Zinc Carboxylate Complexes: Structural Characterisation† of some Binuclear and Linear Trinuclear Complexes

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The preparation and structural characteristics of nine air-stable binuclear zinc(II) carboxylate complexes together with 13 air-stable linear trinuclear complexes of general formula [Zn_2M(carboxylate)$_6$(base)$_2$] where M^{II} = Zn, Co, Ni, Cd, Mg, or Ca are reported. The crystal structure of the parent binuclear complex [$Zn_2(MeCH{=}CHCO_2)_4(C_9H_7N)_2$] ($C_9H_7N$ = quinoline) has been determined. The main feature of interest is the flexibility of the tetracarboxylate framework which can bridge across a wide range of metal–metal distances (*e.g.* Zn $\cdots$ Zn 2.976 Å in this complex).

Since Van Niekerk and Schoening[1] determined the binuclear nature of copper(II) acetate monohydrate there has been considerable interest in binuclear transition-metal carboxylate complexes. Such complexes are known for a wide range of transition metals,[2] with the emphasis on those which exhibit metal–metal interactions, whether strong (*e.g.* Mo^{II}_2 quadruply bonded species[3]) or relatively weak (*e.g.* Cu^{II}_2 species[2,4]). We have prepared and studied a series of binuclear and linear trinuclear metal carboxylate complexes which possess *syn–syn* bridging carboxylate ligands, and in which no metal–metal bonding interactions are present.

We have recently reported[5a] the crystal structure of the first carboxylate-bridged linear trinuclear zinc(II) complex, [$Zn_3(MeCH{=}CHCO_2)_6(C_9H_7N)_2$], where C_9H_7N = quinoline. The only other example of such a structure is [$Co_3(PhCO_2)_6(C_9H_7N)_2$],[5b] but despite the apparent similarity in the gross structures of these complexes there are subtle differences in the exact nature of the carboxylate bridging modes. The only other known related structure for zinc,[6] containing binuclear units, is the cation [$Zn_2(MeCO_2)_3$]$^+$; monomeric complexes are, of course, much more common.[7–10]

In the course of an extensive study of a variety of oligomeric metal complexes containing carboxylate ligands we have prepared and characterised nine air-stable binuclear zinc(II) complexes together with 13 air-stable linear trinuclear complexes of general formula [Zn_2M(carboxylate)$_6$(base)$_2$] where M^{II} = Zn, Co, Ni, Cd, Mg, or Ca. A structurally similar mixed-metal complex [$(Ph_3P)ClZn(\mu\text{-}Cl)_2(thf)V(thf)(\mu\text{-}Cl)_2ZnCl(PPh_3)$] (thf = tetrahydrofuran) is known,[11] but this does not involve carboxylate ligands. The compounds reported (Tables 1 and 2) substantially extend our knowledge of the structural chemistry of zinc(II) carboxylate complexes.

Results and Discussion

Crystal Structure of [$Zn_2(MeCH{=}CHCO_2)_4(C_9H_7)_2$].—Figure 1 shows the molecular structure of the binuclear complex. The molecule has the same general form as many metal carboxylates of formula M_2(carboxylate)$_4$(base)$_2$, with four bidentate bridging carboxylate ligands and two axial ligands. This structure is not in itself unusual, although the metal separation of 2.976 Å is one of the largest reported, but it is the first example of such a structure reported for Zn^{II}, and it is not immediately obvious why such structures should form in the absence of metal–metal bonding.

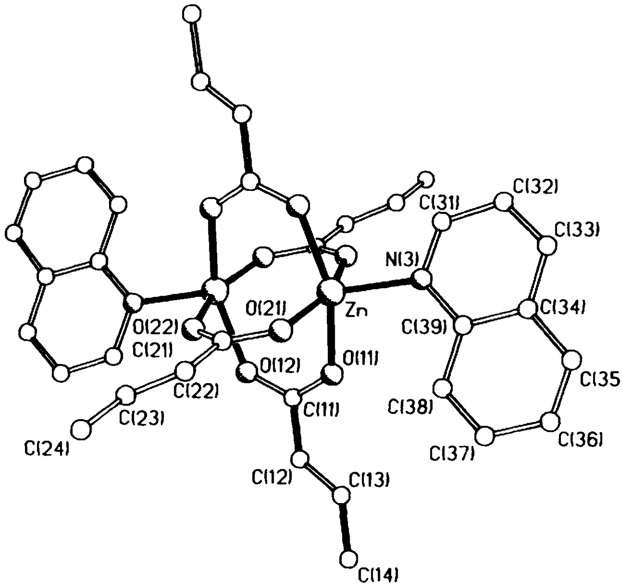

Figure 1. Solid-state structure and numbering scheme for [$Zn_2(MeCH{=}CHCO_2)_4(C_9H_7N)_2$]

