Data collection

Siemens *P*4 diffractometer
$2\theta/\omega$ scans
Absorption correction:
empirical *via* ψ scans (*SHELXL*93; Sheldrick, 1993)
$T_{min} = 0.666$, $T_{max} = 0.760$
2409 measured reflections
2183 independent reflections
1933 reflections with $I > 2\sigma(I)$
$R_{int} = 0.013$
$\theta_{max} = 24.99°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 13$
$l = -22 \rightarrow 22$
3 standard reflections every 97 reflections intensity decay: 3.19%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.064$
$S = 1.052$
2182 reflections
191 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0286P)^2 + 0.4364P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.253$ e Å^{-3}
$\Delta\rho_{min} = -0.278$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. *Selected geometric parameters (Å, °) for (II)*

Pd—S2	2.2496 (6)	S2—C2	1.712 (2)
Pd—S1	2.2501 (6)	C1—C2	1.400 (3)
S1—C1	1.695 (2)		
S2^{i}—Pd—S1	92.08 (2)	C2—S2—Pd	105.93 (8)
S2—Pd—S1	87.92 (2)	C2—C1—S1	121.6 (2)
C1—S1—Pd	105.32 (8)	C1—C2—S2	119.2 (2)

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

For both compounds, data collection: *XSCANS* (Siemens, 1994*a*); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *XP* (Siemens, 1994*b*); software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1234). Services for accessing these data are described at the back of the journal.

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A linear trinuclear Cd^{II}–Cd^{II}–Cd^{II} complex with a μ-acetato bridge: bis{(μ-acetato)[μ-bis(salicylidene)-1,3-propanediaminato]cadmium(II)}cadmium(II)

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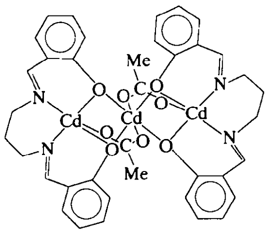
Abstract

The title complex, bis(μ-acetato)-1:2$\kappa^2 O$:O';2:3$\kappa^2 O$:O'-bis{μ-2,2'-[1,3-propanediylbis(nitrilomethylidene)]diphenolato}-1$\kappa^4 N$,N',O,O':2$\kappa^2 O$,O';3$\kappa^4 N$,N',O,O':2$\kappa^2 O$,O'-tricadmium(II), $[Cd\{Cd(C_{17}H_{16}N_2O_2)(CH_3CO_2)\}_2]$, consists of a doubly oxygen-bridged linear homotrinuclear complex. The outer Cd^{II} ions, related by an inversion centre, have an irregular square-pyramidal coordination. The central Cd^{II} ion has an irregular octahedral coordination and lies on an inversion centre. The metal–metal bridging distance is 3.2582 (3) Å.

Comment

The structures and syntheses of several oxygen-bridged dimeric and trimeric linear homo- or heteronuclear metal complexes have been studied in our laboratories recently; examples include $[Cu_2(C_{11}H_{10}ClNO_2)_2]$ (Tahir *et al.*, 1996), $[Cu_2(C_{14}H_{11}NO_2)_2]$ (Ülkü, Ercan, Atakol, Ercan & Gencer, 1997), $[Ni_3\{(SALPD)(CH_3CO_2)[(CH_3)_2SO]\}_2]$ (Ülkü, Ercan, Atakol & Dinçer, 1997), $[Cd\{Ni(SALPD)(CH_3CO_2)[(CH_3)_2NCHO]\}_2]$ (Ülkü, Tahir *et al.*, 1997), $[Cu_2(C_{12}H_{13}NO_2)_2]$ (Atakol *et al.*, 1997), $[Cu_2(C_{12}H_{13}NO_2)_2]$ (Ülkü *et al.*, 1998), $[Ni_2\{Cu-$

