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Zinc Carboxylate Complexes: Structural Characterization of the Mixed-Metal Linear Trinuclear Complexes $MZn_2(crot)_6(base)_2$ (M = Mn, Co, Ni, Zn, Cd, Mg, Ca, Sr; crot$^-$ = Crotonate(1–); Base = Quinoline, 6-Methylquinoline)

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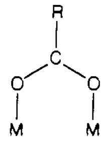
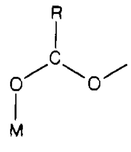
Received October 29, 1987

The crystal structures of eight $MZn_2(crot)_6(base)_2$ complexes have been determined (crot$^-$ = crotonate(1–), $MeCH{=}CHCO_2^-$; base = Q = quinoline, C_9H_7N, or base = 6-MeQ = 6-methylquinoline, $C_{10}H_9N$). All eight complexes crystallize solvent-free in centrosymmetric space groups, with the central M atom on a crystallographic inversion center, a linear array of three metal atoms linked by crotonate bridges, and terminal Q or 6-MeQ ligands attached to Zn. $MnZn_2(crot)_6Q_2$ ($C_{42}H_{44}N_2O_{12}Zn_2Mn$, **1**) crystallizes in the monoclinic space group $P2/c$, with a = 10.9126 (5) Å, b = 9.6913 (5) Å, c = 20.7505 (9) Å, β = 100.527 (5)°, and Z = 2. $CoZn_2(crot)_6Q_2$ ($C_{42}H_{44}N_2O_{12}Zn_2Co$, **2**) crystallizes in the monoclinic space group $P2_1/c$, with a = 10.6062 (5) Å, b = 11.9598 (5) Å, c = 17.7779 (8) Å, β = 98.203 (5)°, and Z = 2. $NiZn_2(crot)_6Q_2$ ($C_{42}H_{44}N_2O_{12}Zn_2Ni$, **3**) crystallizes in the monoclinic space group $P2_1/c$, with a = 10.660 (2) Å, b = 14.050 (3) Å, c = 15.046 (3) Å, β = 104.50 (2)°, and Z = 2. $Zn_3(crot)_6Q_2$ ($C_{42}H_{44}N_2O_{12}Zn_3$, **4**) is isostructural with compound **1**, with a = 10.832 (1) Å, b = 9.635 (1) Å, c = 20.784 (2) Å, β = 100.29 (1)°, and Z = 2 in the monoclinic space group $P2/c$. $CdZn_2(crot)_6Q_2$ ($C_{42}H_{44}N_2O_{12}Zn_2Cd$, **5**) is isostructural with compound **2**, with a = 10.7402 (5) Å, b = 11.8731 (5) Å, c = 17.8351 (7) Å, β = 98.966 (4)°, and Z = 2 in the monoclinic space group $P2_1/c$. $MgZn_2(crot)_6Q_2$ ($C_{42}H_{44}N_2O_{12}Zn_2Mg$, **6**) crystallizes in the triclinic space group $P\bar{1}$, with a = 10.965 (3) Å, b = 10.977 (3) Å, c = 11.075 (3) Å, α = 104.85 (1)°, β = 111.82 (1)°, γ = 101.86 (1)°, and Z = 1. $CaZn_2(crot)_6(6\text{-}MeQ)_2$ ($C_{44}H_{48}N_2O_{12}Zn_2Ca$, **7**) crystallizes in the triclinic space group $P\bar{1}$, with a = 10.170 (1) Å, b = 10.397 (1) Å, c = 12.064 (1) Å, α = 93.230 (5)°, β = 90.666 (6)°, γ = 113.518 (5)°, and Z = 1. $SrZn_2(crot)_6(6\text{-}MeQ)_2$ ($C_{44}H_{48}N_2O_{12}Zn_2Sr$, **8**) crystallizes in the triclinic space group $P\bar{1}$, with a = 9.695 (2) Å, b = 11.188 (2) Å, c = 11.777 (2) Å, α = 65.97 (1)°, β = 86.88 (1)°, γ = 86.80 (1)°, and Z = 1. The molecular structures of $MZn_2(crot)_6Q_2$ (M = Mn, Co, Ni, Zn, Cd) do not differ significantly from each other. The central M atom is octahedrally coordinated and linked to each Zn atom by three crotonate bridges: of these two are of the syn–syn bidentate type, and the third is monodentate (monatomic), bridging through only one oxygen atom; the other oxygen atom forms a weak, secondary interaction with the Zn atom, distorting the tetrahedral coordination of Zn. The C–O bond lengths of the monodentate bridging crotonate differ significantly, corresponding to localized single and double bonds, while the bidentate bridges have essentially equivalent C–O bonds. In the series $MgZn_2(crot)_6Q_2$, $CaZn_2(crot)_6(6\text{-}MeQ)_2$, and $SrZn_2(crot)_6(6\text{-}MeQ)_2$, there is a systematic change from monodentate to bidentate bridging for the third crotonate, the secondary Zn···O interaction increasing in importance at the expense of the originally stronger Zn–O bond. In $SrZn_2(crot)_6(6\text{-}MeQ)_2$ all crotonate bridges are equivalent, syn–syn bidentate. In this series (M = Mg, Ca, Sr), coordination of M becomes increasingly distorted from ideal octahedral, and M–O–C angles increase considerably, while Zn–O–C angles remain approximately constant. The observed differences in geometry are rationalized in terms of variation in the balance of covalent and ionic nature of the metal–crotonate bonding for different central metal atoms M.

We have recently reported[1] the crystal structure of the first carboxylate-bridged linear trinuclear Zn(II) complex $[Zn_3(crot)_6Q_2]$, where crot$^-$ = crotonate anion, $MeCH{=}CHCO_2^-$, and Q = quinoline, C_9H_7N. This was one of a series of mixed-metal trinuclear species of general formula $[MZn_2(carboxylate)_6(base)_2]$, where M = Co, Ni, Zn, Cd, Mg, or Ca, carboxylate(1–) = $MeCH{=}CHCO_2^-$, $Me_2C{=}CHCO_2^-$, or $H_2C{=}C(Me)CO_2^-$, and base = quinoline, isoquinoline, or 2-methylpyridine, for which we have described preparations and spectroscopic characterizations.[2]

These studies are part of an ongoing investigation into zinc carboxylate complexes of various types, which has a number of motivations and aims. First, "simple" anhydrous zinc(II) carboxylates of empirical formula $Zn(carboxylate)_2$ have been found to crystallize in a variety of polymeric forms, with bridging carboxylates between tetrahedrally coordinated Zn atoms:[3] the bridges may be of syn–syn or syn–anti configuration,[4] with formation of polymer chains, sheets, or three-dimensional networks. Polymorphism has been observed for some of these complexes and is likely for others, with quite different structures being formed under different or even nominally similar conditions [e.g. $Zn(2\text{-}ClOBz)_2$ crystallizes from acetone solution to give two different chain polymers: one with only syn–syn bridges;[3f] the other with triply-bridged $Zn_2(carboxylate)_3^+$ units linked together by syn–anti carboxylates,[3g] as in $Zn(crot)_2$[3h]]. The factors affecting the choice of structure adopted by each compound under different conditions remain largely a mystery.


syn-syn


syn-anti

Second, if the carboxylate substituent is unsaturated, there is potential scope for further polymerization in the solid state by cross-linking of the substituents.[5] Such reactions have been promoted in the case of metal propiolate complexes by irradiation.[6] One important application of such polymerization reactions is in the quest for dental filling materials as a substitute for amalgams.[7] Current research involves ionic polymer cements that incorporate unsaturated polycarboxylic acids and metals, including zinc.[8]

The molecular structure of $Zn_3(crot)_6Q_2$ in the solid state is similar to that reported for $Co_3(OBz)_6Q_2$,[9] but there are significant

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differences in detail,[1] in the bridging modes of the carboxylate groups. Vibrational spectroscopy of the mixed-metal complexes $MZn_2(carboxylate)_6(base)_2$ indicates some variation in the carboxylate bridging for different metals M.[2] For this reason, we have investigated crystallographically a series of complexes with different M, but with the carboxylate restricted to one example, that of crotonate. As far as possible, the base has also been kept constant, but the minor modification of replacing quinoline Q by 6-methylquinoline (6-MeQ) was necessary in order to obtain satisfactory single crystals of two of the complexes. We present here the structures of $MZn_2(crot)_6Q_2$ (M = Mn, Co, Ni, Zn, Cd, Mg) and $MZn_2(crot)_6(6\text{-MeQ})_2$ (M = Ca, Sr) and attempt to rationalize the variations observed as the central metal atom is changed.

