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 μ_3 -Oxido-hexa- μ_2 -pivalato-tris-
[(methanol- κ O)cobalt(III)] chloride
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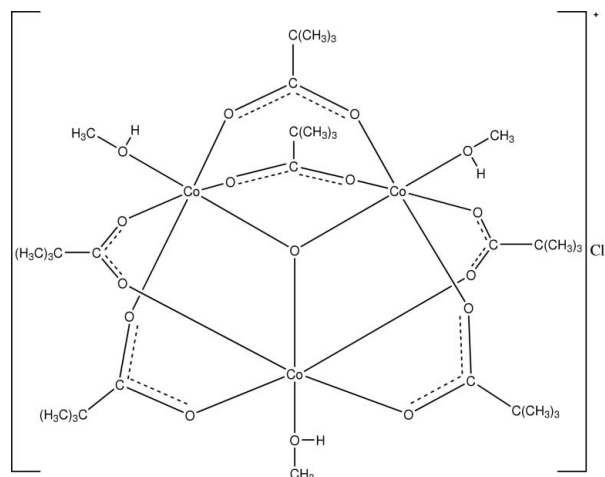
Received 22 September 2009; accepted 13 October 2009

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.037; wR factor = 0.102; data-to-parameter ratio = 14.8.

The crystal structure of the title compound, $[\text{Co}_3(\text{C}_5\text{H}_9\text{O}_2)_6\text{O}(\text{CH}_4\text{O})_3]\text{Cl}$, consists of trinuclear Co^{III} complex cations and chloride anions. The Co^{III} cation has site symmetry m , and is coordinated by four oxygen atoms from four bridging pivalate groups, one central O anion and a methanol oxygen atom, forming a distorted octahedral geometry. The coordinated methanol molecule is located on a crystallographic special position, the C and O atoms being located on the mirror plane. The central O anion lies in the crystallographic $\bar{6}$ position, and acts as a μ_3 -O bridge, linking three equivalent Co^{III} cations and generating the oxo-centered trinuclear Co^{III} complex. The chloride anion, which acts as the counter-ion, is located on crystallographic $\bar{6}$ position. $\text{O}-\text{H}\cdots\text{Cl}$ hydrogen bonding between the Cl anion and hydroxyl group of the coordinated methanol molecule links the molecules into a supramolecular network.

Related literature

For oxido-centered triangular Co complexes, see: Aromì *et al.* (2003); Fursova *et al.* (2007). For related structures, see: Beattie *et al.* (1996).



Experimental

Crystal data

$[\text{Co}_3(\text{C}_5\text{H}_9\text{O}_2)_6\text{O}(\text{CH}_4\text{O})_3]\text{Cl}$
 $M_r = 931.10$
 Hexagonal, $P6_3/m$
 $a = 10.4868$ (15) Å
 $c = 22.794$ (5) Å
 $V = 2170.9$ (6) Å³

$Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 1.26$ mm⁻¹
 $T = 293$ K
 $0.16 \times 0.14 \times 0.11$ mm

Data collection

Rigaku SCXmini 1K CCD area-detector diffractometer
 Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
 $T_{\text{min}} = 0.818$, $T_{\text{max}} = 0.871$

9038 measured reflections
 1317 independent reflections
 1133 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.046$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.102$
 $S = 1.11$
 1317 reflections
 89 parameters
 1 restraint

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.40$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.33$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O3}-\text{H3D}\cdots\text{Cl1}$	0.90 (2)	2.17 (2)	3.070 (3)	175 (6)

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2614).

References

- Aromi, G., Batsanov, A. S., Christian, P., Helliwell, M., Parkin, A., Parsons, S., Smith, A. A., Timco, G. A. & Winpenny, R. E. P. (2003). *Chem. Eur. J.* **9**, 5142–5161.
- Beattie, J. K., Hambley, T. W., Kleptko, J. A., Masters, A. F. & Turner, P. (1996). *Polyhedron* **15**, 2141–2150.
- Fursova, E., Kuznetsova, O., Ovcharenko, V., Romanenko, G., Ikorskii, V., Eremenko, I. & Sidorov, A. (2007). *Polyhedron*, **26**, 2079–2088.
- Rigaku (2005). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

supplementary materials

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μ_3 -Oxido-hexa- μ_2 -pivalato-tris[(methanol- κO)cobalt(III)] chloride

