π conjugation between the cage and the ring, the poor p-type surface orbital overlap in the fused C–B edge in **3** makes a ring current unlikely. In other words, π conjugation between the ring and the cage through the bridged "hypercarbon" atom does not necessarily lead to aromaticity of the exo ring in **3**. A crucial test might be the observation of an induced upfield shift in the bridge protons of the as yet unknown carborane **15**.

15

Experimental Section

General Remarks. ^{1}H NMR spectra were recorded on a Bruker WM250 spectrometer at 250 MHz in $CDCl_3$, with signals referenced to Me_4Si. ^{11}B NMR spectra were recorded on a Bruker WM250 spectrometer (80 MHz for ^{11}B) in $CDCl_3$, with signals referenced to external boron trifluoride etherate. Chemical shifts were measured on decoupled spectra and multiplicities on coupled spectra. Ultraviolet and visible spectra (UV) were taken with a Hewlett Packard 8450A spectrophotometer. Analytical gas chromatography was performed on a Hewlett-Packard 5890A gas chromatograph with helium as carrier gas, using 2-mm-i.d. stainless-steel columns. GC/MS runs were conducted on a Hewlett-Packard 5992B instrument, using packed 2-mm-i.d. glass columns. Preparative gas chromatography was performed on a Varian A90A gas chromatograph with helium as carrier gas, using a $^1/_4$-in. by 4-ft aluminum column packed with 15% OV-101 on 80/100 Chromosorb W-HP. Mass spectra were obtained on a KRATOS MS 50 RFA high-resolution mass spectrometer. In general, reactions were conducted under an inert atmosphere of argon. All solvents were purified and dried by using standard procedures.

Preparation of 6. To a solution of **4** (1 g, 0.005 mol) in methanol (25 mL) was added *p*-toluenesulfonic acid hydrazide (0.93 g, 0.005 mol). The mixture was refluxed for 12 h. The methanol was removed. The resulting gummy mass was triturated with dry pentane to remove the residual methanol. A yellow sticky solid (1.65 g) was obtained for further reaction.

The crude product (1 g, about 2.5 mmol) was dissolved in freshly distilled dry THF (30 mL). *n*-Butyllithium (3 mL, 2.5 M in hexane; 7.5 mmol) was added by a syringe to the THF solution under argon flow at 0 °C. The solution was refluxed for 8 h and cooled. The reaction mixture was quenched with water, the organic layer was separated, and the aqueous layer was extracted with four 50-mL portions of ether. The combined organic extracts were washed with a saturated sodium bicarbonate solution and dried over magnesium sulfate, and the solvent was removed. The residual material was vacuum-distilled by a Kugelrohr apparatus (150 °C; 0.1 Torr) to yield 200 mg (40%) of slightly yellow oil. This sample (with 95% purity by GC) was suitable for preparation of **3**. Further purification by preparative GC provided analytic sample of **6**, a colorless oil. ^{1}H NMR ($CDCl_3$): δ 6.15 (br m, 1 H), 5.87 (br d, 1 H, J = 13.2 Hz), 3.63 (br s, 1 H), 2.52–2.19 (m, 4 H). ^{11}B NMR ($CDCl_3$): δ −3.7 (d, 2 B), −7.6 (d, 2 B), −9.7 (s, 1 B), −10.8 to −13.2 (d, 3 B), −15.1 (d, 1 B), −16.2 (d, 1 B).

When the reaction was run at room temperature for 3 h, a second isomer **7** was also isolated in about equal yield. ^{1}H NMR ($CDCl_3$): δ 5.88 (br m, 1 H), 5.45 (br m, 1 H), 3.66 (br s, 1 H), 2.80 (AB quartet, 2 H), 1.72 (br m, 2 H).