Experimental Section

All complexes are stable to air at room temperature. The preparations, analytical and spectroscopic data for $MZn_2(crot)_6Q_2$ (M = Co, Ni, Zn, Cd, Mg, Ca) have already been reported.[2] Of these all except the Ca complex were suitable for single-crystal X-ray diffraction studies as prepared. $MZn_2(crot)_6Q_2$ (M = Mn, Sr) and $MZn_2(crot)_6(6\text{-MeQ})_2$(M = Ca, Sr) were prepared in an exactly analogous manner.

$MnZn_2(crot)_6Q_2$. Anal. Calcd for $C_{42}H_{44}MnN_2O_{12}Zn_2$: C, 52.9; H, 4.7; N, 2.9; Mn, 5.8. Found: C, 53.1; H, 4.6; N, 2.9; Mn, 5.6.

$SrZn_2(crot)_6Q_2$. Anal. Calcd for $C_{42}H_{44}N_2O_{12}SrZn_2$: C, 51.1; H, 4.5; N, 2.8; Zn, 13.3. Calcd for $C_{42}H_{44}H_2O_{12}SrZn_2 \cdot 0.5C_9H_7N$: C, 53.1; H, 4.6; N, 3.3; Zn, 12.4. Found: C, 52.7; H, 4.4; N, 3.1; Zn, 12.5.

$CaZn_2(crot)_6(6\text{-MeQ})_2$. Anal. Calcd for $C_{44}H_{48}CaN_2O_{12}Zn_2$: C, 54.6; H, 5.0; N, 2.9. Found: C, 54.6; H, 4.8; N, 2.8.

$SrZn_2(crot)_6(6\text{-MeQ})_2$. Anal. Calcd for $C_{44}H_{48}N_2O_{12}SrZn_2$: C, 52.1; H, 4.8; N, 2.8; Zn, 12.9. Found: C, 52.1; H, 4.7; N, 2.7; Zn, 13.4.

Crystal Structure Determinations. Crystallographic data are given in Table I. Unit cell parameters were obtained by least-squares refinement from 2θ values of 24–36 reflections measured at $\pm\omega$ ($20 < 2\theta < 25°$). Data were collected at 22 °C on a Siemens AED2 diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å), in a ω/θ scan mode. Online profile fitting was performed for compound **4**, which was examined on an older Siemens AED machine.[10] Crystals were mounted with epoxy resin on glass fibers. For each data set, three standard reflections were measured approximately every hour to monitor stability; small decay corrections (ca. 5% in total) were applied in some cases. Data reduction also included standard Lp corrections and semiempirical absorption corrections based on sets of equivalent reflections measured at a range of azimuthal angles.[11] Reflections with $F > 4\sigma(F)$ were used for structure determination and refinement.

In all structures, the central metal atom lies on a crystallographic inversion center. Zinc atoms were located from Patterson syntheses; all other atoms were located from successive difference syntheses. Refinement was by blocked-cascade least squares on F, with anisotropic thermal parameters for all non-hydrogen atoms and a weighting scheme $w^{-1} = \sigma^2(F) + gF^2$, the parameter g being automatically optimized. H atoms, most of which were revealed in difference syntheses, were constrained to give C–H = 0.96 Å, aromatic and olefinic H on external angle bisectors, H–C–H = 109.5° for methyl H, and $U(H) = 1.2U_{eq}(C)$. The rigid methyl groups were allowed rotational freedom; they were found to be approximately staggered with respect to the adjacent olefinic CH group, as in other complexes with crotonate ligands.[2,3h] The refined isotropic extinction parameter x is defined by $F_c' = F_c/(1 + xF_c^2/\sin 2\theta)^{1/4}$. In structure **8**, one crotonate group is probably disordered, leading to an unreasonable observed geometry. The disorder is essentially in the double-bonded carbon atoms C(32) and C(33). Attempts to resolve the disorder into alternative atomic sites, to give a simple model with two possible orientations of the ligand, were unsuccessful, and only broad electron density maxima were found, corresponding to the results given here. No H atoms were included for this group. Complex scattering factors were taken from ref 12.

Final atomic coordinates are given in Tables II–IX, with bond lengths and angles for the metal coordination spheres and crotonate bridges given in Tables X–XVII. Lists of complete bond lengths and angles, anisotropic thermal parameters, and H atom parameters, and a table of $|F_o|$, $|F_c|$, and $\sigma(F)$ are available as supplementary material.

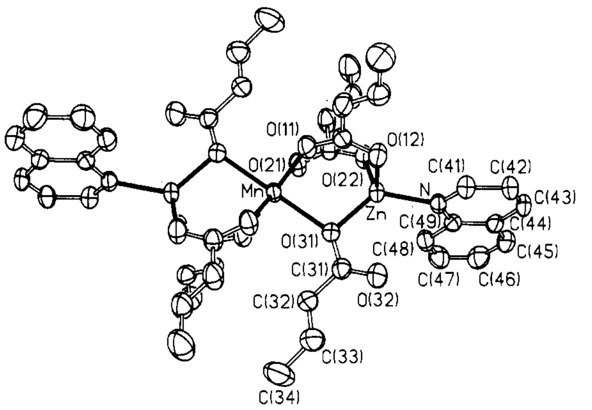


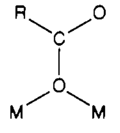
Figure 1. Molecular structure of $MnZn_2(crot)_6Q_2$ (**1**). Thermal motion is represented in all diagrams as 50% probability ellipsoids; H atoms are omitted. All the crotonate ligands follow an atom numbering scheme analogous to that shown for ligand 3, and the same scheme is used for all eight structures. The central metal atom lies on a crystallographic inversion center.

X-ray single-crystal diffraction data were also measured for the compound $SrZn_2(crot)_6Q_2$, but this was found to contain additional quinoline in the solid-state structure (0.5 Q per molecule), and the extra quinoline, together with some of the crotonate groups, was disordered so a satisfactory refinement could not be achieved. Compound **8** was synthesized as a substitute for this compound.

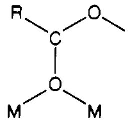
Results and Discussion

All eight molecular structures contain a linear array of three metal atoms, with the central one on a crystallographic inversion center. The central M atom is linked to each Zn atom by three crotonate bridges, and the coordination of Zn is completed by a terminal quinoline or 6-methylquinoline ligand. The coordination geometry and the nature of the bridging by the crotonates are not, however, constant over the whole series of structures, but show significant variation. Close inspection shows that structures **1–5** are all very similar, while structures **6–8** manifest a systematic change in molecular geometry as the central metal is varied from Mg through Ca and Sr.

Compounds 1–5. Here the central metal is a transition or post transition metal. The structure of compound **1**, representative of the whole group, is shown in Figure 1. Compounds **2–5** are very similar except for the orientations of crotonate side chains and the quinoline ligands. Variations in the molecular geometry for the central core of these five compounds are small, and there is no clear pattern in the differences observed (Table XVIII). In each set of three crotonate bridges between M and one of the Zn atoms, two are of the commonly observed syn–syn type, with approximately equal C–O bond lengths. The third crotonate functions primarily as a monatomic (M–O–Zn) bridge. This type of bridge (A) is rare in metal carboxylate chemistry;[4,13a,13b] in most cases, the other oxygen atom is also directly involved in coordination to a metal atom, so that the carboxylate is simultaneously



A



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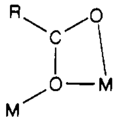

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Table I. Crystallographic Data[a]

