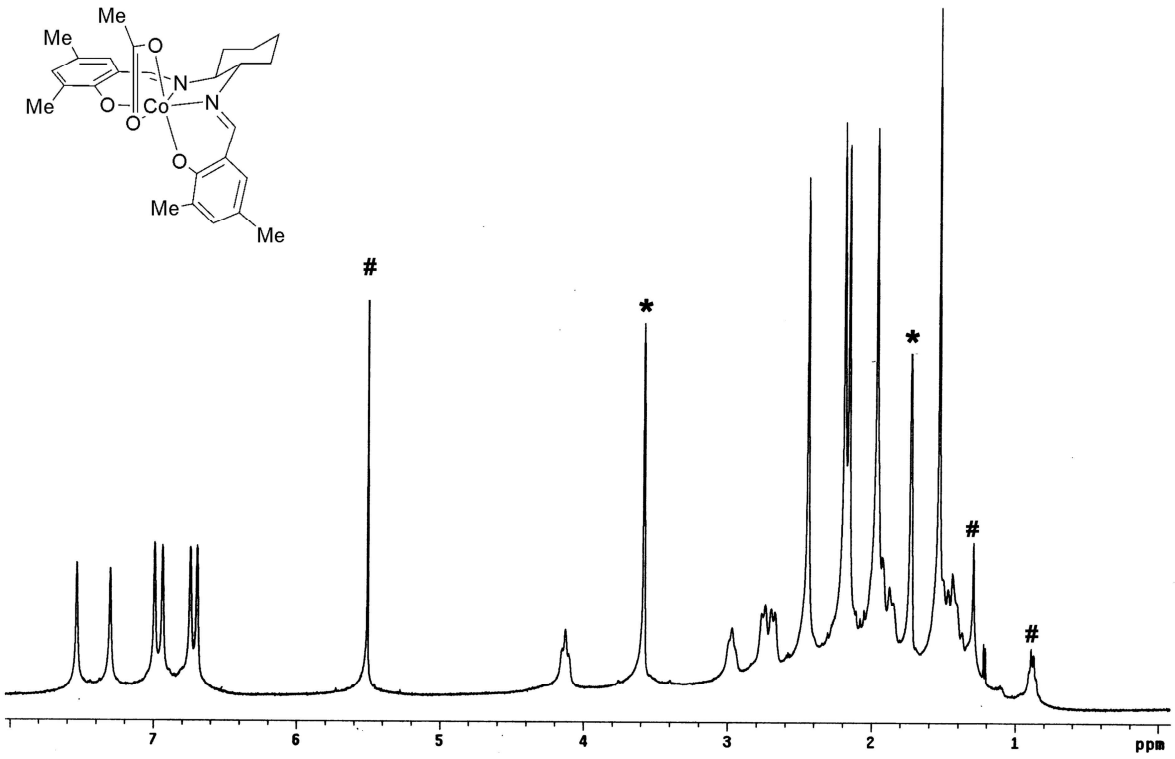

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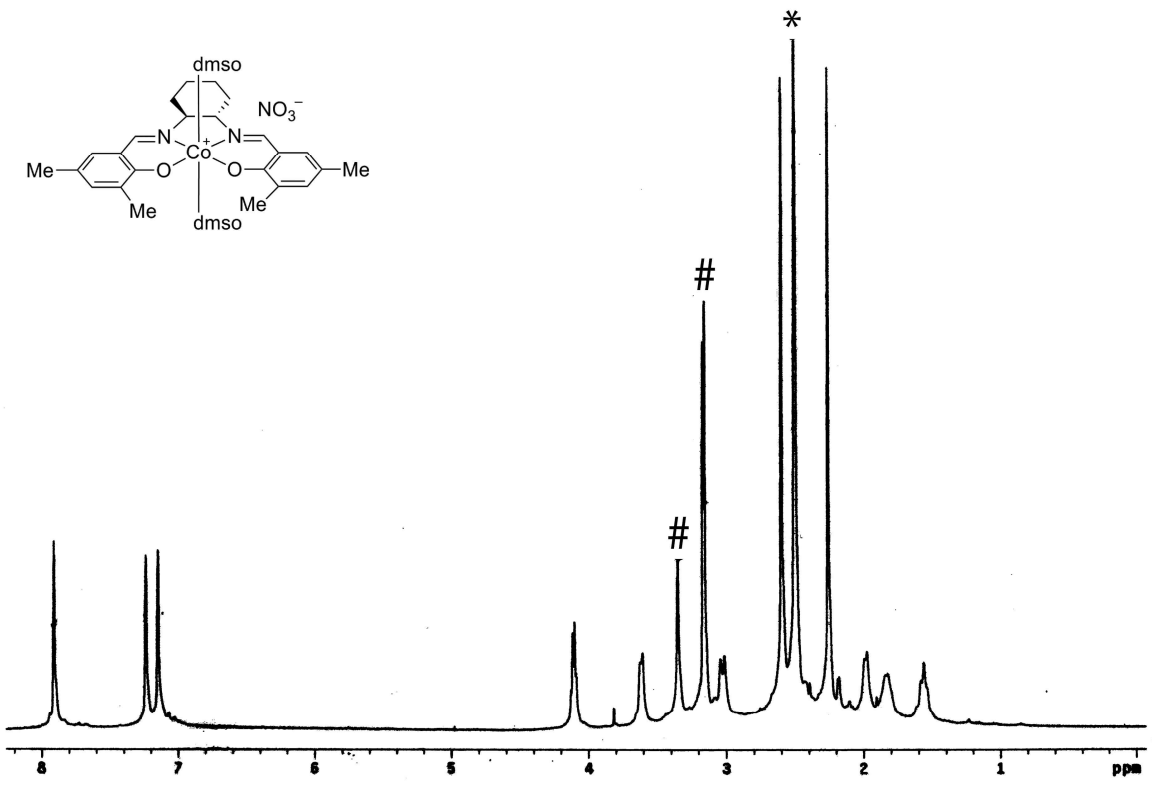

