C—Sn—C angle in molecule (1) is 128·7 (3)° approaching the ideal value in a trigonal bipyramid. From short N···O distances the presence of H bonds is inferred. They are in some cases markedly shorter than the sum of the van der Waals radii (3·11 Å; Kitaigorodskii, 1979). Thus, intermolecular distances N(12)···O(13) of 2·768 Å and intramolecular distances N(22)···O(22) of 3·029 Å, and N(12)···O(12) of 2·998 Å are observed. It is noteworthy that the MeOH molecule is independent and is not involved in the hydrogen-bonding system.

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Structures of the Mixed-Metal Carboxylate Base Adducts [MgZn$_2$(crotonate)$_6$(4-vinylpyridine)$_2$] and [MgCo$_2$(crotonate)$_6$(4-vinylpyridine)$_4$]

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Abstract. (1) [MgZn$_2$(C$_4$H$_5$O$_2$)$_6$(C$_7$H$_7$N)$_2$], M_r = 875·8, monoclinic, $P2_1/c$, a = 10·251 (1), b = 14·315 (2), c = 14·382 (2) Å, β = 106·52 (1)°, V = 2023·4 Å^3, Z = 2, D_x = 1·437 g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 12·9 cm^{-1}, F(000) = 908, T = 295 K, R = 0·063 for 2829 unique observed reflections. (2) [MgCo$_2$(C$_4$H$_5$O$_2$)$_6$(C$_7$H$_7$N)$_4$], M_r = 1073·2, monoclinic, $C2/c$, a = 24·623 (2), b = 11·855 (1), c = 18·855 (1) Å, β = 104·640 (6)°, V = 5325·2 Å^3, Z = 4, D_x = 1·338 g cm^{-3}, μ(Mo $K\alpha$) = 6·9 cm^{-1}, F(000) = 2240, T = 295 K, R = 0·030 for 3709 unique observed reflections. The molecules contain an exactly (1) or approximately (2) linear array of three metal atoms linked by six crotonate bridges. Four of the bridges are of the *syn–syn* type, coordinating to one metal atom through each of their two O atoms. The other two crotonates are simultaneously chelating to one metal (Zn or Co) and bridging through one O atom also to Mg. In (1), Zn is five-coordinate, and in (2), Co is six-coordinate, with one or two 4-vinylpyridine terminal ligands respectively. The Mg atom is octahedrally coordinated in both structures.

Introduction. The first crystal structure of a trinuclear metal carboxylate complex of formula [MM'_2(O$_2$CR)$_6L_2$] was reported by Catterick, Hursthouse, New & Thornton (1974): in this case, all three metal atoms were cobalt. Several other compounds of this kind have been studied since then, with M' = Zn and a variety of different central metals M = Zn, Mn, Co, Ni, Cd, Mg, Ca, Sr, Ba; L is a heterocyclic nitrogen base, and the carboxylates include benzoate, crotonate and pivalate (Clegg, Little & Straughan, 1985, 1986, 1988; Clegg, Hunt, Straughan & Mendiola, 1989; Catterick & Thornton, 1976). In each case, the three metal atoms are arranged in a linear array within a centrosymmetric molecule. The L base ligands are attached terminally to the outer metal atoms, and the carboxylates form bridges between the central and the outer metal atoms. These bridges vary in their bonding characteristics, from one extreme of bridging *via* one O atom to each metal, to the other extreme of bridging both metals through a single O atom with the second O atom uncoordinated, and intermediate modes of bridging are found within the series. The main factor influencing the nature of the bridging ligands is the size of the central metal atom and its position in the periodic table (main-group or transition metal).

In metal carboxylate complexes containing unsaturated carboxylate substituents, such as crotonate, there is the possibility of solid-state reactions involving the unsaturated centres. Such reactions, either spontaneous or triggered by irradiation, have been observed for metal propiolate complexes (Foxman & Jaufmann, 1983). The complexes reported here were prepared with terminal base ligands containing further unsaturated groups, in order to enhance the possibilities for solid-state polymerization reactions.