	$MnZn_2(crot)_6Q_2$ (**1**)	$CoZn_2(crot)_6Q_2$ (**2**)	$NiZn_2(crot)_6Q_2$ (**3**)	$Zn_3(crot)_6Q_2$ (**4**)	$CdZn_2(crot)_3Q_2$ (**5**)	$MgZn_2(crot)_6Q_2$ (**6**)	$CaZn_2(crot)_6$-(6-MeQ)$_2$ (**7**)	$SrZn_2(crot)_6$-(6-MeQ) (**8**)
chem formula	$C_{42}H_{44}N_2O_{12}Zn_2Mn$	$C_{42}H_{44}N_2O_{12}Zn_2Co$	$C_{42}H_{44}N_2O_{12}Zn_2Ni$	$C_{42}H_{44}N_2O_{12}Zn_3$	$C_{42}H_{44}N_2O_{12}Zn_2Cd$	$C_{42}H_{44}N_2O_{12}Zn_2Mg$	$C_{44}H_{48}N_2O_{12}Zn_2Ca$	$C_{44}H_{48}N_2O_{12}Zn_2Sr$
fw	954.5	958.5	958.3	965.0	1012.0	923.9	967.7	1015.3
cryst color	pale pink	purple	pale yellow	colorless	colorless	colorless	colorless	colorless
cryst size, mm	0.20 × 0.27 × 0.42	0.17 × 0.27 × 0.54	0.15 × 0.23 × 0.38	0.15 × 0.38 × 0.54	0.12 × 0.27 × 0.44	0.19 × 0.31 × 0.50	0.16 × 0.19 × 0.46	0.19 × 0.38 × 0.46
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic	triclinic
space group	$P2/c^b$	$P2_1/c^c$	$P2_1/c$	$P2/c^b$	$P2_1/c^c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	10.9126 (5)	10.6062 (5)	10.660 (2)	10.832 (1)	10.7402 (5)	10.965 (3)	10.170 (1)	9.695 (2)
b, Å	9.6913 (5)	11.9598 (5)	14.050 (3)	9.635 (1)	11.8731 (5)	10.977 (3)	10.397 (1)	11.188 (2)
c, Å	20.7505 (9)	17.7779 (8)	15.046 (3)	20.784 (2)	17.8351 (7)	11.075 (3)	12.064 (1)	11.777 (2)
α, deg						104.85 (1)	93.230 (5)	65.97 (1)
β, deg	100.527 (5)	98.203 (5)	104.50 (2)	100.29 (1)	98.966 (4)	111.82 (1)	90.666 (6)	86.88 (1)
γ, deg						101.86 (1)	113.518 (5)	86.80 (1)
V, Å^3	2157.6	2232.0	2181.7	2134.3	2246.5	1127.0	1167.0	1164.2
Z	2	2	2	2	2	1	1	1
d_{calcd}, g cm^{-3}	1.469	1.426	1.459	1.501	1.496	1.361	1.377	1.448
μ, mm^{-1}	1.47	1.52	1.61	1.78	1.61	1.16	1.22	2.21
$F(000)$	982	986	988	992	1028	478	502	520
2θ range, deg	3–50	3–50	3–50	3–50	3–50	3–50	3–50	3–50
index ranges								
h	0 to +12	−12 to +2	−13 to 0	−12 to +12	−12 to +12	−13 to 0	−12 to +12	−11 to +3
k	−11 to +1	0 to +14	0 to +17	0 to +11	0 to +14	−13 to +13	−12 to +12	−13 to +13
l	−24 to +24	−21 to +21	−18 to +18	−24 to +24	−21 to +21	−13 to +13	−14 to +14	−13 to +13
no. of reflcns measd	4177	4628	3864	5868	7563	4113	8210	5880
no. of unique reflcns	3806	3913	3838	3748	3945	3952	4105	4098
no. with $F > 4\sigma(F)$	3062	2453	2457	3158	2725	3275	3196	2839
transmissn factors	0.55–0.58	0.50–0.53	0.60–0.66	0.41–0.53	0.53–0.62	0.78–0.87	0.76–0.82	0.47–0.62
R_{int}	0.018	0.020	0.015	0.034	0.022	0.031	0.028	0.022
weighting g	0	0	0	0.00002	0	0.00019	0	0.00009
R	0.030	0.043	0.048	0.033	0.039	0.035	0.049	0.050
wR	0.029	0.033	0.033	0.031	0.030	0.044	0.035	0.046
no. of params	278	277	277	278	277	277	290	287
shift/esd: max, mean	0.05, 0.01	0.09, 0.01	0.08, 0.02	0.02, 0.004	0.01, 0.003	0.007, 0.001	0.01, 0.001	0.24, 0.02
extinction param x	4.4 (4) × 10^{-7}	0	0	1.6 (1) × 10^{-6}	0	0	2.4 (10) × 10^{-7}	1.3 (3) × 10^{-6}
slope of norm prob plot	1.64	1.68	1.43	1.27	1.61	1.63	1.49	1.67
max, min in diff map, e Å^{-3}	0.55, −0.25	0.34, −0.42	0.55, −0.40	0.25, −0.23	0.48, −0.58	0.43, −0.24	0.63, −0.45	0.62, −0.45

[a] The standard deviation of the least significant figure is given in parentheses in this and subsequent tables. [b] Compounds **1** and **4** are isomorphous and isostructural. [c] Compounds **2** and **5** are isomorphous and isostructural.

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^4$) for $MnZn_2(crot)_6Q_2$ (**1**)

atom	*x*	*y*	*z*	U_{eq}[a]
Mn	5000	5000	5000	347 (2)
Zn	7708.2 (2)	3444.8 (3)	5034.6 (1)	379 (1)
O(11)	5966 (1)	5310 (2)	4189 (1)	521 (7)
O(12)	7941 (1)	4634 (2)	4313 (1)	509 (7)
C(11)	7005 (2)	5303 (2)	4018 (1)	408 (9)
C(12)	7163 (2)	6106 (3)	3438 (1)	521 (10)
C(13)	8222 (2)	6278 (3)	3235 (1)	505 (10)
C(14)	8395 (3)	7121 (4)	2660 (1)	734 (13)
O(21)	4776 (1)	2868 (2)	4768 (1)	498 (7)
O(22)	6591 (1)	1934 (2)	4647 (1)	508 (6)
C(21)	5406 (2)	1950 (3)	4568 (1)	430 (9)
C(22)	4723 (2)	789 (3)	4202 (1)	558 (11)
C(23)	5163 (3)	−83 (3)	3839 (1)	637 (11)
C(24)	4478 (3)	−1255 (4)	3468 (2)	879 (16)
O(31)	6816 (1)	4430 (2)	5633 (1)	436 (6)
O(32)	8678 (2)	4999 (2)	6159 (1)	675 (8)
C(31)	7556 (2)	5052 (3)	6109 (1)	421 (9)
C(32)	6931 (2)	5826 (3)	6576 (1)	511 (10)
C(33)	7527 (3)	6530 (3)	7066 (1)	629 (11)
C(34)	6951 (3)	7325 (4)	7549 (2)	905 (16)
N	9412 (2)	2544 (2)	5246 (1)	372 (7)
C(41)	10256 (2)	2907 (3)	4896 (1)	439 (9)
C(42)	11398 (2)	2225 (3)	4930 (1)	466 (10)
C(43)	11655 (2)	1117 (3)	5329 (1)	468 (9)
C(44)	10801 (2)	705 (3)	5728 (1)	408 (9)
C(45)	11001 (2)	−421 (3)	6162 (1)	525 (10)
C(46)	10149 (3)	−762 (3)	6539 (1)	613 (12)
C(47)	9049 (3)	9 (3)	6500 (1)	590 (11)
C(48)	8816 (2)	1098 (3)	6079 (1)	492 (10)
C(49)	9678 (2)	1468 (2)	5679 (1)	373 (8)

[a] U_{eq} is equal to one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ matrix.

