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Structural and Spectroscopic Properties of the Cobalt(II) 3,5-Di-*tert*-butylcatecholate Tetramer Having a Distorted Co_4O_4 Cubane Core

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Reaction of the metal amide $[Co\{N(SiMe_3)_2\}_2]_2$ with 3,5-di-*tert*-butylcatechol ($DBCatH_2$) in THF/toluene solution affords the neutral metal catecholate tetramer $[Co_4(DBCat)_4(THF)_{5.5}]$ in moderate yield. A crystal structure determination reveals a distorted cubane Co_4O_4 array. Each cobalt is bonded to three triply bridging oxygens and a terminal oxygen from the catecholate ligands. Further coordination to THF donor molecules gives rise to two cobalts with a pseudooctahedral geometry and two with a distorted trigonal-bipyramidal geometry. The closest metal-metal distance is 3.121 (10) Å. All four ligands are present in the catecholate form. ESR, NMR, IR, magnetic, and UV-vis data are also reported. Crystallographic data at 130 K: $a = 15.078$ (7) Å, $b = 16.080$ (6) Å, $c = 19.344$ (6) Å, $\alpha = 85.43$ (3)°, $\beta = 83.67$ (3)°, $\gamma = 81.78$ (3)°, $Z = 2$, space group $P\bar{1}$, $R = 0.098$.

Over the past few years there has been considerable interest in the characterization of transition-metal catecholate and semiquinone complexes.[1-3] Some metal catecholates, for example, have been shown to be excellent model compounds for in vivo biological microbial iron transport and sequestering agents.[4-8] For instance, the synthetic ferric ion sequestering agent 1,5,10-tris-(5-sulfo-2,3-dihydroxybenzoyl)-1,5,10-triazadecane (3,4-LI-CAMS) contains three catechol moieties that strongly chelate the Fe^{3+} ion in the same manner as the microbial iron transport agent enterobactin.[5,6] Such novel synthetic analogues are potentially important for treatment of β-thalassemia (high levels of iron in blood) and as chelating agents for Ga(III) and In(III) in radiopharmaceuticals.[4,6] The role of catecholate ligands in catalytic processes is also of considerable interest.[8] One such example is the Cu(II) species $[Cu(bpy)(DBCat)]_2$ (DBCat = 3,5-di-*tert*-butylcatecholate), which has been shown to be a catalyst for the oxidation of catechols to lactones.[9,10] Recently, $Co^{II}(acac)_2$ was shown to catalyze the oxidation of $DBCatH_2$ by oxygen in nonaqueous solutions.[11] The proposed reaction scheme leads to the formation of a ternary $(DBCat)-Co^{II}-O_2$ complex, which undergoes an intramolecular reaction to give the quinone in the rate-determining step.

Table I. Crystal Data and Summary of Data Collection and Refinement for $[Co_4(DBCat)_4(THF)_{5.5}]$

formula	$Co_4O_{13.5}C_{78}H_{124}$
fw	1513.57
cryst system	triclinic
space group	$P\bar{1}$
based on conditions	none
cryst dimens, mm	0.30 × 0.50 × 0.60
cryst color and habit	green plates
a, Å	15.078 (7)
b, Å	16.080 (6)
c, Å	19.344 (6)
α, deg	85.43 (3)
β, deg	83.67 (3)
γ, deg	81.78 (3)
Z	2
V, Å^3	4604 (4)
d(130 K)calcd, g/cm^3	1.09
radiation	Mo Kα (λ = 71069 Å)
linear abs coeff, cm^{-1}	7.5
temp, K	130
instrument	Syntex $P2_1$
scan speed, deg/min	20
scan width, deg	1.6
type of scan	ω
ω offset for bkgds, deg	1.2
2θ(max), deg	45
range of transmission factors	0.70-0.83
octants	$+h, \pm k, \pm l$
no. of variables	448
data/variable ratio	10.0
programs	SHELXTL, Version 4
no. of reflcns collected	12 167
no. of unique data	12 167
R(merge)	0.005
no. of data used in refinement	4457 ($I > 3\sigma(I)$)
$R(F)$	0.098
$R_w(F)$	0.108
largest feature on final diff map	0.96 e Å^{-3}, 1.55 Å from O(13)

