Crystal Structure of Anhydrous Barium Methacrylate

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The crystal structure of anhydrous barium methacrylate, $Ba[O_2C{\cdot}C(:CH_2)CH_3]_2$, has been determined by the heavy-atom method from *X*-ray diffractometer data and refined by full-matrix least squares to *R* 0.042 for 1 578 reflections. Crystals are monoclinic, space group $P2_1/c$, $a = 12.162(1)$, $b = 8.017(1)$, $c = 10.373(1)$ Å, $\beta = 102.87(1)°$, $Z = 4$. The structure is comprised of sheets of almost coplanar barium ions bridged as an infinite two-dimensional polymer normal to a^* by the carboxylate groups. Ba–O distances range from 2.766 to 3.030(5) Å about the irregularly eight-co-ordinate cation; in the ligands, the central C–C bond is long [1.498(10), 1.511(9) Å] and one of the ligands is grossly twisted about the bond.

It has been previously reported that barium methacrylate monohydrate when irradiated by γ- and *X*-rays undergoes polymerization;[1,2] subsequent to a structure determination by neutron diffraction (which, incidentally, established that the compound was the mono- rather than the di-hydrate as had been previously re-reported) it was suggested that photodecomposition of the lattice water molecules into H and OH radicals occurs and that these initiate the polymerization process.[3] Independent e.s.r. evidence has shown the presence of $Me_2\dot{C}CO_2^-$ radicals in the lattice of the irradiated complex.[4] In contrast, the anhydrous salt barium methacrylate does not polymerize appreciably when irradiated.[1] In order clearly to define any further differences between the two structures, other than that of the presence of water, a structure determination of the latter has been undertaken by *X*-ray diffraction methods and is reported here.

TABLE 1

Atomic positional ($\times 10^4$; for H, $\times 10^3$; for Ba, $\times 10^5$) and thermal parameters ($\times 10^3$ Å^2), with least-squares estimated standard deviations in parentheses

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba	03 733(3)	46 701(5)	21 326(3)	30.0(3)	10.6(3)	21.4(3)	−0.6(2)	5.0(2)	−0.2(1)
(*a*) Ligand (1)									
O(1)	−0 934(4)	2 987(6)	3 576(4)	38(3)	24(3)	24(2)	2(2)	10(2)	2(2)
O(2)	−0 456(4)	3 189(6)	5 791(4)	39(3)	19(3)	27(2)	5(2)	4(2)	−1(2)
C(1)	−1 161(6)	3 292(8)	4 674(6)	35(3)	10(3)	25(3)	2(3)	6(3)	2(3)
C(2)	−3 017(9)	4 674(13)	3 483(10)	52(6)	49(6)	47(5)	21(5)	7(4)	4(4)
C(3)	−2 334(6)	3 827(10)	4 709(7)	35(4)	26(4)	31(4)	8(3)	3(3)	−2(3)
C(4)	−2 740(7)	3 504(12)	5 772(8)	38(4)	45(5)	39(4)	2(4)	8(4)	−2(4)
H(1) *	−348(8)	382(13)	575(8)						
H(2)	−237(7)	285(12)	648(8)						
H(3)	−326(7)	387(13)	281(9)						
H(4)	−241(9)	545(11)	323(10)						
H(5)	−372(9)	490(12)	381(10)						
(*b*) Ligand (2)									
O(1)	1 350(4)	4 557(6)	0 023(5)	33(3)	22(3)	33(3)	2(2)	9(2)	−3(2)
O(2)	1 625(4)	2 974(7)	−1 609(5)	41(3)	32(3)	35(3)	−7(2)	10(2)	−12(2)
C(1)	1 984(6)	3 747(9)	−0 535(6)	29(3)	20(4)	27(3)	1(3)	6(3)	8(3)
C(2)	3 585(10)	4 553(15)	1 334(11)	53(6)	64(8)	56(6)	−7(5)	−11(5)	−8(5)
C(3)	3 230(6)	3 716(10)	0 098(8)	29(4)	29(4)	41(4)	−2(3)	0(3)	9(3)
C(4)	3 957(9)	2 955(15)	−0 506(12)	39(5)	59(7)	86(7)	7(5)	17(5)	1(6)
H(1)	470(8)	299(12)	−018(8)						
H(2)	375(7)	254(13)	−138(9)						
H(3)	317(7)	385(12)	205(9)						
H(4)	324(9)	541(12)	138(10)						
H(5)	440(8)	419(12)	185(9)						