Y. Sun, L.-L. Zhu and H.-H. Zhang

Comment

Oxo-centered triangular Co complexes, $\text{Co}_3(\mu_3\text{-O})$, have been considered as effective models for studying $M-M$ interactions in metal clusters (Aromi *et al.*, 2003; Fursova *et al.*, 2007). We report here the synthesis and crystal structure of the title complex, (I). The complex is a typical oxo-centered carboxylate triangle, featuring exclusively, Co^{III} sites around a central μ_3 -oxide. Each edge of the triangle is further bridged by two pivalates with a terminal methanol ligand completing the coordination environment around each octahedral cobalt site (Fig. 1). The Co^{III} cation has site symmetry m . The central μ_3 -O lies in the -6 rotoinversion axis. The coordinated methanol molecule is located on a crystallographic special position, the C and O atoms have site symmetry m . A similar oxo-centered cobalt(III) triangle has been reported for acetate (Beattie *et al.*, 1996). The $\text{O}-\text{H}\cdots\text{Cl}$ hydrogen bond between the Cl ion serving as a trifurcated acceptor and hydroxyl of the coordinated methanol molecule as donor link molecules into two-dimensional hydrogen-bonded networks (Fig. 2).

Experimental

Hydrochloric acid (0.01 mmol) was added with constant stirring to a methanol solution (15 ml) containing $\text{Co}(\text{O}(\text{OCC}(\text{CH}_3)_3)_2\cdot 4\text{H}_2\text{O})$ (0.5 mmol), then filtered off. After a few days, red well shaped single crystals in the form of rectangular blocks deposited in the mother liquid. They were separated off, washed with cold methanol and dried in air at room temperature.

Refinement

H atoms of the methyl groups were included in calculated positions and treated in the subsequent refinement as riding atoms, with $\text{C}-\text{H} = 0.96 \text{ \AA}$, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The hydride H3D was refined isotropically.

Figures

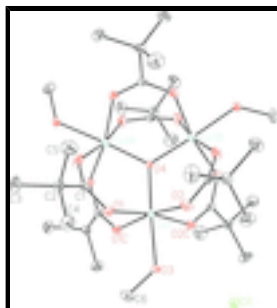


Fig. 1. The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 20% probability level. H atoms have been omitted for clarity [symmetry codes: (A) $x, y, -z + 1/2$; (B) $-y + 1, x - y + 1, z$; (C) $-x + y, -x + 1, z$].

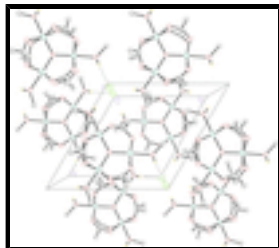


Fig. 2. Crystal packing of the compound (I). The tertbutyl methyl groups and H atoms, except for those of the methanol ligands, have been omitted for clarity. Hydrogen bonds are shown as dashed lines.

μ_3 -Oxido-hexa- μ_2 -pivalato-tri(methanol- κ O) tricobalt(III) chloride

Crystal data

$[\text{Co}_3(\text{C}_5\text{H}_9\text{O}_2)_6\text{O}(\text{CH}_4\text{O})_3]\text{Cl}$

$M_r = 931.10$

Hexagonal, $P6_3/m$

Hall symbol: $-P\ 6c$

$a = 10.4868\ (15)\ \text{\AA}$

$b = 10.4868\ (15)\ \text{\AA}$

$c = 22.794\ (5)\ \text{\AA}$

$\alpha = 90^\circ$

$\beta = 90^\circ$

$\gamma = 120^\circ$

$V = 2170.9\ (6)\ \text{\AA}^3$

$Z = 2$

$F_{000} = 980$

$D_x = 1.424\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 1832 reflections

$\theta = 2.8\text{--}25.3^\circ$

$\mu = 1.26\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Block, red

$0.16 \times 0.14 \times 0.11\ \text{mm}$

Data collection

Rigaku SCXmini 1K CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: $8.192\ \text{pixels mm}^{-1}$

$T = 293\ \text{K}$

thin-slice ω scans

Absorption correction: multi-scan (CrystalClear; Rigaku, 2005)

$T_{\min} = 0.818$, $T_{\max} = 0.871$

9038 measured reflections

1317 independent reflections

1133 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.046$

$\theta_{\max} = 25.0^\circ$

$\theta_{\min} = 1.8^\circ$

$h = -12 \rightarrow 10$

$k = -12 \rightarrow 12$

$l = -23 \rightarrow 26$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.102$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0515P)^2 + 1.7379P]$

where $P = (F_o^2 + 2F_c^2)/3$

$S = 1.11$ $(\Delta/\sigma)_{\max} < 0.001$
 1317 reflections $\Delta\rho_{\max} = 0.40 \text{ e } \text{\AA}^{-3}$
 89 parameters $\Delta\rho_{\min} = -0.33 \text{ e } \text{\AA}^{-3}$
 1 restraint Extinction correction: none
 Primary atom site location: structure-invariant direct methods