Numerous semiquinone and catecholate complexes have been synthesized and characterized by X-ray crystallography. The differences in M-O, C-O, and (O)C-C(O) bond lengths readily allows a distinction to be made between catecholate and semiquinone complexation.[1] First-row transition-metal catecholate derivatives that have appeared in the literature include Cr,[12,13] Mn,[14] Fe,[13] Co,[15-17] Ni,[17] and Cu.[1,18,19] With regard to the title compound, the cobalt complexes $[Co_4(DBSQ)_8]$[17] and $[Co(DBCat)(DBSQ)(bpy)]$ (DBSQ = 3,5-di-tert-butylsemiquinone) are particularly relevant.[16] Our synthesis of the cobalt catecholate complex is a natural extension of our interest in low-coordinate cobalt alkoxides and in the tetradentate aryloxide *p*-*tert*-butylcalix[4]arene. Structural determinations of mononuclear[20] as well as dimeric[21] and trinuclear[22] $[Co_3$(p-*tert*-butylcalix[4]arene)$_2$-

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Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $[Co_4(DBCat)_4(THF)_{5.5}]$

	x	*y*	*z*	*U*
Co(1)	4048 (2)	2201 (1)	2647 (1)	48 (1)[a]
Co(2)	1997 (2)	2137 (1)	3378 (1)	51 (1)[a]
Co(3)	2542 (2)	3749 (1)	2497 (1)	46 (1)[a]
Co(4)	2432 (2)	2122 (1)	1749 (1)	48 (1)[a]
O(1)	3317 (7)	2944 (6)	1855 (5)	45 (3)
O(2)	4942 (7)	2059 (6)	1836 (5)	49 (3)
O(3)	2967 (8)	1482 (7)	2598 (6)	55 (3)
O(4)	2147 (8)	1035 (7)	3821 (6)	60 (3)
O(5)	3051 (7)	2825 (6)	3326 (5)	42 (3)
O(6)	2592 (7)	4515 (6)	3192 (5)	48 (3)
O(7)	1633 (7)	2938 (6)	2538 (5)	48 (3)
O(8)	1390 (8)	2488 (7)	1285 (6)	53 (3)
O(9)	4865 (8)	3138 (6)	2947 (5)	53 (3)
O(10)	4826 (8)	1301 (7)	3278 (6)	53 (3)
O(11)	1168 (8)	2637 (7)	4237 (6)	61 (3)
O(12)	2249 (7)	4737 (6)	1742 (5)	49 (3)
O(13)	2986 (9)	1406 (7)	913 (6)	70 (4)
C(1)	3929 (11)	3043 (9)	1248 (8)	39 (4)
C(2)	4785 (11)	2572 (9)	1275 (8)	39 (4)
C(3)	5426 (11)	2711 (9)	713 (8)	38 (4)
C(4)	5143 (11)	3211 (8)	139 (8)	34 (4)
C(5)	4299 (11)	3628 (9)	89 (8)	38 (4)
C(6)	3652 (11)	3583 (9)	706 (8)	40 (4)
C(7)	6397 (13)	2209 (11)	721 (9)	60 (5)
C(8)	6789 (13)	2497 (11)	1368 (9)	58 (5)
C(9)	6332 (15)	1247 (11)	781 (11)	75 (6)
C(10)	6958 (13)	2464 (11)	62 (9)	64 (5)
C(11)	4024 (11)	4135 (9)	−567 (8)	37 (4)
C(12)	3267 (14)	4901 (11)	−396 (11)	74 (6)
C(13)	4749 (12)	4483 (11)	−1000 (10)	65 (5)
C(14)	3597 (15)	3582 (12)	−1002 (11)	75 (6)
C(15)	3019 (11)	618 (9)	2798 (8)	44 (4)
C(16)	2608 (12)	415 (10)	3446 (9)	51 (5)
C(17)	2647 (12)	−438 (10)	3670 (9)	51 (5)
C(18)	3150 (12)	−1022 (11)	3245 (9)	59 (5)
C(19)	3587 (13)	−826 (11)	2612 (9)	60 (5)
