

Two mixed-metal carboxylate–base adducts

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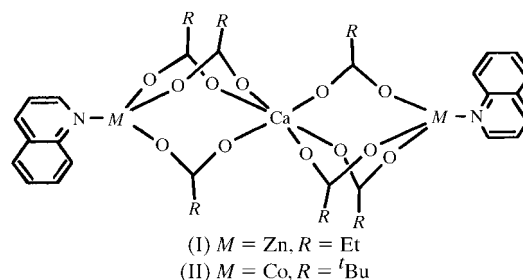
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The crystal structures of hexa- μ -propionato-1:2 κ^6 O':-1:3 κ^6 O':O'-diquinoline-2 κ N,3 κ N-calcium(II)dizinc(II), [CaZn₂(C₃H₅O₂)₆(C₉H₇N)₂], and hexa- μ -pivalato-1:2 κ^6 O':-1:3 κ^6 O':O'-diquinoline-2 κ N,3 κ N-calcium(II)dicobalt(II), [CaCo₂(C₅H₉O₂)₆(C₉H₇N)₂], are described. Both contain a linear array of one Ca^{II} ion and two M^{II} (M = Zn, Co) ions connected by two sets of three carboxylate ligands in *syn-syn* bridging modes. The distorted tetrahedral geometry around the M^{II} ion is completed by a quinoline N atom. The central Ca^{II} ion occupies a crystallographic inversion centre and is octahedrally coordinated by six carboxyl O atoms in each structure. The Zn^{II}...Ca^{II} and Co^{II}...Ca^{II} distances are 3.8504 (9) and 3.7929 (5) Å, respectively.

Comment

For some time, a type of novel linear trinuclear assembly of general formula [M^{II}M'^{II}(O₂CR)₆L₂] (M = M' = Mn, Fe, Co, Zn; M' = Zn, M = Mn, Co, Ni, Zn, Cd, Mg, Ca, Sr, Ba; L is a heterocyclic base) has been the subject of considerable attention in the literature (Catterick *et al.*, 1974; Catterick & Thornton, 1976; Clegg *et al.*, 1985, 1986, 1988, 1989). The first example characterized by single-crystal X-ray diffraction was the cobalt complex [Co₃(O₂CPh)₆(C₉H₇N)₂] reported by Catterick *et al.* (1974). In each case, the three divalent metal ions are arranged in a linear array within a centrosymmetric molecule. The ligands L are bound terminally to the outer metal ions, and the carboxylates form bridges between the



central and outer metal ions. Several Schiff base derivatives, such as [Mn^{II}(O₂CCH₃)₄(L¹)₂(CH₃OH)₂] and [M^{II}(O₂C-CH₃)(L²)₂(dmf)₂] [M = Fe, Co; L¹ = 1,3-dihydroxy-2-methyl-2-(5-chlorosalicylideneamino)propane, L² = N,N'-bis(salicylidene)-2,2'-dimethylpropylenediamine], have also been synthesized and characterized (Li *et al.*, 1988; Gerli *et al.*, 1991; Tangoulis *et al.*, 1996). These complexes not only provide a wealth of data about steric interactions and spectroscopic and magnetic properties, but can also serve as structural models for biological systems and solid materials.

The title complexes, (I) and (II) (Figs. 1 and 2, respectively), consist of a centrosymmetric linear trinuclear molecule, with