* U_{iso} for H atoms fixed at 0.05 Å^2.

EXPERIMENTAL

A single prismatic crystal 0.20 × 0.30 × 0.20 mm coated with 'Formvar' to exclude moisture, was used. Unit-cell dimensions were obtained by a least-squares fit of the angular parameters of 15 reflections with 2θ *ca.* 25° centred in the counter aperture of a Syntex $P\bar{1}$ four-circle diffractometer. A unique data set was collected in the range $2\theta < 50°$ by a conventional 2θ—θ scan, yielding 1 715 independent reflections, of which 1 578 with $I > 2\sigma(I)$ were considered observed and used in the structure solution and refinement, after absorption correction.

Crystal Data.—$C_8H_{10}BaO_4$, $M = 307.5$. Monoclinic, $a = 12.162(1)$, $b = 8.017(1)$, $c = 10.373(1)$ Å, $\beta = 102.87(1)°$,

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[1] J. B. Lando and H. Morawetz, *J. Polymer. Sci.*, 1964, **C4**, 789.

[2] N. W. Isaacs, C. H. L. Kennard, and J. H. O'Donnell, *Nature*, 1967, **216**, 1104.

[3] N. W. Isaacs, J. J. vander Zee, K. G. Shields, J. V. Tillack, D. Wheeler, F. H. Moore, and C. H. L. Kennard, *Cryst. Struct. Comm.*, 1972, **1**, 193.

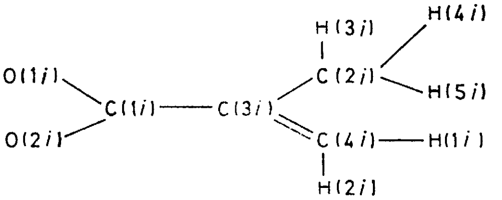
[4] J. H. O'Donnell, B. McGarvey, and H. Morawetz, *J. Amer. Chem. Soc.*, 1964, **86**, 2322.

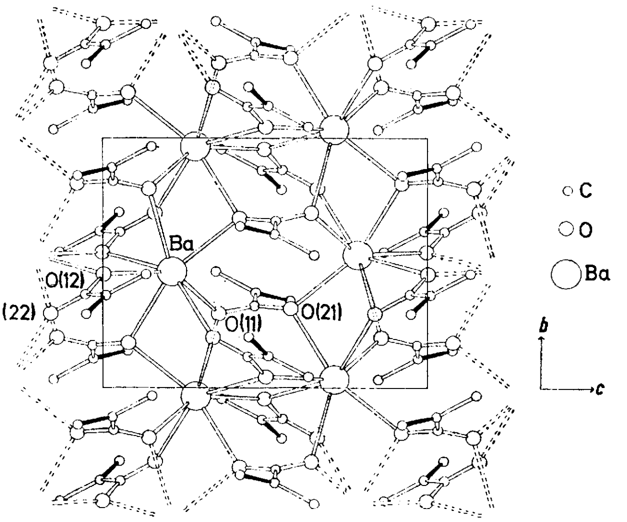
$U = 986.1(1)$ Å^3, $D_m = 2.05_4$, $Z = 4$, $D_c = 2.066$ g cm^{-3}, $F(000) = 584$. Monochromatic Mo-K_α radiation, $\lambda = 0.710\,69$ Å; μ (Mo-K_α) = 41.2 cm^{-1}, neutral atom scattering factors,[5] that for Ba being corrected for anomalous dispersion, ($\Delta f'$, $\Delta f''$).[6] Space group $P2_1/c$ (No. 14, C^5_{2h}).

