Tetra-μ_3-methanolato-tetrakis[(2-formylphenolato-O)-(methanol-O)cobalt(II)]

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The title complex, [Co$_4$(CH$_3$O)$_4$$L_4$(CH$_4$O)$_4$] ($L$H = 2-hydroxybenzaldehyde, C$_7$H$_6$O$_2$), has a cubane-type structural topology with four Co atoms and four O atoms, each derived from MeO$^-$, at alternate corners. Each Co atom is coordinated in a distorted octahedral geometry defined by three bridging O atoms, two O atoms from chelating L, and one O atom from a methanol molecule.
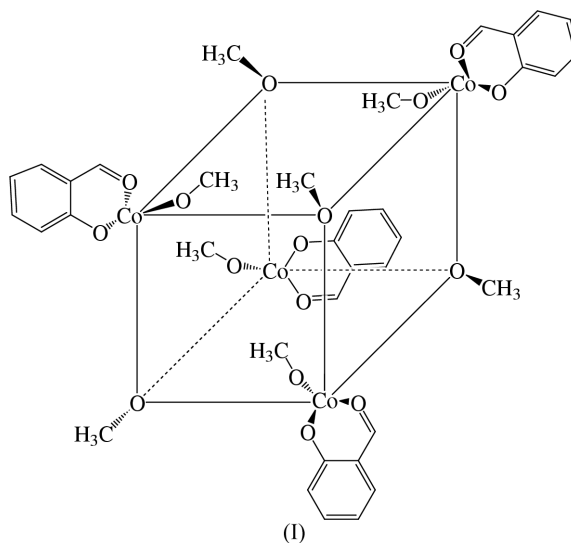
Comment

In the past two decades, cubane-type polynuclear complexes have received much attention owing to their magnetic and optical properties, as well their biological relevance. Complexes of the type Mn$_4$O$_4$ and their derivatives have been extensively studied for they are thought to have relevance to the Water Oxidation Center (WOC) in the photosynthetic apparatus of green plants and cyanobacteria (Christou, 1989; Brudrig *et al.*, 1991; Dimitrou *et al.*, 1993; Taft *et al.*, 1993; Wieghardt, 1989). Recently, several cubane-type complexes of

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cobalt and other transition metals, such as nickel, zinc and cadmium, have been reported. For example, Christou and others have reported biologically relevant cubane complexes, *e.g.* [Co$_4$O$_4$(OAc)$_2$bpy$_4$(ClO$_4$)$_2$], containing the [Co$_4$O$_4$]$^{4+}$ core, which is structurally analogous to, but more stable than, that of Mn^{III}Mn^{IV} or Mn$_4^{IV}$ species (Dimitrou *et al.*, 1993). Two mixed-valence clusters, [Co$_8$O$_4$(O$_2$CPh)$_{12}$solv$_4$] (solv = DMF, MeCN, H$_2$O) containing the [Co$_4^{III}$O$_4$]$^{4+}$ core, [Co$_8$O$_4$(O-H)$_4$(OAc)$_6$$L_2$](ClO$_4$)$_2$ [L = 1,2-bis(2,2'-bipyridyl-6-yl)ethane] containing a [Co$_8$$\mu_4$-O$_4$($\mu_3$-OH)$_4$]$^{8+}$ core with an unusual face-sharing triple-cubane architecture, as well as [Co$_4$(2,2-PyC-(O)(OH)$_4$(OAc)$_3$(H$_2$O)](ClO$_4$), containing the [Co$_4^{II}$O$_4$]$^{4+}$

cubane unit, have been also reported (Dimitrou *et al.*, 1995; Grillo *et al.*, 1996; Tong *et al.*, 1999). In an attempt to prepare Schiff base complexes, the unexpected complex, [Co$_4$(OMe)$_4$-L$_4$(MeOH)$_4$] (LH = 2-hydroxybenzaldehyde), was isolated and characterized crystallographically.

