Preparation and Characterisation of Linear Mixed-metal Trinuclear Carboxylate Complexes of General Formula $[M_2M'(O_2CR)_6(C_9H_7N)_2]$; Crystal Structure of $[Zn_2Ba(O_2CCMe_3)_6(C_9H_7N)_2]$ *

William Clegg, Paul A. Hunt, and Brian P. Straughan
Department of Chemistry, The University, Newcastle upon Tyne NE1 7RU
Maria Antonia Mendiola
Departmento de Quimica (C-VIII), Universidad Autonoma, Canto Blanco, 28049 Madrid, Spain

---

The complexes $[Co_2M(O_2CCH{=}CHMe)_6(C_9H_7N)_2]$ where M = Zn or Mn, C_9H_7N = quinoline, $[Zn_2Co(O_2CPh)_6(C_9H_7N)_2]$, $[Zn_2M(O_2CMe)_6(C_9H_7N)_2]$ where M = Zn or Mn, and $[Zn_2Ba(O_2CCMe_3)_6(C_9H_7N)_2]$ have been prepared by the stoicheiometric addition of metal carboxylate salts to an ethanolic solution of quinoline. Solid-state u.v.–visible, i.r., and magnetic measurements are all consistent with the presence of linear arrays of three metal ions bonded by bridging carboxylates and terminal quinoline ligands. An *X*-ray crystallographic investigation of the barium complex shows that all of the carboxylates are of the *syn–syn* bridging type across Ba • • • Zn separations of 4.13(1) and 4.22(1) Å.

The binuclear complexes $[Cu_2L_2(O_2CMe)_4]$, where L = H_2O, MeOH, quinoline, *etc*., and related complexes have received a lot of attention in the literature,[1,2] not least because they provide a large body of information about magnetic interactions for metal complexes which have two spins of 0.5. Cobalt(II) carboxylates provide a similar series of binuclear complexes [3] and the latter can be readily enlarged to give a linear trinuclear array of cobalt(II) ions held together by six bridging carboxylates and terminated by two heterocyclic bases.[3]

More recently, we have reported an extensive series of linear trinuclear zinc complexes with the general formula $[Zn_2M(O_2CR)_6L_2]$, where M = Zn, Cd, Ni, Co, Mg, Ca, or Sr, RCO_2 = tiglate [(*E*)-2-methylbut-2-enoate], crotonate, or 3,3-dimethylacrylate, and L = quinoline, isoquinoline, or 6-methylquinoline.[4–6] The crotonate complexes have been characterised by *X*-ray crystallography. The constant feature for all of the structures is that the three divalent metals are linked by six unsaturated carboxylate ligands and they again provide a wealth of data about steric interactions, as well as vibrational, electronic, and magnetic properties.

We have now prepared a further series of complexes to establish that linear mixed-metal Co_2M^{II} trinuclear complexes can be prepared. We also wish to demonstrate that mixed-metal trinuclear complexes can be prepared with bridging ligands such as acetate, pivalate, and benzoate as well as unsaturated aliphatic carboxylates. Herein we report the preparation of $[Co_2M(O_2CCH{=}CHMe)_6(C_9H_7N)_2]$, where M = Mg or Mn, $[Zn_2Co(O_2CPh)_6(C_7H_9N)_2]$, $[Zn_2M(O_2CMe)_6(C_9H_7N)_2]$ where M = Zn or Mn, and $[Zn_2Ba(O_2CCMe_3)_6(C_9H_7N)_2]$; in all cases C_9H_7N = quinoline. We discuss the *X*-ray crystal structure of $[Zn_2Ba(O_2CCMe_3)_6(C_9H_7N)_2]$ and the solid-state u.v.–visible, i.r., and magnetic data for the entire series.