Table III. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^4$) for $CoZn_2(crot)_6Q_2$ (**2**)

atom	*x*	*y*	*z*	U_{eq}[a]
Co	5000	5000	5000	387 (2)
Zn	7973.2 (4)	4951.9 (4)	5898.4 (2)	454 (1)
O(11)	5086 (2)	5692 (2)	6080 (1)	521 (10)
O(12)	7099 (3)	5624 (3)	6675 (1)	631 (12)
C(11)	5945 (4)	5908 (3)	6617 (2)	500 (16)
C(12)	5647 (4)	6582 (5)	7281 (3)	876 (23)
C(13)	4609 (4)	7060 (4)	7327 (3)	823 (22)
C(14)	4314 (6)	7755 (7)	7999 (3)	1456 (37)
O(21)	6209 (2)	6270 (2)	4698 (1)	527 (10)
O(22)	8264 (2)	6088 (2)	5162 (1)	477 (10)
C(21)	7354 (4)	6561 (3)	4746 (2)	429 (14)
C(22)	7669 (4)	7499 (3)	4278 (2)	599 (17)
C(23)	8823 (4)	7835 (3)	4217 (2)	636 (18)
C(24)	9184 (5)	8748 (4)	3721 (3)	1047 (27)
O(31)	6598 (2)	3964 (2)	5387 (1)	481 (10)
O(32)	8260 (3)	3044 (3)	5247 (3)	1321 (22)
C(31)	7118 (4)	3096 (4)	5167 (2)	506 (16)
C(32)	6281 (5)	2209 (4)	4800 (3)	675 (19)
C(33)	6645 (6)	1307 (4)	4548 (3)	1069 (28)
C(34)	5808 (8)	408 (5)	4138 (5)	1706 (46)
N	9775 (3)	4772 (2)	6464 (2)	450 (11)
C(41)	10717 (3)	5247 (3)	6168 (2)	514 (16)
C(42)	11986 (4)	5209 (4)	6510 (3)	621 (18)
C(43)	12256 (4)	4657 (4)	7178 (3)	734 (20)
C(44)	11302 (4)	4137 (4)	7516 (2)	603 (17)
C(45)	11519 (5)	3547 (4)	8213 (3)	892 (23)
C(46)	10557 (5)	3066 (4)	8509 (3)	980 (25)
C(47)	9320 (5)	3132 (4)	8128 (3)	848 (23)
C(48)	9063 (4)	3701 (3)	7461 (2)	655 (18)
C(49)	10045 (4)	4209 (3)	7141 (2)	512 (15)

[a] U_{eq} is equal to one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ matrix.

Table IV. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^4$) for $NiZn_2(crot)_6Q_2$ (3)

atom	*x*	*y*	*z*	U_{eq}[a]
Ni	5000	5000	5000	398 (3)
Zn	1989.0 (5)	4334.5 (4)	4213.4 (4)	457 (2)
O(11)	3696 (3)	6105 (2)	4660 (2)	577 (13)
O(12)	1632 (2)	5662 (2)	4409 (2)	525 (11)
C(11)	2524 (4)	6282 (3)	4540 (3)	428 (17)
C(12)	2141 (4)	7296 (3)	4527 (3)	561 (20)
C(13)	956 (5)	7595 (3)	4343 (3)	660 (22)
C(14)	557 (6)	8620 (4)	4294 (5)	1156 (34)
O(21)	4693 (3)	4589 (2)	3670 (2)	565 (12)
O(22)	2620 (3)	4204 (2)	3092 (2)	593 (13)
C(21)	3764 (4)	4376 (3)	3033 (3)	504 (18)
C(22)	4082 (6)	4327 (4)	2105 (4)	769 (24)
C(23)	3332 (7)	4081 (5)	1432 (5)	1125 (36)
C(24)	3751 (9)	4013 (7)	491 (4)	1826 (56)
O(31)	3566 (2)	4031 (2)	5180 (2)	487 (11)
O(32)	2031 (3)	3480 (3)	5731 (2)	832 (16)
C(31)	3180 (4)	3655 (3)	5845 (3)	443 (16)
C(32)	4139 (4)	3498 (3)	6718 (3)	464 (17)
C(33)	3819 (4)	3226 (3)	7462 (3)	588 (20)
C(34)	4706 (5)	3097 (4)	8399 (3)	784 (25)
N	170 (3)	3819 (2)	3732 (2)	426 (13)
C(41)	−804 (4)	4407 (3)	3641 (3)	505 (18)
C(42)	−2094 (4)	4146 (3)	3268 (3)	641 (21)
C(43)	−2353 (4)	3239 (3)	2997 (3)	650 (21)
C(44)	−1365 (4)	2566 (3)	3091 (3)	471 (17)
C(45)	−1562 (5)	1602 (3)	2850 (3)	626 (21)
C(46)	−574 (5)	989 (4)	2955 (3)	678 (23)
C(47)	700 (4)	1311 (3)	3320 (3)	675 (22)
C(48)	946 (4)	2232 (3)	3573 (3)	575 (19)
C(49)	−79 (4)	2877 (3)	3471 (3)	435 (17)

[a] U_{eq} is equal to one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ matrix.

Table V. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^4$) for $Zn_3(crot)_6Q_2$ (**4**)

atom	*x*	*y*	*z*	U_{eq}[a]
Zn(1)	5000	5000	5000	340 (2)
Zn(2)	7708.8 (3)	3479.2 (3)	5053.9 (2)	347 (1)
O(11)	5937 (2)	5351 (2)	4206 (1)	470 (8)
O(12)	7935 (2)	4689 (2)	4339 (1)	467 (8)
C(11)	6985 (3)	5332 (3)	4037 (1)	375 (10)
C(12)	7130 (3)	6121 (3)	3448 (1)	466 (12)
C(13)	8205 (3)	6276 (3)	3244 (1)	473 (12)
C(14)	8376 (3)	7102 (4)	2660 (2)	695 (16)
O(21)	4726 (2)	2958 (2)	4760 (1)	436 (8)
O(22)	6567 (2)	1986 (2)	4662 (1)	469 (8)
C(21)	5367 (3)	2024 (3)	4572 (1)	398 (11)
C(22)	4684 (3)	856 (3)	4205 (2)	480 (12)
C(23)	5149 (3)	−41 (3)	3854 (2)	537 (13)
C(24)	4483 (3)	−1217 (4)	3479 (2)	795 (18)
O(31)	6753 (2)	4438 (2)	5633 (1)	400 (7)
O(32)	8631 (2)	5009 (2)	6153 (1)	621 (9)
C(31)	7494 (2)	5073 (3)	6107 (1)	381 (10)
C(32)	6877 (3)	5842 (3)	6580 (1)	452 (11)
C(33)	7493 (3)	6546 (3)	7066 (2)	567 (13)
C(34)	6932 (4)	7343 (5)	7559 (2)	836 (19)
N	9414 (2)	2550 (2)	5251 (1)	331 (8)
C(41)	10257 (2)	2908 (3)	4891 (1)	391 (11)
C(42)	11401 (2)	2216 (3)	4921 (1)	440 (12)
C(43)	11659 (2)	1100 (3)	5319 (1)	447 (12)
C(44)	10813 (2)	694 (3)	5725 (1)	367 (10)
C(45)	11014 (3)	−437 (3)	6159 (1)	464 (12)
C(46)	10160 (3)	−778 (4)	6542 (2)	574 (14)
C(47)	9068 (3)	22 (3)	6505 (2)	543 (13)
C(48)	8829 (3)	1113 (3)	6087 (1)	441 (11)
C(49)	9680 (2)	1469 (3)	5684 (1)	344 (10)

[a] U_{eq} is equal to one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ matrix.

monatomic and either bidentate (B) or chelating (C).[13c–j] It is significant that the C–O bond lengths for the single-atom bridging crotonates in these structures are characteristic of localized single and double bonds, in contrast to the syn–syn bridges.

The C═O bond of the monatomic crotonate bridge can not, however, be considered totally free and uninvolved in coordination. The relatively short Zn⋯O distances given in Table XVIII indicate a weak, secondary interaction between zinc and the carbonyl

Table VI. Atomic Coordinates (×10⁴) and Equivalent Isotropic Thermal Parameters (Å² × 10⁴) for $CdZn_2(crot)_6Q_2$ (**5**)

atom	*x*	*y*	*z*	U_{eq}[a]
Cd	5000	5000	5000	349 (1)
Zn	8006.3 (3)	4984.9 (4)	5871.8 (2)	343 (1)
O(11)	5108 (2)	5683 (2)	6162 (1)	456 (10)
O(12)	7160 (2)	5715 (2)	6633 (1)	488 (10)
C(11)	6021 (4)	5974 (3)	6637 (2)	411 (14)
C(12)	5796 (4)	6696 (4)	7285 (2)	589 (18)
C(13)	4717 (4)	7100 (4)	7371 (2)	657 (20)
C(14)	4442 (5)	7842 (6)	8010 (3)	1215 (32)
O(21)	6297 (2)	6405 (2)	4731 (1)	487 (11)
O(22)	8342 (2)	6117 (2)	5145 (1)	410 (9)
C(21)	7430 (4)	6652 (3)	4756 (2)	359 (13)
C(22)	7758 (4)	7609 (3)	4306 (2)	502 (16)
C(23)	8897 (4)	7903 (4)	4227 (2)	578 (18)
C(24)	9253 (6)	8845 (5)	3749 (3)	994 (28)
O(31)	6741 (2)	3890 (2)	5417 (1)	420 (9)
O(32)	8301 (3)	3021 (3)	5033 (2)	959 (17)
C(31)	7196 (3)	3055 (3)	5094 (2)	435 (14)
C(32)	6289 (4)	2188 (3)	4771 (2)	558 (17)
C(33)	6571 (5)	1280 (4)	4458 (3)	854 (25)
C(34)	5657 (8)	409 (5)	4089 (4)	1344 (38)
N	9757 (3)	4716 (2)	6447 (2)	343 (11)
C(41)	10726 (3)	5177 (3)	6184 (2)	404 (14)
C(42)	11961 (4)	5116 (4)	6561 (2)	520 (16)
C(43)	12192 (4)	4567 (4)	7232 (3)	612 (19)
C(44)	11209 (4)	4071 (4)	7540 (2)	500 (16)
C(45)	11372 (4)	3474 (4)	8239 (3)	732 (21)
C(46)	10376 (5)	3009 (4)	8500 (3)	807 (22)
C(47)	9183 (5)	3078 (4)	8086 (3)	724 (21)
C(48)	8970 (4)	3633 (3)	7407 (2)	529 (16)
C(49)	9977 (3)	4139 (3)	7125 (2)	381 (13)

[a] U_{eq} is equal to one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ matrix.