(SALPD)(NO_2)$_2$[$(CH_3)_2NCHO$]}$_2$]·2[$(CH_3)_2NCHO$] (Tahir *et al.*, 1998), [Mn{Ni(SALPD)(CH_3CO_2)[$(CH_3)_2$-NCHO]}$_2$] (Ercan & Atakol, 1998), [Cd{Cu(SALPD)-(CH_3CO_2)}$_2$]·$C_4H_8O_2$ (Ercan *et al.*, 1998), [Cu$_3$-{(SALPD)(CH_3CO_2)}$_2$]·$C_4H_8O_2$ (Atakol *et al.*, 1999), [Cu{Zn($C_{23}H_{21}I_2N_3O_2$)}] (Ercan *et al.*, 1999) and [Ni{Zn($C_{31}H_{34}I_2N_4O_2$)}] (Arıcı *et al.*, 1999), where H_2SALPD is *N*,*N'*-bis(salicylidene)-1,3-propanediamine {alternative name: 2,2'-[1,3-propanediylbis-(nitrilomethylidene)]diphenol}. Structural studies of some other oxygen-bridged homonuclear complexes have been reported previously by other workers (Kato *et al.*, 1964; Barclay & Hoskins, 1965; Butcher & Sinn, 1976; Kato & Muto, 1988). We report here a new linear homonuclear trimeric complex, [Cd$_3${(SALPD)(CH_3CO_2)}$_2$], (I).



(I)

The monoclinic unit cell of (I) contains two centrosymmetric trimer complexes, whose central Cd^{II} ion is located on the inversion centre at the origin. The coordination around the central Cd^{II} ion is an irregular octahedron, involving four bridging O atoms from two SALPD^{2-} ligands in the equatorial plane and an O atom from each of the two bridging acetate groups in the apical positions. The inversion-related outer Cd^{II} ions have irregular square-pyramidal coordination polyhedra, with the four equatorial positions occupied by the two N and two O atoms of the SALPD^{2-} ligand. There is an O atom from each bridging acetate group in the axial positions of these irregular square-pyramidal polyhedra.

The Cd···Cd distance is 3.2582 (3) Å; this is longer than the Cu···Cd distance [3.244 (3) Å] in the similar structure described by Ercan *et al.* (1998). The SALPD^{2-} ligand in (I) is not planar. The dihedral angles between the best plane of the salicylaldimine residues (N1, C1–C7, O1 and N2, C11–C17, O2) and the equatorial plane (O1, O2, N1, N2) are 143.4 (1) and 40.7 (1)°, respectively. The dihedral angle between the equatorial planes of the neighbouring polyhedra [O1, O2, N1, N2 and O1, O2, O1^{i}, O2^{i}; symmetry code: (i) $-x, -y, -z$] is 13.7 (1)°. The outer Cd^{II} ion is 0.7407 (1) Å out of its equatorial plane. The Cd1—O1, Cd1—O2 and Cd1—O4 bond lengths are 2.269 (3), 2.297 (3) and 2.353 (3) Å, respectively, while the Cd—O distances were 2.280 (3), 2.310 (3) and 2.238 (2) Å, respectively, in our previous investigation (Ercan *et al.*, 1998). The average Cd2—O bond length in (I) is 2.207 (3) Å, and the Cd2—N1 and Cd2—N2 bond lengths are 2.258 (4) and 2.236 (4) Å, respectively. The chelate ring formed by atoms Cd2, N1, C8–C10 and N2 has a chair conformation. The distances