The explanation for this behaviour comes from the preparation of the binuclear complexes; it is important that the Zn:base ratio is not significantly greater than 1:1, otherwise crystallisation of the binuclear product does not result. Instead, an intractable mixture of complexes forms with Zn:base ratios of 1:2 and greater. In the absence of sufficient N-donor bases, the Zn atoms satisfy their co-ordination requirement by sharing carboxylate ligands in a bidentate manner rather than forming discrete mononuclear complexes with chelating carboxylates. Although bidentate chelating carboxylates are known[2,12] they are rare; the formation of a four-membered M–O–C–O ring, with the high angular strain involved, is not expected to be energetically favourable.

There has been extensive discussion[3,13–15] of factors affecting the binuclear tetracarboxylate structure. The effect of axial ligands on metal separations in metal–metal bonded complexes varies according to the type of metal. However, even for systems where a noticeable trend of increasing metal separation with increasing electron-donor ability of the axial ligand exists, it is a small effect compared with the effect on the

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† *Supplementary data available* (No. SUP 56514, 3 pp.): thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

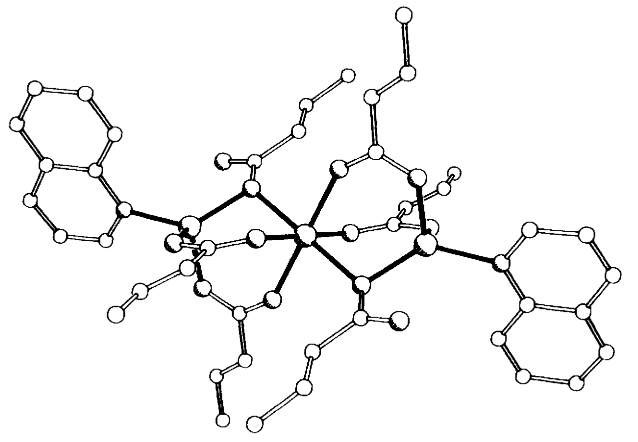


Figure 2. Solid-state structure for $[Zn_3(MeCH{=}CHCO_2)_6(C_9H_7N)_2]$

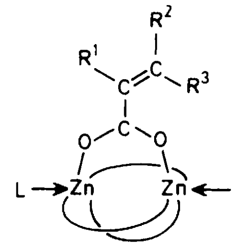
metal separation of changing the electronic properties of the carboxylate groups. There is no evidence to suggest that the metal separation in non-metal-bonded binuclear complexes is affected by the axial ligands, although the co-ordination geometry around each metal may be severely distorted by bulky ligands such as triphenylphosphine.[16]

Discussion has concentrated on the relative importance of the carboxylate framework compared with the strength of the metal–metal bond in determining the overall structure. Koh and Christoph[13] have studied a wide range of binuclear tetracarboxylate complexes possessing metal–metal interactions, with metal separations in the range 2.050—2.886 Å. They have shown empirically that there is a linear relationship between metal separation and M–M–O angles, and conclude that the M–O–C angles are the most responsive to change in the $\overline{\text{M–M–O–C–O}}$ ring. The average Zn–Zn–O angle (79.4°) in $[Zn_2(MeCH{=}CHCO_2)_4(C_9H_7N)_2]$ agrees well with the empirically predicted value (79.3°) for Zn $\cdots$ Zn 2.976 Å. The metal separation[16] of 3.452 Å in $[Cd_2(CF_3CO_2)_4(PPh_3)_2]$ is the largest currently known for a binuclear tetracarboxylate complex; the average Cd–Cd–O angle (73.9°) also agrees well with the predicted value (72.4°), despite severe distortion of the carboxylate framework.

Thus for binuclear tetracarboxylate complexes devoid of metal–metal bonding interactions, the structures of which are solely dependent upon the electronic and steric constraints of the carboxylate ligands and isolated metal atoms, the flexible tetracarboxylate framework will accommodate metal separation at least as large as 3.452 Å with the same trends in angle deformations as observed for complexes possessing metal–metal bonding interactions.