Experimental. The compounds were prepared from a mixture of the corresponding metal crotonates (obtained from the carbonates and crotonic acid) and 4-vinylpyridine in ethanol solution. Crystals were obtained from the reaction mixtures. Data for (2) are given in parentheses where they differ from those for (1).

Crystal size 0·4 × 0·4 × 0·4 mm (0·3 × 0·4 × 0·4 mm), Stoe–Siemens diffractometer, unit-cell parameters from 2θ values of 32 reflections (20–25°) measured at $\pm\omega$. Data collection in ω/θ scan mode with on-line profile fitting (Clegg, 1981), $2\theta_{\max} = 50°$, index ranges h −12→12 (−29→29), k 0→17 (0→14), l 0→17 (0→22), together with a partial equivalent set of reflections with $k < 0$; approximately 13% (18%) decay in intensities of three standard reflections, semi-empirical absorption corrections, transmission 0·44–0·61 (0·74–0·76). 5599 (6960) reflections measured, 3556 (4707) unique, 2829 (3709) with $F > 4\sigma_c(F)$ (σ_c from counting statistics only), R_{int} = 0·029 (0·014).

Structure solution by Patterson and difference syntheses, blocked-cascade least-squares refinement on F, weighting $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 27 - 253G + 460G^2 - 48H + 23H^2 + 224GH$ ($\sigma_c^2(F) + 14 + 25G + 45G^2 - 29H + 17H^2 - 59GH$) where $G = F_o/F_{\max}$, $H = \sin\theta/\sin\theta_{\max}$ (Wang & Robertson, 1985); anisotropic thermal parameters for all non-H atoms, H atoms constrained to give C—H 0·96 Å, H—C—H 109·5 or 120° as appropriate, aromatic H on ring angle external bisectors, U(H) = 1·2U_{eq}(C); extinction effects insignificant. R = 0·063 (0·030), wR = 0·027 (0·031), S = 1·86 (1·03) for 259 (331) parameters, mean Δ/σ = 0·010 (0·006), max. Δ/σ = 0·039 (0·019), $(\Delta\rho)_{\max}$ = 0·82 (0·23), $(\Delta\rho)_{\min}$ = −0·83 (−0·17) e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99, 149); *SHELXTL* (Sheldrick, 1985) and local computer programs.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å$^2 \times 10^3$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
(1)				
Mg	5000	5000	5000	49·3 (7)
Zn	5852·7 (4)	7167·8 (3)	5911·0 (3)	52·7 (2)
O(11)	6832 (2)	6467 (1)	7068 (1)	65 (1)
O(12)	6497 (2)	5088 (1)	6333 (1)	65 (1)
C(11)	7002 (3)	5601 (2)	7022 (2)	57 (2)
C(12)	7926 (3)	5187 (2)	7937 (3)	63 (2)
C(13)	8183 (3)	4307 (2)	8052 (3)	67 (2)
C(14)	9087 (3)	3862 (2)	8963 (2)	79 (2)