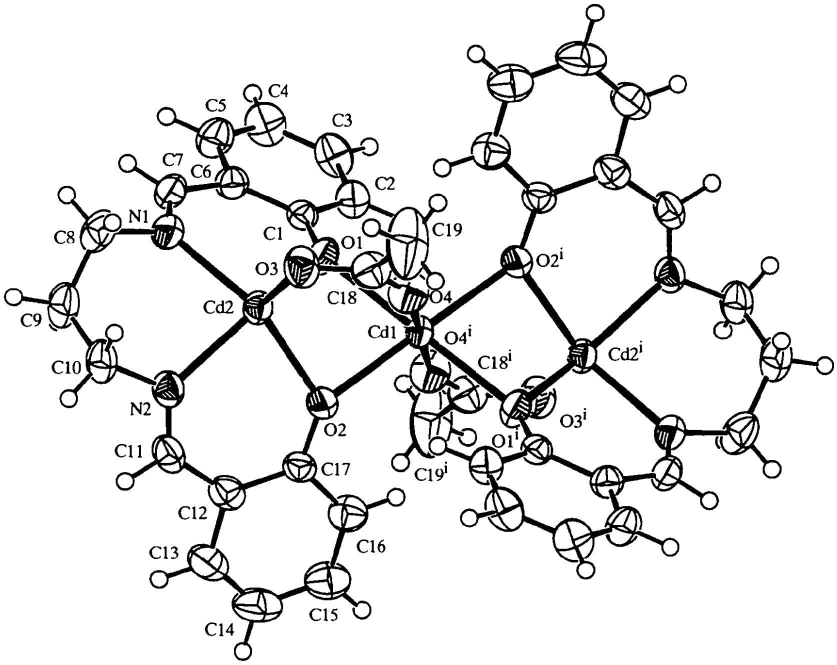


Fig. 1. *PLATON* (Spek, 1998) drawing of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small circles of arbitrary radii [symmetry code: (i) $-x, -y, -z$].

of the two *para*-positioned chair atoms, Cd2 and C9, from the plane of the other four atoms are −1.035 (6) and 0.697 (6) Å, respectively. Although the type of metal ions and some of the coordinating groups of the metal complexes reported by our previous investigations are different from the case discussed here, the bond lengths, angles and dihedral angles of these structures are similar.

Experimental

N,*N*′-Bis(salicylidene)-1,3-propanediamine (0.282 g, 1 mmol) was dissolved in 75 ml hot methanol. Next, a solution of $Cd(CH_3CO_2)_2$ (0.335 g, 1.5 mmol) in 30 ml hot methanol was added slowly. The resulting mixture was set aside for 1 d and the yellow crystals which formed were filtered off and dried in air.

Crystal data

$[Cd_3(C_{17}H_{16}N_2O_2)_2(C_2H_3O_2)_2]$
$M_r = 1015.95$
Monoclinic
$P2_1/c$
$a = 10.6433 (12)$ Å
$b = 20.6568 (13)$ Å
$c = 8.5187 (11)$ Å
$\beta = 91.762 (2)°$
$V = 1872.0 (3)$ Å^3
$Z = 2$
$D_x = 1.802$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12.04–20.91°$
$\mu = 1.74$ mm^{-1}
$T = 295$ K
Prismatic
0.30 × 0.20 × 0.15 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (Fair, 1990)
$T_{min} = 0.614$, $T_{max} = 0.770$
3669 measured reflections
3195 independent reflections
2772 reflections with $I > 1\sigma(I)$
$R_{int} = 0.014$
$\theta_{max} = 25.08°$
$h = -10 \rightarrow 0$
$k = -24 \rightarrow 0$
$l = -12 \rightarrow 12$
3 standard reflections
frequency: 120 min
intensity decay: −0.78%