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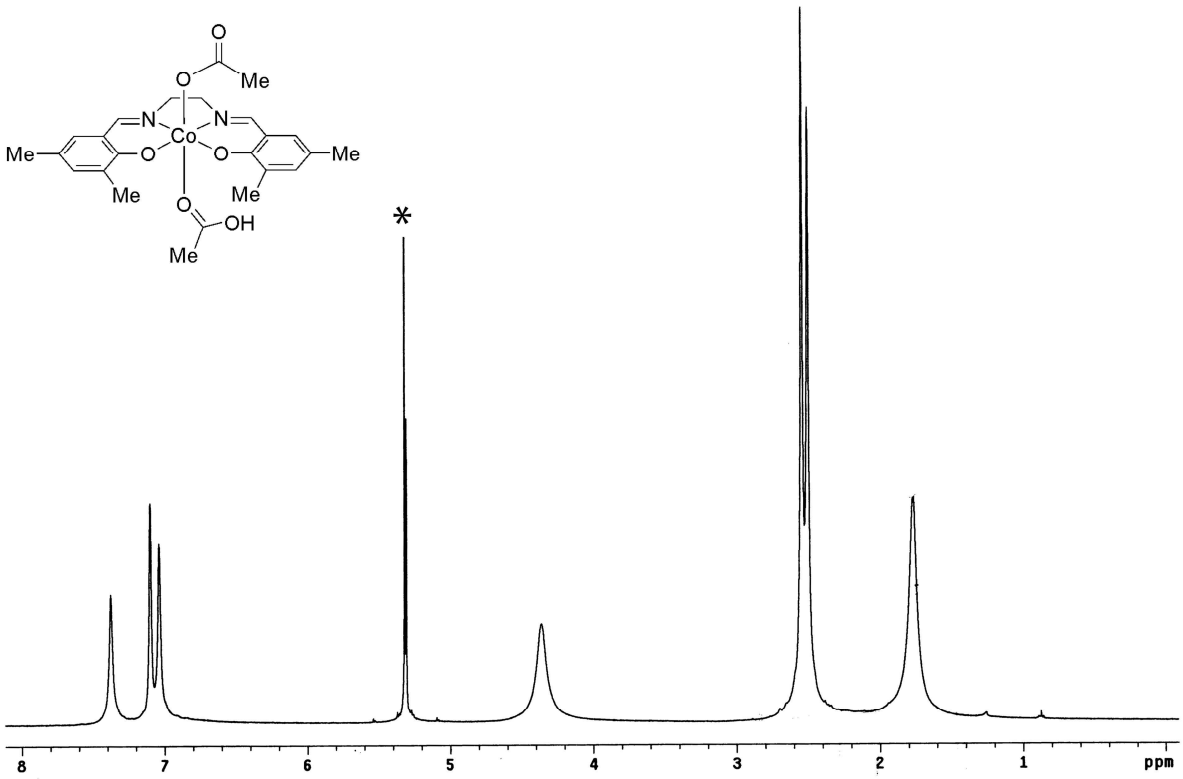
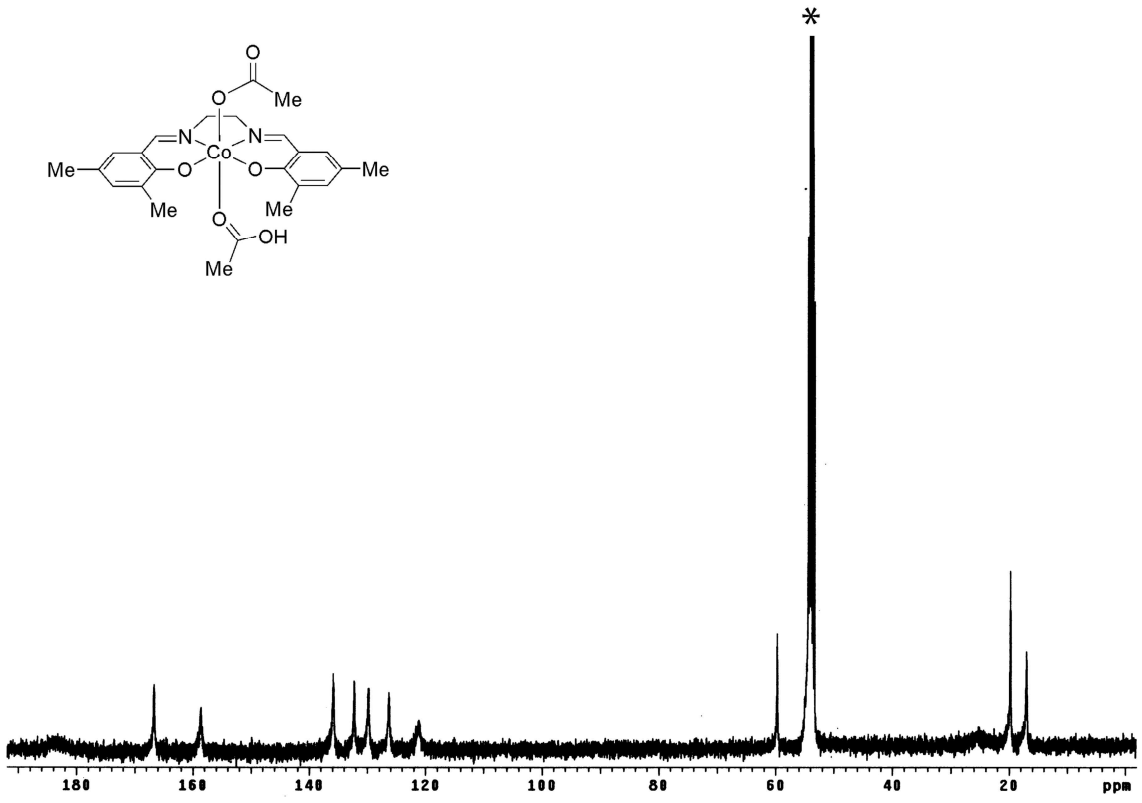


<The ^{13}C NMR spectrum of (Me-salen)Co(OAc)·HOAc in CD_2Cl_2>



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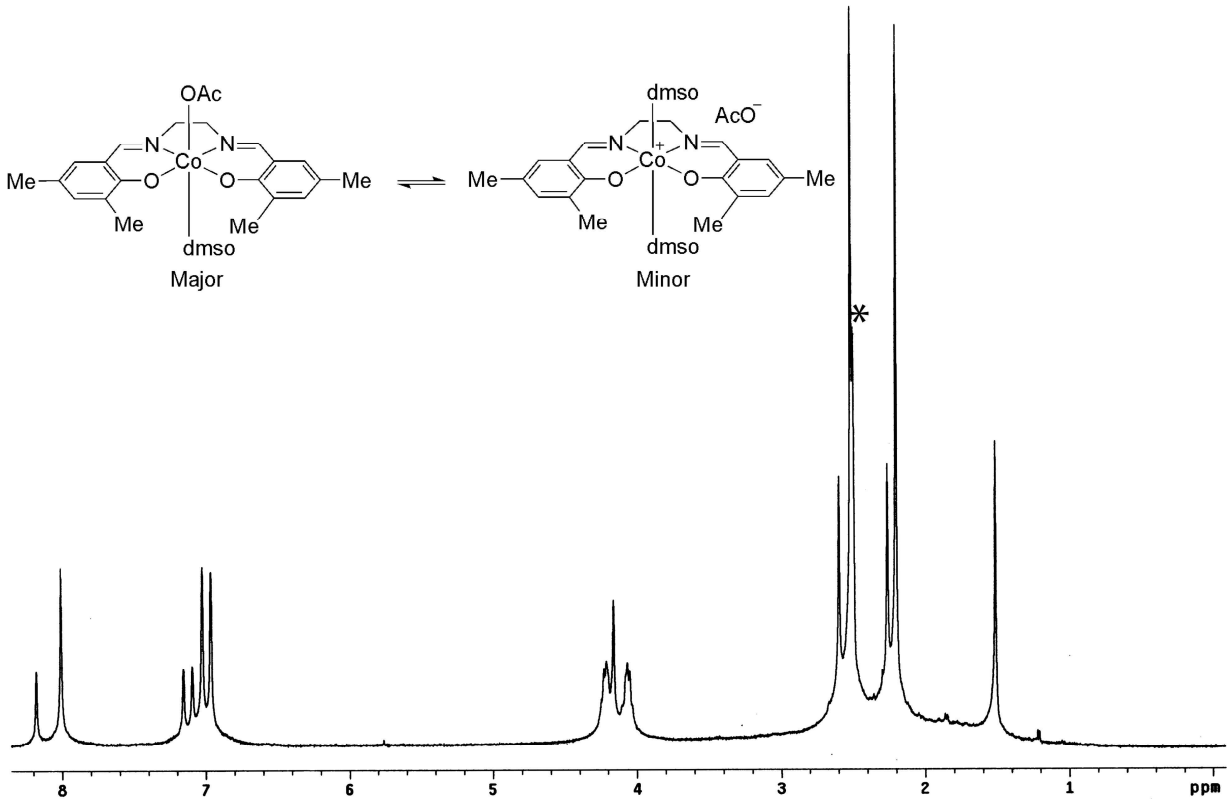