Preparation of 3. To a solution of **6** (60 mg, 0.31 mmol) in dry benzene (8 mL) was added *N*-bromosuccinimide (60 mg, 0.34 mmol) and a catalytic amount of benzoyl peroxide. The mixture was refluxed under argon flow for 12 h. The benzene was removed. The residual material was dissolved in dimethylformamide (3 mL) and then was heated rapidly to reflux for 0.5 h. The solution was cooled and diluted with 20 mL of pentane and washed with 10 mL of water. The organic layer was extracted with four 20-mL portions of pentane. The combined pentane solutions were washed with water and concentrated. Preparative GC yielded an analytical sample of **3** (7.4 mg, 13%; colorless oil). Precise mass for $B_{10}C_6H_{14}$: calcd, 194.2885; found, 194.2091. UV ($CDCl_3$), λ_{max} (ϵ): 266 nm (4700), 274 nm (4000). ^{1}H NMR ($CDCl_3$): δ 6.82 (br d, 1 H, J = 12.4 Hz), 6.69 (br m, 1 H), 6.57 (ddd, 1 H, J = 9.7, 6.1, 1.2 Hz), 6.21 (d, 1 H, J = 9.8 Hz), 3.94 (br s, 1 H). ^{11}B NMR ($CDCl_3$): δ −3.1 (d, 1 B), −9.7 (s, 1 B; d, 2 B), −12.9 (d, 2 B), −15.0 (d, 2 B), −17.0 (d, 1 B), −18.5 (d, 1 B).

Acknowledgment. Support by the National Science Foundation through Grants CHE 83-18345 and 86-17590 is gratefully acknowledged. We thank the Department of Army for a generous supply of decaborane. Our thanks also go to Mary W. Baum for her expert help with the NMR spectroscopy and to Dr. J. E. Jackson for helpful comments upon the manuscript.

Registry No. **3**, 113860-56-3; **4**, 105335-31-7; **5**, 113860-54-1; **6**, 113860-55-2; **7**, 113860-57-4.

Contribution from the Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071

Calcium Binding to γ-Carboxyglutamate and β-Carboxyaspartate Residues: Structure of a Calcium Complex of Benzylmalonic Acid

Yoshinobu Yokomori[1] and Derek J. Hodgson*

Received October 23, 1987

The presence of the modified amino acid residues γ-carboxyglutamic (Gla) and β-carboxyaspartic (Asa) acids in a variety of proteins is well documented,[2-6] and it is well established that Gla residues are implicated in calcium binding in both blood and bone proteins.[7] Since several authors have suggested that a principal role for Gla is in the discrimination between calcium and magnesium,[8] we and others have been investigating the structures of a variety of model complexes designed to probe the modes of binding of calcium, magnesium, and related metals to Gla and/or Asa.[9-12]

The bonding patterns of relevant metals to carboxylate moieties have been reviewed by Einspahr and Bugg,[13] who note that for a monocarboxylate functionality (as in Glu or Asp) a metal can bind in either a unidentate or a bidentate fashion. The unidentate mode involves metal coordination to a single oxygen atom, while the bidentate form involves metal ion binding to both oxygen atoms of a single carboxylate group. In a dicarboxylate like Gla or Asa, however, a third binding mode is possible; in this mode the metal again binds to two oxygen atoms, but the two oxygen atoms are from different carboxylates. This mode of binding is usually referred to as the "malonate" mode since it is available only to a dicarboxylate like malonate (or Gla or Asa).

No definitive crystallographic study of a metal complex of either Asa or Gla has been published, but we and others have modeled these residues by the use of α-substituted malonate derivatives.[9-12] Thus, in recent years the modes of binding of calcium to α-ethylmalonate[9] and α-methylmalonate[10] have been reported, as have the interactions between magnesium and α-methylmalonate[10] and those between barium and several substituted malonates.[12]