It is not clear to what extent the metals may be separated whilst still retaining the bidentate bridging framework; the $[Zn_2(MeCO_2)_3]^+$ cation[6] has a metal separation of 3.538 Å, and retains bidentate bridging carboxylate groups, although there are only three of them. An interesting comparison exists between this cation and $[Zn_3(MeCH{=}CHCO_2)_6(C_9H_7N)_2]$ (Figure 2) which although possessing a smaller metal separation (3.264 Å between central and terminal zinc atoms) has a monodentate bridge on either side of the central, regular octahedral, zinc atom.[5] Thus it is clear that the criteria leading to monodentate or bidentate bridging do not totally depend on metal separation. We are currently carrying out an *X*-ray crystal structure investigation of other linear trinuclear carboxylates to clarify the situation, but it seems likely that steric interactions between the monodentate bridges and bidentate bridges on the other side of the central zinc atom are important.

Table 1. Analytical data[a] for the binuclear zinc(II) carboxylates[b]



Complex	R^1	R^2	R^3	L	Analysis (%) C	H	N	Zn
(1)	H	Me	H	C_9H_7N	56.0 (56.0)	4.6 (4.7)	3.9 (3.8)	17.8 (17.9)
(2)	H	Me	H	2Me-py[c]	50.9 (51.2)	5.2 (5.2)	4.3 (4.3)	
(3)	H	Me	H	*iso*-C_9H_7N[d]	55.5 (56.0)	4.6 (4.7)	3.8 (3.8)	
(4)	Me	H	H	C_9H_7N	56.1 (56.0)	4.7 (4.7)	3.9 (3.8)	17.7 (17.9)
(5)	Me	H	H	2Me-py	50.9 (51.2)	5.2 (5.2)	4.3 (4.3)	
(6)	Me	Me	H	C_9H_7N	57.9 (58.1)	5.4 (5.4)	3.4 (3.6)	
(7)	Me	Me	H	2Me-py	53.5 (53.9)	5.7 (5.9)	3.8 (3.9)	
(8)	Me	Me	H	*iso*-C_9H_7N[d]	57.4 (58.1)	5.2 (5.4)	3.6 (3.6)	16.2 (16.6)
(9)	H	Me	Me	C_9H_7N	57.9 (58.1)	5.2 (5.4)	3.5 (3.6)	16.7 (16.6)

[a] Required values are given in parentheses. [b] All of the complexes were prepared in 30—60% yields. [c] 2-Methylpyridine. [d] Isoquinoline.

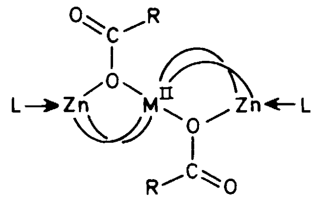
Vibrational Study of Binuclear and Linear Trinuclear Complexes.—The binuclear complexes all have a similar structure to that of $[Zn_2(MeCH{=}CHCO_2)_4(C_7H_9N)_2]$ (Figure 1), and their vibrational data are given in Table 3. The solid-state i.r. spectra show $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ values which are consistent with the presence of bridging carboxylate ligands.[17] Spectra of solutions in $CHCl_3$ or CH_2Cl_2 gave a new band at *ca.* 1 700 cm^{-1} due to the presence of monodentate carboxylate ligands; the band may be assigned to a ν(C=O) terminal mode. Thus the solution i.r. spectrum suggests a binuclear or mononuclear structure is formed in which both monodentate and bidentate (bridging or chelating) crotonate groups are present in rapid equilibrium.

The linear trinuclear complex $[Zn_3(MeCH{=}CHCO_2)_6(C_9H_7N)_2]$ (Figure 2) contains four bidentate and two monodentate crotonate ligands in the solid state. The band at 1 626 cm^{-1} in the solid-state i.r. spectrum is assigned to ν(C=O) of the monodentate crotonate bridges. It is *ca.* 80 cm^{-1} lower in frequency than the 'free' ν(C=O) in α,β-unsaturated esters,[18] and this is due to the weak interaction of the carboxyl groups with the terminal zinc atoms.

In solution ($CHCl_3$ or CH_2Cl_2) the ν(C=O) band occurs at 1 702 cm^{-1} implying either (*i*) cleavage of the C=O $\cdots$ Zn interaction by solvent, with overall retention of the trinuclear structure, or (*ii*) decomposition to a structure with both monodentate and bidentate crotonate ligands, as is possible for the binuclear complexes. However, vibrational data from the Mg^{II}- and Ca^{II}-containing mixed-metal trinuclear complexes have enabled us to propose (*i*) as the most likely situation.