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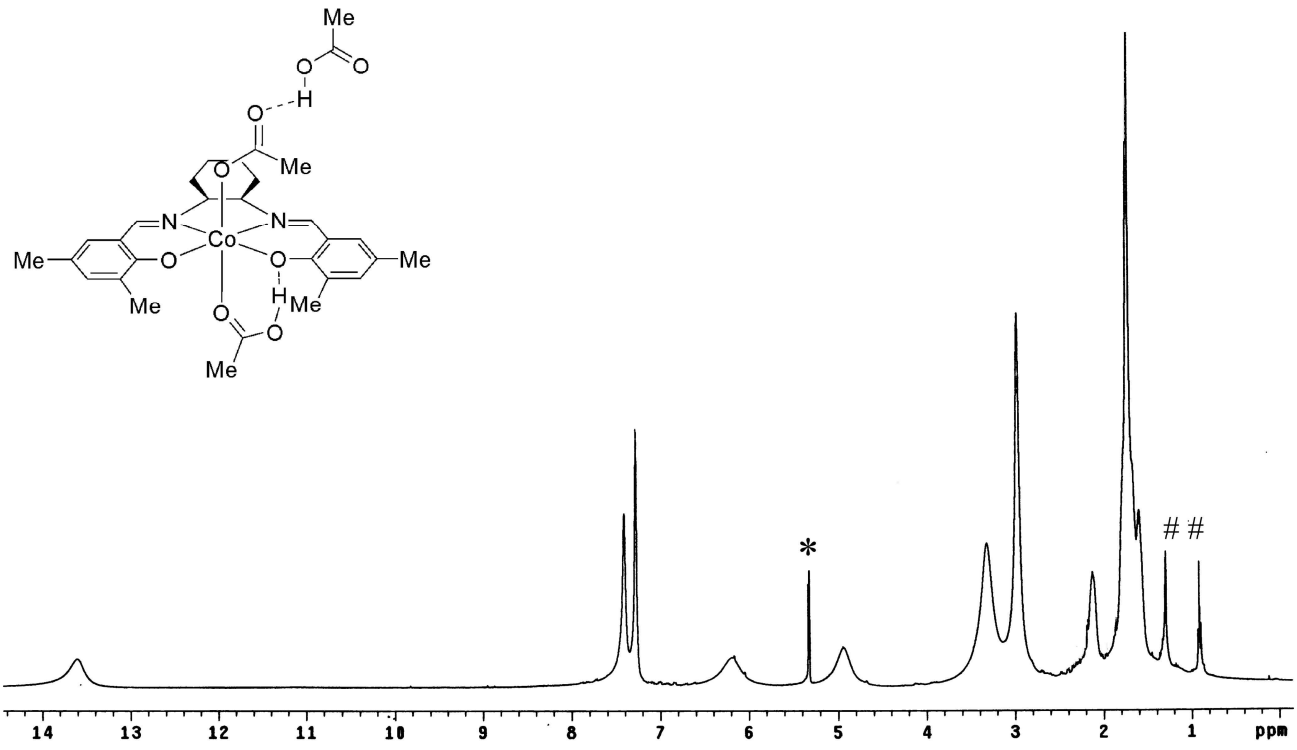

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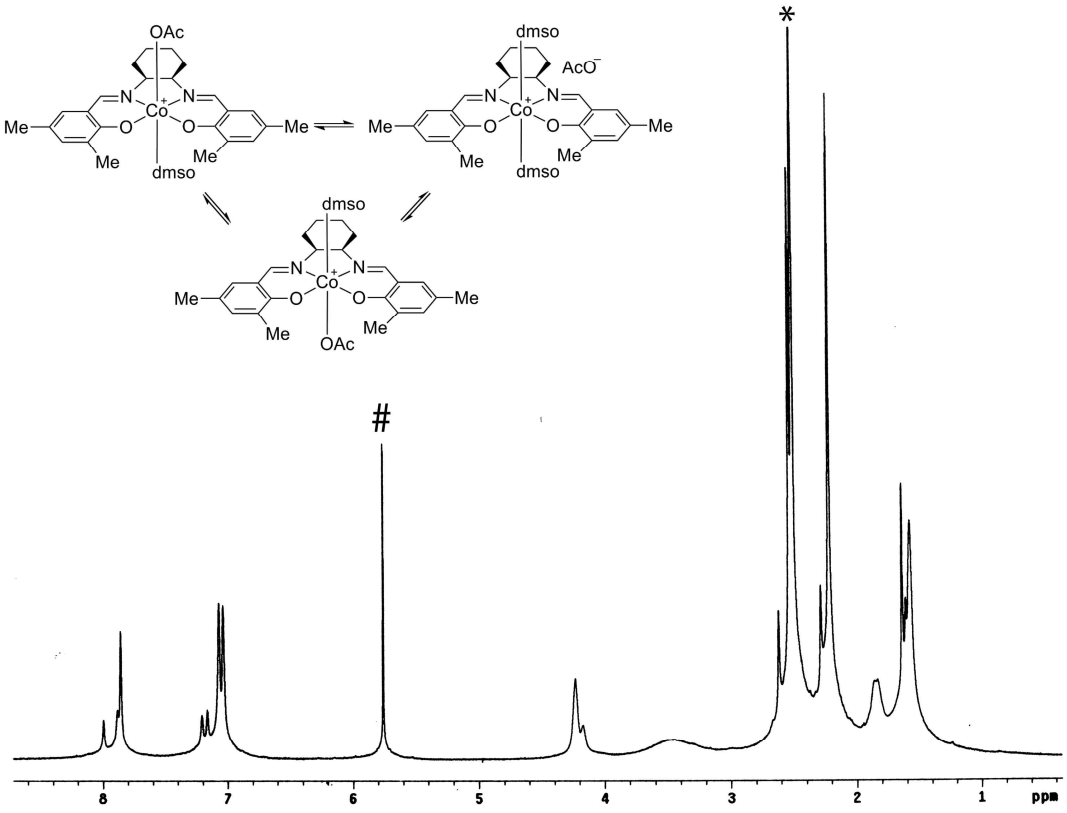

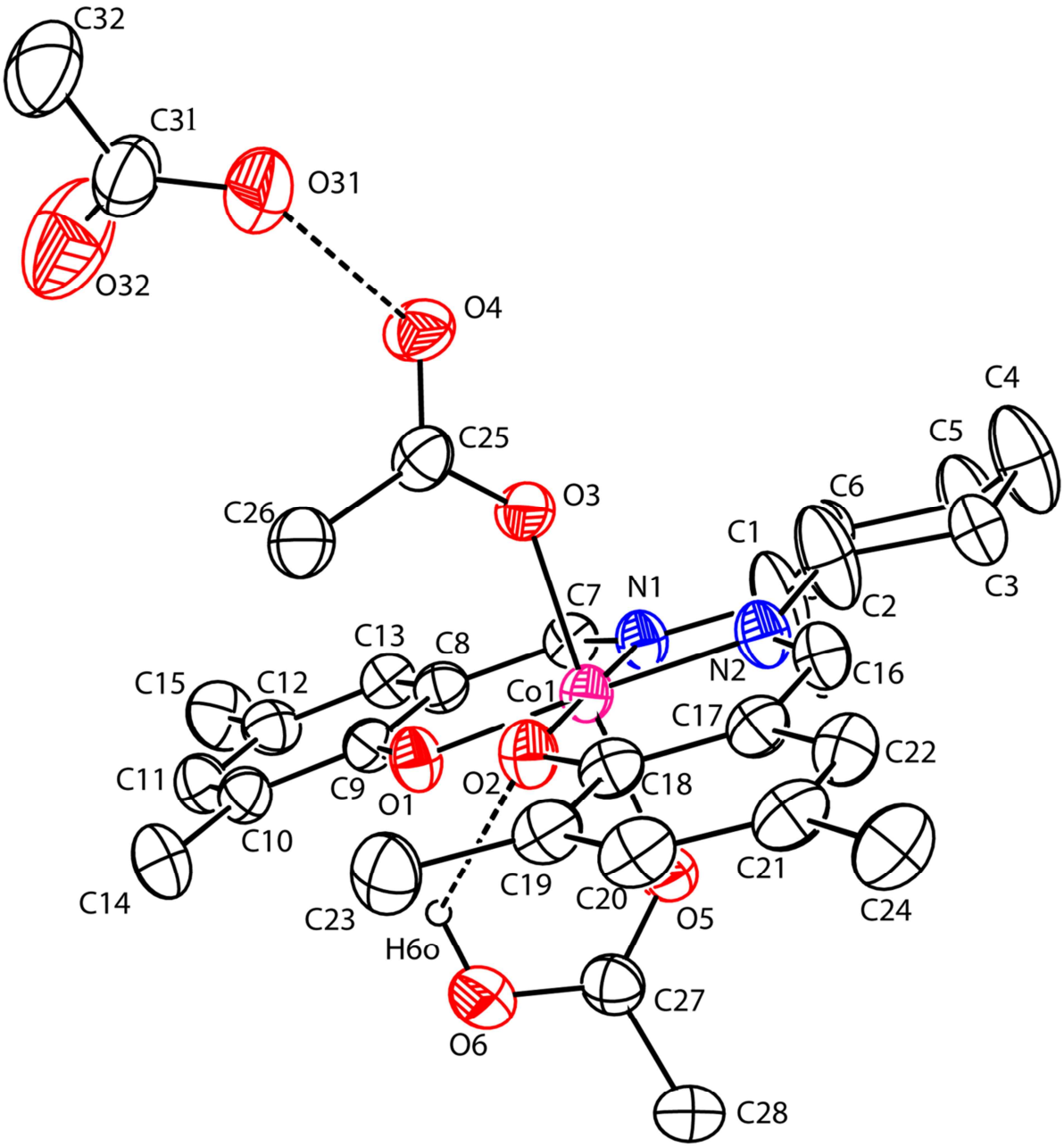

Figure S1. X-ray structures of (Me-salcy)Co(OAc)·2(HOAc).