Refinement

Refinement on F
$R = 0.028$
$wR = 0.037$
$S = 0.90$
2772 reflections
241 parameters
H atoms: see below
$w = 1/[\sigma F^2 + (0.02F)^2 + 0.4]$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Cd1···Cd2	3.2582 (3)	O1—C1	1.318 (5)
Cd1—O1	2.269 (3)	O2—C17	1.319 (5)
Cd1—O2	2.297 (3)	O3—C18	1.271 (6)
Cd1—O4	2.353 (4)	O4—C18	1.229 (6)
Cd2—O1	2.223 (3)	N1—C7	1.284 (6)
Cd2—O2	2.225 (3)	N1—C8	1.475 (6)
Cd2—O3	2.173 (3)	N2—C10	1.472 (6)
Cd2—N1	2.258 (4)	N2—C11	1.273 (6)
Cd2—N2	2.236 (4)		
Cd1—Cd2—O1	44.07 (8)	Cd2—O1—Cd1	93.0 (1)
Cd1—Cd2—O2	44.78 (8)	Cd2—O1—C1	130.3 (3)
Cd1—Cd2—O3	93.0 (1)	Cd1—O1—C1	132.6 (3)
Cd1—Cd2—N1	127.3 (1)	Cd2—O2—Cd1	92.2 (1)
Cd1—Cd2—N2	128.0 (1)	Cd2—O2—C17	129.4 (3)
Cd2—Cd1—O1	42.96 (8)	Cd1—O2—C17	132.6 (3)
Cd2—Cd1—O2	43.04 (8)	Cd1—O4—C18	150.7 (3)
Cd2—Cd1—O4	60.30 (9)	Cd2—O3—C18	110.8 (3)
O1—Cd2—O2	80.8 (1)	Cd2—N1—C7	125.8 (3)
O1—Cd2—O3	105.1 (1)	Cd2—N1—C8	116.6 (3)
O1—Cd2—N1	83.6 (1)	C7—N1—C8	117.5 (4)
O1—Cd2—N2	141.5 (1)	Cd2—N2—C10	114.8 (3)
O2—Cd2—O3	110.0 (1)	Cd2—N2—C11	126.3 (3)
O2—Cd2—N1	140.8 (1)	C10—N2—C11	118.8 (4)
O2—Cd2—N2	83.4 (1)	O1—C1—C2	119.5 (4)
O3—Cd2—N1	108.6 (1)	O1—C1—C6	123.3 (4)
O3—Cd2—N2	113.3 (1)	C1—C6—C7	126.5 (4)
N1—Cd2—N2	87.0 (1)	N1—C7—C6	128.8 (4)
O1—Cd1—O2	78.3 (1)	N1—C8—C9	112.9 (4)
O1—Cd1—O4	82.1 (1)	N2—C10—C9	112.4 (4)
O2—Cd1—O4	81.9 (1)		

All non-H atoms were refined with anisotropic displacement parameters. H atoms H81, H82, H91, H92, H101, H102, H191, H192 and H193 were taken from difference maps, while the other H atoms were placed geometrically 0.95 Å from their parent C atoms, and then a riding model was used for all H atoms, with $U_{iso}(H) = 1.3U_{eq}(C)$.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1993). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MolEN*. Program(s) used to refine structure: *MolEN*. Molecular graphics: *PLATON* (Spek, 1998). Software used to prepare material for publication: *MolEN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1176). Services for accessing these data are described at the back of the journal.

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Three anionic polymeric networks: sodium(I)–ruthenium(III), sodium(I)–rhodium(III) and sodium(I)–aluminium(III) μ-oxalato complexes with tris(2,2′-bipyridine)ruthenium(II) cations

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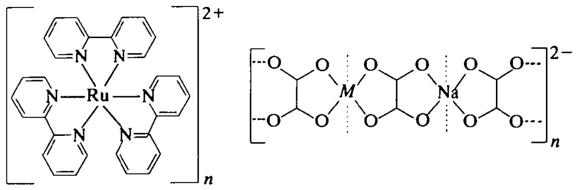
Abstract