(1) Present and permanent address: Department of Chemistry, The National Defense Academy, Hashirimizu, Yokosuka 239, Japan.
(2) Magnusson, S.; Sottrup-Jensen, L.; Peterson, T. E.; Morris, H. R.; Dell, A. *FEBS Lett.* **1974**, *44*, 189-193.
(3) Stenflo, J.; Fernlund, P.; Egan, W.; Roepstorff, P. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 2730-2733.
(4) Prendergast, F. G.; Mann, K. G. *J. Biol. Chem.* **1977**, *252*, 840-850.
(5) Lian, J. B.; Hauschka, P. V.; Gallop, P. M. *Fed. Proc., Fed. Am. Soc. Exp. Biol.* **1978**, *37*, 2615-2620.
(6) Christy, M. R.; Barkley, R. M.; Koch, T. H.; Van Buskirk, J. J.; Kirsch, W. M. *J. Am. Chem. Soc.* **1981**, *103*, 3935-3937. Christy, M. R.; Koch, T. H. *J. Am. Chem. Soc.* **1982**, *104*, 1771-1772.
(7) Jackson, C. M.; Nemerson, Y. *Annu. Rev. Biochem.* **1980**, *49*, 765-811.
(8) Williams, R. J. In *Calcium Binding Proteins and Calcium Function*; Wasserman, R. H., et al., Eds.; Elsevier: New York, 1977; pp 1-12.
(9) Zell, A.; Einspahr, H.; Bugg, C. E. *Biochemistry* **1985**, *24*, 533-537.
(10) Curry, M. E.; Eggleston, D. S.; Hodgson, D. J. *J. Am. Chem. Soc.* **1985**, *107*, 8234-8238.
(11) Eggleston, D. S.; private communication.
(12) Yokomori, Y.; Flaherty, K. A.; Hodgson, D. J. *Inorg. Chem.*, in press.
(13) Einspahr, H.; Bugg, C. E. *Acta Crystallogr., Sect., B: Struct. Crystallogr. Cryst. Chem.* **1981**, *B37*, 1044-1052.

0020-1669/88/1327-2008$01.50/0

Table I. Crystal and Intensity Measurement Data

mol formula	$Ca(C_{10}H_9O_4)_2$
M_r	426.44
crystal dimens, mm	0.20 × 0.05 × 1.3
D_{obsd}, g cm^{-3}	1.40 (2)
Z	4
D_{calcd}, g cm^{-3}	1.388
a, Å	17.326 (5)
b, Å	5.477 (3)
c, Å	23.133 (7)
β, deg	111.65 (2)
V, Å^3	2040 (3)
$F(000)$	888
μ(Mo Kα), cm^{-1}	3.452
space group	$P2_1/n$
no. of data collcd	2895
no. of data used in refinement	1630
	$I > 3\sigma(I)$
octants collcd	$\pm h,+k,+l$
max value of 2θ, deg	45
temp, °C	20
no. of variables	262
R	0.076
wR	0.089
$(\Delta/\sigma)_{max}$	0.01
error in observn of unit weight	4.016
max peak in DF, e/Å^{-3}	0.191

Table II. Atomic Positional Parameters for $[Ca(bzmalH)_2]$

atom	x	y	z
Ca	0.1015 (1)	0.1876 (4)	0.5687 (1)
O(1a)	0.1695 (3)	−0.1434 (9)	0.7512 (2)
O(2a)	0.0876 (3)	0.1295 (10)	0.6868 (2)
O(3a)	0.2721 (3)	0.3327 (10)	0.8910 (2)
O(4a)	0.2599 (3)	−0.0416 (10)	0.8542 (2)
O(1b)	0.0816 (3)	−0.1019 (10)	0.4667 (2)
O(2b)	0.1674 (3)	−0.4121 (10)	0.5057 (2)
O(3b)	0.0160 (3)	−0.7580 (10)	0.3441 (2)
O(4b)	−0.0122 (3)	−0.6271 (10)	0.4245 (2)
C(1a)	0.1402 (4)	0.074 (1)	0.7389 (3)
C(2a)	0.1707 (4)	0.268 (1)	0.7888 (3)
C(3a)	0.2392 (4)	0.185 (1)	0.8493 (3)
C(4a)	0.0977 (5)	0.375 (1)	0.8045 (3)
C(5a)	0.0583 (4)	0.198 (2)	0.8344 (3)
C(6a)	0.0818 (5)	0.206 (2)	0.8986 (4)
C(7a)	0.0442 (6)	0.039 (3)	0.9275 (4)
C(8a)	−0.0113 (6)	−0.132 (2)	0.8946 (5)
C(9a)	−0.0323 (5)	−0.135 (2)	0.8318 (5)
C(10a)	0.0019 (5)	0.025 (2)	0.8018 (4)
C(1b)	0.1131 (4)	−0.292 (1)	0.4601 (3)
C(2b)	0.0903 (4)	−0.415 (1)	0.3972 (3)
C(3b)	0.0266 (4)	−0.611 (1)	0.3907 (3)
C(4b)	0.1670 (5)	−0.503 (2)	0.3845 (4)
C(5b)	0.2193 (4)	−0.294 (2)	0.3776 (3)
C(6b)	0.2820 (5)	−0.193 (2)	0.4274 (4)
C(7b)	0.3278 (5)	0.005 (2)	0.4174 (5)
C(8b)	0.3109 (5)	0.098 (2)	0.3605 (5)
C(9b)	0.2503 (6)	−0.003 (2)	0.3116 (5)
C(10b)	0.2052 (5)	−0.193 (2)	0.3193 (4)