C(20)	3529 (13)	47 (11)	2395 (10)	60 (5)
C(21)	2231 (13)	−678 (11)	4398 (10)	64 (5)
C(22)	1167 (15)	−402 (14)	4439 (12)	97 (7)
C(23)	2644 (15)	−296 (12)	4953 (10)	72 (6)
C(24)	2332 (16)	−1650 (12)	4564 (11)	85 (7)
C(25)	4181 (14)	−1480 (12)	2158 (10)	69 (6)
C(26)	5200 (17)	−1397 (15)	2149 (13)	107 (8)
C(27)	4134 (22)	−2367 (18)	2486 (16)	147 (11)
C(28)	3999 (19)	−1339 (17)	1428 (13)	127 (10)
C(29)	3159 (11)	3278 (10)	3880 (8)	46 (4)
C(30)	2889 (11)	4194 (9)	3803 (8)	40 (4)
C(31)	2964 (12)	4663 (10)	4362 (8)	48 (4)
C(32)	3298 (11)	4249 (10)	4951 (8)	46 (4)
C(33)	3564 (12)	3390 (10)	5047 (9)	48 (5)
C(34)	3458 (11)	2897 (10)	4488 (8)	44 (4)
C(35)	2679 (13)	5637 (11)	4304 (9)	61 (5)
C(36)	1644 (15)	5788 (13)	4194 (11)	84 (7)
C(37)	3211 (14)	6062 (12)	3701 (10)	73 (6)
C(38)	2780 (14)	6035 (11)	4966 (10)	66 (6)
C(39)	3933 (11)	2945 (9)	5696 (8)	44 (4)
C(40)	3970 (14)	3554 (11)	6267 (9)	66 (6)
C(41)	4873 (12)	2496 (11)	5504 (9)	59 (5)
C(42)	3337 (14)	2303 (12)	6009 (10)	72 (6)
C(43)	845 (11)	3237 (9)	2277 (8)	45 (4)
C(44)	762 (11)	3043 (10)	1596 (8)	44 (4)
C(45)	−48 (12)	3392 (10)	1274 (9)	52 (5)
C(46)	−679 (12)	3936 (10)	1650 (9)	52 (5)
C(47)	−586 (13)	4178 (11)	2322 (10)	62 (5)
C(48)	199 (13)	3796 (11)	2629 (10)	69 (6)
C(49)	−147 (14)	3190 (11)	549 (10)	69 (6)
C(50)	637 (16)	3478 (14)	21 (12)	91 (7)
C(51)	−188 (16)	2237 (14)	509 (12)	92 (7)
C(52)	−1070 (14)	3638 (12)	273 (10)	73 (6)
C(53)	−1323 (15)	4814 (13)	2684 (11)	82 (6)
C(54)	−2175 (21)	4432 (18)	2832 (15)	135 (10)
C(55)	−1112 (17)	5054 (15)	3370 (13)	103 (8)
C(56)	−1467 (21)	5626 (18)	2157 (16)	139 (10)
C(57)	4945 (13)	3900 (10)	2544 (9)	61 (5)
C(58)	5339 (16)	4475 (14)	2926 (11)	96 (7)
C(59)	5498 (14)	3964 (11)	3622 (10)	68 (6)
C(60)	5466 (13)	3084 (10)	3458 (9)	56 (5)
C(61)	5622 (14)	826 (12)	2940 (11)	82 (6)
C(62)	5905 (14)	131 (12)	3450 (10)	75 (6)
C(63)	5035 (12)	−33 (10)	3884 (9)	51 (5)
C(64)	4576 (12)	878 (10)	3937 (9)	52 (5)
C(65)	824 (15)	3509 (12)	4399 (11)	83 (6)
C(66)	930 (17)	3637 (14)	5151 (12)	101 (8)
C(67)	719 (20)	2714 (15)	5432 (14)	124 (9)
C(68)	1162 (16)	2153 (13)	4924 (11)	92 (7)
C(69)	2805 (14)	5388 (11)	1666 (11)	76 (6)
C(70)	2139 (18)	6201 (15)	1720 (14)	115 (9)
C(71)	1245 (18)	5949 (14e	1811 (13)	109 (8)
C(72)	1400 (14)	5099 (12)	1541 (11)	79 (6)
C(73)	3871 (23)	1096 (22)	622 (19)	176 (14)
C(74)	4095 (23)	1130 (22)	−99 (18)	172 (14)
C(75)	3290 (19)	1144 (18)	−294 (15)	141 (11)
C(76)	2674 (25)	1685 (21)	187 (17)	174 (13)
O(14)	531	1712	3246	100
C(77)	−370	1967	3579	100
C(78)	−989	1781	2948	100
C(79)	−608	1354	2649	100
C(80)	527	1019	2691	100