O(21)	6180 (2)	5714 (2)	4322 (2)	61 (1)
O(22)	6993 (2)	7053 (1)	5028 (1)	59 (1)
C(21)	6966 (3)	6406 (2)	4451 (2)	48 (2)
C(22)	7904 (3)	6424 (2)	3851 (2)	56 (2)
C(23)	8789 (3)	7076 (2)	3874 (2)	68 (2)
C(24)	9787 (4)	7158 (3)	3276 (3)	113 (3)
O(31)	4236 (2)	6290 (1)	5304 (1)	51 (1)
O(32)	3778 (2)	7341 (1)	6242 (2)	69 (1)
C(31)	3420 (3)	6624 (2)	5754 (2)	48 (2)
C(32)	2125 (3)	6143 (2)	5695 (2)	49 (2)
C(33)	1422 (3)	6328 (2)	6299 (2)	53 (2)
C(34)	155 (3)	5843 (3)	6339 (3)	78 (2)
N	6108 (2)	8587 (2)	6091 (2)	48 (1)
C(41)	5559 (3)	9097 (2)	6649 (2)	60 (2)
C(42)	5667 (3)	10058 (2)	6732 (2)	60 (2)
C(43)	6341 (3)	10534 (2)	6193 (2)	57 (2)
C(44)	6927 (3)	10010 (2)	5619 (3)	72 (2)
C(45)	6789 (3)	9044 (2)	5604 (2)	71 (2)
C(46)	6449 (3)	11581 (2)	6160 (2)	70 (2)
C(47)	5796 (4)	12153 (2)	6513 (2)	89 (2)
(2)				
Mg	5000	6197·0 (7)	2500	33·4 (3)
Co	6465·5 (1)	6468·9 (2)	2763·3 (1)	38·5 (1)
O(11)	5260·7 (6)	7490 (1)	1930·3 (10)	59·4 (6)
O(12)	6171·0 (6)	7715 (1)	2022·3 (9)	50·1 (5)
C(11)	5660·8 (8)	7994 (2)	1796 (1)	41·0 (6)
C(12)	5554·5 (9)	9036 (2)	1349 (1)	54·8 (8)
C(13)	5104 (1)	9635 (3)	1249 (2)	77 (1)
C(14)	4992 (2)	10745 (4)	857 (3)	116 (2)
O(21)	5319·6 (6)	4995 (1)	1938·9 (9)	51·1 (5)
O(22)	6247·0 (6)	5128 (1)	2081·3 (9)	49·5 (5)
C(21)	5770·4 (8)	4714 (2)	1798 (1)	41·5 (6)
C(22)	5737·5 (9)	3814 (2)	1239 (1)	49·8 (7)
C(23)	6167 (1)	3446 (2)	1013 (1)	55·0 (8)
C(24)	6151 (1)	2573 (3)	439 (2)	74 (1)
O(31)	5781·7 (5)	6182 (1)	3278·0 (7)	40·8 (4)
O(32)	6588·2 (6)	5346 (1)	3715·2 (9)	52·0 (5)
C(31)	6086·5 (8)	5505 (2)	3735 (1)	41·4 (6)
C(32)	5840·4 (9)	4956 (2)	4280 (1)	50·8 (7)
C(33)	6090 (1)	4166 (2)	4730 (1)	59·7 (8)
C(34)	5845 (2)	3565 (3)	5274 (3)	79 (1)
N(4)	7265·4 (6)	6503 (2)	2527 (1)	45·8 (5)
C(41)	7450 (1)	7419 (2)	2260 (2)	63·1 (9)
C(42)	7978 (1)	7514 (2)	2138 (2)	66 (1)
C(43)	8338·6 (9)	6612 (2)	2283 (1)	52·2 (7)
C(44)	8143 (1)	5649 (2)	2540 (2)	74 (1)
C(45)	7611 (1)	5631 (2)	2658 (2)	69 (1)
C(46)	8915 (1)	6667 (3)	2184 (2)	70 (1)
C(47)	9150 (1)	7548 (3)	1990 (2)	79 (1)
N(5)	6737·5 (7)	7838 (2)	3571 (1)	46·5 (6)
C(51)	6353·3 (9)	8562 (2)	3668 (1)	59·1 (8)
C(52)	6473 (1)	9447 (2)	4156 (2)	65·7 (9)
C(53)	7016 (1)	9614 (2)	4582 (1)	56·3 (8)
C(54)	7405 (1)	8849 (3)	4488 (2)	71 (1)
C(55)	7255 (1)	7995 (2)	3986 (1)	64·4 (9)
C(56)	7174 (1)	10527 (3)	5120 (2)	81 (1)
C(57)	6887 (2)	11405 (4)	5156 (3)	146 (2)