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Co1	0.51834 (5)	0.84488 (5)	0.2500	0.0226 (2)	
Cl1	1.0000	1.0000	0.2500	0.0400 (5)	
O4	0.3333	0.6667	0.2500	0.0196 (9)	
O3	0.7249 (3)	1.0326 (3)	0.2500	0.0325 (7)	
O2	0.6044 (2)	0.7791 (2)	0.18650 (10)	0.0401 (6)	
O1	0.4642 (2)	0.9451 (2)	0.18684 (9)	0.0343 (5)	
C1	0.3430 (3)	0.9136 (3)	0.16434 (12)	0.0249 (6)	
C2	0.3400 (3)	0.9828 (3)	0.10576 (13)	0.0303 (7)	
C3	0.2450 (4)	1.0559 (4)	0.11139 (17)	0.0530 (10)	
H3A	0.1473	0.9838	0.1234	0.079*	
H3B	0.2408	1.0966	0.0742	0.079*	
H3C	0.2876	1.1331	0.1401	0.079*	
C4	0.4953 (4)	1.0946 (4)	0.08584 (16)	0.0508 (9)	
H4B	0.5528	1.0470	0.0821	0.076*	
H4C	0.5402	1.1723	0.1143	0.076*	
H4D	0.4908	1.1351	0.0486	0.076*	
C6	0.7597 (6)	1.1820 (5)	0.2500	0.0530 (14)	
H6A	0.8647	1.2450	0.2500	0.080*	
H6B	0.7190	1.2010	0.2844	0.080*	0.50
H6C	0.7190	1.2010	0.2156	0.080*	0.50
C5	0.2695 (5)	0.8587 (5)	0.06128 (16)	0.0605 (11)	
H5A	0.3284	0.8126	0.0574	0.091*	
H5B	0.2630	0.8977	0.0240	0.091*	
H5C	0.1726	0.7873	0.0743	0.091*	
H3D	0.801 (5)	1.016 (7)	0.2500	0.08 (2)*	

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0220 (3)	0.0214 (3)	0.0235 (3)	0.0101 (2)	0.000	0.000
Cl1	0.0312 (6)	0.0312 (6)	0.0575 (13)	0.0156 (3)	0.000	0.000
O4	0.0184 (13)	0.0184 (13)	0.022 (2)	0.0092 (7)	0.000	0.000
O3	0.0204 (14)	0.0222 (14)	0.0514 (19)	0.0081 (12)	0.000	0.000
O2	0.0346 (12)	0.0285 (11)	0.0463 (14)	0.0076 (9)	0.0183 (10)	-0.0086 (10)
O1	0.0280 (11)	0.0297 (11)	0.0382 (13)	0.0091 (9)	-0.0056 (9)	0.0128 (9)
C1	0.0303 (15)	0.0219 (13)	0.0251 (15)	0.0150 (11)	-0.0001 (12)	0.0010 (11)
C2	0.0311 (16)	0.0334 (15)	0.0274 (16)	0.0170 (13)	0.0008 (12)	0.0073 (12)
C3	0.061 (2)	0.068 (2)	0.049 (2)	0.047 (2)	0.0104 (18)	0.0244 (19)
C4	0.045 (2)	0.057 (2)	0.046 (2)	0.0223 (17)	0.0121 (17)	0.0272 (18)
C6	0.052 (3)	0.028 (2)	0.067 (4)	0.011 (2)	0.000	0.000
C5	0.081 (3)	0.064 (2)	0.032 (2)	0.032 (2)	-0.0127 (19)	-0.0090 (18)

Geometric parameters (\AA , $^\circ$)