Table VII. Atomic Coordinates (×10⁴) and Equivalent Isotropic Thermal Parameters (Å² × 10⁴) for $MgZn_2(crot)_6Q_2$ (**6**)

atom	*x*	*y*	*z*	U_{eq}[a]
Mg	5000	5000	5000	474 (6)
Zn	3855.3 (3)	7247.8 (3)	3468.7 (3)	493 (1)
O(11)	4459 (2)	4476 (2)	2901 (2)	667 (11)
O(12)	3483 (2)	5741 (2)	1842 (2)	601 (9)
C(11)	3931 (3)	4766 (2)	1863 (3)	517 (12)
C(12)	3808 (3)	3943 (3)	504 (3)	666 (16)
C(13)	4384 (4)	3047 (3)	357 (4)	767 (19)
C(14)	4321 (6)	2210 (4)	−998 (5)	1216 (31)
O(21)	6490 (2)	6747 (2)	5423 (2)	680 (11)
O(22)	5831 (2)	8254 (2)	4574 (2)	575 (9)
C(21)	6739 (3)	7829 (2)	5260 (3)	488 (12)
C(22)	8208 (3)	8676 (3)	5905 (3)	621 (14)
C(23)	8643 (4)	9912 (3)	6030 (3)	742 (17)
C(24)	10144 (4)	10798 (4)	6750 (5)	1147 (25)
O(31)	3531 (2)	5936 (2)	4800 (2)	763 (12)
O(32)	2585 (3)	7405 (2)	4466 (3)	855 (15)
C(31)	2769 (3)	6548 (3)	5006 (3)	532 (13)
C(32)	2055 (4)	6352 (4)	5871 (4)	949 (24)
C(33)	2102 (5)	5568 (5)	6493 (5)	1155 (30)
C(34)	1397 (5)	5393 (7)	7429 (5)	1524 (40)
N	3323 (2)	8559 (2)	2465 (2)	471 (10)
C(41)	4270 (3)	9727 (2)	2854 (3)	510 (12)
C(42)	4039 (3)	10633 (3)	2185 (3)	644 (15)
C(43)	2798 (3)	10299 (3)	1054 (3)	700 (16)
C(44)	1766 (3)	9065 (3)	587 (3)	589 (14)
C(45)	453 (3)	8645 (3)	−574 (3)	777 (17)
C(46)	−532 (4)	7462 (3)	−950 (4)	832 (17)
C(47)	−260 (3)	6645 (3)	−170 (4)	745 (16)
C(48)	1001 (3)	7004 (3)	953 (3)	619 (14)
C(49)	2044 (3)	8217 (2)	1340 (3)	493 (12)

[a] U_{eq} is equal to one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ matrix.

Table VIII. Atomic Coordinates (×10⁴) and Equivalent Isotropic Thermal Parameters (Å² × 10⁴) for $CaZn_2(crot)_6(6\text{-}MeQ)_2$ (**7**)

atom	*x*	*y*	*z*	U_{eq}[a]
Ca	5000	5000	5000	467 (4)
Zn	3590.5 (4)	4943.7 (4)	7956.9 (3)	494 (2)
O(11)	2973 (3)	5278 (3)	5522 (2)	911 (16)
O(12)	2271 (2)	5564 (2)	7189 (2)	653 (12)
C(11)	2307 (3)	5726 (3)	6156 (3)	535 (15)
C(12)	1478 (4)	6481 (4)	5728 (3)	697 (19)
C(13)	1560 (4)	6917 (4)	4749 (3)	826 (22)
C(14)	790 (6)	7748 (6)	4285 (4)	1198 (31)
O(21)	4348 (3)	3038 (2)	6016 (2)	945 (16)
O(22)	3602 (2)	3090 (2)	7721 (2)	604 (11)
C(21)	4036 (3)	2548 (3)	6911 (3)	529 (14)
C(22)	4200 (4)	1222 (3)	7157 (3)	605 (16)
C(23)	4814 (4)	618 (3)	6537 (3)	688 (18)
C(24)	5073 (5)	−653 (4)	6769 (4)	894 (23)
O(31)	5991 (3)	6254 (3)	6634 (2)	806 (13)
O(32)	5458 (2)	6478 (2)	8361 (2)	650 (11)
C(31)	6320 (4)	6804 (3)	7574 (3)	522 (15)
C(32)	7776 (4)	7896 (3)	7834 (3)	594 (16)
C(33)	8733 (4)	8359 (4)	7087 (4)	736 (19)
C(34)	10244 (4)	9430 (4)	7296 (4)	1033 (25)
N	2677 (3)	4764 (2)	9510 (2)	454 (11)
C(41)	3357 (4)	5673 (3)	10338 (3)	587 (16)
C(42)	2731 (4)	5777 (4)	11353 (3)	658 (18)
C(43)	1356 (4)	4911 (4)	11495 (3)	617 (18)
C(44)	576 (3)	3893 (3)	10652 (2)	465 (14)
C(45)	−859 (4)	2930 (3)	10746 (3)	587 (16)
C(46)	−1563 (4)	1946 (4)	9925 (3)	641 (17)
C(47)	−834 (4)	1888 (4)	8953 (3)	666 (17)
C(48)	548 (3)	2805 (3)	8821 (3)	555 (15)
C(49)	1281 (3)	3831 (3)	9655 (2)	455 (14)
C(40)	−3099 (4)	924 (4)	10015 (4)	962 (23)

[a] U_{eq} is equal to the trace of the orthogonalized $\mathbf{U}_{ij}$ matrix.

Table IX. Atomic Coordinates (×10⁴) and Equivalent Isotropic Thermal Parameters (Å² × 10⁴) for $SrZn_2(crot)_6(6\text{-}MeQ)_2$ (**8**)

atom	*x*	*y*	*z*	U_{eq}[a]
Sr	5000	5000	5000	597 (3)
Zn	6817.3 (6)	5423.7 (5)	7824.2 (5)	549 (2)
O(11)	5132 (4)	3467 (3)	7198 (3)	808 (17)
O(12)	5926 (4)	3800 (3)	8753 (3)	743 (16)
C(11)	5215 (5)	3194 (4)	8318 (4)	529 (20)
C(12)	4431 (5)	2077 (4)	9216 (4)	593 (21)
C(13)	4410 (5)	1693 (4)	10407 (4)	621 (22)
C(14)	3635 (6)	566 (5)	11330 (5)	892 (29)
O(21)	4520 (4)	6656 (3)	5870 (3)	810 (18)
O(22)	5607 (4)	6979 (3)	7309 (3)	696 (16)
C(21)	4764 (5)	7301 (4)	6466 (4)	563 (21)
C(22)	4019 (6)	8593 (6)	6216 (5)	832 (29)
C(23)	3184 (7)	9129 (7)	5406 (6)	1025 (36)
C(24)	2474 (8)	10489 (6)	5137 (7)	1437 (42)
O(31)	7386 (4)	5621 (4)	5050 (3)	936 (22)
O(32)	8370 (3)	5627 (3)	6671 (3)	744 (17)
C(31)	8325 (5)	5891 (5)	5533 (5)	633 (23)
C(32)	9586 (9)	6557 (6)	4793 (8)	1429 (47)
C(33)	10073 (10)	7136 (7)	4116 (11)	1990 (67)
C(34)	11325 (6)	7801 (6)	3304 (6)	1040 (33)
N	7721 (3)	5576 (3)	9328 (3)	523 (16)
C(41)	7303 (5)	4749 (5)	10458 (4)	625 (22)
C(42)	7809 (5)	4739 (5)	11553 (4)	727 (25)
C(43)	8764 (5)	5594 (5)	11475 (4)	742 (25)
C(44)	9226 (4)	6508 (4)	10313 (4)	573 (21)
C(45)	10212 (5)	7467 (6)	10149 (6)	778 (30)
C(46)	10625 (5)	8348 (5)	9035 (6)	762 (29)
C(47)	10076 (5)	8282 (5)	7994 (5)	740 (26)
C(48)	9141 (5)	7388 (4)	8071 (4)	624 (22)
C(49)	8667 (4)	6479 (4)	9235 (4)	502 (19)
C(40)	11659 (7)	9374 (6)	8899 (7)	1142 (40)