Experimental

Materials.—$[Co_2M(O_2CCH{=}CHMe)_6(C_9H_7N)_2]$ (M = Mn *or* Mg). Solid cobalt(II) crotonate (2 mol) and solid metal(II) crotonate (1 mol) (both previously produced from the reaction of the respective carbonates with crotonic acid in water) were dissolved in the minimum volume of ethanol. Quinoline (2 mol) was added directly and the resulting mixture was refluxed for 3—4 h. The resulting solution was then filtered (a small amount of solid residue was left behind in the Co/Mn reaction) and the filtrate was concentrated until only 10—20% of the initial volume remained. On cooling to *ca*. 10 °C, crystals were formed over a period of time. The latter were collected by vacuum filtration, washed with ethanol, and finally dried under vacuum over P_2O_5 at room temperature. Both of the complexes were obtained in a yield of 80% (with respect to the cobalt crotonate starting material) and they appeared as microcrystalline blue-purple solids. Attempts to recrystallise the solids from ethanol did not produce crystals suitable for *X*-ray studies.

$[Zn_2M(O_2CMe)_6(C_9H_7N)_2]$ (M = Zn *or* Mn). The hydrated zinc and metal(II) acetates (mole ratio 2:1) were suspended in ethanol. Quinoline was added to give a Zn:quinoline ratio of 1:1. The resulting mixture was refluxed for 4—5 h, filtered whilst hot, and then concentrated to half the initial volume of solvent. The filtrate was finally left at room temperature and crystals were deposited over a period of several days. The crystals were vacuum dried over P_2O_5. Both complexes were obtained in >80% yields as microcrystalline, white powders. The manganese-containing complex gave a magnetic moment of 6.2 μ_B at room temperature which is in the range expected for a manganese(II) complex.

$[Zn_2Co(O_2CPh)_6(C_9H_7N)_2]$. Cobalt(II) carbonate (1 mol) reacted with benzoic acid (2 mol) in ethanol under reflux for 2.5 h. The reaction mixture was filtered to give a solution of cobalt benzoate. Zinc benzoate was prepared by a corresponding reaction with zinc carbonate. The latter (2 mol) was added to a solution of cobalt benzoate (1 mol) and quinoline (2 mol). The resulting mixture was refluxed for 2 h, filtered while hot, and the filtrate was then allowed to cool to room temperature. A purple solid was precipitated as the filtrate cooled. It was dried over P_2O_5 in a vacuum desiccator to give a pink microcrystalline solid (60% yield) which was insoluble in the common organic solvents.

$[Zn_2Ba(O_2CCMe_3)_6(C_9H_7N)_2]$. Zinc pivalate (2 mmol) and barium pivalate (1 mmol) were dissolved in EtOH (100 cm^3). Quinoline (2 mmol) was added and the resulting solution was refluxed for 6 h. The volume of the filtrate from the reaction mixture was reduced to 20 cm^3; crystals formed over a period of 6 weeks. The crystals were washed with EtOH and dried over P_2O_5 (yield 80%).

---

* 1,2;1,2;1,2;2,3;2,3;2,3-Hexa-μ-pivalato-*OO′*-1,3-bis(quinoline)-1,3-dizincbarium.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Analytical data (%) for the trinuclear metal complexes; calculated values in parentheses

Complex	C	H	N	Zn	Co	Mn
$[Zn_2Ba(O_2CCMe_3)_6(C_9H_7N)_2]$	51.00	6.00	2.45			
	(50.90)	(6.05)	(2.45)			
$[Zn_3(O_2CMe)_6(C_9H_7N)_2]$	44.20	3.65	3.35	23.7		
	(44.55)	(4.00)	(3.45)	(24.2)		
$[Zn_2Mn(O_2CMe)_6(C_9H_7N)_2]$	45.30	3.95	3.45	13.8		7.0
	(45.15)	(4.05)	(3.50)	(16.4)		(6.9)
$[Zn_2Co(O_2CPh)_6(C_9H_7N)_2]$	61.50	3.65	2.40	13.6	3.9	
	(61.35)	(3.75)	(2.40)	(11.1)	(5.0)	
$[Co_2Mg(O_2CCH{=}CHMe)_6(C_9H_7N)_2]$	55.00	4.70	3.00		12.6	
	(55.35)	(4.85)	(3.05)		(12.9)	
$[Co_2Mn(O_2CCH{=}CHMe)_6(C_9H_7N)_2]$	53.75	4.55	2.95		12.1	4.7
	(53.55)	(4.70)	(2.95)		(12.5)	(5.8)