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

(THF)] species have been carried out. In this paper, we describe the first structure of a neutral cobalt(II) catecholate, $[Co_4(DBCat)_4(THF)_{5.5}]$, and some of its magnetic and spectroscopic properties.

Experimental Section

All manipulations were performed by using modified Schlenk techniques under an atmosphere of N_2. Solvents were freshly distilled from drying agents and degassed twice before use. 3,5-Di-*tert*-butylcatechol ($DBCatH_2$) was purchased from Aldrich and used without further purification; $[Co\{N(SiMe_3)_2\}_2]_2$ was synthesized by a literature procedure.[23]

Preparation of $[Co_4(DBCat)_4(THF)_{5.5}]$. Addition of $[Co\{N(SiMe_3)_2\}_2]_2$ (5.25 g, 6.93 mmol) in THF (40 mL) to $DBCatH_2$ (3.08 g, 13.85 mmol) in toluene (60 mL) at ca. −40 °C initially gave a purple solution that changed almost immediately to green. The solution was then stirred overnight at room temperature. After brief heating to 40 °C, filtration, and slow cooling over 20 h to −20 °C, green plates were obtained that were suitable for X-ray diffraction studies. These were separated and dried in vacuo under reduced pressure: yield 2.51 g, 48%; mp >250 °C dec.

X-ray Crystallographic Studies. X-ray data were collected by using a Syntex P2$_1$ diffractometer equipped with a locally modified Syntex LT-1 device. Calculations were carried out on a Data General Eclipse computer using the SHELXTL program system. The atom form factors, including anomalous scattering, were from ref 24.

Green plates of $[Co_4(DBCat)_4(THF)_{5.5}]$, were transferred from the Schlenk tube under N_2 and immediately covered with a layer of hydrocarbon oil. Crystals exposed to air rapidly turn brown with loss of crystallinity. A single green platelet was selected and attached to a glass fiber that was immediately placed in the low-temperature N_2 stream. A 2% decay in the intensity of two standard reflections was observed during data collection, and the data were scaled accordingly. The data were corrected for Lorentz, polarization, and absorption effects.[25] The structure was solved by the Patterson technique. Of the 4457 reflections with $I > 3\sigma(I)$, 12 low-angle reflections were affected by extinction and were omitted. One of the THF molecules, which is comprised of O(14) and C(77) to C(80), has only partial occupancy and did not refine well. This THF also has a very long Co–O distance. Its positional parameters were taken from a final difference map and fixed. The thermal parameter was fixed at 0.10 $Å^2$, and the occupancy was allowed to refine. It converged at 52 (1)% occupancy for the group; hence, a nonintegral number of THF molecules, $(THF)_{5.5}$, appears in the formula. In the final

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(25) Program XABS by H. Hope and B. Moezzi. The program obtains an absorption tensor from F_o–F_c differences.

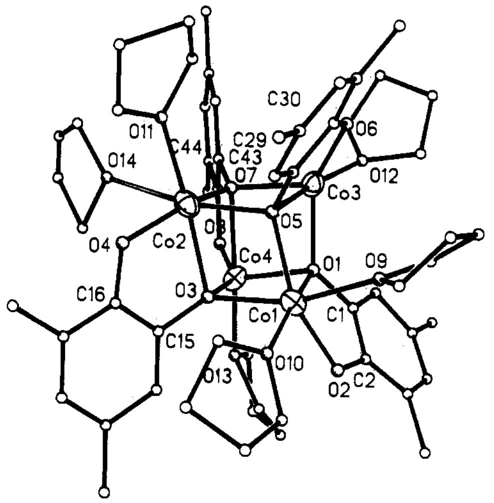

Figure 1. Computer-generated plot of $[Co_4(DBCat)_4(THF)_{5.5}]$. *tert*-Butyl groups have been indicated by a single carbon for clarity. Cobalt atoms are plotted with 35% probability thermal ellipsoids. The remaining atoms are shown with an arbitrary size.