[a] U_{eq} is equal to one-third of the orthogonalized $\mathbf{U}_{ij}$ matrix.

oxygen atom, and this interaction considerably distorts the zinc coordination from simple tetrahedral geometry. It also affects the carbonyl stretching frequency, which for these compounds occurs ca. 80 cm⁻¹ lower in frequency than would be expected for an unperturbed α,β-unsaturated carboxylate group, such as in methyl crotonate ($\nu_{C=O}$ = 1705 cm⁻¹).[1,2]

The central M atom enjoys almost perfect octahedral coordination in all five compounds, *cis*-O–M–O angles deviating only

Table X. Selected Bond Lengths (Å) and Angles (deg) for MnZn$_2$(crot)$_6$Q$_2$ (**1**)

Mn–O(11)	2.164 (2)	Mn–O(21)	2.125 (2)
Mn–O(31)	2.238 (2)	Zn–O(12)	1.941 (2)
Zn–O(22)	1.980 (2)	Zn–O(31)	1.960 (2)
Zn–N	2.029 (2)		

O(11)–Mn–O(21)	90.6 (1)	O(11)–Mn–O(31)	89.2 (1)
O(21)–Mn–O(31)	86.9 (1)	O(12)–Zn–O(22)	106.5 (1)
O(12)–Zn–O(31)	110.4 (1)	O(22)–Zn–O(31)	106.1 (1)
O(12)–Zn–N	100.3 (1)	O(22)–Zn–N	104.0 (1)
O(31)–Zn–N	127.9 (1)	Mn–O(11)–C(11)	144.8 (1)
Zn–O(12)–C(11)	117.9 (2)	O(11)–C(11)–O(12)	124.0 (2)
Mn–O(21)–C(21)	136.4 (2)	Zn–O(22)–C(21)	125.4 (2)
O(21)–C(21)–O(22)	125.2 (2)	Mn–O(31)–Zn	103.8 (1)
Mn–O(31)–C(31)	133.6 (2)	Zn–O(31)–C(31)	113.3 (2)
O(31)–C(31)–O(32)	121.4 (2)		

Table XI. Selected Bond Lengths (Å) and Angles (deg) for CoZn$_2$(crot)$_6$Q$_2$ (**2**)

Co–O(11)	2.081 (3)	Co–O(21)	2.107 (3)
Co–O(31)	2.133 (2)	Zn–O(12)	1.944 (3)
Zn–O(22)	1.942 (3)	Zn–O(31)	1.993 (3)
Zn–N	2.040 (3)		

O(11)–Co–O(21)	90.0 (1)	O(11)–Co–O(31)	90.3 (1)
O(21)–Co–O(31)	90.9 (1)	O(12)–Zn–O(22)	109.1 (1)
O(12)–Zn–O(31)	100.2 (1)	O(22)–Zn–O(31)	106.5 (1)
O(12)–Zn–N	101.6 (1)	O(22)–Zn–N	100.3 (1)
O(31)–Zn–N	137.4 (1)	Co–O(11)–C(11)	135.9 (3)
Zn–O(12)–C(11)	127.5 (2)	O(11)–C(11)–O(12)	127.0 (4)
Co–O(21)–C(21)	143.2 (2)	Zn–O(22)–C(21)	121.8 (2)
O(21)–C(21)–O(22)	124.6 (4)	Co–O(31)–Zn	107.4 (1)
Co–O(31)–C(31)	137.7 (2)	Zn–O(31)–C(31)	107.8 (2)
O(31)–C(31)–O(32)	118.9 (4)		

Table XII. Selected Bond Lengths (Å) and Angles (deg) for NiZn$_2$(crot)$_6$Q$_2$ (**3**)

Ni–O(11)	2.061 (3)	Ni–O(21)	2.028 (3)
Ni–O(31)	2.114 (3)	Zn–O(12)	1.941 (3)
Zn–O(22)	1.975 (3)	Zn–O(31)	1.974 (2)
Zn–N	2.026 (3)		

O(11)–Ni–O(21)	92.1 (1)	O(11)–Ni–O(31)	93.0 (1)
O(21)–Ni–O(31)	90.0 (1)	O(12)–Zn–O(22)	109.9 (1)
O(12)–Zn–O(31)	105.0 (1)	O(22)–Zn–O(31)	101.5 (1)
O(12)–Zn–N	101.0 (1)	O(22)–Zn–N	99.3 (1)
O(31)–Zn–N	138.4 (1)	Ni–O(11)–C(11)	141.1 (3)
Zn–O(12)–C(11)	121.0 (3)	O(11)–C(11)–O(12)	125.0 (4)
Ni–O(21)–C(21)	137.5 (3)	Zn–O(22)–C(21)	125.5 (3)
O(21)–C(21)–O(22)	126.3 (4)	Ni–O(31)–Zn	106.1 (1)
Ni–O(31)–C(31)	138.2 (2)	Zn–O(31)–C(31)	106.4 (2)
O(31)–C(31)–O(32)	118.6 (4)		

Table XIII. Selected Bond Lengths (Å) and Angles (deg) for Zn$_3$(crot)$_6$Q$_2$ (**4**)

Zn(1)–O(11)	2.113 (2)	Zn(1)–O(21)	2.038 (2)
Zn(1)–O(31)	2.177 (2)	Zn(2)–O(12)	1.938 (2)
Zn(2)–O(22)	1.976 (2)	Zn(2)–O(31)	1.954 (2)
Zn(2)–N	2.027 (2)		

O(11)–Zn(1)–O(21)	91.9 (1)	O(11)–Zn(1)–O(31)	91.3 (1)
O(21)–Zn(1)–O(31)	88.9 (1)	O(12)–Zn(2)–O(22)	106.1 (1)
O(12)–Zn(2)–O(31)	110.0 (1)	O(22)–Zn(2)–O(31)	103.7 (1)
O(12)–Zn(2)–N	100.6 (1)	O(22)–Zn(2)–N	104.0 (1)
O(31)–Zn(2)–N	130.4 (1)	Zn(1)–O(11)–C(11)	143.7 (2)
Zn(2)–O(12)–C(11)	118.0 (2)	O(11)–C(11)–O(12)	124.6 (3)
Zn(1)–O(21)–C(21)	135.3 (2)	Zn(2)–O(22)–C(21)	125.6 (2)
O(21)–C(21)–O(22)	125.9 (3)	Zn(1)–O(31)–Zn(2)	104.2 (1)
Zn(1)–O(31)–C(31)	133.8 (2)	Zn(2)–O(31)–C(31)	111.4 (2)
O(31)–C(31)–O(32)	120.8 (3)		

Table XIV. Selected Bond Lengths (Å) and Angles (deg) for CdZn$_2$(crot)$_6$Q$_2$ (**5**)

Cd–O(11)	2.212 (3)	Cd–O(21)	2.272 (3)
Cd–O(31)	2.314 (2)	Zn–O(12)	1.951 (3)
Zn–O(22)	1.940 (3)	Zn–O(31)	1.963 (2)
Zn–N	2.022 (3)		