Table S3. Bond lengths [Å] and angles [deg] for (Me-salcy)Co(OAc)·2(HOAc)

Co(1)-O(2)	1.880(3)	Co(1)-O(5)	1.969(3)	O(1)-C(9)	1.339(5)
Co(1)-N(2)	1.889(4)	N(1)-C(7)	1.274(5)	O(2)-C(18)	1.318(5)
Co(1)-O(3)	1.902(3)	N(1)-C(1)	1.460(6)	C(1)-C(2)	1.379(8)
Co(1)-N(1)	1.902(3)	N(2)-C(16)	1.287(6)	C(1)-C(6)	1.509(7)
Co(1)-O(1)	1.910(3)	N(2)-C(2)	1.475(6)	C(2)-C(3)	1.510(7)

C(3)-C(4)	1.522(8)	O(3)-Co(1)-N(1)	87.49(14)	C(11)-C(10)-C(9)	118.6(4)
C(4)-C(5)	1.385(8)	O(2)-Co(1)-O(1)	85.24(13)	C(11)-C(10)-C(14)	121.6(4)
C(5)-C(6)	1.511(7)	N(2)-Co(1)-O(1)	177.34(14)	C(9)-C(10)-C(14)	119.8(4)
C(7)-C(8)	1.442(6)	O(3)-Co(1)-O(1)	94.82(13)	C(12)-C(11)-C(10)	123.5(4)
C(8)-C(13)	1.409(6)	N(1)-Co(1)-O(1)	94.44(14)	C(13)-C(12)-C(11)	117.5(4)
C(8)-C(9)	1.410(6)	O(2)-Co(1)-O(5)	88.33(13)	C(13)-C(12)-C(15)	120.5(5)
C(9)-C(10)	1.403(6)	N(2)-Co(1)-O(5)	86.83(15)	C(11)-C(12)-C(15)	122.0(5)
C(10)-C(11)	1.390(6)	O(3)-Co(1)-O(5)	174.38(13)	C(12)-C(13)-C(8)	121.5(4)
C(10)-C(14)	1.503(6)	N(1)-Co(1)-O(5)	90.58(14)	N(2)-C(16)-C(17)	125.6(4)
C(11)-C(12)	1.389(7)	O(1)-Co(1)-O(5)	90.59(13)	C(22)-C(17)-C(18)	120.0(4)
C(12)-C(13)	1.374(6)	C(7)-N(1)-C(1)	122.4(4)	C(22)-C(17)-C(16)	117.4(4)
C(12)-C(15)	1.523(7)	C(7)-N(1)-Co(1)	125.7(3)	C(18)-C(17)-C(16)	122.6(4)
C(16)-C(17)	1.431(6)	C(1)-N(1)-Co(1)	111.8(3)	O(2)-C(18)-C(17)	124.5(4)
C(17)-C(22)	1.410(6)	C(16)-N(2)-C(2)	122.9(4)	O(2)-C(18)-C(19)	116.9(4)
C(17)-C(18)	1.412(6)	C(16)-N(2)-Co(1)	125.3(3)	C(17)-C(18)-C(19)	118.5(4)
C(18)-C(19)	1.422(6)	C(2)-N(2)-Co(1)	111.8(3)	C(20)-C(19)-C(18)	118.0(5)
C(19)-C(20)	1.380(6)	C(9)-O(1)-Co(1)	126.5(3)	C(20)-C(19)-C(23)	123.2(4)
C(19)-C(23)	1.508(7)	C(18)-O(2)-Co(1)	125.5(3)	C(18)-C(19)-C(23)	118.8(4)
C(20)-C(21)	1.392(7)	C(2)-C(1)-N(1)	111.9(5)	C(19)-C(20)-C(21)	124.9(4)
C(21)-C(22)	1.375(6)	C(2)-C(1)-C(6)	118.4(5)	C(22)-C(21)-C(20)	116.4(4)
C(21)-C(24)	1.503(6)	N(1)-C(1)-C(6)	119.0(4)	C(22)-C(21)-C(24)	121.4(5)
O(3)-C(25)	1.280(5)	C(1)-C(2)-N(2)	110.4(5)	C(20)-C(21)-C(24)	122.2(4)
O(4)-C(25)	1.240(5)	C(1)-C(2)-C(3)	117.2(5)	C(21)-C(22)-C(17)	122.1(5)
C(25)-C(26)	1.494(7)	N(2)-C(2)-C(3)	117.9(5)	C(25)-O(3)-Co(1)	132.4(3)
O(5)-C(27)	1.235(5)	C(2)-C(3)-C(4)	111.2(5)	O(4)-C(25)-O(3)	118.7(4)
O(6)-C(27)	1.293(6)	C(5)-C(4)-C(3)	117.0(6)	O(4)-C(25)-C(26)	118.5(4)
C(27)-C(28)	1.480(7)	C(4)-C(5)-C(6)	118.9(5)	O(3)-C(25)-C(26)	122.7(4)
O(31)-C(31)	1.246(7)	C(1)-C(6)-C(5)	110.8(4)	C(27)-O(5)-Co(1)	126.8(3)
O(32)-C(31)	1.217(8)	N(1)-C(7)-C(8)	126.6(4)	O(5)-C(27)-O(6)	122.3(5)
C(31)-C(32)	1.498(9)	C(13)-C(8)-C(9)	119.8(4)	O(5)-C(27)-C(28)	122.2(5)
O(2)-Co(1)-N(2)	95.34(14)	C(13)-C(8)-C(7)	117.0(4)	O(6)-C(27)-C(28)	115.3(4)
O(2)-Co(1)-O(3)	93.63(13)	C(9)-C(8)-C(7)	123.1(4)	O(32)-C(31)-O(31)	122.7(7)
N(2)-Co(1)-O(3)	87.74(15)	O(1)-C(9)-C(10)	117.8(4)	O(32)-C(31)-C(32)	121.5(6)
O(2)-Co(1)-N(1)	178.86(14)	O(1)-C(9)-C(8)	123.2(4)	O(31)-C(31)-C(32)	115.8(7)
N(2)-Co(1)-N(1)	84.93(15)	C(10)-C(9)-C(8)	119.0(4)		