The structure was solved by the heavy-atom method and refined by least squares, the last few cycles being full matrix; anisotropic thermal parameters were of the form exp-$[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. Hydrogen atoms were located in difference maps and their positional parameters refined, with isotropic thermal parameters fixed at 0.05 Å^2. In the final refinement cycle no parameter shift was $>0.2\sigma$, those for the Ba atoms being considerably less, and refinement terminated at $R = 0.043$ $R'[=(\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}}]$ 0.052. The weighting scheme was of the form $w = (\sigma^2|F_o| + n|F_o|^2)^{-1}$, a value of 7×10^{-4} for n being found appropriate.

Data processing was carried out by use of a local adaptation of the '*X*-Ray '72' system[7] on a CDC 6200 machine at the University of Western Australia.

Ligand numbering follows the scheme given below; *i* is 1 or 2, and denotes the ligand numbering used in the Discussion section and Tables. Structure amplitude tables and hydrogen atom geometries are deposited as Supplementary Publication No. SUP 21489 (8 pp., 1 microfiche).* Results are given in Tables 1—3 and the Figure.





Unit-cell contents projected down *a**; the ethylenic bonds of the vinyl groups are shown as solid bonds

TABLE 2

Interatomic distances (Å) and angles (°), with least-squares estimated standard deviations in parentheses

(*a*) The Ba environment (deviations of the Ba from the corresponding ligand plane are also given in square brackets)

Ba–O(11)	2.766(5) [1.265]	Ba–O(22$^{\text{II}}$)	3.030(5) [1.243]
Ba–O(12)	2.714(6) [1.345]	Ba–O(22$^{\text{III}}$)	2.763(5) [1.694]
Ba–O(21$^{\text{I}}$)	2.739(5) [2.186]	Ba–O(21$^{\text{IV}}$)	2.753(5) [1.415]
Ba–O(12$^{\text{II}}$)	2.772(5) [1.243]	Ba–O(11$^{\text{V}}$)	2.881(5) [2.679]
O(11)–Ba–O(12)	145.9(1)	O(12)–Ba–O(O11$^{\text{V}}$)	69.8(1)
O(11)–Ba–O(21$^{\text{I}}$)	78.8(1)	O(21$^{\text{I}}$)–Ba–O(12$^{\text{II}}$)	112.5(1)
O(11)–Ba–O(12$^{\text{II}}$)	97.1(1)	O(21$^{\text{I}}$)–Ba–O(22$^{\text{II}}$)	68.8(1)
O(11)–Ba–O(22$^{\text{II}}$)	82.3(1)	O(21$^{\text{I}}$)–Ba–O(22$^{\text{III}}$)	100.9(1)
O(11)–Ba–O(22$^{\text{III}}$)	72.1(2)	O(21$^{\text{I}}$)–Ba–O(21$^{\text{IV}}$)	149.8(2)
O(11)–Ba–O(21$^{\text{IV}}$)	71.2(1)	O(21$^{\text{I}}$)–Ba–O(11$^{\text{V}}$)	69.7(1)
O(11)–Ba–O(11$^{\text{V}}$)	141.8(1)	O(12$^{\text{II}}$)–Ba–O(22$^{\text{II}}$)	44.3(1)
O(22$^{\text{III}}$)–Ba–O(21$^{\text{IV}}$)	72.6(1)	O(12$^{\text{II}}$)–Ba–O(22$^{\text{III}}$)	142.2(1)
O(22$^{\text{III}}$)–Ba- O(11$^{\text{V}}$)	133.8(1)	O(12$^{\text{II}}$)–Ba–O(21$^{\text{IV}}$)	69.7(1)
O(12)–Ba–O(21$^{\text{I}}$)	135.2(1)	O(12$^{\text{II}}$)–Ba–O(11$^{\text{V}}$)	76.5(1)
O(12)–Ba–O(12$^{\text{II}}$)	75.2(2)	O(22$^{\text{II}}$)–Ba–O(22$^{\text{III}}$)	154.0(2)
O(12)–Ba–O(22$^{\text{II}}$)	110.7(1)	O(22$^{\text{II}}$)–Ba–O(21$^{\text{IV}}$)	103.8(1)
O(12)–Ba–O(22$^{\text{III}}$)	93.5(2)	O(22$^{\text{II}}$)–Ba–O(11$^{\text{V}}$)	66.7(1)
O(12)–Ba–O(21$^{\text{IV}}$)	75.0(1)	O(21$^{\text{IV}}$)–Ba–O(11$^{\text{V}}$)	136.1(1)
Ba–O(11)–C(11)	131.7(4)	Ba$^{\text{I}}$–O(21)–C(11)	124.8(4)
Ba$^{\text{VI}}$–O(11)–C(11)	121.6(4)	Ba$^{\text{III}}$–O(21)–C(11)	127.4(4)
Ba–O(11)–Ba$^{\text{VI}}$	96.6(2)	Ba$^{\text{III}}$–O(21)–Ba$^{\text{I}}$	100.3(1)
Ba–O(12)–C(12)	144.9(4)	Ba$^{\text{II}}$–O(22)–C(12)	87.7(4)
Ba$^{\text{II}}$–O(12)–C(12)	100.2(4)	Ba$^{\text{IV}}$–O(22)–C(12)	146.9(5)
Ba–O(12)–Ba$^{\text{II}}$	104.8(2)	Ba$^{\text{II}}$–O(22)–Ba$^{\text{IV}}$	93.3(1)