O(11)–Cd–O(21)	89.1 (1)	O(11)–Cd–O(31)	89.2 (1)
O(21)–Cd–O(31)	89.7 (1)	O(12)–Zn–O(22)	108.2 (1)
O(12)–Zn–O(31)	102.4 (1)	O(22)–Zn–O(31)	111.8 (1)
O(12)–Zn–N	102.4 (1)	O(22)–Zn–N	101.2 (1)
O(31)–Zn–N	129.4 (1)	Cd–O(11)–C(11)	131.5 (3)
Zn–O(12)–C(11)	132.0 (2)	O(11)–C(11)–O(12)	126.3 (4)
Cd–O(21)–C(21)	142.5 (2)	Zn–O(22)–C(21)	120.1 (2)
O(21)–C(21)–O(22)	124.3 (3)	Cd–O(31)–Zn	103.2 (1)
Cd–O(31)–C(31)	130.0 (2)	Zn–O(31)–C(31)	114.2 (2)
O(31)–C(31)–O(32)	121.0 (4)		

Table XV. Selected Bond Lengths (Å) and Angles (deg) for MgZn$_2$(crot)$_6$Q$_2$ (**6**)

Mg–O(11)	2.058 (2)	Mg–O(21)	2.061 (2)
Mg–O(31)	2.057 (3)	Zn–O(12)	1.949 (2)
Zn–O(22)	1.940 (2)	Zn–O(31)	2.376 (3)
Zn–O(32)	2.081 (3)	Zn–N	2.081 (3)

O(11)–Mg–O(21)	90.1 (1)	O(11)–Mg–O(31)	90.6 (1)
O(21)–Mg–O(31)	91.0 (1)	O(12)–Zn–O(22)	112.1 (1)
O(12)–Zn–O(31)	95.3 (1)	O(22)–Zn–O(31)	100.3 (1)
O(12)–Zn–O(32)	126.0 (1)	O(22)–Zn–O(32)	117.4 (1)
O(31)–Zn–O(32)	56.5 (1)	O(12)–Zn–N	98.3 (1)
O(22)–Zn–N	97.4 (1)	O(31)–Zn–N	151.7 (1)
O(32)–Zn–N	95.7 (1)	Mg–O(11)–C(11)	144.5 (2)
Zn–O(12)–C(11)	126.0 (2)	O(11)–C(11)–O(12)	125.7 (3)
Mg–O(21)–C(21)	147.1 (2)	Zn–O(22)–C(21)	125.4 (2)
O(21)–C(21)–O(22)	125.1 (2)	Mg–O(31)–Zn	104.8 (1)
Mg–O(31)–C(31)	165.1 (2)	Zn–O(31)–C(31)	85.8 (2)
Zn–O(32)–C(31)	99.0 (2)	O(31)–C(31)–O(32)	118.7 (4)

Table XVI. Selected Bond Lengths (Å) and Angles (deg) for CaZn$_2$(crot)$_6$(6-MeQ)$_2$ (**7**)

Ca–O(11)	2.284 (3)	Ca–O(21)	2.308 (3)
Ca–O(31)	2.284 (3)	Zn–O(12)	1.951 (3)
Zn–O(22)	1.937 (3)	Zn–O(32)	1.965 (2)
Zn–N	2.086 (2)		

O(11)–Ca–O(21)	89.6 (1)	O(11)–Ca–O(31)	85.0 (1)
O(21)–Ca–O(31)	85.7 (1)	O(12)–Zn–O(22)	124.2 (1)
O(12)–Zn–O(32)	113.2 (1)	O(22)–Zn–O(32)	115.7 (1)
O(12)–Zn–N	97.5 (1)	O(22)–Zn–N	100.0 (1)
O(32)–Zn–N	98.6 (1)	Ca–O(11)–C(11)	152.5 (2)
Zn–O(12)–C(11)	122.6 (3)	O(11)–C(11)–O(12)	123.3 (4)
Ca–O(21)–C(21)	147.3 (2)	Zn–O(22)–C(21)	130.5 (2)
O(21)–C(21)–O(22)	125.5 (3)	Ca–O(31)–C(31)	170.0 (2)
Zn–O(32)–C(31)	114.2 (2)	O(31)–C(31)–O(32)	122.6 (3)

Table XVII. Selected Bond Lengths (Å) and Angles (deg) for SrZn$_2$(crot)$_6$(6-MeQ)$_2$ (**8**)

Sr–O(11)	2.461 (3)	Sr–O(21)	2.469 (4)
Sr–O(31)	2.462 (4)	Zn–O(12)	1.923 (3)
Zn–O(22)	1.940 (3)	Zn–O(32)	1.930 (3)
Zn–N	2.090 (4)		

O(11)–Sr–O(21)	83.8 (1)	O(11)–Sr–O(31)	89.4 (1)
O(21)–Sr–O(31)	81.0 (1)	O(12)–Zn–O(22)	115.3 (1)
O(12)–Zn–O(32)	124.5 (2)	O(22)–Zn–O(32)	111.9 (1)
O(12)–Zn–N	97.0 (1)	O(22)–Zn–N	99.4 (2)
O(32)–Zn–N	102.5 (1)	Sr–O(11)–C(11)	153.6 (3)
Zn–O(12)–C(11)	126.4 (3)	O(11)–C(11)–O(12)	124.1 (4)
Sr–O(21)–C(21)	155.9 (3)	Zn–O(22)–C(21)	124.9 (4)
O(21)–C(21)–O(22)	125.6 (4)	Sr–O(31)–C(31)	153.2 (4)
Zn–O(32)–C(31)	126.9 (3)	O(31)–C(31)–O(32)	124.6 (5)

slightly from 90°. In each case the M–O bonds to the single-atom bridging ligand are longer than the others. The M···Zn separations of ca. 3.3 Å do not indicate any significant direct interaction between the metal atoms; this distance is constrained by the bridging geometry. A similar Zn···Zn separation of 3.25 Å is observed in polymeric zinc crotonate, which contains Zn$_2$(crotonate)$_3$ units with three syn–syn bridges,[3h] and the Zn$_2$(OAc)$_3$$^+$ cation has a rather larger Zn···Zn distance of 3.54 Å.[14]

Compounds 6–8. Ignoring the unimportant difference between Q and 6-MeQ ligands, we have here a homologous series of compounds in which the successive alkaline-earth metals Mg, Ca,

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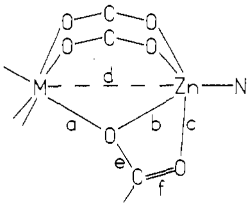
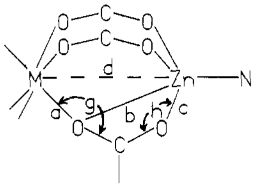
[14] Birnbaum, A.; Cotton, F. A.; Dori, Z.; Kapon, M. *Inorg. Chem.* **1984**, *23*, 1617.

Table XVIII. Selected Interatomic Distances (Å) in Compounds **1**–**5**, $MZn_2(crot)_6Q_2$



compd	M	*a*	*b*	*c*	*d*	*e*	*f*
1	Mn	2.238 (2)	1.960 (2)	2.815 (3)	3.306 (2)	1.304 (3)	1.211 (3)
2	Co	2.133 (2)	1.993 (3)	2.596 (4)	3.325 (2)	1.263 (5)	1.201 (5)
3	Ni	2.114 (3)	1.974 (2)	2.570 (3)	3.268 (3)	1.287 (6)	1.219 (5)
4	Zn	2.177 (2)	1.954 (2)	2.752 (3)	3.264 (2)	1.306 (3)	1.219 (3)
5	Cd	2.314 (2)	1.963 (2)	2.815 (3)	3.358 (2)	1.281 (5)	1.209 (5)

Table XIX. Selected Interatomic Distances (Å) and Interbond Angles (deg) in Compounds **4** and **6**–**8**, $MZn_2(crot)_6(base)_2$



compd	M	*a*	*b*	*c*	*d*	*g*	*h*
4	Zn	2.177 (2)	1.954 (2)	2.752 (3)	3.264 (2)	226.2 (2)	75.5 (2)
6	Mg	2.057 (3)	2.376 (3)	2.081 (3)	3.518 (3)	194.9 (2)	99.0 (2)
7	Ca	2.284 (3)	2.836 (3)	1.965 (2)	3.855 (3)	170.0 (2)	114.2 (2)
8	Sr	2.462 (4)	3.203 (5)	1.930 (3)	4.050 (5)	153.2 (4)	126.9 (3)

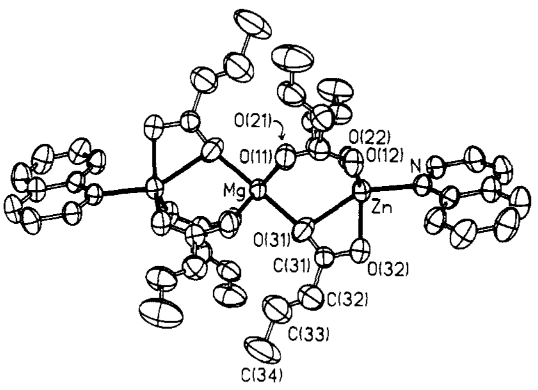


Figure 2. Molecular structure of $MgZn_2(crot)_6Q_2$ (**6**).