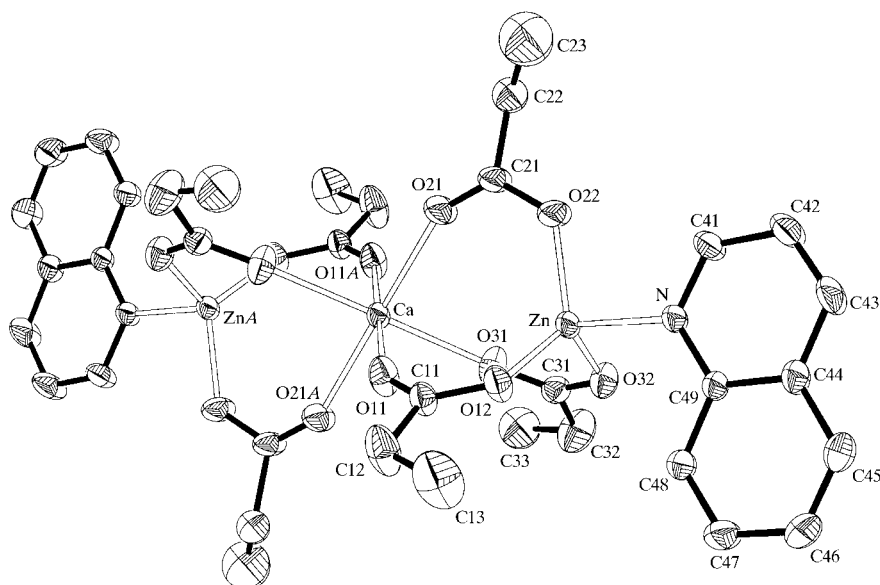


Figure 1

A view of the molecular structure of (I) showing the atom-numbering scheme and 30% probability displacement ellipsoids. Only one component of the disordered C atoms of the propionate groups is shown for clarity. [Symmetry code: (A) $-1 - x, 1 - y, 1 - z$.]

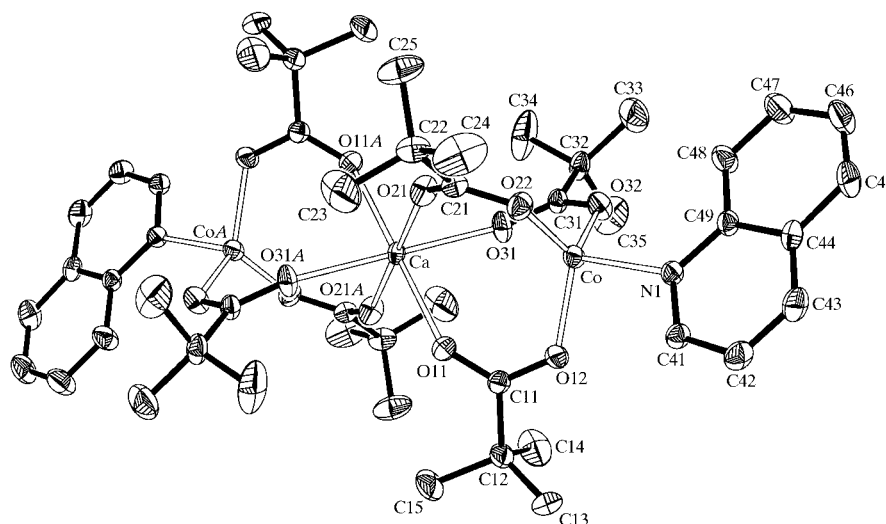


Figure 2

A view of the molecular structure of (II) showing the atom-numbering scheme and 30% probability displacement ellipsoids. [Symmetry code: (A) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$.]