(*b*) Intraligand geometries; values for ligand (2) follow those for ligand (1)

C(1)–O(1)	1.255(8), 1.247(9)	C(3)–C(2)	1.516(11), 1.426(13)
C(1)–O(2)	1.281(7), 1.262(8)	C(3)–C(4)	1.331(12), 1.340(15)
C(1)–C(3)	1.498(10), 1.511(9)		
O(1)–C(1)–O(2)	124.8(6), 122.5(6)	C(2)–C(3)–C(4)	123.1(8), 122.4(8)
C(3)–C(1)–O(1)	118.7(5), 118.0(6)	C(2)–C(3)–C(1)	117.1(7), 117.2(8)
C(3)–C(1)–O(2)	116.5(6), 119.5(7)	C(4)–C(3)–C(1)	119.7(6), 120.4(7)

(*c*) Interligand ethylenic contacts <5 Å

C(31) ··· C(32$^{\text{VI}}$)	4.26(1)	C(31) ··· C(32$^{\text{V}}$)	4.09(1)
C(31) ··· C(41$^{\text{IV}}$)	4.42(1)	C(31) ··· C(42$^{\text{VII}}$)	4.69(1)

Transformations of the asymmetric unit at x,y,z:

I $\bar{x}, 1 - y, 1 - z$
II $\bar{x}, 1 - y, z$
III $x, \frac{1}{2} - y, \frac{1}{2} + z$
IV $x, \frac{1}{2} - y, z - \frac{1}{2}$
V $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$
VI $\bar{x}, y - \frac{1}{2}, \frac{1}{2} - z$
VII $x - 1, \frac{1}{2} - y, \frac{1}{2} + z$

DISCUSSION

As in the structure of the monohydrate, the co-ordination geometry of the barium ion is irregular; in the present case it is comprised of eight oxygen atoms at distances ranging from 2.766(5) to 3.030(5) Å and drawn from a variety of adjacent ligands. This is a consequence of the fact that ligand oxygen atoms act as bridges between adjacent pairs of barium atoms. The overall structure is composed of sheets of barium ions lying close to the plane $x = 0$ and linked by bridging methacrylate ligands each of which is thus associated with three or four different barium ions. The ligand axes are directed approximately parallel to *a*, so that the overall result is a two-dimensional polymer with the hydrocarbon moieties protruding on either side; this is consistent with the observation of a facile cleavage normal to *a** in the crystals, presumably

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* For details, see Notice to Authors No. 7, in *J.C.S. Perkin II*, 1975, Index issue.