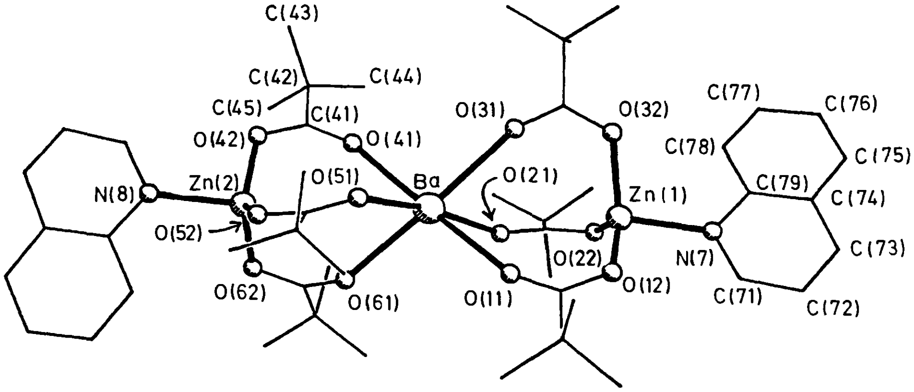

Figure. Molecular structure of $[Zn_2Ba(O_2CCMe_3)_6(C_9H_7N)_2]$. The complete labelling scheme is shown for one pivalate and one quinoline; other ligands are labelled correspondingly. Hydrogen atoms are omitted for clarity

All six complexes are stable in air at room temperature and all except $[Zn_2Co(O_2CPh)_6(C_9H_7N)_2]$ are readily soluble in ethanol and methanol; the benzoate complex is only soluble in molar HNO_3.

Analyses.—Carbon, H, and N analyses (Table 1) were carried out using a Carlo Erba 1106 Elemental Analyser. Cobalt, zinc, and manganese analyses were performed on a Perkin-Elmer model 2380 atomic absorption spectrophotometer using wavelengths λ = 240.7, 213.9, and 279.5 nm respectively.

Spectral Measurements.—Infrared spectra were recorded as KBr discs on a Perkin-Elmer model 598 spectrometer, visible and u.v. spectra on a Perkin-Elmer model 550 spectrophotometer using a diffuse reflectance solid-state sample attachment. The near-i.r. region was measured on a Cary 17D spectrophotometer.

Magnetic Measurements.—Magnetic susceptibility measurements were carried out using the Faraday method with a MAGNET B-4 Brucker balance except for $[Zn_2Mn(O_2CMe)_6(C_9H_7N)_2]$ which was studied on a small Johnson-Matthey magnetic susceptibility balance.

X-Ray Structure Determination for $[Zn_2Ba(O_2CCMe_3)_6(C_9H_7N)_2]$.—*Crystal data.* $C_{48}H_{68}BaN_2O_{12}Zn_2$, M_r = 1 133.2, triclinic, space group $P\bar{1}$, a = 12.260(2), b = 12.323(2), c = 18.776(3) Å, α = 81.75(1), β = 75.93(1), γ = 86.80(1)° (from 2θ values of 32 reflections measured at $\pm\omega$; 2θ 20—22°), U = 2 722.5 Å^3, Z = 2, D_c = 1.382 g cm^{-3}, $F(000)$ = 1 164, Mo-K_α radiation, λ = 0.710 73 Å, μ = 1.67 mm^{-1}, T = 293 K.