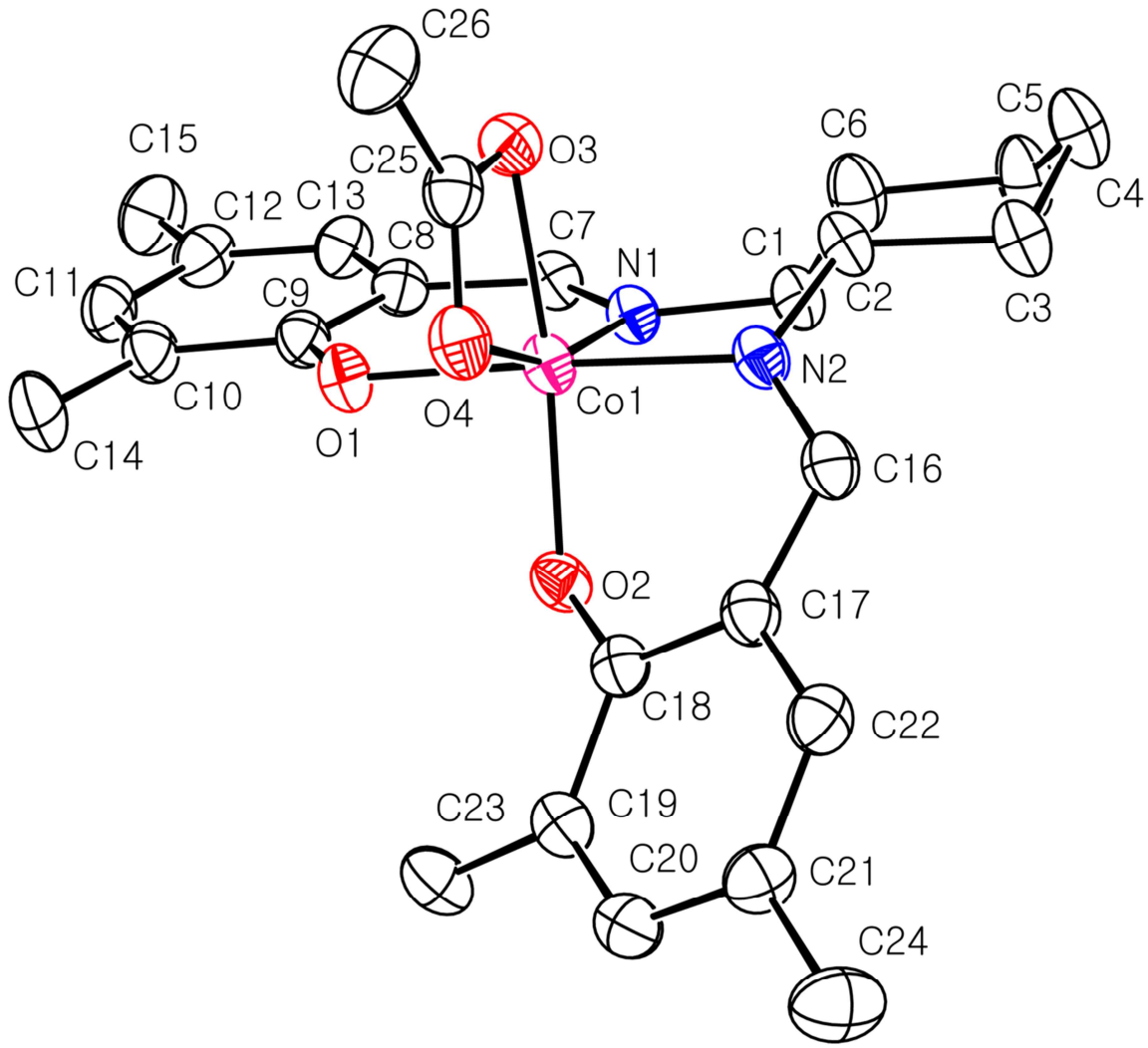

Figure S2. X-ray structure of (Me-salcy)Co(κ^2-OAc).

Table S4. Bond lengths [Å] and angles [deg] for (Me-salcy)Co(κ^2-OAc).

Co(1)-O(1)	1.878(2)	O(2)-C(18)	1.322(4)	C(9)-C(10)	1.421(4)
Co(1)-O(2)	1.880(2)	O(3)-C(25)	1.269(4)	C(10)-C(11)	1.376(5)
Co(1)-N(2)	1.891(3)	O(4)-C(25)	1.264(4)	C(10)-C(14)	1.503(5)
Co(1)-N(1)	1.892(2)	C(1)-C(6)	1.522(4)	C(11)-C(12)	1.407(5)
Co(1)-O(3)	1.962(2)	C(1)-C(2)	1.542(4)	C(12)-C(13)	1.363(5)
Co(1)-O(4)	1.990(2)	C(2)-C(3)	1.512(4)	C(12)-C(15)	1.513(5)
Co(1)-C(25)	2.311(3)	C(3)-C(4)	1.525(5)	C(16)-C(17)	1.435(4)
N(1)-C(7)	1.289(4)	C(4)-C(5)	1.523(6)	C(17)-C(22)	1.408(4)
N(1)-C(1)	1.480(4)	C(5)-C(6)	1.533(5)	C(17)-C(18)	1.421(4)
N(2)-C(16)	1.289(4)	C(7)-C(8)	1.431(4)	C(18)-C(19)	1.421(4)
N(2)-C(2)	1.473(4)	C(8)-C(9)	1.418(4)	C(19)-C(20)	1.379(5)
O(1)-C(9)	1.310(4)	C(8)-C(13)	1.420(5)	C(19)-C(23)	1.514(5)

C(20)-C(21)	1.402(5)	C(7)-N(1)-Co(1)	123.9(2)	C(10)-C(11)-C(12)	123.6(3)
C(21)-C(22)	1.371(5)	C(1)-N(1)-Co(1)	113.55(19)	C(13)-C(12)-C(11)	116.9(3)
C(21)-C(24)	1.504(5)	C(16)-N(2)-C(2)	123.7(3)	C(13)-C(12)-C(15)	122.0(4)
C(25)-C(26)	1.493(5)	C(16)-N(2)-Co(1)	124.0(2)	C(11)-C(12)-C(15)	121.1(4)
C(101)-Cl(02)	1.707(8)	C(2)-N(2)-Co(1)	110.27(19)	C(12)-C(13)-C(8)	122.4(3)
C(101)-Cl(01)	1.726(6)	C(9)-O(1)-Co(1)	125.47(19)	N(2)-C(16)-C(17)	122.8(3)
		C(18)-O(2)-Co(1)	117.81(19)	C(22)-C(17)-C(18)	120.2(3)
O(1)-Co(1)-O(2)	88.05(10)	C(25)-O(3)-Co(1)	88.63(19)	C(22)-C(17)-C(16)	120.0(3)
O(1)-Co(1)-N(2)	177.80(11)	C(25)-O(4)-Co(1)	87.55(19)	C(18)-C(17)-C(16)	119.0(3)
O(2)-Co(1)-N(2)	89.76(10)	N(1)-C(1)-C(6)	116.4(3)	O(2)-C(18)-C(17)	123.8(3)
O(1)-Co(1)-N(1)	96.23(10)	N(1)-C(1)-C(2)	105.8(2)	O(2)-C(18)-C(19)	118.5(3)
O(2)-Co(1)-N(1)	98.76(10)	C(6)-C(1)-C(2)	111.1(3)	C(17)-C(18)-C(19)	117.5(3)
N(2)-Co(1)-N(1)	83.94(11)	N(2)-C(2)-C(3)	117.8(3)	C(20)-C(19)-C(18)	119.3(3)
O(1)-Co(1)-O(3)	89.69(10)	N(2)-C(2)-C(1)	102.0(2)	C(20)-C(19)-C(23)	122.1(3)
O(2)-Co(1)-O(3)	166.07(9)	C(3)-C(2)-C(1)	111.1(3)	C(18)-C(19)-C(23)	118.6(3)
N(2)-Co(1)-O(3)	92.48(10)	C(2)-C(3)-C(4)	108.8(3)	C(19)-C(20)-C(21)	123.9(3)
N(1)-Co(1)-O(3)	95.15(10)	C(5)-C(4)-C(3)	111.5(3)	C(22)-C(21)-C(20)	116.7(3)
O(1)-Co(1)-O(4)	87.57(9)	C(4)-C(5)-C(6)	112.5(3)	C(22)-C(21)-C(24)	122.0(3)
O(2)-Co(1)-O(4)	99.81(10)	C(1)-C(6)-C(5)	109.8(3)	C(20)-C(21)-C(24)	121.3(3)
N(2)-Co(1)-O(4)	92.97(10)	N(1)-C(7)-C(8)	126.2(3)	C(21)-C(22)-C(17)	122.3(3)
N(1)-Co(1)-O(4)	161.15(10)	C(9)-C(8)-C(13)	119.7(3)	O(4)-C(25)-O(3)	117.3(3)
O(3)-Co(1)-O(4)	66.35(9)	C(9)-C(8)-C(7)	122.9(3)	O(4)-C(25)-C(26)	121.9(3)
O(1)-Co(1)-C(25)	86.97(11)	C(13)-C(8)-C(7)	117.3(3)	O(3)-C(25)-C(26)	120.9(3)
O(2)-Co(1)-C(25)	132.81(11)	O(1)-C(9)-C(8)	124.3(3)	O(4)-C(25)-Co(1)	59.34(17)
N(2)-Co(1)-C(25)	94.65(11)	O(1)-C(9)-C(10)	117.9(3)	O(3)-C(25)-Co(1)	58.08(17)
N(1)-Co(1)-C(25)	128.43(12)	C(8)-C(9)-C(10)	117.8(3)	C(26)-C(25)-Co(1)	176.6(3)
O(3)-Co(1)-C(25)	33.29(10)	C(11)-C(10)-C(9)	119.5(3)	Cl(02)-C(101)-Cl(01)	113.9(4)
O(4)-Co(1)-C(25)	33.11(10)	C(11)-C(10)-C(14)	122.1(3)		
C(7)-N(1)-C(1)	121.9(3)	C(9)-C(10)-C(14)	118.3(3)		