[5] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[6] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[7] '*X*-Ray' System, version of June 1972, Technical Report, TR 192, University of Maryland Computer Science Centre.

due to weak van der Waals interactions between adjacent sheets.

TABLE 3

Equations of least-squares planes through the two ligands, in the present structure and the monohydrate, in the form $pX + qY + rZ = S$ where the orthogonal Å frame (X,Y,Z) is defined by the transformation $X = ax + cz \cos \beta$, $Y = by$, $Z = cz \sin \beta$. The numbering convention defined in this paper is used for both structures. Atomic deviations, Δ, are in Å; barium atom deviations are given in Table 2

	$Ba[CO_2{\cdot}C(\vdots CH_2)CH_3]_2$		$Ba[CO_2{\cdot}C(\vdots CH_2)CH_3]_2{\cdot}H_2O$	
Ligand (i)	(1)	(2)	(1)	(2)
10^4p	2 846	2 441	5 833	−2 860
10^4q	9 411	8 345	0 883	3 717
10^4r	1 826	−4 941	−8 080	8 832
s	2.6414	3.3977	0.974	3.227
σ/Å	0.246	0.030	0.06	0.02
χ^2 *	5 126	62.3	19.4	8.52
ΔO(1)	−0.29	0.04	−0.06	0.03
ΔO(2)	0.30	−0.03	0.07	−0.03
ΔC(1)	0.00	−0.01	−0.00	0.00
ΔC(2)	0.26	−0.03	0.00	−0.00
ΔC(3)	0.00	−0.01	−0.06	0.02
ΔC(4)	−0.26	0.04	0.06	−0.02

* Five degrees of freedom.

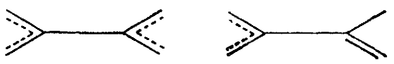
In spite of the lower residual and more extensive data set of the present structure, the full-matrix standard deviations of the light-atom geometry are inferior to those for the monohydrate,[3] presumably a consequence of the greater evenness of the scattering lengths in the neutron determination. Nevertheless, a number of interesting conclusions concerning the intraligand geometries may be drawn in the present case.

As expected, the carboxy-groups both in the present structure and the monohydrate are highly conjugated; no individual C–O distance in either structure differs significantly at the 3σ level from the mean of 1.26_0 Å which in turn is typical of carboxylate groups [8] [although in ligand (1) the sum of the two C–O distances is rather larger than the usual value of 2.51 Å, 2.53_6 *vs.* 2.50_2 for ligand (2)]. The same is true of the O–C–O angle, mean 123.0°. The ethylenic C–C distances in the present structure determination are in agreement with each other [1.33(1) and 1.34(1) Å] and with the usual localised ethylenic-bond value; [9] the significant lengthening of this bond, which is apparent compared with the structure of the monohydrate, may be attributable to the fact that whereas in the latter, it is the carbon nuclei which are located, the X-ray determination of the atomic positions is biased towards the localized electron distribution in the double bond, giving an apparently shorter value. The geometry about the α-carbon in both structures is as expected, the smallest angle being opposed to the ethylenic bond; the mean is 118.0 for the two structures with no single value deviating significantly at the 3σ level.