Data collection and processing. Siemens AED2 diffractometer, crystal size 0.12 × 0.27 × 0.27 mm, ω—θ scan, scan range 0.68° below α_1 to 0.68° above α_2, scan time 14—56 s, $2\theta_{max.}$ 45°; index ranges h −13 to 0, k −13 to 13, l −20 to 20. Semiempirical absorption correction (transmission 0.66—0.69), crystal decay correction (total *ca.* 11%), 7 092 unique reflections, 4 297 with $F > 4\sigma(F)$.

Structure solution and refinement.[7] Patterson and difference syntheses, block-cascade least squares on F, $w = 1/\sigma^2(F)$, anisotropic thermal parameters, H atoms constrained [C–H 0.96 Å, H–C–H 109.5°, aromatic H on ring angle external bisectors, $U(H) = 1.2U_{eq}(C)$], extinction negligible; 586 parameters, R = 0.051, R' = 0.042, mean shift/estimated standard deviation (e.s.d.) = 0.019, maximum = 0.065, largest features in final difference synthesis +0.71 and −0.41 e Å^{-3}, slope of normal probability plot = 1.63. Refined atomic co-ordinates are given in Table 2, selected bond lengths and angles in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

The analytical data for all six complexes are shown in Table 1. They are in close agreement with the calculated data and strongly support the presence of trinuclear metal complexes (isostructural with those reported previously).[5,6] The diffuse reflectance spectra of the cobalt-containing complexes are the most diagnostic for structural purposes (see Table 4).

The solid-state spectrum of $[Co(H_2O)_6]^{2+}$ which contains Co^{2+} in an octahedral field shows a broad band at *ca.* 515 nm

Table 2. Atomic co-ordinates (× 10^4) for $[Zn_2Ba(O_2CCMe_3)_6(C_9H_7N)_2]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ba	6 983(1)	5 029(1)	2 505(1)	C(51)	8 988(7)	2 790(7)	2 845(5)
Zn(1)	5 933(1)	8 000(1)	3 367(1)	C(52)	9 928(7)	2 566(8)	3 229(5)
Zn(2)	8 108(1)	2 167(1)	1 633(1)	C(53)	10 759(12)	1 773(12)	2 937(9)
O(11)	8 051(5)	6 546(5)	2 870(4)	C(54)	10 418(15)	3 525(12)	3 280(14)
O(12)	7 480(4)	7 989(4)	3 429(3)	C(55)	9 470(11)	2 069(20)	3 970(8)
C(11)	8 225(6)	7 301(7)	3 180(4)	O(61)	8 216(6)	4 555(5)	1 217(3)
C(12)	9 401(7)	7 418(7)	3 285(5)	O(62)	8 424(5)	3 091(5)	665(3)
C(13)	9 410(8)	6 921(9)	4 071(5)	C(61)	8 252(7)	4 112(7)	664(5)
C(14)	10 279(8)	6 881(9)	2 727(6)	C(62)	8 049(7)	4 806(6)	−30(5)
C(15)	9 666(8)	8 653(8)	3 193(6)	C(63)	8 352(9)	5 984(8)	−73(6)
O(21)	5 993(6)	6 788(5)	1 940(4)	C(64)	6 777(8)	4 750(9)	32(6)
O(22)	5 395(4)	8 243(4)	2 468(3)	C(65)	8 678(10)	4 356(9)	−722(5)
C(21)	5 367(6)	7 580(6)	2 018(4)	N(7)	5 537(5)	9 554(5)	3 717(3)
C(22)	4 532(7)	7 845(8)	1 540(5)	C(71)	6 379(7)	10 196(7)	3 695(4)
C(23)	3 475(8)	8 406(9)	1 947(6)	C(72)	6 249(8)	11 196(7)	3 967(5)
C(24)	5 110(10)	8 645(12)	891(6)	C(73)	5 203(9)	11 517(7)	4 313(5)
C(25)	4 187(13)	6 857(12)	1 304(9)	C(74)	4 282(7)	10 877(6)	4 352(5)
O(31)	5 338(6)	5 561(5)	3 582(4)	C(75)	3 146(8)	11 185(8)	4 685(5)
O(32)	4 847(5)	7 042(4)	4 076(3)	C(76)	2 281(8)	10 583(8)	4 669(5)
C(31)	4 673(7)	6 094(7)	3 986(5)	C(77)	2 470(7)	9 638(7)	4 328(5)
C(32)	3 524(7)	5 593(7)	4 368(5)	C(78)	3 530(6)	9 291(6)	4 019(4)
C(33)	3 608(9)	4 379(8)	4 467(7)	C(79)	4 463(6)	9 905(6)	4 033(4)
C(34)	3 135(9)	5 958(10)	5 130(6)	N(8)	8 675(6)	601(5)	1 388(3)
C(35)	2 731(9)	6 010(11)	3 912(8)	C(81)	7 943(7)	−184(7)	1 537(4)
O(41)	5 944(6)	3 442(6)	2 202(5)	C(82)	8 198(7)	−1 254(7)	1 389(5)
O(42)	6 513(5)	1 876(5)	1 845(4)	C(83)	9 255(7)	−1 488(7)	1 042(5)
C(41)	5 790(7)	2 615(7)	1 988(5)	C(84)	10 101(7)	−694(7)	865(4)
C(42)	4 620(7)	2 434(8)	1 877(5)	C(85)	11 235(7)	−883(7)	520(5)
C(43)	4 088(8)	1 506(9)	2 418(6)	C(86)	12 003(7)	−100(7)	393(5)
C(44)	3 933(9)	3 440(9)	1 919(9)	C(87)	11 680(7)	925(7)	598(5)
C(45)	4 747(11)	2 148(13)	1 113(6)	C(88)	10 586(7)	1 153(7)	924(4)
O(51)	8 254(5)	3 484(5)	3 025(3)	C(89)	9 779(7)	350(6)	1 070(4)
O(52)	8 993(5)	2 203(5)	2 342(4)				