The solid-state i.r. spectra of $[Zn_2Mg(MeCH{=}CHCO_2)_6(C_9H_7N)_2]$ and $[Zn_2Ca(MeCH{=}CHCO_2)_6(C_9H_7N)_2]$ show

Table 2. Analytical data for the linear trinuclear complexes*



Complex	M^{II}	R	L	Analysis (%) C	H	N	Zn
(10)	Zn	MeCH=CH	C_9H_7N	52.0	4.4	2.8	19.7
				(52.3)	(4.6)	(2.9)	(20.3)
(11)	Zn	Me_2C=CH	2Me-py	51.6	5.6	2.8	20.0
				(51.6)	(5.8)	(2.9)	(20.1)
(12)	Co	MeCH=CH	C_9H_7N	52.2	4.5	3.0	13.2
				(52.6)	(4.6)	(2.9)	(13.6)
(13)	Co	Me_2C=CH	C_9H_7N	54.6	5.2	2.6	13.1
				(55.3)	(5.4)	(2.7)	(12.5)
(14)	Co	Me_2C=CH	2Me-py	51.8	5.8	2.9	13.5
				(52.0)	(5.8)	(2.9)	(13.5)
(15)	Ni	MeCH=CH	C_9H_7N	52.5	4.5	2.9	14.7
				(52.6)	(4.6)	(2.9)	(13.7)
(16)	Cd	MeCH=CH	C_9H_7N	49.6	4.2	2.7	13.4
				(49.9)	(4.4)	(2.8)	(12.9)
(17)	Cd	MeCH=CH	2Me-py	46.2	4.6	2.9	
				(46.0)	(4.7)	(3.0)	
(18)	Cd	MeCH=CH	*iso*-C_9H_7N	49.5	4.2	2.8	
				(49.9)	(4.4)	(2.8)	
(19)	Cd	CH_2=CMe	C_9H_7N	50.0	4.3	2.7	
				(49.9)	(4.4)	(2.8)	
(20)	Mg	MeCH=CH	C_9H_7N	54.6	4.7	3.0	14.2
				(54.6)	(4.8)	(3.0)	(14.2)
(21)	Mg	MeCH=CH	*iso*-C_9H_7N	55.0	4.6	2.9	
				(54.6)	(4.8)	(3.0)	
(22)	Ca	MeCH=CH	C_9H_7N	53.9	4.6	3.0	
				(53.7)	(4.7)	(3.0)	
(23)	Ca	MeCH=CH	2Me-py	49.9	5.0	3.1	
				(49.8)	(5.1)	(3.2)	

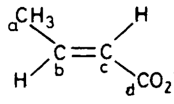
* See Table 1 for details.

Table 3. Selected vibrational data (cm^{-1})[a] for binuclear and trinuclear carboxylate complexes

Complex[b]	I.r. bands assigned to CO_2 modes: Solid state	Solution[c]
$[Zn_2(RCO_2)_4(C_9H_7N)_2]$	1 608br, 1 411br	1 703br, 1 579br
$[Zn_3(RCO_2)_6(C_9H_7N)_2]$	1 626, 1 568br, 1 409br	1 702br, 1 577br
$[Zn_2Co(RCO_2)_6(C_9H_7N)_2]$	1 622, 1 568br, 1 410br	1 724br, 1 693br, 1 580br
$[Zn_2Cd(RCO_2)_6(C_9H_7N)_2]$	1 632, 1 562br, 1 411br	1 700br, 1 573br
$[Zn_2Ni(RCO_2)_6(C_9H_7N)_2]$	1 622, 1 573br, 1 413br	
$[Zn_2Mg(RCO_2)_6(C_9H_7N)_2]$	1 599br, 1 401br	1 586br
$[Zn_2Ca(RCO_2)_6(C_9H_7N)_2]$	1 591br, 1 401br	1 581br

[a] All absorptions are strong; br = broad. [b] R = MeCH=CH. [c] Bands $< 1\ 550\ cm^{-1}$ obscured by those due to solvent ($CHCl_3$).

Table 4. Room-temperature ^{13}C n.m.r. chemical shifts (p.p.m. relative to $SiMe_4$)



Complex*	C_a	C_b	C_c	C_d
$[Zn(RCO_2)_2]$	17.80	145.82	124.87	174.75
$[Zn_2(RCO_2)_4(C_9H_7N)_2]$	17.69	144.09	125.72	174.53
$[Zn_3(RCO_2)_6(C_9H_7N)_2]$	17.70	144.36	125.57	174.53
$[Zn_2Cd(RCO_2)_6(C_9H_7N)_2]$	17.69	143.91	125.74	174.43
$[Zn_2Mg(RCO_2)_6(C_9H_7N)_2]$	17.57	142.37	126.75	173.52
$[Zn_2Ca(RCO_2)_6(C_9H_7N)_2]$	17.58	142.50	126.56	173.73

* R = MeCH=CH.

no peaks in the region 1 620—1 630 cm^{-1}. There is no evidence for the presence of monodentate crotonate bridges, and these complexes are believed to possess six bidentate bridges. Significantly, the i.r. solution spectra show no ν(C=O) bands which would indicate the presence of a monodentate carboxylate group; this has been confirmed by solution Raman spectroscopy.

