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A linear trinuclear Co^{II}–Co^{II}–Co^{II} complex with μ-acetate bridges: di-μ-acetato-bis[μ-*N*,*N*′-bis(salicylidene)-1,4-butanediaminato]tricobalt(II)

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The title linear trinuclear complex, di-μ-acetato-1:2κ^2*O*,*O*′;-2:3κ^2*O*,*O*′-bis{2,2′-[1,4-butanediylbis(nitrilomethylidyne)]-diphenolato}-1:2κ^6O,*N*,*N*,*O*′:*O*,*O*′;2,3κ^6*O*,*O*′:*O*,*N*,*N*,*O*′-tricobalt(II), $[Co_3(C_{18}H_{18}N_2O_2)_2(C_2H_3O_2)_2]$, was prepared by the reaction of the tetradentate Schiff base ligand bis(salicylidene)-1,4-diaminobutane and $Co(CH_3COO)_2{\cdot}2H_2O$ in a methanol solution. The central Co^{II} ion, which is located on an inversion center, has a distorted octahedral coordination involving four bridging O atoms from two Schiff base ligands in the equatorial plane and one O atom from each bridging acetate group in the axial positions. The coordination around the terminal Co^{II} ion is irregular square pyramidal, with two O and two N atoms of the ligand in the basal plane and one O atom from an acetate group in the apical position. The acetate bridges linking the central and terminal Co^{II} ions are mutually *trans*. The closest Co$\cdots$Co separation is 3.125 (4) Å.

Key indicators

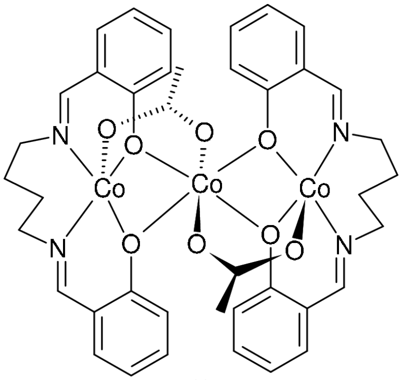
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.008 Å
R factor = 0.069
wR factor = 0.171
Data-to-parameter ratio = 13.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Investigations into the magnetic properties of molecule-based materials containing a polymetallic assembly have become a fascinating subject in the field of condensed matter physics and materials chemistry (Dalai *et al.*, 2002; Bhaduri *et al.*, 2003). Much attention has been focused on coordination complexes with novel magnetic properties, which may have potentially useful applications in materials science (Ray *et al.*, 2003). The prime strategy for designing these molecular materials is to use a suitable bridging ligand that determines the nature of the magnetic interactions (Koner *et al.*, 2003). The structure and magnetic properties of the trinuclear complex $[Zn\{Cu(CH_3CO_2)(Salpd)\}_2]$, where Salpd is bis(salicylidene)-1,3-diaminopropane, has been reported previously (Fukuhara *et al.*, 1990). Similar examples of trihomo- and heteronuclear complexes derived from the Schiff base ligand Salpd have also been reported (Ülkü *et al.*, 1997; Atakol *et al.*, 1999; Ercan & Atakol, 1998). However, trinuclear Schiff base complexes derived from bis(salicylidene)-1,4-diaminobutane have rarely been seen. As an extension of the work on the structural characterization of trinuclear Schiff base compounds, we report here the title trinuclear cobalt(II) compound, (I), which is isostructural with the previously reported zinc complex bis{(μ-acetato-κ^2*O*,*O*′)[μ-*N*,*N*′-bis(salicylidene)-1,4-butanediamine]zinc}zinc, (II) (Reglinski *et al.*, 2002).