Table 3. Selected bond lengths (Å) and angles (°)

Ba–O(11)	2.600(7)	Ba–O(21)	2.640(7)
Ba–O(31)	2.615(7)	Ba–O(41)	2.592(8)
Ba–O(51)	2.623(6)	Ba–O(61)	2.646(6)
Zn(1)–O(12)	1.928(6)	Zn(1)–O(22)	1.935(6)
Zn(1)–O(32)	1.949(5)	Zn(1)–N(7)	2.107(6)
Zn(2)–O(42)	1.942(6)	Zn(2)–O(52)	1.917(7)
Zn(2)–O(62)	1.965(5)	Zn(2)–N(8)	2.091(7)
O(11)–Ba–O(21)	80.3(2)	O(11)–Ba–O(31)	83.9(2)
O(21)–Ba–O(31)	74.1(2)	O(11)–Ba–O(41)	176.8(2)
O(21)–Ba–O(41)	102.6(2)	O(31)–Ba–O(41)	95.5(2)
O(11)–Ba–O(51)	91.5(2)	O(21)–Ba–O(51)	170.6(2)
O(31)–Ba–O(51)	109.7(2)	O(41)–Ba–O(51)	85.7(2)
O(11)–Ba–O(61)	105.9(2)	O(21)–Ba–O(61)	95.4(2)
O(31)–Ba–O(61)	164.5(2)	O(41)–Ba–O(61)	75.4(2)
O(51)–Ba–O(61)	82.4(2)	O(12)–Zn(1)–O(22)	126.3(2)
O(12)–Zn(1)–O(32)	120.8(2)	O(22)–Zn(1)–O(32)	105.8(2)
O(12)–Zn(1)–N(7)	94.9(3)	O(22)–Zn(1)–N(7)	98.9(2)
O(32)–Zn(1)–N(7)	103.6(2)	O(42)–Zn(2)–O(52)	126.8(3)
O(42)–Zn(2)–O(62)	104.6(3)	O(52)–Zn(2)–O(62)	122.5(3)
O(42)–Zn(2)–N(8)	96.4(3)	O(52)–Zn(2)–N(8)	94.7(3)
O(62)–Zn(2)–N(8)	104.3(2)	Ba–O(11)–C(11)	159.9(5)
Zn(1)–O(12)–C(11)	125.0(6)	Ba–O(21)–C(21)	150.7(6)
Zn(1)–O(22)–C(21)	129.2(5)	Ba–O(31)–C(31)	161.8(6)
Zn(1)–O(32)–C(31)	123.3(5)	Ba–O(41)–C(41)	160.4(6)
Zn(2)–O(42)–C(41)	121.2(6)	Ba–O(51)–C(51)	143.6(6)
Zn(2)–O(52)–C(51)	135.0(6)	Ba–O(61)–C(61)	146.5(6)
Zn(2)–O(62)–C(61)	117.1(5)		