Co1—O4	1.9055 (5)	C2—C5	1.519 (5)
Co1—O2 ⁱ	2.002 (2)	C2—C4	1.524 (4)
Co1—O2	2.002 (2)	C2—C3	1.537 (4)
Co1—O1 ⁱ	2.0244 (19)	C3—H3A	0.9600
Co1—O1	2.0244 (19)	C3—H3B	0.9600
Co1—O3	2.074 (3)	C3—H3C	0.9600
Cl1—Cl1	0.0000	C4—H4B	0.9600
O4—Co1 ⁱⁱ	1.9055 (6)	C4—H4C	0.9600
O4—Co1 ⁱⁱⁱ	1.9055 (6)	C4—H4D	0.9600
O3—C6	1.420 (5)	C6—H6A	0.9600
O3—H3D	0.90 (2)	C6—H6B	0.9600
O2—C1 ⁱⁱⁱ	1.252 (3)	C6—H6C	0.9600
O1—C1	1.251 (3)	C5—H5A	0.9600
C1—O2 ⁱⁱ	1.252 (3)	C5—H5B	0.9600
C1—C2	1.528 (4)	C5—H5C	0.9600
O4—Co1—O2 ⁱ	94.33 (6)	C4—C2—C1	111.0 (2)
O4—Co1—O2	94.33 (6)	C5—C2—C3	108.9 (3)
O2 ⁱ —Co1—O2	92.60 (15)	C4—C2—C3	110.5 (3)
O4—Co1—O1 ⁱ	95.56 (6)	C1—C2—C3	109.7 (3)
O2 ⁱ —Co1—O1 ⁱ	87.52 (10)	C2—C3—H3A	109.5
O2—Co1—O1 ⁱ	170.07 (9)	C2—C3—H3B	109.5
O4—Co1—O1	95.56 (6)	H3A—C3—H3B	109.5
O2 ⁱ —Co1—O1	170.07 (9)	C2—C3—H3C	109.5
O2—Co1—O1	87.52 (10)	H3A—C3—H3C	109.5
O1 ⁱ —Co1—O1	90.66 (13)	H3B—C3—H3C	109.5
O4—Co1—O3	177.12 (8)	C2—C4—H4B	109.5
O2 ⁱ —Co1—O3	83.69 (8)	C2—C4—H4C	109.5

O2—Co1—O3	83.69 (8)	H4B—C4—H4C	109.5
O1 ⁱ —Co1—O3	86.46 (8)	C2—C4—H4D	109.5
O1—Co1—O3	86.46 (8)	H4B—C4—H4D	109.5
Co1 ⁱⁱ —O4—Co1	120.0	H4C—C4—H4D	109.5
Co1 ⁱⁱ —O4—Co1 ⁱⁱⁱ	120.0	O3—C6—H6A	109.5
Co1—O4—Co1 ⁱⁱⁱ	120.0	O3—C6—H6B	109.5
C6—O3—Co1	128.1 (3)	H6A—C6—H6B	109.5
C6—O3—H3D	117 (4)	O3—C6—H6C	109.5
Co1—O3—H3D	115 (4)	H6A—C6—H6C	109.5
C1 ⁱⁱⁱ —O2—Co1	134.27 (18)	H6B—C6—H6C	109.5
C1—O1—Co1	131.72 (18)	C2—C5—H5A	109.5
O1—C1—O2 ⁱⁱ	123.9 (3)	C2—C5—H5B	109.5
O1—C1—C2	119.5 (2)	H5A—C5—H5B	109.5
O2 ⁱⁱ —C1—C2	116.6 (2)	C2—C5—H5C	109.5
C5—C2—C4	109.6 (3)	H5A—C5—H5C	109.5
C5—C2—C1	107.0 (3)	H5B—C5—H5C	109.5
O2 ⁱ —Co1—O4—Co1 ⁱⁱ	133.53 (7)	O1—Co1—O2—C1 ⁱⁱⁱ	-111.7 (3)
O2—Co1—O4—Co1 ⁱⁱ	-133.53 (7)	O3—Co1—O2—C1 ⁱⁱⁱ	161.6 (3)
O1 ⁱ —Co1—O4—Co1 ⁱⁱ	45.60 (6)	O4—Co1—O1—C1	12.6 (3)
O1—Co1—O4—Co1 ⁱⁱ	-45.60 (6)	O2—Co1—O1—C1	106.7 (3)
O2 ⁱ —Co1—O4—Co1 ⁱⁱⁱ	-46.47 (7)	O1 ⁱ —Co1—O1—C1	-83.1 (3)
O2—Co1—O4—Co1 ⁱⁱⁱ	46.47 (7)	O3—Co1—O1—C1	-169.5 (3)
O1 ⁱ —Co1—O4—Co1 ⁱⁱⁱ	-134.40 (6)	Co1—O1—C1—O2 ⁱⁱ	16.6 (4)
O1—Co1—O4—Co1 ⁱⁱⁱ	134.40 (6)	Co1—O1—C1—C2	-162.2 (2)
O2 ⁱ —Co1—O3—C6	-133.34 (7)	O1—C1—C2—C5	114.9 (3)
O2—Co1—O3—C6	133.34 (7)	O2 ⁱⁱ —C1—C2—C5	-64.0 (3)
O1 ⁱ —Co1—O3—C6	-45.44 (6)	O1—C1—C2—C4	-4.6 (4)
O1—Co1—O3—C6	45.44 (6)	O2 ⁱⁱ —C1—C2—C4	176.5 (3)
O4—Co1—O2—C1 ⁱⁱⁱ	-16.3 (3)	O1—C1—C2—C3	-127.0 (3)
O2 ⁱ —Co1—O2—C1 ⁱⁱⁱ	78.2 (3)	O2 ⁱⁱ —C1—C2—C3	54.0 (4)