The title compound, (I), is a trinuclear cobalt(II) compound (Fig. 1). The neutral compound consists of two Co(Salbu) units [Salbu is bis(salicylidene)-1,4-butanediaminate] connected to each other by a completely encapsulated third metal ion Co2, which is located on a crystallographic inversion center. All the bond lengths and angles are comparable to those in complex (II). The cage of the central metal atom is formed by two oxygen bridges, O1 and O2, from each Co(Salbu) moiety and by two acetate functions that further connect the central metal with the two outer metal ions, resulting in an octahedral environment for Co2. The coordination geometry around the central metal ion displays only slight distortions. The bond distances Co2—O are similar and range from 2.170 (4) to 2.218 (4) Å (Table 1). The greatest deviations of the bond angles from those expected for an ideal geometry are 77.22 (13)° for O1—Co2—O2 and 102.78 (13)° O1^{i}—Co2—O2 [symmetry code: (i) $1 - x$, $-y$, $2 - z$]. The remaining bond angles around Co2 are close to ideal values for octahedral geometry.



(I)

The coordination polyhedra around the inversion-related terminal Co^{II} ions are slightly distorted square pyramids, whose basal planes are formed by two bridging O atoms and two N atoms of the Schiff base ligand. The O atoms of the acetate groups occupy the apical positions. The substantial distortion of the square pyramids is revealed by the bond angles between apical and basal donor atoms, which show deviations of approximately 15.5° from the ideal 90° angle in a regular square pyramid. On the other hand, the bond angles between the donor atoms in basal positions are closer to 90°. A similar pattern can be found for the bond lengths. The unique bond length between Co1 and the apical donor atom O3 is 2.088 (4) Å, which is slightly shorter than the average bond length between Co1 and the basal donor atoms [2.136 (4) Å]. The Co atoms are displaced out of the least-squares plane defined by the basal donor atoms in the direction of the oxygen of the acetate moiety by 0.576 (4) Å. For the basal ligands in each polyhedron, the average deviation from their least-squares plane was calculated to be 0.254 (4) Å, indicating the lack of planarity of this group of atoms in the complex. The greater distortion of the coordination geometry around the terminal metal atoms in comparison with the central one is attributed to the steric effects of the chelate ligands for the complex. The four-membered bridging ring Co1—O1—Co2—O2 is not planar but is folded. The dihedral angle between the benzene rings C2–C7 and C13–C18 is 67.4 (3)°.

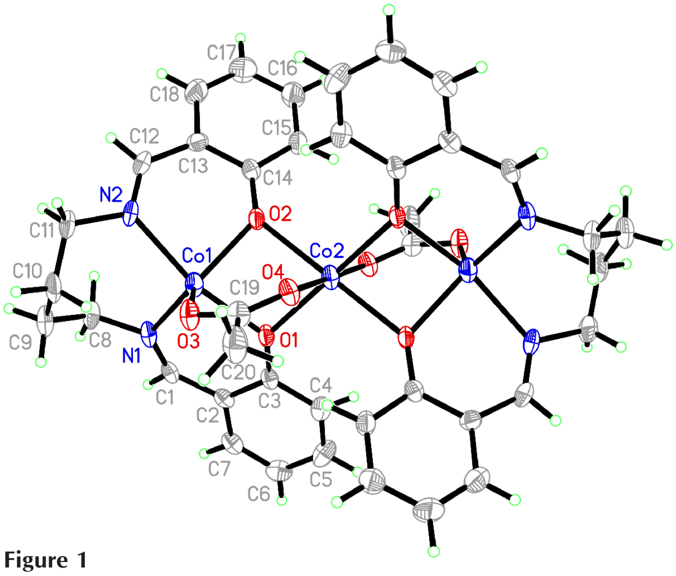


Figure 1
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Unlabeled atoms are related by the symmetry code $(1 - x, -y, 2 - z)$.