In both the anhydrous compound and the monohydrate, the central C–C distances have a mean value of 1.50_4 Å; in view of the lack of correction for thermal motion it is clear that there is little, if any, difference between this value and that of a simple C–C bond. This is somewhat surprising; it might reasonably be expected on a molecular orbital picture that the two π systems at either end of the molecule might overlap to give an extended conjugated system throughout the molecule, with the exception of the methyl group. However, whereas in acrolein and butadiene, the central C–C bond is of the order of 1.47 Å, in glyoxal it increases to *ca.* 1.51,[10-12] presumably as a result of withdrawal of π electrons from the bond by virtue of the greater number of highly electronegative atoms at the ends of the conjugated system. In oxalamide, it is further increased to 1.54(1) Å.[13] A more extreme and well studied case is that of the oxalate anion in which the central C–C bond is usually of the order of 1.56—1.57 Å; a theoretical study by Brown and Harcourt [14] has suggested that this phenomenon is due to delocalization of oxygen $2p$ lone-pair electrons into an antibonding σ orbital between the carbon atoms. If the present case can reasonably be regarded as an isoelectronic parallel, then it might be expected that a similar effect would militate against contraction of the central C–C bond due to conjugation. The present phenomenon, in fact, appears to be widespread and largely unrecognized. For example, in aromatic carboxylates and nitro-compounds, the aromatic C–C (carboxylate) and aromatic C–N(nitro) distances differ very little from the usual single-bond distances (Table 4).

TABLE 4

A selection of literature values (chosen as far as possible on the basis of accuracy, simplicity, recency, and representativeness) for the central bond-length (l Å) in systems of types: *



System	Example	
$^-O_2C{-}CO_2^-$	Oxalates [a]	*ca.* 1.56
$O_2N{-}NO_2$	N_2O_4 [b]	1.75_0
$Ph{-}CO_2^-$	Anisate [c]	1.50(2)
$Ph{-}NO_2$	*p*-Nitrotoluene [d]	1.482(7)
Ph–Ph	Diphenyls [e]	*ca.* 1.50
$^-O_2C{-}C(\vdots CH_2){-}$	Methacrylates [f,g]	*ca.* 1.50
	Maleates, fumarates	
$^-O_2C{-}CO{-}$	Pyruvates [h]	1.58(4)

[a] H. Küppers, *Acta Cryst.*, 1973, **B29**, 318, and references therein. [b] D. W. Smith and K. Hedberg, *J. Chem. Phys.*, 1956, **25**, 1282. [c] D. R. McGregor and J. C. Speakman, *J. Chem. Soc.* (*A*), 1968, 2016. [d] J. V. Bane and L. M. Pant, *Acta Cryst.*, 1971, **B27**, 1158. [e] Ref. 8, p. S13. [f] This work, and ref. 3. [g] R. D. Ellison and H. A. Levy, *Acta Cryst.*, 1965, **19**, 520; M. P. Gupta, S. M. Prasad, R. G. Sahu, and B. N. Sahu, *Acta Cryst.*, 1972, **B28**, 135. [h] S. S. Tavole, L. M. Pant, and A. A. Biswas, *Acta Cryst.*, 1961, **14**, 1281.

* [For comparison the 'normal' single-bond (sp^3–sp^3) distances (Å) in the systems concerned are C–C 1.54, N–N, 1.46, C–N 1.48. sp^2-sp^2 single-bond distances appear to be *ca.* 0.01—0.02 Å less].

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[8] *Chem. Soc. Special Publ.*, No. 11, 1958, p. S18.

[9] Ref. 8, p. S14.

[10] J. Paldus and D. A. Ramsay, *Canad. J. Phys.*, 1967, **45**, 1389.

[11] A. R. H. Cole, G. M. Mohay, and G. A. Osborne, *Spectrochim. Acta*, 1967, **A23**, 909.

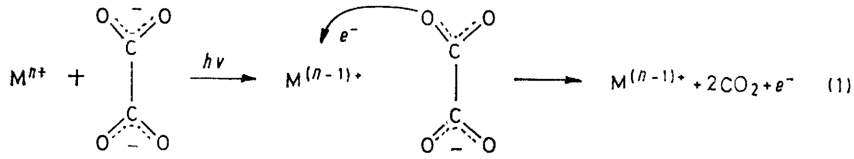
[12] K. Kuchitso, T. Fukuyama, and Y. Morino, *J. Mol. Structure*, 1967—8, **1**, 463.