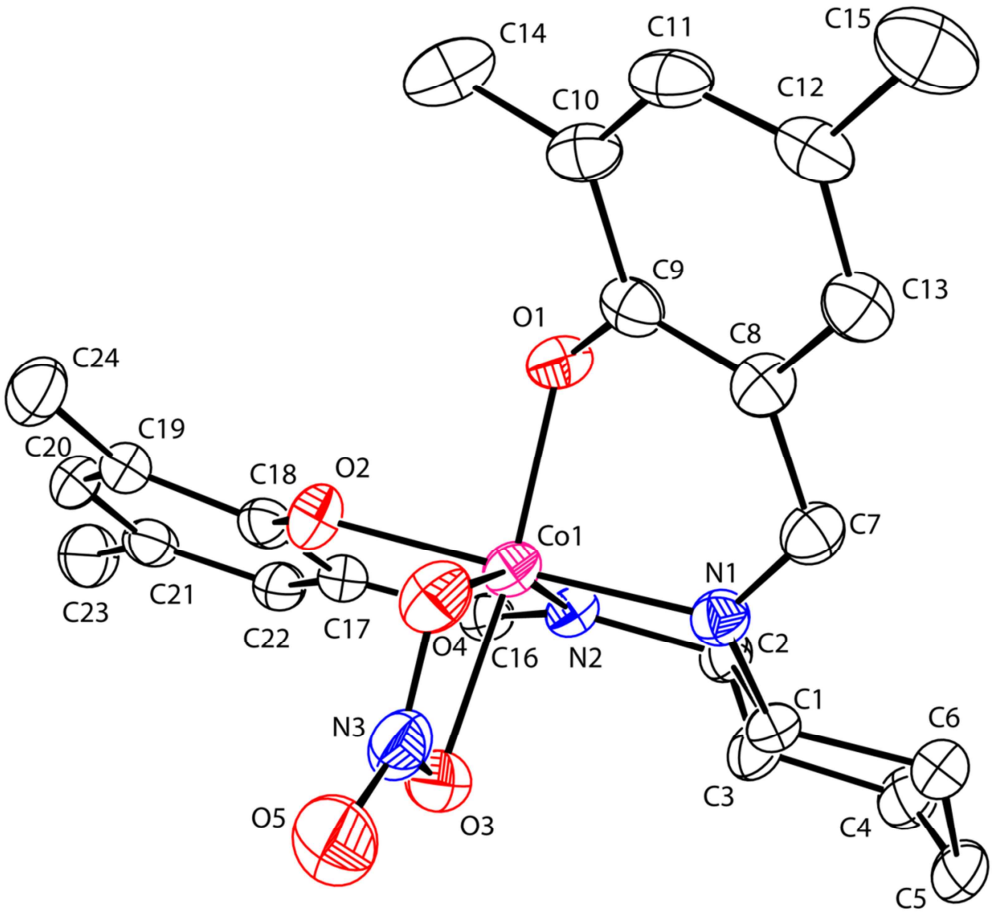

Figure S3. X-ray structure of (Me-salcy)Co(κ^2-NO_3).

Table S5. Bond lengths [Å] and angles [deg] for (Me-salcy)Co(κ^2-NO_3)

Co(1)-O(1)	1.858(2)	C(2)-C(3)	1.516(4)	C(17)-C(18)	1.424(5)
Co(1)-O(2)	1.870(2)	C(3)-C(4)	1.521(5)	C(18)-C(19)	1.418(5)
Co(1)-N(2)	1.883(3)	C(4)-C(5)	1.513(5)	C(19)-C(20)	1.368(5)
Co(1)-N(1)	1.904(3)	C(5)-C(6)	1.532(4)	C(19)-C(23)	1.509(4)
Co(1)-O(4)	1.980(2)	C(7)-C(8)	1.441(4)	C(20)-C(21)	1.414(5)
Co(1)-O(3)	1.990(2)	C(8)-C(13)	1.401(5)	C(21)-C(22)	1.370(5)
Co(1)-N(3)	2.379(4)	C(8)-C(9)	1.404(5)	C(21)-C(24)	1.517(5)
N(1)-C(7)	1.277(4)	C(9)-C(10)	1.420(5)	N(3)-O(5)	1.210(4)
N(1)-C(1)	1.471(4)	C(10)-C(11)	1.385(5)	N(3)-O(3)	1.283(4)
N(2)-C(16)	1.288(4)	C(10)-C(14)	1.503(5)	N(3)-O(4)	1.290(4)
N(2)-C(2)	1.490(4)	C(11)-C(12)	1.388(5)	O(1)-Co(1)-O(2)	88.77(10)
O(1)-C(9)	1.341(4)	C(12)-C(13)	1.369(5)	O(1)-Co(1)-N(2)	100.39(11)
O(2)-C(18)	1.301(4)	C(12)-C(15)	1.513(5)	O(2)-Co(1)-N(2)	96.09(12)
C(1)-C(6)	1.519(4)	C(16)-C(17)	1.429(5)	O(1)-Co(1)-N(1)	89.69(11)
C(1)-C(2)	1.520(4)	C(17)-C(22)	1.402(5)	O(2)-Co(1)-N(1)	178.42(11)

N(2)-Co(1)-N(1)	83.84(12)	N(1)-C(1)-C(6)	118.2(3)	C(12)-C(13)-C(8)	122.3(4)
O(1)-Co(1)-O(4)	98.34(11)	N(1)-C(1)-C(2)	102.7(3)	N(2)-C(16)-C(17)	127.0(3)
O(2)-Co(1)-O(4)	87.60(10)	C(6)-C(1)-C(2)	111.9(3)	C(22)-C(17)-C(18)	120.0(3)
N(2)-Co(1)-O(4)	160.98(11)	N(2)-C(2)-C(3)	116.2(3)	C(22)-C(17)-C(16)	118.4(3)
N(1)-Co(1)-O(4)	92.97(11)	N(2)-C(2)-C(1)	105.8(3)	C(18)-C(17)-C(16)	121.5(3)
O(1)-Co(1)-O(3)	163.71(11)	C(3)-C(2)-C(1)	111.8(3)	O(2)-C(18)-C(19)	117.9(3)
O(2)-Co(1)-O(3)	88.99(10)	C(2)-C(3)-C(4)	110.4(3)	O(2)-C(18)-C(17)	124.5(3)
N(2)-Co(1)-O(3)	95.89(11)	C(5)-C(4)-C(3)	112.9(3)	C(19)-C(18)-C(17)	117.6(3)
N(1)-Co(1)-O(3)	92.59(11)	C(4)-C(5)-C(6)	110.9(3)	C(20)-C(19)-C(18)	119.5(3)
O(4)-Co(1)-O(3)	65.45(11)	C(1)-C(6)-C(5)	108.1(3)	C(20)-C(19)-C(23)	122.2(3)
O(1)-Co(1)-N(3)	131.12(12)	N(1)-C(7)-C(8)	123.2(3)	C(18)-C(19)-C(23)	118.3(3)
O(2)-Co(1)-N(3)	87.27(11)	C(13)-C(8)-C(9)	119.8(3)	C(19)-C(20)-C(21)	123.8(3)
N(2)-Co(1)-N(3)	128.48(13)	C(13)-C(8)-C(7)	121.4(4)	C(22)-C(21)-C(20)	116.4(4)
N(1)-Co(1)-N(3)	94.01(12)	C(9)-C(8)-C(7)	118.6(3)	C(22)-C(21)-C(24)	123.2(4)
O(4)-Co(1)-N(3)	32.83(10)	O(1)-C(9)-C(8)	123.2(3)	C(20)-C(21)-C(24)	120.4(4)
O(3)-Co(1)-N(3)	32.63(10)	O(1)-C(9)-C(10)	117.8(4)	C(21)-C(22)-C(17)	122.5(3)
C(7)-N(1)-C(1)	123.6(3)	C(8)-C(9)-C(10)	118.8(3)	O(5)-N(3)-O(3)	123.9(4)
C(7)-N(1)-Co(1)	123.9(2)	C(11)-C(10)-C(9)	118.0(4)	O(5)-N(3)-O(4)	123.0(4)
C(1)-N(1)-Co(1)	109.9(2)	C(11)-C(10)-C(14)	122.4(3)	O(3)-N(3)-O(4)	113.1(3)
C(16)-N(2)-C(2)	122.1(3)	C(9)-C(10)-C(14)	119.6(4)	O(5)-N(3)-Co(1)	178.5(3)
C(16)-N(2)-Co(1)	123.8(2)	C(10)-C(11)-C(12)	124.1(3)	O(3)-N(3)-Co(1)	56.79(18)
C(2)-N(2)-Co(1)	113.7(2)	C(13)-C(12)-C(11)	116.9(4)	O(4)-N(3)-Co(1)	56.33(18)
C(9)-O(1)-Co(1)	115.5(2)	C(13)-C(12)-C(15)	121.8(4)	N(3)-O(3)-Co(1)	90.6(2)
C(18)-O(2)-Co(1)	126.2(2)	C(11)-C(12)-C(15)	121.3(4)	N(3)-O(4)-Co(1)	90.8(2)