As shown in Fig. 1, four Co atoms and four O atoms, each from MeO$^-$, occupy alternate corners of the cubane unit where each Co atom is surrounded by three bridging O atoms derived from MeO$^-$, one from MeOH and two O atoms from chelating 2-formylphenolate so as to form a distorted octahedral geometry. Each of the bridging O atoms has a remarkably distorted tetrahedral geometry. The Co—O(MeOH) bond lengths are longer than those for Co—O(MeO$^-$).

Experimental

A solution of melamine (0.04 g, 0.33 mmol) and salicylaldehyde (0.12 g, 1 mmol) in methanol solution (20 ml) was heated to 333 K for 3 h with vigorous stirring. After cooling, NaOH (0.04 g, 1 mmol) in methanol (5 ml) was added to the colorless solution. Co(NO$_3$)$_2$·6H$_2$O (0.15 g, 0.5 mmol) was then added and the reaction mixture was stirred for 1 h to give a red solution which was filtered. Deep-red and pale-red crystalline complexes were obtained by keeping the resultant solution open to the air for a week. A deep-red single-crystal was selected for X-ray diffraction.

Crystal data

[Co$_4$(CH$_3$O)$_4$(C$_7$H$_5$O$_2$)$_4$(CH$_4$O)$_4$]	$D_x = 1.518$ Mg m^{-3}
$M_r = 972.46$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 154
$a = 14.6546$ (5) Å	reflections
$b = 14.7082$ (5) Å	$\theta = 3.1$–$20.7°$
$c = 20.3235$ (7) Å	$\mu = 1.60$ mm^{-1}
$\beta = 103.789$ (1)°	$T = 293$ (2) K
$V = 4254.3$ (3) Å^3	Block, dark-red
$Z = 4$	$0.50 \times 0.45 \times 0.45$ mm

Data collection

Siemens SMART CCD	7411 independent reflections
diffractometer	5377 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.039$
Absorption correction: empirical	$\theta_{max} = 24.9°$
(*SADABS*; Sheldrick, 1996)	$h = -17 \rightarrow 17$
$T_{min} = 0.454$, $T_{max} = 0.487$	$k = -12 \rightarrow 17$
15 156 measured reflections	$l = -10 \rightarrow 24$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0537P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.037$	$+ 0.6296P]$
$wR(F^2) = 0.103$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} = 0.001$
7411 reflections	$\Delta\rho_{max} = 0.58$ e Å^{-3}
521 parameters	$\Delta\rho_{min} = -0.37$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Co1—O1	2.147 (3)	Co2—O8	2.114 (2)
Co1—O5	2.131 (2)	Co2—O21	2.115 (2)
Co1—O6	2.116 (2)	Co2—O22	2.035 (2)
Co1—O7	2.054 (2)	Co3—O3	2.165 (3)
Co1—O11	2.101 (2)	Co3—O5	2.103 (2)
Co1—O12	2.030 (2)	Co3—O7	2.114 (2)
Co2—O2	2.152 (3)	Co3—O8	2.076 (2)
Co2—O5	2.064 (2)	Co3—O31	2.125 (2)
Co2—O6	2.102 (2)	Co3—O32	2.022 (2)
Co4—O4	2.194 (3)	Co4—O8	2.141 (2)
Co4—O6	2.052 (2)	Co4—O41	2.088 (2)
Co4—O7	2.107 (2)	Co4—O42	2.024 (2)
O12—Co1—O5	91.51 (8)	O5—Co3—O3	166.01 (11)
O12—Co1—O6	93.66 (9)	O5—Co3—O7	83.52 (8)
O12—Co1—O7	173.41 (9)	O5—Co3—O31	99.04 (9)
O12—Co1—O11	88.30 (9)	O7—Co3—O3	88.13 (10)
O5—Co1—O1	91.44 (10)	O7—Co3—O31	175.72 (8)
O6—Co1—O1	168.34 (9)	O8—Co3—O3	88.19 (10)
O6—Co1—O5	83.07 (8)	O8—Co3—O5	79.88 (8)
O7—Co1—O1	88.44 (10)	O8—Co3—O7	84.54 (8)
O7—Co1—O5	84.30 (8)	O8—Co3—O31	99.25 (9)
O7—Co1—O6	80.81 (8)	O31—Co3—O3	90.01 (11)
O7—Co1—O11	95.88 (9)	O32—Co3—O3	95.88 (11)
O11—Co1—O1	88.68 (10)	O32—Co3—O5	95.24 (9)
O11—Co1—O5	179.78 (9)	O32—Co3—O7	89.46 (9)
O11—Co1—O6	96.84 (9)	O32—Co3—O8	172.64 (9)
O12—Co1—O1	96.77 (10)	O32—Co3—O31	86.90 (9)
O5—Co2—O2	87.72 (10)	O6—Co4—O4	89.08 (10)
O5—Co2—O6	85.07 (8)	O6—Co4—O7	81.07 (8)
O5—Co2—O8	79.89 (8)	O6—Co4—O8	84.32 (8)
O5—Co2—O21	98.71 (9)	O6—Co4—O41	93.95 (9)
O6—Co2—O2	90.07 (10)	O7—Co4—O4	168.73 (10)
O6—Co2—O8	83.79 (8)	O7—Co4—O8	83.12 (8)
O6—Co2—O21	176.18 (8)	O8—Co4—O4	90.50 (9)
O8—Co2—O2	166.58 (10)	O41—Co4—O4	87.92 (10)
O8—Co2—O21	97.34 (9)	O41—Co4—O7	98.16 (9)
O21—Co2—O2	89.57 (10)	O41—Co4—O8	177.67 (9)
O22—Co2—O2	98.48 (11)	O42—Co4—O4	96.68 (11)
O22—Co2—O5	171.91 (9)	O42—Co4—O6	173.63 (10)
O22—Co2—O6	89.70 (9)	O42—Co4—O7	92.92 (9)
O22—Co2—O8	93.42 (9)	O42—Co4—O8	92.88 (8)
O22—Co2—O21	86.59 (9)	O42—Co4—O41	89.00 (9)