the central Ca^{II} ion on a crystallographic inversion centre. Two M^{II} ($M = \text{Zn}, \text{Co}$) ions are each coordinated by three carboxyl O atoms and a quinoline molecule to form a distorted tetrahedron, whose most distorted angles are $\text{O22}-\text{Zn}-\text{N}$ of $95.84(13)^\circ$ and $\text{O12}-\text{Co}-\text{N1}$ of $94.42(12)^\circ$. Each terminal M^{II} ion is connected to the central Ca^{II} ion by three carboxylate bridges in a *syn-syn* mode. The Ca^{II} ion occupies a slightly distorted octahedron of O atoms, with $\text{Ca}-\text{O}$ bond lengths in the range 2.287(3)–2.323(3) Å for (I) and 2.261(3)–2.279(3) Å for (II), and with all $\text{O}-\text{Ca}-\text{O}$ angles within 4.5° of ideal octahedral values for both (I) and (II). The two structures are therefore similar to those observed for $[\text{MZn}_2(\text{O}_2\text{CCH}=\text{CHCH}_3)_6(\text{C}_{10}\text{H}_9\text{N})_2]$ ($M = \text{Ca}, \text{Sr}$) and $[\text{BaZn}_2(\text{O}_2\text{CCMe}_3)_6(\text{C}_9\text{H}_7\text{N})_2]$ (Clegg *et al.*, 1988, 1989), but are different from that of $[\text{MgZn}_2(\text{O}_2\text{CCH}=\text{CHCH}_3)_6(\text{C}_9\text{H}_7\text{N})_2]$ (Clegg *et al.*, 1988), where the central Mg^{II} ion is linked to each Zn^{II} ion by three crotonate bridges: two of these are *syn-syn* bidentate and the third is monodentate and bridging through only one O atom. The $\text{Zn}-\text{O}$ [1.924(3)–1.951(3) Å], $\text{Zn}-\text{N}$ [2.086(2) Å] and $\text{Zn}\cdots\text{Ca}$ [3.8504(9) Å] distances in (I) are in good agreement with the corresponding values in $[\text{CaZn}_2(\text{O}_2\text{CCH}=\text{CHCH}_3)_6(\text{C}_{10}\text{H}_9\text{N})_2]$ (Clegg *et al.*, 1988) and slightly longer than the $\text{Co}-\text{O}$ [1.904(3)–1.914(3) Å], $\text{Co}-\text{N}$ [2.065(3) Å] and $\text{Co}\cdots\text{Ca}$ [3.7929(5) Å] distances in (II) as a consequence of the smaller radius of cobalt. The present $\text{Zn}\cdots\text{Ca}$ and $\text{Co}\cdots\text{Ca}$ distances are considerably longer than the $\text{Zn}\cdots\text{Mg}$ distance of 3.518(3) Å found in MgZn_2 crotonate (Clegg *et al.*, 1988), but significantly shorter than the corresponding separations in SrZn_2 crotonate [4.050(5) Å; Clegg *et al.*, 1988] and BaZn_2 pivalate [4.18(1) Å; Clegg *et al.*, 1989].

Experimental

For the preparation of (I), a mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, propionic acid and quinoline (molar ratio 2:1:6:2) in

EtOH was refluxed for 10 h. The resulting solution was allowed to stand in air and colourless crystals were deposited after one week. For the preparation of (II), a mixture of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, pivalic acid and quinoline (molar ratio 2:1:6:2) in ethanol was refluxed for 12 h. The resulting solution was allowed to stand in air and purple prismatic crystals were deposited after three days.

Compound (I)

Crystal data

$[\text{CaZn}_2(\text{C}_3\text{H}_5\text{O}_2)_6(\text{C}_9\text{H}_7\text{N})_2]$
 $M_r = 867.55$
 Monoclinic, $P2_1/n$
 $a = 8.614(2)$ Å
 $b = 19.363(4)$ Å
 $c = 12.473(3)$ Å
 $\beta = 95.59(3)^\circ$
 $V = 2070.4(7)$ Å³
 $Z = 2$

$D_x = 1.392$ Mg m⁻³

Mo $K\alpha$ radiation

Cell parameters from 25 reflections

$\theta = 1.95$ – 25.00°

$\mu = 1.341$ mm⁻¹

$T = 293(2)$ K

Triangular prism, colourless

$0.15 \times 0.10 \times 0.10$ mm

Data collection

Enraf-Nonius CAD-4 diffractometer

ω scans

Absorption correction: empirical ω scans (Fair, 1990)

$T_{\text{min}} = 0.735$, $T_{\text{max}} = 0.875$

3633 measured reflections

3633 independent reflections

3007 reflections with $I > 2\sigma(I)$

$\theta_{\text{max}} = 25.00^\circ$

$h = 0 \rightarrow 10$

$k = 0 \rightarrow 23$

$l = -14 \rightarrow 14$

3 standard reflections

frequency: 120 min

intensity decay: none

Table 1

Selected geometric parameters (Å, °) for (I).