We conclude that these complexes retain their linear trinuclear structure in solution and consider it unlikely that $[Zn_3(MeCH{=}CHCO_2)_6(C_9H_7N)_2]$ undergoes a decomposition reaction.

The vibrational spectra of compounds **(12)**, **(15)**, and **(16)**, where M^{II} = Co, Ni, or Cd, are very similar to **(10)** (Table 3); *X*-ray crystal-structure studies are planned to elucidate precisely the solid-state structures of the mixed-metal trinuclear complexes.

The vibrational modes due to the heterocyclic nitrogen bases are typical for bases co-ordinated to a metal. Bonding *via* the N atom can be recognised by a positive shift in frequency (5—10 cm^{-1}) for certain bands.[19,20] The ν(C=C) frequency for the co-ordinated α,β-unsaturated carboxylate groups shows only minor variations across the series (1 656—1 662 cm^{-1}).

^{13}C *N.M.R. Measurements.*—The ^{13}C n.m.r. chemical shift values for $CDCl_3$ solutions of several selected binuclear and trinuclear complexes are given in Table 4. As $[Zn_3(MeCH{=}CHCO_2)_6(C_9H_7N)_2]$ possesses two distinct types of bridging crotonate ligands in both the solid state and in solution, it should be possible to distinguish them by ^{13}C n.m.r. spectroscopy. However, only four crotonate peaks were observed in the temperature range 200—300 K, suggesting the presence of a facile bridge-exchange process resulting in averaged chemical shifts for the crotonate carbon atoms. From Table 4 it can be concluded that the ^{13}C resonances are insensitive to the mode of carboxylate co-ordination.

Mass Spectrometry.—A general feature of metal carboxylate mass spectra is that clusters larger than the parent molecule are commonly observed; this feature is present in the mass spectra of the bi- and tri-nuclear carboxylate complexes reported in this paper.

The complexes $[Zn_2(MeCH{=}CHCO_2)_4(C_9H_7N)_2]$ and $[Zn_3(MeCH{=}CHCO_2)_6(C_9H_7N)_2]$ give very similar mass spectra (Table 5). Assignment of the fragments was carried out by inspection, and simulation of observed zinc and carbon isotope patterns (^{64}Zn, 48.9, ^{66}Zn, 27.8, ^{67}Zn, 4.1, ^{68}Zn, 18.6, ^{70}Zn, 0.6, and ^{13}C, 1.1%) confirmed the assignments (Table 6).

No fragments due to the original zinc crotonate frameworks were observed for these species; rearrangement to basic zinc crotonate, $[Zn_4O(MeCH{=}CHCO_2)_6]$, occurred on the spectrometer probe, and the fragments observed correspond closely to those observed in the mass spectrum of basic zinc carboxylates,[21,22] and normal zinc acetate.[23]

The complex $[Zn_2Co(MeCH{=}CHCO_2)_6(C_9H_7N)_2]$ has a complicated spectrum which shows the presence of mixed-metal

Table 5. Assignment of major fragments in the mass spectra of $[Zn_2(MeCH{=}CHCO_2)_4(C_9H_7N)_2]$ and $[Zn_3(MeCH{=}CHCO_2)_6(C_9H_7N)_2]$

Fragment m/e[a]	Assignment[b]
697	$[Zn_4O(RCO_2)_5]^+$
543	$[Zn_4O_2(RCO_2)_3]^+$
499	$[Zn_4O_2(RCO_2)_2R]^+$
463	$[Zn_3O(RCO_2)_3]^+$
419	$[Zn_3O(RCO_2)_2R]^+$
395	$[Zn_3O(OH)(RCO_2)_2]^+$
379	$[Zn_3O(RCO_2)_2]^+$
348.5	$[Zn_4O(RCO_2)_5]^{2+}$
321	$[Zn_3O(OH)(RCO_2)]^+$
306	$[Zn_4O(RCO_2)_4]^{2+}$

[a] First peak in the isotope pattern, corresponding to ^{64}Zn and ^{12}C. [b] R = MeCH=CH.