$[^4T_{1g}(P) \longleftarrow {}^4A_2(F)]$ with shoulders on both the high- and low-energy sides. In addition, a weak band has been observed[3] in the near-i.r. region at *ca.* 1 250 nm $[^4T_{2g}(F) \longleftarrow {}^4T_{1g}(F)]$.

We have previously reported[6] the crystal structure of $[Zn_2Co(O_2CCH{=}CHMe)_6(C_9H_7N)_2]$ and this confirms the presence of a central octahedrally co-ordinated cobalt ion on a crystallographic inversion centre linked by crotonate bridges to two zinc(II) ions. The three metal ions form a linear array and the zinc atoms each have a terminal quinoline attached to them. The solid-state reflectance spectrum of this complex shows an absorption band at 559 nm[8] with prominent shoulders at 532 and 580 nm (see Table 4). There is no evidence for an end absorption on the low-energy side of these bands. The solid-state spectrum of $[Zn_2Co(O_2CPh)_6(C_9H_7N)_2]$ shows bands at 530, 552, and 585 nm with no evidence for end absorptions. This provides good evidence for the presence of a linear trinuclear mixed-metal complex, isostructural with the Zn_2Co crotonate system.

$[Zn_2Mn(O_2CMe)_6(C_9H_7N)_2]$.—The solid-state electronic spectrum of this complex is characteristically weak in the visible region due to octahedrally co-ordinated Mn^{II}. The weak bands at 394, 400, *ca.* 450, and *ca.* 535 nm are readily assigned by comparison with the spectrum of $[Mn(H_2O)_6]^{2+}$.

$[Co_2MgL_6(C_9H_7N)_2]$ *and* $[Co_2MnL_6(C_9H_7N)_2]$ ($L = O_2CCH{=}CHMe$). Catterick and Thornton[3] have demonstrated that $[Co_3(O_2CPh)_6(C_9H_7N)_2]$, which has a linear array of three cobalt atoms with a central six-co-ordinate ion and two five-co-ordinate cobalt(II) end ions, exhibits solid-state absorptions at *ca.* 520, 555, and 580 nm with an additional band in the near-i.r. region at 940 nm. The presence of the latter band appears to be a diagnostic feature associated with the presence of cobalt(II) ions in essentially a trigonal bipyramidal environment. The above two complexes show significant absorptions in

Table 4. Solid-state electronic spectra (350—1 200 nm) of some linear trinuclear mixed-metal carboxylate complexes

Complex	Absorptions/nm				
$[Co(H_2O)_6]^{2+}$	454	506	590 (sh)		*ca.* 1 250
$[Zn_2Co(O_2CCH{=}CHMe)_6(C_9H_7N)_2]$	532	559	580		No end absorption
$[Zn_2Co(O_2CPh)_6(C_9H_7N)_2]$	530	552	585		No end absorption
$[Zn_2Mn(O_2CMe)_6(C_9H_7N)_2]$	394	400	*ca.* 450	*ca.* 535	No end absorption
$[Co_2Mg(O_2CCH{=}CHMe)_6(C_9H_7N)_2]$	525	550	574		1 000 (br)
$[Co_2Mn(O_2CCH{=}CHMe)_6(C_9H_7N)_2]$	526	555	580		1 040 (br)