We here report the structure of the 1:2 complex of calcium and hydrogen α-benzylmalonate, $Ca(bzmalH)_2$.

Experimental Section

Colorless, needle-shaped crystals of the complex were grown at room temperature by slow evaporation of a filtered aqueous solution of 1:1 molar quantities of benzylmalonic acid and calcium bromide; the pH of the solution was adjusted to 3.0 by addition of potassium hydroxide. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer equipped with a molybdenum tube [$\lambda(K\alpha_1)$ = 0.709 26 Å, $\lambda(K\alpha_2)$ = 0.713 54 Å]. Data were corrected for Lorentz–polarization effects but not for absorption. Additional details of our data collection and reduction procedures have been presented elsewhere,[14,15] and data specific to the present experiment are tabulated in Table I.

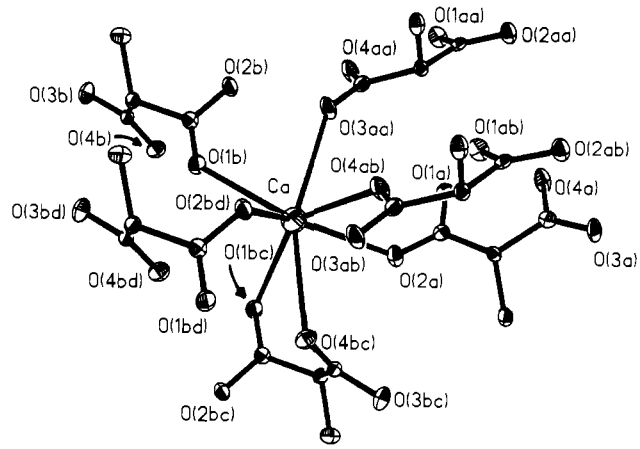


Figure 1. Coordination around a single calcium ion in $[Ca(bzmalH)_2]$. Phenyl rings and hydrogen atoms have been omitted for clarity. Carbon atoms are unlabelled, the apparently terminal carbon atoms being the benzylic atoms C(4) to which the phenyl rings are attached. Thermal ellipsoids in this figure and all subsequent figures are drawn at the 25% probability level. Symmetry relationships are as given in Table III.

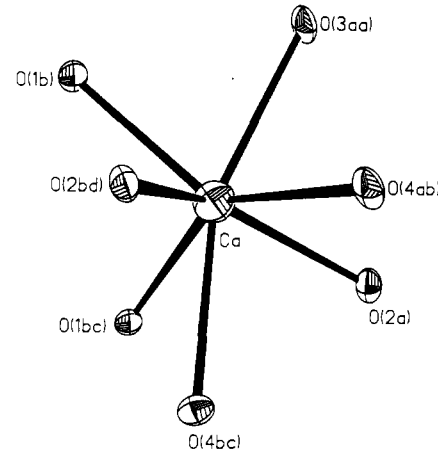


Figure 2. Inner coordination sphere around a single calcium ion in $[Ca(bzmalH)_2]$.