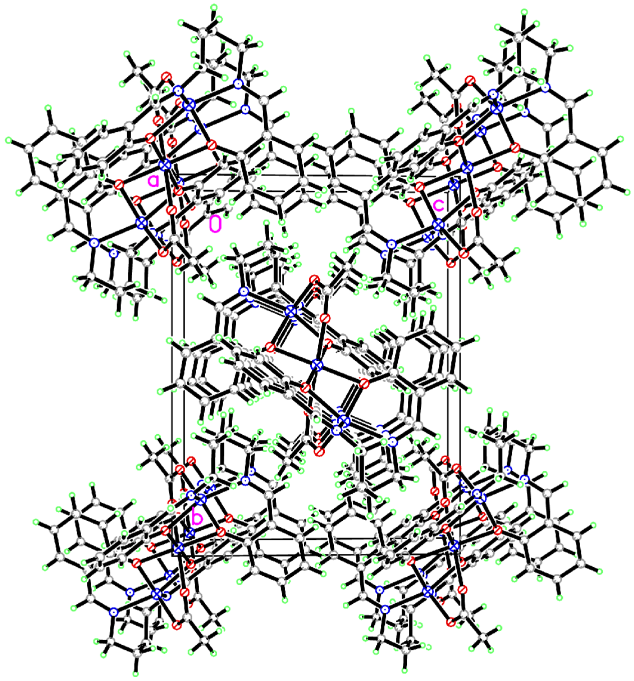


Figure 2
The crystal packing of (I), viewed along the *a* axis.

Experimental

1,4-Diaminobutane (0.1 mmol, 8.6 mg) and salicylaldehyde (0.2 mmol, 24.4 mg) were dissolved in MeOH (3 ml). The mixture was stirred for 1 h to give a clear orange solution of *N*,*N*′-bis(salicylidene)-1,4-butanediaminate. To the above solution was added an MeOH solution (2 ml) of $Co(CH_3COO)_2 \cdot 4H_2O$ (0.2 mmol, 49.9 mg), with stirring for 10 min. The mixture was transferred to a stainless steel bomb, which was sealed, heated at 423 K for 12 h, and cooled gradually to room temperature. Red block-shaped crystals of the complex were formed at the bottom of the vessel.

Crystal data

$[Co_3(C_{18}H_{18}N_2O_2)_2(C_2H_3O_2)_2]$
$M_r = 883.57$
Monoclinic, $P2_1/c$
$a = 9.193$ (9) Å
$b = 16.726$ (17) Å
$c = 12.729$ (13) Å
$\beta = 95.314$ (18)°
$V = 1949$ (3) Å^3
$Z = 2$

$D_x = 1.506$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2101 reflections
$\theta = 2.5$–22.7°
$\mu = 1.32$ mm^{-1}
$T = 298$ (2) K
Block, red
0.38 × 0.32 × 0.22 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.621$, $T_{max} = 0.745$
9778 measured reflections

3360 independent reflections
1992 reflections with $I > 2\sigma(I)$
$R_{int} = 0.137$
$\theta_{max} = 25.0°$
$h = -9 \rightarrow 10$
$k = -19 \rightarrow 17$
$l = -15 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.070$
$wR(F^2) = 0.171$
$S = 0.91$
3360 reflections
251 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0878P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.04$ e Å^{-3}
$\Delta\rho_{min} = -0.69$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—O3	2.088 (4)	Co1—N2	2.184 (5)
Co1—O2	2.090 (4)	Co2—O1	2.170 (4)
Co1—O1	2.104 (4)	Co2—O4	2.193 (4)
Co1—N1	2.167 (5)	Co2—O2	2.218 (4)
O3—Co1—O2	108.87 (16)	O1—Co2—O1^i	180
O3—Co1—O1	94.64 (16)	O1—Co2—O4	88.04 (15)
O2—Co1—O1	81.51 (15)	O1^i—Co2—O4	91.96 (15)
O3—Co1—N1	116.64 (17)	O4—Co2—O4^i	180
O2—Co1—N1	133.56 (16)	O1—Co2—O2	77.22 (13)
O1—Co1—N1	86.05 (15)	O1^i—Co2—O2	102.78 (13)
O3—Co1—N2	101.88 (18)	O4—Co2—O2	87.67 (14)
O2—Co1—N2	84.91 (17)	O4^i—Co2—O2	92.33 (14)
O1—Co1—N2	161.32 (17)	O2—Co2—O2^i	180
N1—Co1—N2	94.17 (17)		

Symmetry code: (i) $1 - x, -y, 2 - z$.

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.93–0.97 Å, and with $U_{iso}(H) = 1.2$ or $1.5U_{eq}(C)$. The unassigned maximum residual density is near atom Co2, while the minimum residual density is 0.90 Å from atom Co1.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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