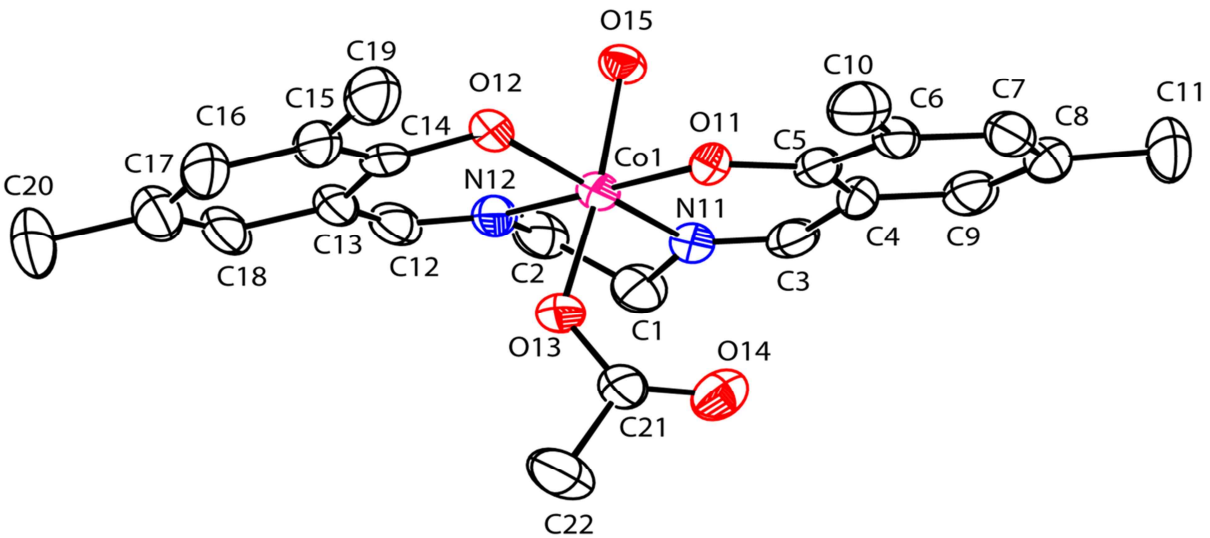

Figure S4. X-ray structure of (Me-salen)Co(OAc)(H_2O).

Table S6. Bond lengths [Å] and angles [deg] for (Me-salen)Co(OAc)(H_2O)

Co(1)-O(13)	1.875(7)	C(17)-C(18)	1.358(16)	C(5)-C(4)-C(9)	119.3(10)
Co(1)-N(11)	1.882(9)	C(17)-C(20)	1.536(17)	C(3)-C(4)-C(9)	118.4(11)
Co(1)-N(12)	1.895(9)	C(21)-C(22)	1.537(17)	O(11)-C(5)-C(6)	118.6(10)
Co(1)-O(11)	1.905(7)	O(13)-Co(1)-N(11)	96.6(3)	O(11)-C(5)-C(4)	123.2(10)
Co(1)-O(12)	1.908(7)	O(13)-Co(1)-N(12)	88.8(3)	C(6)-C(5)-C(4)	118.2(10)
Co(1)-O(15)	1.970(6)	N(11)-Co(1)-N(12)	86.2(4)	C(7)-C(6)-C(5)	119.1(12)
N(11)-C(3)	1.266(12)	O(13)-Co(1)-O(11)	93.0(3)	C(7)-C(6)-C(10)	120.1(11)
N(11)-C(1)	1.449(12)	N(11)-Co(1)-O(11)	93.6(3)	C(5)-C(6)-C(10)	120.7(11)
N(12)-C(12)	1.311(13)	N(12)-Co(1)-O(11)	178.3(3)	C(6)-C(7)-C(8)	123.5(11)
N(12)-C(2)	1.469(14)	O(13)-Co(1)-O(12)	86.7(3)	C(9)-C(8)-C(7)	118.7(11)
O(11)-C(5)	1.328(11)	N(11)-Co(1)-O(12)	175.6(3)	C(9)-C(8)-C(11)	120.8(13)
O(12)-C(14)	1.341(11)	N(12)-Co(1)-O(12)	91.1(4)	C(7)-C(8)-C(11)	120.4(12)
O(13)-C(21)	1.282(13)	O(11)-Co(1)-O(12)	89.1(3)	C(8)-C(9)-C(4)	121.0(11)
O(14)-C(21)	1.207(15)	O(13)-Co(1)-O(15)	173.7(3)	N(12)-C(12)-C(13)	124.8(11)
C(1)-C(2)	1.536(15)	N(11)-Co(1)-O(15)	89.1(3)	C(18)-C(13)-C(14)	121.2(11)
C(3)-C(4)	1.432(14)	N(12)-Co(1)-O(15)	89.0(3)	C(18)-C(13)-C(12)	115.8(11)
C(4)-C(5)	1.406(14)	O(11)-Co(1)-O(15)	89.3(3)	C(14)-C(13)-C(12)	122.7(10)
C(4)-C(9)	1.434(14)	O(12)-Co(1)-O(15)	87.4(3)	O(12)-C(14)-C(13)	123.1(10)
C(5)-C(6)	1.396(15)	C(3)-N(11)-C(1)	120.4(10)	O(12)-C(14)-C(15)	119.1(10)
C(6)-C(7)	1.369(15)	C(3)-N(11)-Co(1)	126.5(8)	C(13)-C(14)-C(15)	117.7(10)
C(6)-C(10)	1.487(15)	C(1)-N(11)-Co(1)	113.1(7)	C(16)-C(15)-C(14)	118.0(12)
C(7)-C(8)	1.372(16)	C(12)-N(12)-C(2)	122.2(10)	C(16)-C(15)-C(19)	122.3(12)
C(8)-C(9)	1.330(15)	C(12)-N(12)-Co(1)	126.6(8)	C(14)-C(15)-C(19)	119.7(10)
C(8)-C(11)	1.539(15)	C(2)-N(12)-Co(1)	111.1(8)	C(15)-C(16)-C(17)	125.7(13)
C(12)-C(13)	1.407(15)	C(5)-O(11)-Co(1)	126.8(7)	C(18)-C(17)-C(16)	114.9(12)
C(13)-C(18)	1.380(15)	C(14)-O(12)-Co(1)	124.9(6)	C(18)-C(17)-C(20)	125.2(13)
C(13)-C(14)	1.393(14)	C(21)-O(13)-Co(1)	128.7(8)	C(16)-C(17)-C(20)	119.8(14)
C(14)-C(15)	1.399(14)	N(11)-C(1)-C(2)	106.0(9)	C(17)-C(18)-C(13)	122.1(12)
C(15)-C(16)	1.352(15)	N(12)-C(2)-C(1)	107.1(9)	O(14)-C(21)-O(13)	128.0(13)
C(15)-C(19)	1.505(15)	N(11)-C(3)-C(4)	126.5(11)	O(14)-C(21)-C(22)	118.4(12)
C(16)-C(17)	1.398(17)	C(5)-C(4)-C(3)	122.3(10)	O(13)-C(21)-C(22)	113.4(13)