Table 6. Comparison of observed and calculated isotope patterns for the fragment $[Zn_4O(RCO_2)_5]^+$ in the mass spectrum of $[Zn_3(RCO_2)_6(C_9H_7N)_2]$ where R = MeCH=CH

	Relative intensity	
m/e	Observed	Calculated
697	27	27
698	10	6
699	62	63
700	28	23
701	96	98
702	41	37
703	100	100
704	45	41
705	80	78
706	34	31
707	47	45
708	20	17
709	22	20
710	8	7
711	7	6

basic carboxylate species. The parent peak consists of the overlapping isotope patterns of $[Zn_nCo_{4-n}O(MeCH{=}CHCO_2)_6]^+$ (n = 0—4). Basic cobalt carboxylates are known,[24] but no mixed-metal basic tetranuclear carboxylate complex has yet been isolated.

The spectrum of $[Zn_2Ni(MeCH{=}CHCO_2)_6(C_9H_7N)_2]$ gives the only example we have of retention of the linear trinuclear unit; a pattern of peaks beginning at m/e 776 is assigned to $[Zn_2Ni(MeCH{=}CHCO_2)_6]^+$. The highest peak observed is assigned to $[Zn_3NiO(MeCH{=}CHCO_2)_6]^+$, and it is interesting that, in contrast to the $[Zn_2Co(MeCH{=}CHCO_2)_6(C_9H_7N)_2]$ spectrum, there is no evidence for any mixed-metal fragment containing a different Zn:Ni ratio. Apart from these two fragments, the spectrum is similar to those of $[Zn_2(MeCH{=}CHCO_2)_4(C_9H_7N)_2]$ and $[Zn_3(MeCH{=}CHCO_2)_6(C_9H_7N)_2]$. Unlike zinc and cobalt, basic nickel carboxylates are unknown so the presence of $[Zn_3NiO(MeCH{=}CHCO_2)_6]^+$ is surprising. We are currently attempting to isolate a mixed zinc–nickel basic carboxylate based on this mass spectral evidence.

Investigation of the mixed-metal trinuclear carboxylates is hindered by the rearrangements occurring in the spectrometer. We hope to prevent these in future by using the milder ionisation technique of fast atom bombardment.

Experimental

All of the complexes are crystalline and stable to air at room temperature. They are readily soluble in methanol, ethanol, chloroform, and dichloromethane but are insoluble in the relatively non-polar solvents diethyl ether, benzene, and carbon tetrachloride.

The C, H, and N microanalyses were carried out using a Carlo Erba 1106 elemental analyser. Zinc analysis was performed on a Perkin-Elmer model 2380 atomic absorption spectrophotometer (λ = 213.9 nm). Infrared spectra were recorded from KBr discs or from solutions in a 0.2-mm KBr liquid cell on a Perkin-Elmer model 598 spectrometer and the bands assigned to $\nu(CO_2)$ modes of the bridging carboxylate ligands are given in Table 3. ^{13}C N.m.r. spectra were recorded on a Brucker WM 300/WB at 300 K. The field was 7.05 T and the sample-tube diameter was 5 mm. Some typical ^{13}C n.m.r. chemical shifts are shown in Table 4. Mass spectra were measured with an AEI MS9 mass spectrometer. Solution Raman spectra were recorded with a modified Cary 81 instrument. The spectra were excited using the green line (514.8 nm) of a Coherent Radiation model CR3 argon-ion laser and the spectra were calibrated by reference to the positions of well documented solvent bands. Electronic spectra were run on a Perkin-Elmer 550 spectrometer using a diffuse reflectance attachment for samples in the solid state. Both solid-state and solution spectra (in $CHCl_3$ and EtOH) for the mixed-metal linear trinuclear complexes containing Co^{II} and Ni^{II} as central metal ions indicate that the transition-metal ions are in regular octahedral environments. For example, in the solid state, the following transitions were observed in the visible region: for compound (**12**), ${}^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ 17 889 cm^{-1}; compound (**15**), ${}^3A_{2g} \longrightarrow {}^3T_{1g}(P)$ 23 696 cm^{-1}, ${}^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ 13 351 cm^{-1}.

X-Ray Crystallography.—*Crystal data.* $C_{34}H_{34}N_2O_8Zn_2$, M = 729.4, monoclinic, a = 10.532(1), b = 10.910(1), c = 14.623(2) Å, β = 99.10(1)°, U = 1 659.1 Å^3 (by least-squares refinement on 2θ angles for 32 reflections, λ = 0.710 73 Å), space group $P2_1/n$, Z = 2, D_c = 1.460 g cm^{-3}, F(000) = 752, crystal dimensions 0.27 × 0.30 × 0.50 mm, μ(Mo-K_α) = 1.53 mm^{-1}, T = 298 K.