Table 5. Selected vibrational data/cm^{-1} for some trinuclear carboxylate complexes

	$\nu_{asym}(CO_2)$		$\nu_{sym}(CO_2)$
$Na(O_2CCH{=}CHMe)$	1 588		1 436
$[Zn_3(O_2CCH{=}CHMe)_6(C_9H_7N)_2]$	1 568br	1 626s	1 409br
$[Zn_2Co(O_2CPh)_6(C_9H_7N)_2]$	1 558s		
	1 570	1 610s	1 400br,s
$[Co_2Mn(O_2CCH{=}CHMe)_6$-$(C_9H_7N)_2]$	1 530s	1 572s	1 401s
$[Co_2Mg(O_2CCH{=}CHMe)_6$-$(C_9H_7N)_2]$	1 546br,m	1 592br,s	1 400br,s
$[Zn_2Ba(O_2CCMe_3)_6(C_9H_7N)_2]$	1 578br,m	1 604br,s	1 406br,s
$[Zn_3(O_2CMe)_6(C_9H_7N)_2]$	1 592br,s	1 639m	1 398br,s
$[Zn_2Mn(O_2CMe)_6(C_9H_7N)_2]$	1 600br,s	1 647m	1 407br,m

the near-i.r. region at 1 000 and 1 040 nm respectively and hence we may conclude that they both have linear trinuclear structures.

Vibrational Data for Trinuclear Species.—The solid-state i.r. spectra of the complexes all show the presence of co-ordinated carboxylate and quinoline ligands; the characteristic vibrational frequencies for the latter show small shifts of 5 to 10 cm^{-1} and bonding *via* the N atom can be recognised by the direction of these shifts.[9,10] The observed solid-state vibrational frequencies $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ for the co-ordinated carboxylates are given in Table 5. Data for sodium crotonate and $[Zn_3(O_2CCH{=}CHMe)_6(C_9H_7N)_2]$ are included for reference purposes. The *X*-ray crystal structure of the trinuclear zinc complex reveals the presence of four bidentate and two monodentate crotonate ligands and the latter show a characteristic band in the solid-state i.r. spectrum at 1 626 cm^{-1}. It is *ca.* 80 cm^{-1} lower in frequency than the free $\nu(C{=}O)$ in $\alpha\beta$-unsaturated esters[11] and this has been interpreted as due to a weak interaction of the carbonyl group with the terminal zinc atoms. The other two bands at 1 568 and 1 409 cm^{-1} have been assigned to $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ respectively of the four bidentate carboxylate ligands.

The i.r. spectrum of $[Zn_2Co(O_2CPh)_6(C_9H_7N)_2]$ again shows characteristic $\nu(CO_2)$ modes indicative of bridging benzoate ligands. The lower frequency at 1 610 cm^{-1} suggests a stronger interaction of the carbonyl groups on the monodentate benzoate ligands with the terminal zinc atoms.

For mixed-metal complexes involving cobalt terminal atoms, it appears from the carboxylate stretching frequencies that all six crotonate ligands are approximately equivalent and they are best represented as bidentate bridges. This conclusion is borne out by the Zn_2Ba pivalate complex where all the $\nu(CO_2)$ modes lie in adjacent positions to those of the cobalt complexes and, though unsymmetrical, the crystal structure indicates six equivalent bidentate pivalate ligands.

Finally the positions of the $\nu(CO_2)$ modes for two acetate complexes provide strong evidence for the presence of two kinds of acetate ligand in these structures. The bands at *ca.* 1 640 cm^{-1} are strongly indicative of a monodentate acetate ligand with only a very weak interaction between the carbonyl oxygen and the terminal zinc atoms, while the other two bands are assigned to bridging carboxylate ligands.