The structure was determined by using MULTAN80.[16] The hydrogen atoms associated with the protonated carboxylate moieties were located in a difference Fourier map. The hydrogen atom associated with molecule B is disordered and is associated with O(2b) and O(3b). The situation in molecule A is less clear; there is no evidence in the difference Fourier for any disorder, the only proton position being bonded to O(4a). Examination of the C–O bond lengths, however, suggests that O(1a) may also be partially protonated. All other hydrogen atoms were placed in calculated portions, and non-hydrogen atoms were refined anisotropically while hydrogen atom parameters were not refined. Atomic scattering factors are taken from ref 17, hydrogen scattering factors from ref 18. The atomic positional parameters are presented in Table II; lists of hydrogen atom parameters, anisotropic thermal parameters (U_{ij}), and observed and calculated structure amplitudes are available as supplementary material.

Discussion

The structure consists of Ca^{2+} cations coordinated to two independent hydrogen benzylmalonate ions (A and B). As is invariably the case for calcium and barium complexes of malonate derivatives,[9,10,12,19–21] the structure is polymeric. A view of the

(14) Graves, B. J.; Hodgson, D. J. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *B38*, 135–139.
(15) Eggleston, D. S.; Hodgson, D. J. *Int. J. Pept. Protein Res.* **1985**, *25*, 242–253.
(16) Main, P. Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declerq, J. P.; Woolfson, M. M. "MULTAN80, A System of Computer Programmes for the Automatic Solution of Crystal Structures from X-ray Diffraction Data"; University of York, England, and University of Louvain, Belguim, 1980.
(17) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.
(18) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–3187.

Table III. Bond Lengths (Å) in $[Ca(bzmalH)_2]$[a]

Ca–O(2a)	2.848 (2)	C(4a)–C(5a)	1.497 (5)
Ca–O(3aa)	2.818 (3)	C(5a)–C(6a)	1.389 (5)
Ca–O(4ab)	2.827 (3)	C(5a)–C(10a)	1.367 (5)
Ca–O(1b)	2.755 (3)	C(6a)–C(7a)	1.423 (7)
Ca–O(1bc)	3.006 (3)	C(7a)–C(8a)	1.357 (8)
Ca–O(2bd)	3.076 (3)	C(8a)–C(9a)	1.361 (8)
Ca–O(4bc)	2.897 (3)	C(9a)–C(10a)	1.382 (7)
O(1a)–C(1a)	1.283 (4)	C(1b)–C(2b)	1.518 (5)
O(2a)–C(1a)	1.251 (4)	C(2b)–C(3b)	1.505 (5)
O(3a)–C(3a)	1.226 (4)	C(2b)–C(4b)	1.540 (5)
O(4a)–C(3a)	1.285 (4)	C(4b)–C(5b)	1.505 (6)
O(1b)–C(1b)	1.211 (4)	C(5b)–C(6b)	1.375 (6)
O(2b)–C(1b)	1.303 (4)	C(5b)–C(10b)	1.392 (6)
O(3b)–C(3b)	1.303 (4)	C(6b)–C(7b)	1.409 (8)
O(4b)–C(3b)	1.208 (4)	C(7b)–C(8b)	1.340 (9)
C(1a)–C(2a)	1.515 (5)	C(8b)–C(9b)	1.345 (9)
C(2a)–C(3a)	1.533 (5)	C(9b)–C(10b)	1.352 (8)
C(2a)–C(4a)	1.555 (5)		

[a] The second lower case letter associated with some of the oxygen atoms indicates their symmety relationship to the parent atom: a = 0.5 − x, y − 0.5, 1.5 − z; b = 0.5 − x, y + 0.5, 1.5 − z; c = −x, −y, 1 − z; d = x, y + 1, z.