Table 2. *Selected bond lengths* (Å) *and angles* (°)

(1)			
Mg—O(12)	2·091 (2)	Mg—O(21)	2·032 (3)
Mg—O(31)	2·100 (2)	Zn—O(11)	1·957 (2)
Zn—O(22)	1·963 (2)	Zn—O(31)	2·065 (2)
Zn—O(32)	2·320 (3)	Zn—N	2·056 (3)
O(11)—C(11)	1·256 (4)	O(12)—C(11)	1·224 (4)
O(21)—C(21)	1·257 (4)	O(22)—C(21)	1·238 (4)
O(31)—C(31)	1·286 (4)	O(32)—C(31)	1·238 (4)
O(12)—Mg—O(21)	91·6 (1)	O(12)—Mg—O(31)	88·6 (1)
O(21)—Mg—O(31)	88·0 (1)	O(11)—Zn—O(22)	104·6 (1)
O(11)—Zn—O(31)	101·8 (1)	O(22)—Zn—O(31)	103·3 (1)
O(11)—Zn—O(32)	99·2 (1)	O(22)—Zn—O(32)	153·0 (1)
O(31)—Zn—O(32)	58·6 (1)	O(11)—Zn—N	112·5 (1)
O(22)—Zn—N	94·9 (1)	O(31)—Zn—N	135·5 (1)
O(32)—Zn—N	87·1 (1)	Zn—O(11)—C(11)	120·4 (2)
Mg—O(12)—C(11)	144·1 (2)	O(11)—C(11)—O(12)	127·0 (3)
Mg—O(21)—C(21)	140·4 (2)	Zn—O(22)—C(21)	126·3 (2)
O(21)—C(21)—O(22)	125·4 (3)	Mg—O(31)—Zn	108·7 (1)
Mg—O(31)—C(31)	140·0 (2)	Zn—O(31)—C(31)	96·9 (2)
Zn—O(32)—C(31)	86·4 (2)	O(31)—C(31)—O(32)	117·6 (3)
(2)			
Mg—O(11)	2·065 (2)	Mg—O(21)	2·047 (2)
Mg—O(31)	2·105 (1)	Co—O(12)	2·037 (2)
Co—O(22)	2·030 (2)	Co—O(31)	2·172 (2)
Co—O(32)	2·194 (2)	Co—N(4)	2·127 (2)
Co—N(5)	2·210 (2)	O(11)—C(11)	1·231 (3)
O(12)—C(11)	1·264 (2)	O(21)—C(21)	1·249 (3)
O(22)—C(21)	1·259 (2)	O(31)—C(31)	1·274 (2)
O(32)—C(31)	1·260 (3)		
O(11)—Mg—O(21)	92·1 (1)	O(11)—Mg—O(31)	91·1 (1)
O(21)—Mg—O(31)	87·2 (1)	O(11)—Mg—O(11a)	84·1 (1)
O(11)—Mg—O(21a)	175·0 (1)	O(21)—Mg—O(21a)	91·8 (1)
O(11)—Mg—O(31a)	89·6 (1)	O(21)—Mg—O(31a)	92·1 (1)
O(31)—Mg—O(31a)	179·0 (1)	O(12)—Co—O(22)	98·2 (1)
O(12)—Co—O(31)	103·8 (1)	O(22)—Co—O(31)	92·8 (1)
O(12)—Co—O(32)	162·4 (1)	O(22)—Co—O(32)	90·1 (1)
O(31)—Co—O(32)	60·1 (1)	O(12)—Co—N(4)	91·8 (1)
O(22)—Co—N(4)	89·6 (1)	O(31)—Co—N(4)	163·7 (1)
O(32)—Co—N(4)	103·9 (1)	O(12)—Co—N(5)	86·2 (1)
O(22)—Co—N(5)	175·6 (1)	O(31)—Co—N(5)	86·6 (1)
O(32)—Co—N(5)	85·8 (1)	N(4)—Co—N(5)	89·7 (1)
Mg—O(11)—C(11)	146·8 (1)	Co—O(12)—C(11)	124·9 (1)
O(11)—C(11)—O(12)	125·6 (2)	Mg—O(21)—C(21)	140·7 (1)
Co—O(22)—C(21)	130·0 (1)	O(21)—C(21)—O(22)	126·1 (2)
Mg—O(31)—Co	111·3 (1)	Mg—O(31)—C(31)	139·1 (1)
Co—O(31)—C(31)	90·6 (1)	Co—O(32)—C(31)	90·0 (1)
O(31)—C(31)—O(32)	119·2 (2)		

Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1, selected bond lengths and angles in Table 2.*

Discussion. The molecular structures are shown in Figs. 1 and 2. Complex (1) closely resembles the previously reported structure of $MgZn_2$(crotonate)$_6$(quinoline)$_2$ (Clegg, Little & Straughan, 1988), the 4-vinylpyridine base replacing quinoline in an otherwise essentially identical centrosymmetric molecule. Four of the crotonates bridge between magnesium and zinc in the *syn–syn* mode. The other two have one O atom bonded to both Mg and Zn, while the second O atom coordinates only Zn, to give ligands which are simultaneously bridging (between Mg and Zn) and bidentate (to Zn). Coordination of Mg is essentially octahedral; Zn is five-coordinate, and the geometry may be considered as derived from tetrahedral with the small-bite chelating carboxylate ligand occupying one of the four coordination sites.

The structure of the central $MgCo_2$(crotonate)$_6$ part of (2) is similar, with the same two types of bridging ligands. Here, however, there are two base ligands attached to each Co atom, to give six-coordination of these atoms. The coordination is distorted from octahedral mainly as a consequence of the small bite of the chelating crotonate ligand. The two 4-vinylpyridine ligands occupy mutually *cis* sites. The two Co—N bond lengths differ significantly, the longer Co—N(5) bond lying *trans* to the shortest Co—O bond.

The molecule of (2) has twofold rotation symmetry, in contrast to the centrosymmetry observed in (1) and in previous trinuclear structures of this type. Exact linearity of the tri-metal skeleton is not imposed in this case, and the Co···Mg···Co angle is 169·5 (1)°. This deviation from linearity is significant statistically, but probably not chemically. The Mg···Co separation of 3·531 (1) Å is similar to the Mg···Zn separation of 3·385 (1) Å in (1) and corresponding *M*···*M′* separations in related structures.

All the crotonate ligands adopt a planar *transoid* conformation in both structures, as is commonly observed for this ligand. The vinyl groups of the base ligands lie close to the pyridine ring planes. Despite

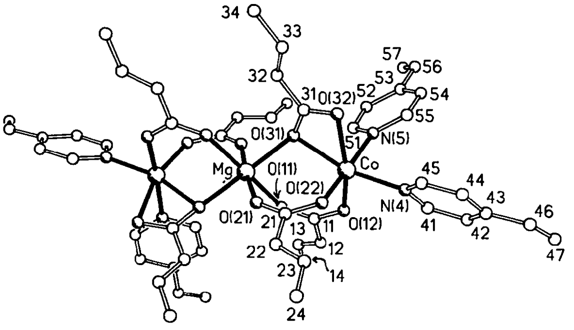

Fig. 1. Molecular structure of (1), without H atoms. C atoms are labelled by number only.