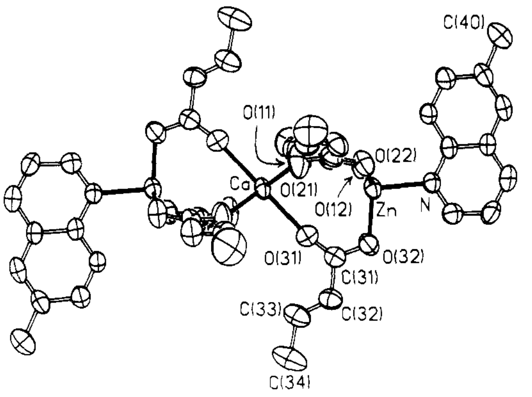


Figure 3. Molecular structure of $CaZn_2(crot)_6(6\text{-}MeQ)_2$ (**7**).

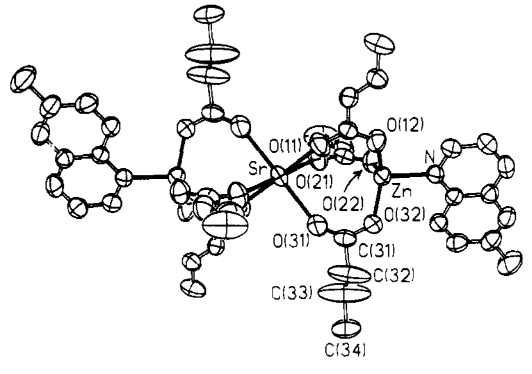


Figure 4. Molecular structure of $SrZn_2(crot)_6(6\text{-}MeQ)_2$ (**8**). Atoms C(32) and C(33) are probably disordered.

and Sr occupy the central site of the $MZn_2(crot)_6Q_2$ molecule. The molecular structures (Figures 2–4) differ markedly from those of compounds **1**–**5** and also from each other: major features are listed in Table XIX, together with the corresponding values for compound **4** for comparison. The major variation is in the nature of the crotonate bridges.

In the magnesium compound (**6**), two of each set of three bridges are of the common syn–syn type. The third has one of its oxygen atoms, O(31), bonded simultaneously to Mg and Zn. In this respect, this bridge resembles the corresponding bridge in **4**. The secondary Zn···O(32) interaction of **4**, however, is a genuine Zn–O bond in **6**, so that the Zn–O(31), Zn–O(32), and Mg–O(31) bonds are all of significant strength. Compared with that in compound **4**, the Zn–O(32) "bond" has strengthened at the expense of Zn–O(31). The observed structure closely resembles that of $Co_3(OBz)_6Q_2$.[9]

If Mg is replaced by Ca, to give compound **7**, the decrease in Zn–O(32) distance and concomitant increase in Zn–O(31) continue, to the extent that the former must now be considered a genuine bond and the latter a much weaker interaction, though still significant, because this bridge clearly differs in its geometry from the other two.

With the replacement of Ca by Sr in compound **8**, the process reaches its logical conclusion, and all the crotonate bridges are of the syn–syn type; none of them can be recognized as significantly different from the others. No C=O stretching mode is seen in the vibrational spectra of compounds **6**–**8**.

The change in the bridging function of the third crotonate ligand of each set in the series **6**–**8** is accompanied by other geometrical changes. Thus, across this series, the coordination geometry of

M becomes increasingly distorted from ideal octahedral, as evidenced by the O–M–O angles; the M–O bonds are all equivalent, as indicated by their lengths; and the M···Zn separation increases markedly. Indeed the Sr···Zn distance of 4.050 Å is believed to be the largest value known for a system where two metal atoms are bridged only by syn–syn carboxylates.[4]

Across the series **4** and **6–8** the increasing M···Zn separation necessarily "stretches" the syn–syn bridges, so that the angles at the oxygen atoms are expected to increase. In fact, the Zn–O–C angles do not change materially, and the increase takes place essentially entirely in the M–O–C angles adjacent to the central metal atom.

These geometrical details and trends can best be understood qualitatively in terms of the nature of the bonding between the crotonate ligands and the metal centers. With a transition or post transition metal in the center of the molecule, the bonding is predominantly covalent, and the essentially invariant observed structure for compounds **1–5** accommodates best an octahedral coordination of the central M atom while simultaneously maintaining reasonable angles at the ligand oxygen atoms. Acceptable angles at metal and oxygen atoms could not be achieved with all the carboxylates acting as syn–syn bridges. For compounds **6–8**, the increasing size and decreasing polarizing power of the central M^{2+} ion suggests more ionic character in the bonding between M and the crotonate bridges, while covalent bonding still predominantly determines the zinc coordination. Thus the O–M–O and, more particularly, M–O–C angles are less strongly constrained by covalency and are more easily distorted to accommodate the larger central M atoms/ions. Since the terminal d^{10} Zn(II) have no crystal-field stabilization effects, these atoms have no strong coordination geometry preferences and the geometry at Zn varies according to the nature of the third crotonate bridge, while maintaining relatively constant Zn–O–C angles for the syn–syn bridges.

In all eight structures, the terminal quinoline ligands adopt positions that minimize steric interactions with the crotonate bridges (one O–Zn–N–C torsion angle is close to 180°), though intermolecular (crystal packing) forces must also influence the exact positions taken up by these ligands.

Quinoline and crotonate ligands (excluding methyl hydrogen atoms) are all essentially planar. The C=C—C=O fragment of the monatomic bridging crotonates is in the cisoid conformation, as in crotonic acid itself.[15] The crotonate C=C bond lengths do not vary significantly with the different bridging modes and are essentially the same as in crotonic acid and in other crotonate ligands.[2,3h,13j,16]

A further feature of interest in these structures is the presence of six unsaturated centers per molecule. The intramolecular separations of these C=C double bonds from each other are large, but short intermolecular separations may lead to the possibility of solid-state polymerization reactions. The ideas used to understand the polymerization of reactive solid phases have been advanced earlier by Schmidt in his "topochemical rule":[5] this states that, for α,β-unsaturated carboxylic acids, centers capable of undergoing stereospecific polymerization must be oriented parallel to one another and at distances of less than ca. 4 Å. The rule has been confirmed by Foxman more recently, with his work on metal propiolates.[6] In the structures described here, several intermolecular separations of <4 Å occur for unsaturated centers. Only in two of the structures, however, are the pairs of double bonds parallel. In **7**, adjacent molecules displaced along the *a* axis have strictly parallel C(12)–C(13) and C(12′)–C(13′) bonds (related by a center of symmetry) 3.66 Å apart. In **8**, such an arrangement is found for C(22)–C(23), 3.71 Å from the centrosymmetrically related bond in the adjacent molecule displaced along *b*, and also for C(32)–C(33), 3.80 Å from the centrosymmetrically related bond in the adjacent molecule displayed along *a*. Thus, these two structures are potential candidates for polymerization reactions, which may lead to chain and sheet polymers respectively. In none of the other structures are double bonds with separations of <4 Å oriented even approximately parallel to each other; angles between such pairs of bonds range from 42 to 90°. We are currently investigating the properties of analogous species with vinyl acetate as bridging ligands; this should permit greater orientational freedom of the double bonds, which may more easily adopt favorable positions for polymerization reactions.

Acknowledgment. We thank the SERC for financial support, including a research studentship to I.R.L. and a research grant toward crystallographic equipment.

Registry No. **1**, 114155-49-6; **2**, 105428-88-4; **3**, 105428-85-1; **4**, 96518-56-8; **5**, 105428-84-0; **6**, 114183-72-1; **7**, 114155-50-9; **8**, 114155-51-0; $SrZn_2(crot)_6Q_2$, 114155-52-1.

Supplementary Material Available: Tables S1–S24, listing complete bond lengths and angles, thermal parameters, and hydrogen atom parameters for all eight structures, together with molecular structure diagrams (Figures S1–S4), for compounds **2–5** (28 pages); tables of observed and calculated structure factors with esd values (129 pages). Ordering information is given on any current masthead page.

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