[13] Ref. 8, p. S13.

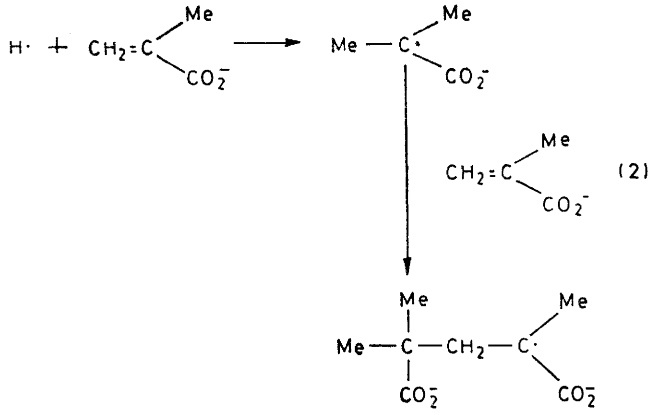
[14] R. D. Brown and R. D. Harcourt, *Austral. J. Chem.*, 1963, **16**, 737.

It appears from crystallographic studies in the foregoing classes of compound that there is little or no barrier to free rotation about the bond connecting the two π bonded systems, since a wide variety of twist angles is found with little or no correlation between the angle of twist and any variation in the bond length, the latter being generally insignificant. In the present case a marked deviation from planarity is found in ligand (1) (Table 3) with no significant change in C–C distance.

In the theory of Brown and Harcourt,[14] the highest occupied orbital in the case of the oxalate is a bonding orbital; in the event of oxidation of the species this bond might be expected to weaken to some extent. Such a proposal is consistent with mechanisms proposed for the decomposition of transition-metal oxalate complexes where typically the process is represented, as in reaction (1).



In the present case, such a mechanism is less likely because of the greater strength of the central bond; by mechanism (1) oxidation might be expected to proceed *via* the OH radical to give CO_2 and $\cdot C(:CH_2)Me$, which would then be expected to polymerize with the possibility of further radical generation by H·. Such a process seems unlikely, however, in view of the fact that the observed reaction products are polymethacrylates and the e.s.r. spectrum is indicative of $Me_2\dot{C}CO_2^-$ and related species; the more probable mechanism is thus initial attack by H· [reaction (2)].



The distances between adjacent ethylenic bonds of the vinyl groups in the present structure are only slightly greater (minimum 4.09 Å) than the corresponding interligand contacts in the monohydrate (minimum 3.85 Å); while in the latter this proximity may be of considerable assistance in permitting polymerization, the anhydrous compound is not so different in this respect as to suggest that the entity responsible for initiating the procedure is other than the H_2O species.

In both structures a wide variation is found in the C(2)–C(3) distances, the differences being highly significant [monohydrate, 1.474(4), 1.437(4) Å; this structure, 1.52(1), 1.43(1) Å]; the distances, with one exception, are less than the expected C(sp^2)–C(sp^3) distance (1.52 Å). In spite of the otherwise generally well-behaved nature of the two structure analyses, we regard these distances with some scepticism as there is no apparent good reason for either the shortening <1.52 Å or the very short values observed in two of the ligands; the diminution seems rather greater than might be expected as a result of lack of correction for thermal motion, although the latter on the peripheral carbon atoms is high.

The environments of the two carboxylate groups are somewhat different: in the case of ligand (2), contacts occur from each oxygen to the same barium (2.763 and 3.030 Å), and may be regarded as chelating it, and, although each oxygen bridges a pair of barium atoms, the contacts are relatively flat, the maximum deviation from the ligand plane being 1.694 Å. By contrast, with ligand (1), each oxygen bridges barium pairs, the four bariums being independent; two of them deviate very considerably from the ligand plane, with deviations of 2.186 and 2.679 Å, and should interact with the oxygen $p\pi$ orbitals more strongly than is the case of the other contacts, correlating with the diminution in CO_2^- π character in ligand (1).

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