The crystal structures of $[\mathrm{Ru(bpy)_3}]_n^{2+}[\mathrm{Na}M(\mathrm{ox})_3]_n^{2n-}$, with M = $\mathrm{Ru^{III}}$ [tris(2,2′-bipyridine)ruthenium(II) tris(μ-oxalato)ruthenium(III)sodium(I), (1)], M = $\mathrm{Rh^{III}}$ [tris(2,2′-bipyridine)ruthenium(II) tris(μ-oxalato)rhodium(III)sodium(I), (2)] and M = $\mathrm{Al^{III}}$ [tris(2,2′-bipyridine)ruthenium(II) tris(μ-oxalato)aluminium(III)sodium(I), (3)], where bpy is 2,2′-bipyridine ($C_{10}H_8N_2$) and ox is oxalate (C_2O_4), represent examples of a specific polymeric three-dimensional network topology. These networks, formally built up from $[M(\mathrm{ox})_{3/2}]$ subunits and $[\mathrm{Ru(bpy)_3}]^{2+}$ counter-ions which template the polymeric structure, are chiral. The absolute configurations of the measured crystals have been determined as the Λ form for (1), and as the Δ form for (2) and (3). The coordinated metal ions form trigonally distorted octahedra. The average distances are 2.060 (2) Å for $\mathrm{Ru^{II}}$—N in the three $[\mathrm{Ru(bpy)_3}]^{2+}$ counter-ions, 2.338 (3) Å for $\mathrm{Na^{I}}$—O, 2.031 (2) Å for $\mathrm{Ru^{III}}$—O, 2.005 (2) Å for $\mathrm{Rh^{III}}$—O and 1.890 (3) Å for $\mathrm{Al^{III}}$—O.

Comment

The anionic oxalate molecule can act as a mono-, bi-, tri- or tetradentate ligand, but is also well known for its ability to form bridged polynuclear complexes (Scott *et al.*, 1973). In particular, several two-dimensional heterometallic layer compounds with network stoichiometries $[M^{\mathrm{II}}M^{\mathrm{III}}(\mathrm{ox})_3]_n^{n-}$ (Tamaki *et al.*, 1992; Decurtins, Schmalle, Oswald *et al.*, 1994; Pellaux *et al.*, 1997), as well as three-dimensional homometallic network compounds with stoichiometries $[M_2^{\mathrm{II}}(\mathrm{ox})_3]_n^{2n-}$ (Decurtins, Schmalle, Schneuwly *et al.*, 1994; Decurtins *et al.*, 1996), have been reported. Both structure types have been realised for many different transition metals and they are of interest in the field of molecule-based magnets due to the ability of the oxalato ligand to act as mediator for magnetic exchange interactions. In addition, a three-dimensional heterometallic structure type with stoichiometries $[M^{\mathrm{I}}M^{\mathrm{III}}(\mathrm{ox})_3]_n^{2n-}$, of which three examples are presented in this report, has been studied mainly because of its specific photophysical properties (Hauser *et al.*, 1996; von Arx *et al.*, 1996). For a general description of the $[M^{\mathrm{I}}M^{\mathrm{III}}(\mathrm{ox})_3]_n^{2n-}$ structures, these anionic networks may be considered as built up from formal $[M(\mathrm{ox})_{3/2}]$ subunits, each representing three-connected points (Wells, 1984). If all subunits have the same chiral configuration, a well defined three-dimensional three-connected decagon network is formed, where the $[\mathrm{Ru(bpy)_3}]^{2+}$ cations occupy the vacancies of the framework.



(1) M=$\mathrm{Ru^{III}}$
(2) M=$\mathrm{Rh^{III}}$
(3) M=$\mathrm{Al^{III}}$

In Fig. 1, a stereoplot of the structure of (1) in the Λ configuration is presented. Strands of bridged metal ions in the oxalato network form left-handed helices along the 2_1 axes. According to the space-group symmetry, all metal ions occupy sites with D_3 point-group symmetry (Wyckoff letter *a*). Contrary to the Λ configuration found in the case of (1), the absolute configurations of the coordinated metal ions in the measured crystals of (2) and (3) represent the Δ form; compound (3) is shown in Fig. 2 as an example. The Na—O 3+3 coordination distances range between 2.315 (2) Å in (1) and 2.388 (3) Å in (3). The most pronounced differences within the Na—O distances are observed in (3). Furthermore, these bond lengths are significantly elongated compared with values in (1) and (2). In a similar way, the Na—O distances reported for $[\mathrm{Ni(bpy)_3}]$-