Data collection and processing. Siemens AED2 diffractometer, ω—θ scan mode, graphite-monochromated Mo-K_α radiation. Scan range 1.19 + α-doublet resolution, scan time 17.5—76 s. 3 331 Reflections measured ($2\theta < 50°$, $h \geqslant 0$, $k \leqslant 1$), of which 2 914 were unique (merging R = 0.015), giving 2 372 with $F > 4\sigma(F)$; an intensity decay of *ca.* 17% was corrected for on the basis of three standard reflections measured every 60 min. Empirical absorption corrections based on azimuthal scan data[25] (transmission factors 0.458—0.516) were employed.

Structure solution and refinement.[25] Patterson and difference syntheses. Blocked-cascade refinement on F, with all non-hydrogen atoms anisotropic, hydrogens in calculated positions with C–H 0.96 Å, H–C–H 109.5°, aromatic and olefinic H on C–C–C external bisectors, U(H) = 1.2U_{eq}(C). Weighting scheme $w = 1/\sigma^2(F)$, giving satisfactory analysis of variance. Final R = 0.030, $R' = (\Sigma w\Delta^2/wF_o)^{\frac{1}{2}}$ = 0.027.

Slope of normal probability plot = 1.56; largest peak in final difference synthesis 0.24 e Å^{-3}, largest hole −0.22 e Å^{-3}. Scattering factors from ref. 26. Refined atomic co-ordinates are given in Table 7, selected bond lengths and bond angles in Table 8.

Preparations of the Binuclear Zinc(II) *Complexes*.—$[Zn_2(MeCH{=}CHCO_2)_4(C_9H_7N)_2]$. Freshly precipitated zinc hydroxide (5 mmol) was refluxed with crotonic acid (11 mmol) in water (100 cm^3) for 1 h. The resulting solution was filtered and concentrated (Rotovap) to 15—20 cm^3 causing precipitation of white zinc(II) crotonate. The product was isolated (in essentially quantitative yield) by vacuum filtration, washed with diethyl ether (50 cm^3), and dried under vacuum over P_2O_5 at

Table 7. Atomic co-ordinates (× 10^4) for the complex [$Zn_2(MeCH{=}CHCO_2)_4(C_9H_7N)_2$]

Atom	*x*	*y*	*z*
Zn	5 830.7(2)	5 914.2(2)	4 624.0(2)
O(11)	6 671(2)	4 322(1)	4 325(1)
O(12)	5 434(2)	2 941(1)	4 875(1)
C(11)	6 411(2)	3 251(2)	4 530(1)
C(12)	7 313(2)	2 262(2)	4 381(2)
C(13)	8 449(2)	2 459(3)	4 152(2)
C(14)	9 439(3)	1 520(3)	4 044(3)
O(21)	6 930(2)	5 882(2)	5 895(1)
O(22)	5 681(2)	4 489(2)	6 420(1)
C(21)	6 629(2)	5 190(2)	6 515(2)
C(22)	7 476(2)	5 220(2)	7 426(2)
C(23)	7 427(2)	4 413(2)	8 083(2)
C(24)	8 245(3)	4 361(3)	9 008(2)
N(3)	6 648(2)	7 235(2)	3 892(1)
C(31)	5 863(2)	8 122(2)	3 556(2)
C(32)	6 212(2)	9 096(3)	3 036(2)
C(33)	7 432(2)	9 137(3)	2 844(2)
C(34)	8 306(2)	8 222(2)	3 175(2)
C(35)	9 594(2)	8 201(3)	3 000(2)
C(36)	10 399(2)	7 296(3)	3 335(2)
C(37)	9 989(2)	6 345(2)	3 863(2)
C(38)	8 756(2)	6 330(2)	4 054(2)
C(39)	7 898(2)	7 263(2)	3 710(1)

Table 8. Bond lengths (Å) and angles (°)

Zn–O(11)	2.028(2)	Zn–O(21)	2.029(2)
Zn–O(12′)	2.044(2)	Zn–O(22′)	2.072(2)
Zn–N(3)	2.063(2)	O(11)–C(11)	1.247(3)
O(12)–C(11)	1.262(3)	C(11)–C(12)	1.476(4)
C(12)–C(13)	1.310(4)	C(13)–C(14)	1.488(5)
O(21)–C(21)	1.258(3)	O(22)–C(21)	1.247(3)
C(21)–C(22)	1.483(3)	C(22)–C(23)	1.311(4)
C(23)–C(24)	1.486(4)	N(3)–C(31)	1.317(3)
N(3)–C(39)	1.384(3)	C(31)–C(32)	1.390(4)
C(32)–C(33)	1.359(4)	C(33)–C(34)	1.391(4)
C(34)–C(35)	1.420(4)	C(34)–C(39)	1.414(3)
C(35)–C(36)	1.342(4)	C(36)–C(37)	1.401(4)
C(37)–C(38)	1.371(4)	C(38)–C(39)	1.401(3)