Table III. Selected Bond Distances (Å) for $[Co_4(DBCat)_4(THF)_{5.5}]$

Co–O(Cat) terminal (av)	1.916 (14)	O(6)–C(30)	1.35 (2)
Co–O(Cat) bridging(av)	2.107 (11)	O(7)–C(43)	1.35 (2)
Co–O(THF)(av)	2.183 (11)	O(8)–C(44)	1.33 (2)
O(1)–C(1)	1.42 (2)	C(1)–C(2)	1.40 (2)
O(2)–C(2)	1.33 (2)	C(15)–C(16)	1.37 (2)
O(3)–C(15)	1.41 (2)	C(29)–C(30)	1.47 (2)
O(4)–C(16)	1.35 (2)	C(43)–C(44)	1.40 (2)
O(5)–C(29)	1.38 (2)		
Co(1)···Co(2)	3.267 (10)	Co(2)–O(5)	2.052 (11)
Co(1)···Co(3)	3.138 (10)	Co(2)–O(7)	2.064 (10)
Co(1)···Co(4)	3.167 (10)	Co(2)–O(11)	2.108 (11)
Co(2)···Co(3)	3.146 (10)	Co(2)–O(14)	2.450 (1)
Co(2)···Co(4)	3.147 (10)	Co(3)–O(1)	2.021 (10)
Co(3)···Co(4)	3.121 (10)	Co(3)–O(5)	2.222 (10)
Co(1)–O(1)	2.168 (10)	Co(3)–O(6)	1.911 (11)
Co(1)–O(2)	1.959 (10)	Co(3)–O(7)	2.013 (12)
Co(1)–O(3)	2.144 (12)	Co(3)–O(12)	2.103 (10)
Co(1)–O(5)	2.081 (10)	Co(4)–O(1)	2.044 (11)
Co(1)–O(9)	2.225 (12)	Co(4)–O(3)	2.047 (11)
Co(1)–O(10)	2.124 (11)	Co(4)–O(7)	2.229 (10)
Co(2)–O(3)	2.202 (11)	Co(4)–O(8)	1.893 (12)
Co(2)–O(4)	1.900 (11)	Co(4)–O(13)	2.089 (12)

cycles of refinement all atoms were refined isotropically except cobalt atoms. These were refined anisotropically. Hydrogen atoms were included at calculated positions by using a riding model, and their thermal parameters were given the value 1.2 times the thermal parameter of the bonded carbon. Further details of data collection and refinement are given in Table I, and positional parameters are given in Table II.

Results and Discussion

Structure. $[Co_4(DBCat)_4(THF)_{5.5}]$, as illustrated in Figure 1, is the first structurally characterized multinuclear cobalt(II) catecholate. Pertinent bond lengths and angles are given in Tables III and IV. Each cobalt(II) is bound to three triply bridging oxygens and a terminal oxygen from the DBCat ligands. Further coordination to two THF donor molecules gives distorted octahedral geometries at Co(1) and Co(2). Co(3) and Co(4), which are coordinated to only one THF, have a distorted tbp environment. The deviations from octahedral geometry at Co(1) and Co(2) can readily be seen in Figure 1. For these two cobalt centers the atoms O(14), O(11), Co(2), O(5), O(3), Co(1), O(2), and O(9) are nearly coplanar. Oxygens O(1) and O(10) and oxygens O(4) and O(7) occupy the coordination sites above and below this plane (O(1)–Co(1)–O(10) = 169.0 (4)°; O(7)–Co(2)–O(4) = 150.0 (5)°). As in mononuclear ionic catecholate complexes, the acute O–M–O angle imposed by the DBCat ligand (average 80.2°) accounts for much of the geometrical distortion at the cobalt atoms. For the five-coordinate cobalts, Co(3) and Co(4), the metals almost form a plane with three oxygens. For example, Co(3) is nearly coplanar with O(1), O(7), and O(6) ($\sum$ angles at Co = 353°). However, the three equatorial angles at Co(3) are quite irregular, with values 85.2 (4), 124.7 (4), and 143.0 (5)°. The axial ligands for Co(3) involve O(12) and O(5), those for Co(4) involve O(7) and O(13), and the degree of deviation from tbp coordination can be gauged from the angles O(2)–Co(3)–O(5) = 169.8 (4)° and O(7)–Co(4)–O(13) = 170.1 (5)°. The Co–O bond lengths range from ca. 1.93 Å for terminal catechol and ca. 2.12 Å for triply bridging catechol to ca. 2.23 Å for the THF ligand in six-coordinate cobalt. The Co_4O_4 cubane core (common to many M_4X_4 systems) is also distorted. As a result, Co(1) and Co(2) are further apart than Co(3) and Co(4). The Co···Co distances are 3.267 (2) and 3.121 (2) Å, respectively. The slight increase in crowding at the latter cobalt may be one of the reasons that Co(3) and Co(4) are five- rather than six-coordinate and have one rather than two THF donors.