H-atom positions were generated geometrically and allowed to ride on their respective parent C atoms. The O—H atoms were
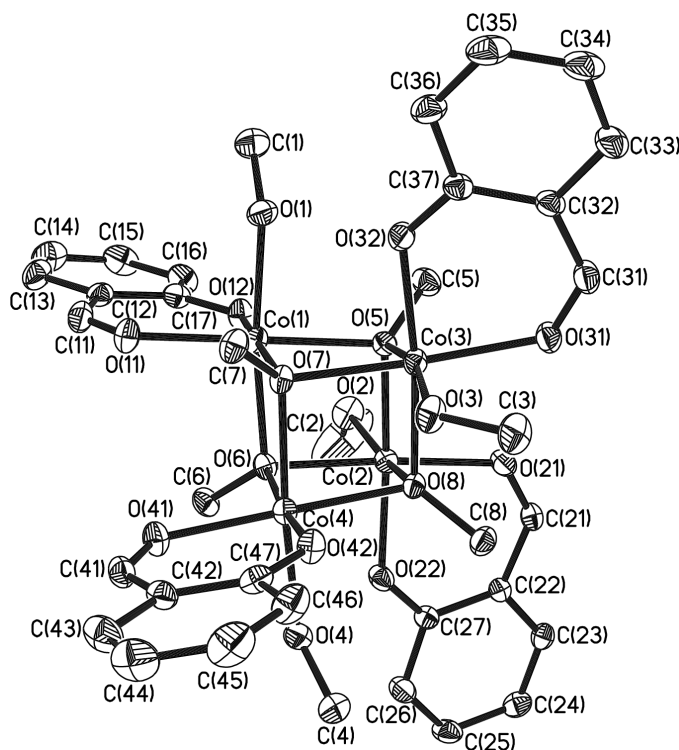

Figure 1
The structure of [Co$_4$(OMe)$_4$L$_4$(MeOH)$_4$]. Displacement ellipsoids are plotted at the 50% probability level (Sheldrick, 1997)

refined with isotropic displacement parameters but fixed in the final cycles of least-squares refinement.

Data collection: *SMART* (Siemens, 1994); cell refinement: *SMART*; data reduction: *SMART*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXL*97; software used to prepare material for publication: *SHELXL*97.

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