Symmetry codes: (i) $x, y, -z+1/2$; (ii) $-y+1, x-y+1, z$; (iii) $-x+y, -x+1, z$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3D \cdots C11	0.90 (2)	2.17 (2)	3.070 (3)	175 (6)

Fig. 1

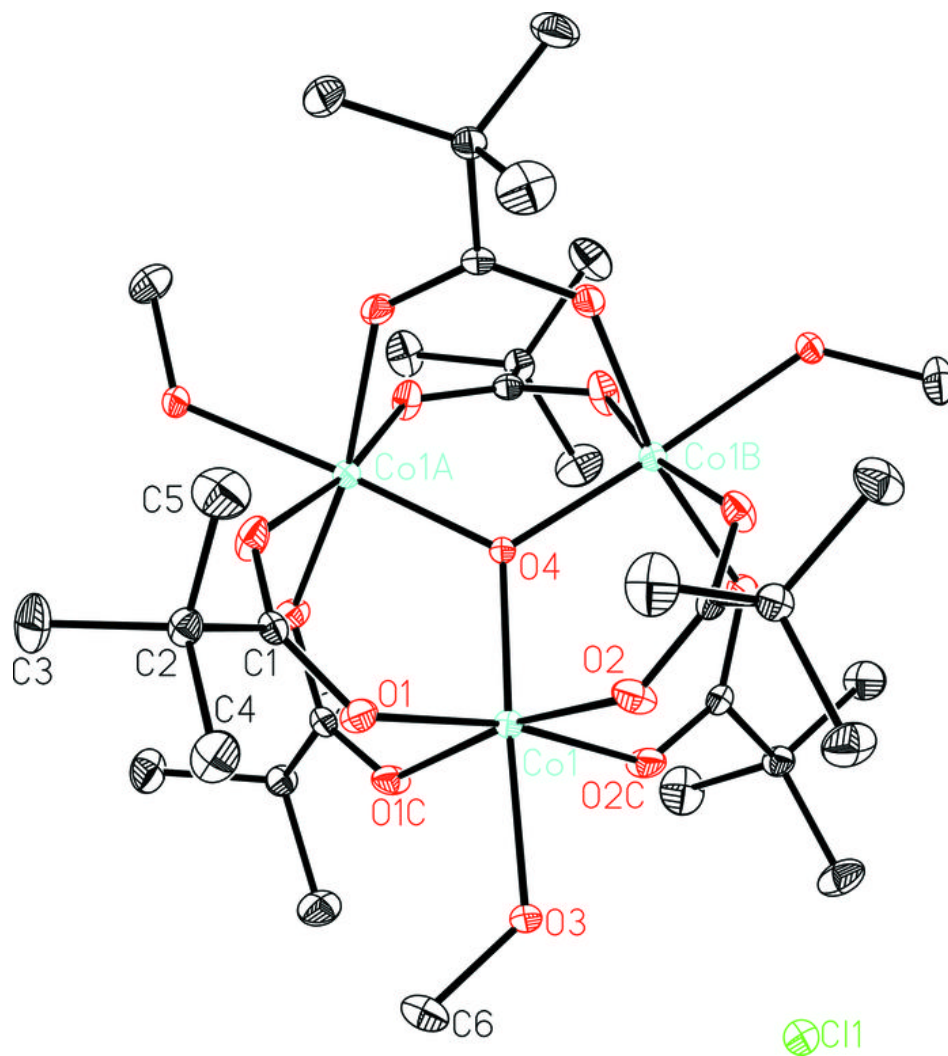


Fig. 2