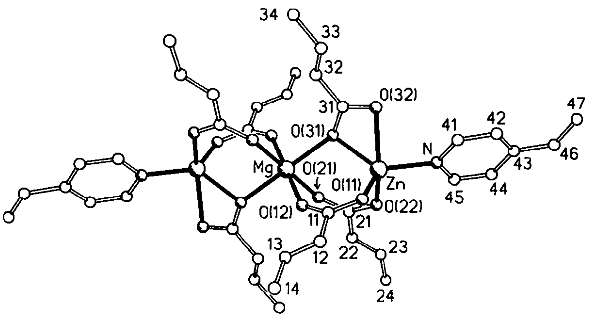

Fig. 2. Molecular structure of (2), without H atoms.

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* Lists of structure factors, anisotropic thermal parameters, full bond lengths and angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53431 (40 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the large number of unsaturated centres in these molecules, there are no notably short contacts (< 4 Å) between any of these centres in adjacent molecules, and the solid compounds do not undergo spontaneous polymerization reactions. The observed intensity decay during data collection is probably due to decomposition involving loss of 4-vinylpyridine ligands.

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Structural Characterization of $Zr_2Cl_8(PPh_3)_2$

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Abstract. Octachlorobis(triphenylphosphane)dizirconium(IV), $[Zr_2Cl_8(C_{18}H_{15}P)_2]$, $M_r = 990{\cdot}65$, monoclinic, $P2_1/c$, $a = 11{\cdot}526\,(3)$, $b = 17{\cdot}530\,(4)$, $c = 20{\cdot}628\,(5)$ Å, $\beta = 106{\cdot}03\,(2)°$, $V = 4006\,(3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}643$ g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71073$ Å, $\mu = 11{\cdot}6$ cm^{-1}, $F(000) = 1968$, $T = 294$ K, $R = 0{\cdot}048$ for 3059 unique observed reflections. The molecule is dinuclear with two Zr atoms bridged by three Cl ligands forming a triangular face perpendicular to the Zr–Zr axis. The Zr—Zr distance is 3·649 (2) Å. The Zr—Cl_{bridge} distances range from 2·582 (3) to 2·612 (3) Å with a mean value of 2·594 (6) Å. The mean Zr—Cl_{bridge}—Zr angle is 89·4 (2)°. The coordination sphere around the first Zr atom is completed by two Cl ligands and two PPh_3 ligands mutually *trans* to each other. The two Cl ligands and two P atoms of the PPh_3 ligands form a distorted square parallel to the plane of the three bridging chlorides. The Zr—Cl_{trans} distances are 2·381 (3) and 2·386 (3) Å, and the Zr—P_{trans} distances are 2·824 (2) and 2·855 (2) Å. The Cl_{trans}—Zr—Cl_{trans} angle is 111·7 (1)° and the P_{trans}—Zr—P_{trans} angle is 134·98 (9)°. Octahedral coordination around the second Zr atom is completed with three terminal Cl ligands with Zr—Cl_{term} distances ranging from 2·337 (3) to 2·343 (3) Å with a mean value of 2·340 (2) Å.

Introduction. In our laboratory we have been actively investigating coordination compounds of Group IV metals with halides and phosphines, especially those of the type *cis,cis*-$M_2Cl_6(PR_3)_4$, where M = Zr and Hf, that contain metal–metal bonds (Cotton, Diebold & Kibala, 1988; Cotton, Kibala & Wojtczak, 1990). The title complex was accidentally synthesized during an attempt to prepare a PPh_3 analog of the $M_2Cl_6(PR_3)_4$ species. We have later prepared $Zr_2Cl_8(PPh_3)_2$ by reacting directly $ZrCl_4$ with PPh_3. Because the compound exhibits rather unusual geometry we report this work here.

Experimental. The compound was prepared by refluxing stoichiometric amounts of $ZrCl_4$ and PPh_3 under argon in toluene. X-ray-quality crystals were obtained upon cooling of the reaction mixture. The quality of the crystals was confirmed by polarized light microscopy. A light-yellow irregularly shaped crystal, 0·45 × 0·40 × 0·40 mm, was mounted in a capillary under argon. Unit-cell dimensions were determined from least-squares analysis of 25 reflec-

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