Table IV. Selected Bond Angles (deg) for $[Co_4(DBCat)_4(THF)_{5.5}]$

Co(1)–O(1)–Co(3)	97.0 (4)	O(4)–Co(2)–O(5)	117.8 (5)
Co(1)–O(1)–Co(4)	97.5 (4)	O(4)–Co(2)–O(7)	150.0 (5)
Co(3)–O(1)–Co(4)	100.3 (5)	O(4)–Co(2)–O(11)	92.8 (5)
Co(1)–O(3)–Co(2)	97.5 (5)	O(4)–Co(2)–O(14)	80.0 (4)
Co(1)–O(3)–Co(4)	98.2 (4)	O(5)–Co(2)–O(7)	83.4 (4)
Co(2)–O(3)–Co(4)	95.5 (4)	O(5)–Co(2)–O(11)	101.1 (4)
Co(1)–O(5)–Co(2)	104.5 (5)	O(7)–Co(2)–O(11)	104.4 (4)
Co(2)–O(5)–Co(3)	94.7 (4)	O(7)–Co(2)–O(14)	80.1 (4)
Co(2)–O(7)–Co(3)	101.0 (5)	O(11)–Co(2)–O(14)	76.8 (4)
Co(2)–O(7)–Co(4)	94.2 (4)	O(1)–Co(3)–O(5)	83.4 (4)
Co(3)–O(7)–Co(4)	94.6 (4)	O(1)–Co(3)–O(6)	143.0 (5)
O(1)–Co(1)–O(2)	79.7 (4)	O(1)–Co(3)–O(7)	85.2 (4)
O(1)–Co(1)–O(3)	79.0 (4)	O(1)–Co(3)–O(12)	97.4 (4)
O(1)–Co(1)–O(5)	83.3 (4)	O(5)–Co(3)–O(6)	81.4 (4)
O(1)–Co(1)–O(9)	100.6 (4)	O(5)–Co(3)–O(7)	80.4 (4)
O(1)–Co(1)–O(10)	169.0 (4)	O(6)–Co(3)–O(12)	92.1 (4)
O(2)–Co(1)–O(3)	111.5 (5)	O(6)–Co(3)–O(7)	124.7 (4)
O(2)–Co(1)–O(5)	157.6 (4)	O(6)–Co(3)–O(12)	92.1 (4)
O(2)–Co(1)–O(9)	85.7 (4)	O(7)–Co(3)–O(12)	109.8 (4)
O(2)–Co(1)–O(10)	92.5 (4)	O(1)–Co(4)–O(3)	84.2 (4)
O(3)–Co(1)–O(5)	79.3 (4)	O(1)–Co(4)–O(7)	79.4 (4)
O(3)–Co(1)–O(9)	162.3 (4)	O(1)–Co(4)–O(8)	120.0 (4)
O(5)–Co(1)–O(9)	113.1 (4)	O(1)–Co(4)–O(13)	106.4 (5)
O(5)–Co(1)–O(10)	106.0 (4)	O(3)–Co(4)–O(7)	84.0 (4)
O(9)–Co(1)–O(10)	86.5 (4)	O(3)–Co(4)–O(8)	147.3 (5)
O(3)–Co(2)–O(4)	79.8 (4)	O(3)–Co(4)–O(13)	104.4 (4)
O(3)–Co(2)–O(5)	78.6 (4)	O(7)–Co(4)–O(8)	80.0 (4)
O(3)–Co(2)–O(4)	79.8 (4)	O(7)–Co(4)–O(13)	170.1 (5)
O(3)–Co(2)–O(7)	84.3 (4)	O(8)–Co(4)–O(13)	90.1 (5)
O(3)–Co(2)–O(14)	106.2 (4)		