$\text{Zn}-\text{O12}$	1.924(3)	$\text{Zn}-\text{N}$	2.086(3)
$\text{Zn}-\text{O22}$	1.924(3)	$\text{Ca}-\text{O11}$	2.323(3)
$\text{Zn}-\text{O32}$	1.951(3)	$\text{Ca}-\text{O21}$	2.310(3)
$\text{O12}-\text{Zn}-\text{O22}$	119.41(17)	$\text{O32}-\text{Zn}-\text{N}$	100.44(14)
$\text{O12}-\text{Zn}-\text{O32}$	116.19(15)	$\text{O11}-\text{Ca}-\text{O21}$	91.10(13)
$\text{O22}-\text{Zn}-\text{O32}$	117.04(17)	$\text{O11}-\text{Ca}-\text{O31}$	85.87(13)
$\text{O12}-\text{Zn}-\text{N}$	101.05(13)	$\text{O21}-\text{Ca}-\text{O31}$	86.64(14)
$\text{O22}-\text{Zn}-\text{N}$	95.84(13)		

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.155$
 $S = 1.149$
 3633 reflections
 238 parameters
 H atoms: see below

$$w = 1/[\sigma^2(F_o^2) + (0.104P)^2 + 0.576P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.64 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.33 \text{ e } \text{\AA}^{-3}$

Compound (II)

Crystal data

$[\text{CaCo}_2(\text{C}_5\text{H}_9\text{O}_2)_6(\text{C}_9\text{H}_7\text{N})_2]$
 $M_r = 1022.98$
 Monoclinic, $C2/c$
 $a = 20.5710 (5) \text{ \AA}$
 $b = 13.9851 (3) \text{ \AA}$
 $c = 18.8102 (4) \text{ \AA}$
 $\beta = 103.814 (7)^\circ$
 $V = 5254.9 (2) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.293 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 5832 reflections
 $\theta = 1.78\text{--}25.53^\circ$
 $\mu = 0.787 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Triangular prism, purple
 $0.15 \times 0.10 \times 0.10 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
 $T_{\min} = 0.879$, $T_{\max} = 0.932$
 12 636 measured reflections

4742 independent reflections
 3269 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.042$
 $\theta_{\max} = 25.53^\circ$
 $h = -24 \rightarrow 24$
 $k = -16 \rightarrow 16$
 $l = -10 \rightarrow 22$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.062$
 $wR(F^2) = 0.135$
 $S = 1.087$
 4742 reflections
 295 parameters
 H atoms: see below

$$w = 1/[\sigma^2(F_o^2) + (0.0480P)^2 + 5.7771P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.33 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.22 \text{ e } \text{\AA}^{-3}$

Table 2

Selected geometric parameters (\AA , $^\circ$) for (II).

Co—O12	1.914 (3)	Ca—O11	2.269 (3)
Co—O22	1.912 (3)	Ca—O21	2.279 (3)
Co—O32	1.904 (3)	Ca—O31	2.261 (3)
Co—N1	2.065 (3)		
O12—Co—O22	118.55 (13)	O32—Co—N1	104.63 (13)
O12—Co—O32	115.87 (14)	O11—Ca—O21	86.43 (11)
O22—Co—O32	118.22 (14)	O11—Ca—O31	87.54 (11)
O12—Co—N1	94.42 (12)	O21—Ca—O31	85.74 (11)
O22—Co—N1	98.22 (13)		

In (I), the C21-ethyl and C33-methyl groups are wholly split into two parts, each having a site-occupancy factor of 0.5. H atoms belonging to the disordered C atoms were not included in the refinement model. Other H atoms were placed geometrically and thereafter refined riding on their parent C atoms; C—H = 0.96 \AA for methyl, 0.97 \AA for methylene and 0.93 \AA for aryl, and $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C})$, where x is 1.5 for methyl H atoms and 1.2 for other H atoms.

For compound (I), data collection: *CAD-4 Software* (Enraf-Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). For compound (II), data collection: *SMART* (Siemens, 1994); cell refinement: *SMART* and *SAINT* (Siemens, 1994); data reduction: *XPREP* (Siemens, 1994); program(s) used to solve structure: *SHELXTL* (Siemens, 1994); program(s) used to refine structure: *SHELXTL*. For both compounds, molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1424). Services for accessing these data are described at the back of the journal.

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