Table IV. Bond Angles (deg) in $[Ca(bzmalH)_2]$[a]

O(2a)–Ca–O(3aa)	86.32 (9)	O(4a)–C(3a)–C(2a)	117.6 (3)
O(2a)–Ca–O(4ab)	78.79 (9)	C(2a)–C(4a)–C(5a)	114.3 (3)
O(2a)–Ca–O(1b)	136.77 (10)	C(4a)–C(5a)–C(6a)	118.1 (4)
O(2a)–Ca–O(1bc)	77.87 (8)	C(4a)–C(5a)–C(10a)	123.2 (3)
O(2a)–Ca–O(2bd)	135.34 (9)	C(6a)–C(5a)–C(10a)	118.7 (4)
O(2a)–Ca–O(4bc)	78.73 (9)	C(5a)–C(6a)–C(7a)	118.5 (5)
O(3aa)–Ca–O(4ab)	77.13 (9)	C(6a)–C(7a)–C(8a)	122.1 (5)
O(3aa)–Ca–O(1b)	73.90 (9)	C(7a)–C(8a)–C(9a)	117.5 (5)
O(3aa)–Ca–O(1bc)	126.57 (9)	C(8a)–C(9a)–C(10a)	122.2 (5)
O(3aa)–Ca–O(2bd)	105.62 (9)	C(5a)–C(10a)–C(9a)	120.9 (4)
O(3aa)–Ca–O(4bc)	157.02 (9)	O(1b)–C(1b)–O(2b)	123.8 (3)
O(4ab)–Ca–O(1b)	130.60 (10)	O(1b)–C(1b)–C(2b)	122.2 (5)
O(4ab)–Ca–O(1bc)	145.02 (9)	O(2b)–C(1b)–C(2b)	113.9 (3)
O(4ab)–Ca–O(2bd)	63.08 (8)	C(1b)–C(2b)–C(3b)	109.6 (3)
O(4ab)–Ca–O(4bc)	82.87 (9)	C(1b)–C(2b)–C(4b)	112.6 (3)
O(1b)–Ca–O(1bc)	83.75 (10)	C(3b)–C(2b)–C(4b)	114.3 (3)
O(1b)–Ca–O(2bd)	87.49 (9)	O(3b)–C(3b)–O(4b)	123.3 (3)
O(1b)–Ca–O(4bc)	128.64 (9)	O(3b)–C(3b)–C(2b)	113.4 (3)
O(1bc)–Ca–O(2bd)	121.42 (8)	O(4b)–C(3b)–C(2b)	123.3 (3)
O(1bc)–Ca–O(4bc)	67.27 (8)	C(2b)–C(4b)–C(5b)	112.4 (3)
O(2bd)–Ca–O(4bc)	74.48 (8)	C(4b)–C(5b)–C(6b)	122.5 (4)
O(1a)–C(1a)–O(2a)	121.9 (3)	C(4b)–C(5b)–C(10b)	120.4 (4)
O(1a)–C(1a)–C(2a)	118.9 (3)	C(6b)–C(5b)–C(10b)	117.1 (4)
O(2a)–C(1a)–C(2a)	119.2 (3)	C(5b)–C(6b)–C(7b)	119.2 (5)
C(1a)–C(2a)–C(3a)	115.0 (3)	C(6b)–C(7b)–C(8b)	121.5 (6)
C(1a)–C(2a)–C(4a)	111.1 (3)	C(7b)–C(8b)–C(9b)	119.2 (7)
C(3a)–C(2a)–C(4a)	108.7 (3)	C(8b)–C(9b)–C(10b)	121.1 (6)
O(3a)–C(3a)–O(4a)	122.3 (3)	C(5b)–C(10b)–C(9b)	121.8 (5)
O(3a)–C(3a)–C(2a)	120.1 (3)		

[a] Symmetry relationships are as given in Table III.

coordination around a single calcium ion is shown in Figure 1; the inner coordination sphere is shown in Figure 2. The significant bond lengths and angles in the complex are collected in Tables III and IV, respectively.

As is shown in Figures 1 and 2, the calcium ion in the complex is seven-coordinate, but does not appear to approximate well to any of the idealized polyhedra.[22] Seven-coordinate calcium ions are also found in one form of calcium malonate dihydrate,[21] in one ion in calcium methylmalonate,[10] and in calcium ethylmalonate,[9] but the binding patterns in the present complex are different from those observed in these related species. In the