The Co_4O_4 cubane core is, to our knowledge, the first structurally characterized example of its type from cobalt. It bears no resemblance to the related semiquinone complex $[Co_4(DBSQ)_8]$[17] (DBSQ = 3,5-di-*tert*-butylsemiquinone) or the cobalt trimer $[Co_3(4\text{-}tert\text{-butylcalix[4]arene})_2(THF)]$.[22] It also differs from the tetranuclear copper(II) catecholate complex $[Cu_4(DBCat)_4(py)_4]$[26] in that it lacks any parallel stacking of the catecholate ligands.

A comparison of cobalt transition-metal catecholate and semiquinone complexes is given in Table V. It can be seen that in $[Co_4(DBCat)_4(THF)_{5.5}]$ all four ligands have structural features that are consistent with their formulation as catecholates. For example, the terminal Co–O bond lengths average 1.916 (14) Å and are significantly shorter than the corresponding terminal Co–O distances in the semiquinone tetramer (Co–O average 2.046 (5) Å).[17] The difference in oxidation state at cobalt can also be reliably determined from Co–O bond lengths. Thus, in the Co(III) mixed semiquinone catecholate complex [Co(DBSQ)(DBCat)(bpy)], terminal Co–O bonds for the catecholate portion are significantly shorter (ca. 1.868 Å) than in $[Co_4(DBCat)_4(THF)_{5.5}]$ as a result of the higher oxidation state of cobalt.[16] In the latter, the Co–O triply bridging distances are, as expected, considerably longer than terminal distances with values ranging from 2.014 (12) to 2.231 (11) Å and similar to those seen elsewhere.[20,22]

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[26] Olmstead, M. M.; Power, P. P.; Speier, G.; Tyeklar, Z. *Polyhedron*, in press.

Table V. Average Bond Lengths (Å) for Semiquinone and Catecholate Complexes

	Co–O[a]	C–O	OC–CO	ref
	Catecholate			
$[Co_4(DBCat)_4(THF)_{5.5}]$	1.916 (14) (trml) 2.107 (11) (tr br)	1.364 (19)	1.412 (22)	this work
[Co(DBSQ)(DBCat)(bpy)]	1.868 (6)	1.358 (10)	1.376 (12)	16
	Semiquinone			
$[Co(DBSQ)_2]_4$	2.046 (5) (trml) 2.055 (4) (db br) 2.191 (4) (tr br)	1.285 (7)	1.448 (9)	17
[Co(DBSQ)(DBCat)(bpy)]	1.897 (6)	1.297 (9)	1.446 (11)	16

[a] Average terminal, doubly bridging, and triply bridging Co–O bond lengths are designated by trml, db br, and tr br, respectively.

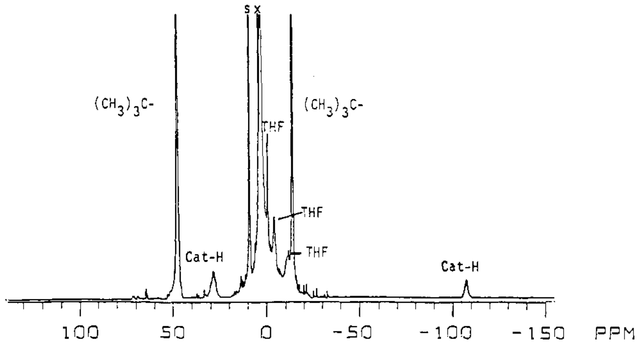

Figure 2. FT ^1H NMR spectrum (360 MHz) in C_6D_6 at 24 °C. Signals due to impurities are designated by ×.