O(11)–Zn–O(21)	88.7(1)	O(11)–Zn–N(3)	104.8(1)
O(21)–Zn–N(3)	105.3(1)	O(11)–Zn–O(12′)	158.7(1)
O(21)–Zn–O(12′)	89.6(1)	N(3)–Zn–O(12′)	96.2(1)
O(11)–Zn–O(22′)	88.3(1)	O(21)–Zn–O(22′)	158.8(1)
N(3)–Zn–O(22′)	95.8(1)	O(12′)–Zn–O(22′)	85.7(1)
Zn–O(11)–C(11)	129.1(2)	C(11)–O(12)–Zn′	126.8(2)
O(11)–C(11)–O(12)	124.8(2)	O(11)–C(11)–C(12)	118.6(2)
O(12)–C(11)–C(12)	116.6(2)	C(11)–C(12)–C(13)	123.6(2)
C(12)–C(13)–C(14)	126.8(3)	Zn–O(21)–C(21)	119.9(1)
C(21)–O(22)–Zn′	136.1(2)	O(21)–C(21)–O(22)	125.2(2)
O(21)–C(21)–C(22)	116.7(2)	O(22)–C(21)–C(22)	118.1(2)
C(21)–C(22)–C(23)	123.8(2)	C(22)–C(23)–C(24)	127.5(3)
Zn–N(3)–C(31)	114.7(2)	Zn–N(3)–C(39)	127.1(1)
C(31)–N(3)–C(39)	118.2(2)	N(3)–C(31)–C(32)	124.1(2)
C(31)–C(32)–C(33)	118.6(2)	C(32)–C(33)–C(34)	120.0(3)
C(33)–C(34)–C(35)	123.2(2)	C(33)–C(34)–C(39)	118.8(2)
C(35)–C(34)–C(39)	118.0(2)	C(34)–C(35)–C(36)	120.9(3)
C(35)–C(36)–C(37)	120.9(3)	C(36)–C(37)–C(38)	120.4(2)
C(37)–C(38)–C(39)	119.8(2)	N(3)–C(39)–C(34)	120.3(2)
N(3)–C(39)–C(38)	119.7(2)	C(34)–C(39)–C(38)	120.1(2)

room temperature. Quinoline (0.5 mmol) was added directly to an ethanolic solution (50 cm^3) of zinc(II) crotonate (0.5 mmol). The solution was refluxed for 10 min, filtered and concentrated (Rotovap) to approximately 5 cm^3. Over a period of 12—24 h white crystals formed, which were isolated as for the parent crotonate. The analytical data are given in Table 1, together with the data for eight other binuclear zinc(II) complexes. The latter were all prepared in the same way from zinc hydroxide, using the appropriate stoicheiometric ratios of carboxylic acid and heterocyclic base.

Preparation of the Linear Trinuclear Zinc(II) *Complex* [$Zn_3(MeCH{=}CHCO_2)_6(C_9H_7N)_2$].—The method was the same as that described for the binuclear complex above except that the stoicheiometric ratio of zinc(II) crotonate : base was 3 : 2. The analytical data are reported in Table 2.

Preparations of Linear Trinuclear Complexes of General Formula [$Zn_2M(carboxylate)_6(base)_2$], *where* M^{II} = Co, Ni, Cd, Mg, *or* Ca.—The complexes were prepared by the same method as described for the linear trinuclear zinc(II) complex except that the zinc : metal(II) carboxylate ratio used was 2 : 1 and the metal(II) carboxylate : base ratio was 3 : 2. There were minor variations, however, in the preparations of the metal(II) carboxylates. When M^{II} = Co, Ni, or Ca the metal carbonates were treated with carboxylic acid, whereas $3MgCO_3{\cdot}Mg(OH)_2{\cdot}3H_2O$ was used to prepare the magnesium carboxylate. Cadmium(II) hydroxide was the preferred starting material for the cadmium complexes (**16**)—(**19**). The analytical data for all of the new complexes are reported in Table 2. The linear trinuclear complexes containing cobalt(II) (**12**)—(**14**) are purple in colour, the nickel(II) complex (**15**) is yellow-green, while the remainder are all white.

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