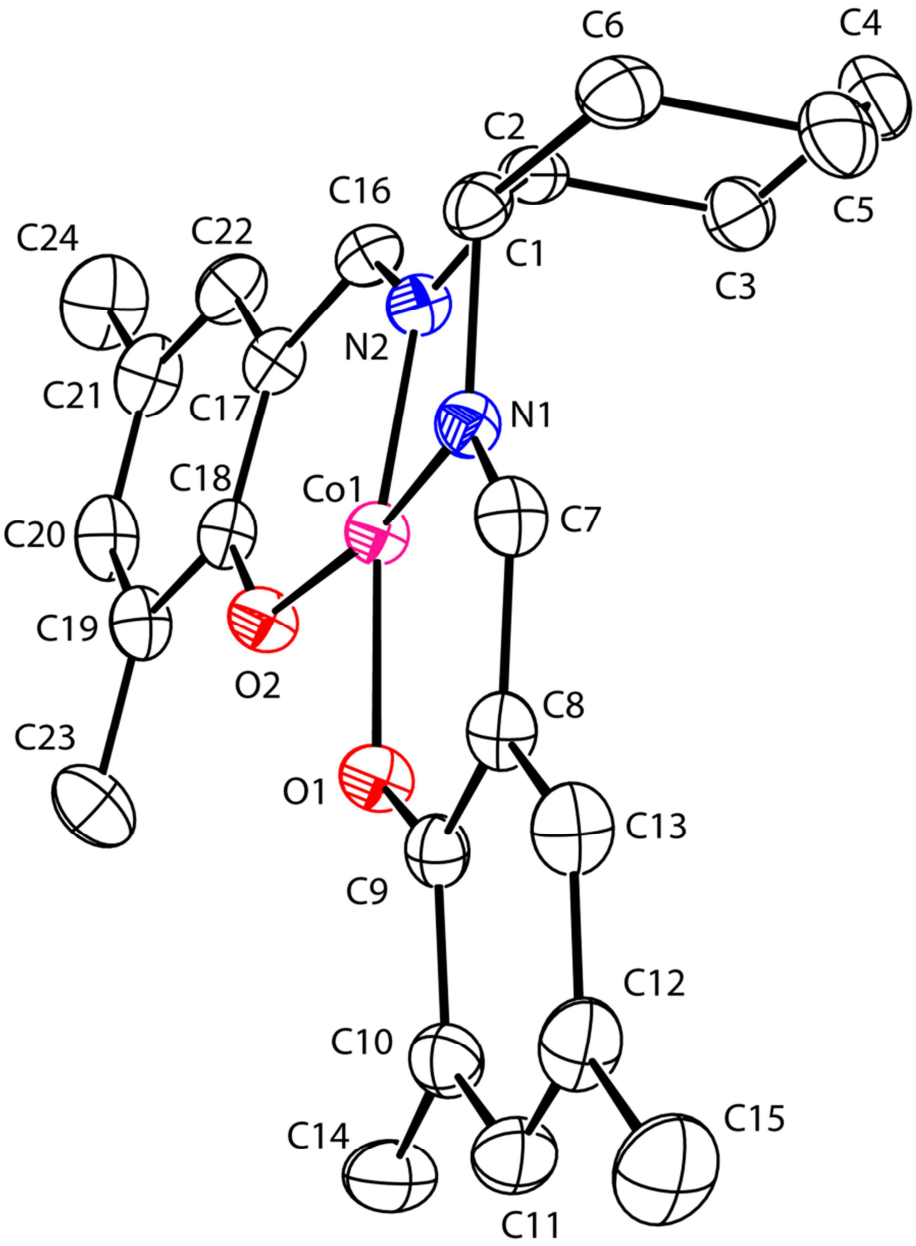

Figure S5. X-ray structure of (Me-sal-*cis*-cy)Co(II).

Table S7. Bond lengths [Å] and angles [deg] for (Me-sal-*cis*-cy)Co(II)

Co(1)-O(1)	1.8436(14)	N(2)-C(2)	1.479(2)	C(4)-C(5)	1.517(4)
Co(1)-O(2)	1.8514(13)	O(1)-C(9)	1.319(2)	C(5)-C(6)	1.514(4)
Co(1)-N(2)	1.8525(17)	O(2)-C(18)	1.316(2)	C(7)-C(8)	1.420(3)
Co(1)-N(1)	1.8687(16)	C(1)-C(2)	1.523(3)	C(8)-C(9)	1.415(3)
N(1)-C(7)	1.297(3)	C(1)-C(6)	1.524(3)	C(8)-C(13)	1.423(3)
N(1)-C(1)	1.494(3)	C(2)-C(3)	1.523(3)	C(9)-C(10)	1.415(3)
N(2)-C(16)	1.307(3)	C(3)-C(4)	1.528(3)	C(10)-C(11)	1.375(3)

C(10)-C(14)	1.514(3)	C(16)-N(2)-Co(1)	127.81(15)	C(9)-C(10)-C(14)	118.7(2)
C(11)-C(12)	1.405(3)	C(2)-N(2)-Co(1)	113.45(13)	C(10)-C(11)-C(12)	123.2(2)
C(12)-C(13)	1.355(3)	C(9)-O(1)-Co(1)	128.44(13)	C(13)-C(12)-C(11)	117.3(2)
C(12)-C(15)	1.517(3)	C(18)-O(2)-Co(1)	128.71(14)	C(13)-C(12)-C(15)	122.6(2)
C(16)-C(17)	1.424(3)	N(1)-C(1)-C(2)	105.07(16)	C(11)-C(12)-C(15)	120.1(2)
C(17)-C(18)	1.414(3)	N(1)-C(1)-C(6)	117.23(17)	C(12)-C(13)-C(8)	122.5(2)
C(17)-C(22)	1.419(3)	C(2)-C(1)-C(6)	110.91(19)	N(2)-C(16)-C(17)	124.6(2)
C(18)-C(19)	1.426(3)	N(2)-C(2)-C(1)	105.38(17)	C(18)-C(17)-C(22)	120.2(2)
C(19)-C(20)	1.379(3)	N(2)-C(2)-C(3)	109.98(18)	C(18)-C(17)-C(16)	121.63(19)
C(19)-C(23)	1.501(3)	C(1)-C(2)-C(3)	112.02(18)	C(22)-C(17)-C(16)	118.2(2)
C(20)-C(21)	1.399(4)	C(2)-C(3)-C(4)	111.8(2)	O(2)-C(18)-C(17)	123.46(18)
C(21)-C(22)	1.358(3)	C(5)-C(4)-C(3)	110.3(2)	O(2)-C(18)-C(19)	118.3(2)
C(21)-C(24)	1.525(3)	C(6)-C(5)-C(4)	110.9(2)	C(17)-C(18)-C(19)	118.24(19)
O(1)-Co(1)-O(2)	87.73(6)	C(5)-C(6)-C(1)	113.46(19)	C(20)-C(19)-C(18)	118.3(2)
O(1)-Co(1)-N(2)	170.07(8)	N(1)-C(7)-C(8)	125.34(19)	C(20)-C(19)-C(23)	121.6(2)
O(2)-Co(1)-N(2)	93.63(7)	C(9)-C(8)-C(7)	121.74(18)	C(18)-C(19)-C(23)	120.1(2)
O(1)-Co(1)-N(1)	94.04(7)	C(9)-C(8)-C(13)	119.1(2)	C(19)-C(20)-C(21)	124.2(2)
O(2)-Co(1)-N(1)	171.76(7)	C(7)-C(8)-C(13)	119.1(2)	C(22)-C(21)-C(20)	117.5(2)
N(2)-Co(1)-N(1)	86.01(7)	O(1)-C(9)-C(8)	123.3(2)	C(22)-C(21)-C(24)	122.3(3)
C(7)-N(1)-C(1)	120.57(17)	O(1)-C(9)-C(10)	118.34(19)	C(20)-C(21)-C(24)	120.2(2)
C(7)-N(1)-Co(1)	126.83(15)	C(8)-C(9)-C(10)	118.33(19)	C(21)-C(22)-C(17)	121.6(2)
C(1)-N(1)-Co(1)	112.44(12)	C(11)-C(10)-C(9)	119.5(2)		
C(16)-N(2)-C(2)	118.68(18)	C(11)-C(10)-C(14)	121.7(2)		