Semiquinone complexes generally have carbon–oxygen lengths of ca. 1.29 Å whereas in catecholate complexes carbon–oxygen bonds are longer, ca. 1.35 Å.[1] The latter value is close to those seen in $[Co_4(DBCat)_4(THF)_{5.5}]$, where the C–O distances average ca. 1.36 Å, further supporting catecholate formulation. A third characteristic that distinguishes catechol from semiquinone bound ligands is the C–C bond length (between the oxygen substituents) within the chelate ring. These distances are ca. 1.40 Å for catecholates and are lengthened to 1.48 Å for semiquinones.[1] For $[Co_4(DBCat)_4(THF)_{5.5}]$, these C–C distances average 1.40 Å with the exception of the C(9)–C(30) value of 1.473 (21) Å. This lengthened value is attributed to thermal motion, as is evident in the high standard deviation in the bond length. Otherwise, bond lengths and bond angles in that particular ring are normal.

Spectra. The electronic spectrum of $[Co_4(DBCat)_4(THF)_{5.5}]$ was obtained in a toluene/THF solution. Three transitions were seen, at 372 nm (ϵ 4000), 494 nm (ϵ 660), and 624 nm (ϵ 700).

The IR spectrum (Nujol) shows two intense absorptions at 1310 and 1261 cm^{-1}, which have been tentatively assigned as terminal ν(C–O) stretching frequences of the catecholate ligand. Generally, terminal ν(C–O) stretching frequencies in chelated catechol ligands are in the range 1226–1270 cm^{-1} whereas in their semiquinone counterparts ν(C–O) frequencies are higher, appearing at ca 1440–1660 cm^{-1}.[27] Two other intense absorptions that appear at 1031 and 970 cm^{-1} are presumed due to ν(C–O) triply bridging frequencies.

As with prior ^1H NMR studies[21] of paramagnetic Co(II) complexes involving alkoxide ligands, the signals are isotropically shifted. No attempt was made to calculate pseudocontact or dipolar contributions. However, Figure 2 shows that there are equally intense *t*-Bu resonances at −17.3 and 50.9 ppm. These have been assigned to the 5-*t*-Bu and 3-*t*-Bu groups, respectively. Assignments for the hydrogens on the catechol ring as well as methylene hydrogens for the THF bound molecules are less clear. For the aromatic protons tentative assignments involve the broadened resonances at 26.5 and −119.5 ppm for DBCat-H on the basis of a 1:9 intensity ratio relative to *tert*-butyl signals. Strong isotropic shifts for catecholate hydrogens have also been reported in the Mo–Fe–S cluster $[Et_4N]_3[MoFe_4S_4(SEt)_3(Cat)_3]$, where similar catechol chelation is observed.[28] Three resonances, of which two integrate 2:9 and the third integrates 4:9, appearing at −1.6, −14.7, and −10.2 ppm are tentatively assigned to methylene protons of the one bound THF molecule. The remaining broad resonance at 0.63 ppm shows no temperature dependence between +25 and −60 °C and seems to be a result of decomposition (or perhaps dissociation of a THF) over a period of 24 h.

No ESR signals were seen for a toluene/THF solution at room temperature. Lowering the temperature to 10 K allowed a powder spectrum to be obtained. This consists of a well-resolved resonance at 3107 G ($g = 2.1699$) and a less intense broad resonance centered at 2500 G ($g = 2.7391$). In accordance with previous ESR studies, these results are characteristic of a high-spin Co(II) ion in a distorted octahedral environment.[27–31] Magnetic susceptibility studies on this and other neutral cobalt alkoxides[21] are currently under way.[32,33]

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Registry No. $[Co_4(DBCat)_4(THF)_{5.5}]$, 111525-60-1; $[Co\{N(SiMe_3)_2\}_2]_2$, 93280-44-5.

Supplementary Material Available: Tables of isotropic thermal parameters, complete bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates (6 pages); a listing of observed and calculated structure factors (27 pages). Ordering information is given on any current masthead page.

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