Magnetic Moments.—The magnetic susceptibility of $[Co_2MgL_6(C_9H_7N)_2]$ and $[Co_2MnL_6(C_9H_7N)_2]$ ($L = O_2CCH{=}CHMe$) have been determined at different temperatures (77—295 K). The value of $\mu_{eff.}$ for $[Co_2Mg(O_2CCH{=}CHMe)_6(C_9H_7N)_2]$ varies from 4.03 at 77 K to 4.43 at 295 K, while $\mu_{eff.}$ for $[Co_2Mn(O_2CCH{=}CHMe)_6(C_9H_7N)_2]$ varies from 7.78 at 77 K to 8.56 at 295 K.

The correlation coefficients of plots of $1/\chi_m^{corr.}$ *versus* T for the two compounds give negative values for $\theta(-27$ and -17 K respectively) and the latter suggest antiferromagnetic interactions between the linear arrays of mixed-metal ions.

Crystal Structure of $[Zn_2Ba(O_2CCMe_3)_6(C_9H_7N)_2]$.—The molecular structure is shown in the Figure. In its essential features it resembles closely the structure of $Zn_2Sr(O_2CCH{=}CHMe)_6(C_9H_6NMe\text{-}6)_2$.[6] Although the molecule does not possess a crystallographic inversion centre, deviations from centrosymmetry are unimportant. All six carboxylate groups are of the *syn–syn* bridging type, and they are all essentially equivalent. This is similar to the situation in the strontium-centred complex, but contrasts with other complexes in the $Zn_2M(O_2CCH{=}CHMe)_6(base)_2$ series, in which one pair of centrosymmetrically related carboxylate bridges differs significantly from the others.[6] The major differences between this barium complex and the previous strontium complex lie in the M–O and M $\cdots$ Zn distances, which are greater for M = Ba, as a consequence of the larger size of the metal atom.

Thus, the observed structure of $[Zn_2Ba(O_2CCMe_3)_6(C_9H_7N)_2]$ supports our interpretation of the balance of covalent and ionic metal–carboxylate bonding in these trinuclear complexes,[6] and demonstrates that unsaturation in the carboxylate substituent is unnecessary for formation of this type of structure.

Acknowledgements

We thank the S.E.R.C. for financial support (to P. A. H) and for a research grant towards the cost of the crystallographic equipment. We also thank M. Ord and I. Brackenridge for assistance, Communidad Autonoma de Madrid (Spain) for a grant (to M. A. M.), and Dr. M. J. Carter for the near-i.r. measurements.

References

1 V. M. Rao, D. N. Sathyanarayana, and H. Manohar, *J. Chem. Soc., Dalton Trans.*, 1983, 2167.
2 M. Bukowska-Strzyzenska, J. Skoweranda, E. Hetbuk, and J. Mrozinski, *Inorg. Chim. Acta*, 1983, **73**, 207.

3 J. Catterick and P. Thornton, *J. Chem. Soc., Dalton Trans.*, 1976, 1634.
4 W. Clegg, I. R. Little, and B. P. Straughan, *J. Chem. Soc., Chem. Commun.*, 1985, 73.
5 W. Clegg, I. R. Little, and B. P. Straughan, *J. Chem. Soc., Dalton Trans.*, 1986, 1283.
6 W. Clegg, I. R. Little, and B. P. Straughan, *Inorg. Chem.*, 1988, **27**, 1916.
7 G. M. Sheldrick, SHELXTL: an integrated system for solving, refining, and displaying crystal structures from diffraction data, University of Göttingen, 1985, Revision 5.
8 I. R. Little, unpublished work.
9 T. Tahaka, Y. Matsumure, R. Okawara, Y. Musya, and S. Kinnimaki, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 1497.
10 W. U. Malik, R. Bembi, and J. K. Dwivedi, *J. Indian Chem. Soc.*, 1976, **53**, 362.
11 A. J. Bowles, W. O. George, and D. B. Cunliffe-Jones, *J. Chem. Soc. B*, 1970, 1070.

Received 1*st August* 1988; *Paper* 8/03129K