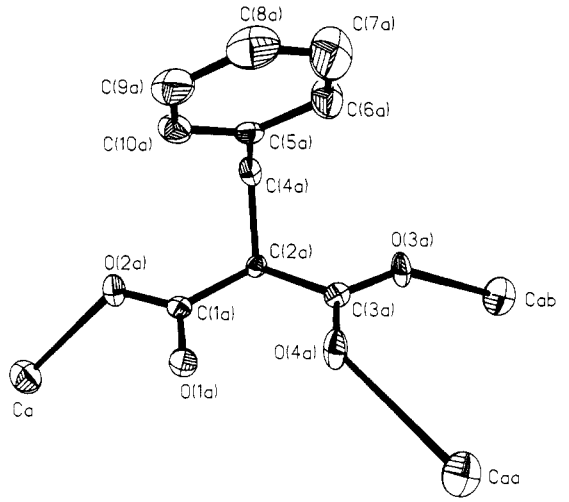


Figure 3. Binding of benzylmalonate ion A in $[Ca(bzmalH)_2]$. Symmetry relationships are as given in Table III.

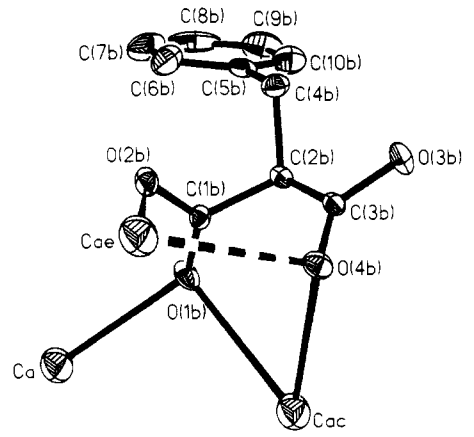


Figure 4. Binding of benzylmalonate ion B in $[Ca(bzmalH)_2]$. Symmetry relationships are as given in Table III, plus e = x, y − 1, z. The dashed line represents the weak interaction (3.344 Å) between O(4b) and Ca(e).

$Ca(bzmalH)_2$ complex, the calcium center forms one malonate interaction and five unidentate bonds; there are no examples of the bidentate mode of binding in this structure. The structure is entirely different from that found in the barium analogue, $Ba(bzmalH)_2 \cdot H_2O$, in which the barium atom is 10-coordinate and both malonate and bidentate binding are observed.[12]

The Ca–O distances in the structure are in the range 2.755 (3)–3.076(3) Å and are much longer than the bond lengths normally associated with calcium carboxylates.[13] Hence, it may be concluded that the binding in the present complex is much weaker than that in related species. In addition to these seven Ca–O bonds, there is an additional Ca–O separation of 3.344 (3) Å. The bond angle of 109.6 (3)° at C(2b) is entirely normal and indicates that the six-membered ring formed by the malonate binding at O(1b) and O(4b) is free from internal strain. Since significant deviations from tetrahedral geomety at C(2) frequently accompany malonate mode binding,[23-26] this absence of any strain may be attributable to the weakness of the interaction.

The binding of the two independent malonate ions is shown in Figures 3 and 4. The weak interaction of 3.344 (3) Å between O(4b) and Ca(e) is shown as the dashed bond in Figure 4. As

(19) Briggman, B.; Oskarsson, A. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 1900–1906.
(20) Karipides, A.; Ault, J.; Reed, A. T. *Inorg. Chem.* **1977**, *16*, 3299–3302; Marsh, R. E.; Schomaker, V. *Inorg. Chem.* **1979**, *18*, 2331–2336.
(21) Albertsson, J.; Oskarsson, A.; Svensson, C. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 2737–2743.
(22) Beauchamp, A. L.; Belanger-Gariepy, F.; Arabi, S. *Inorg. Chem.* **1985**, *24*, 1860–1863.
(23) Briggman, B.; Oskarsson, A. *Acta. Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 3357–3359.
(24) Soriano-Garcia, M.; Rao, S. N. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, *C39*, 850–852.
(25) Duc, G.; Faure, R.; Loiseleur, H. *Acta. Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 2115–2118.
(26) Pajunen, A.; Pajunen, S. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 2425–2428.

can be seen in these figures, both malonate moieties bind to three different calcium ions. The geometries of the hydrogen benzylmalonate ions are comparable with those of the free acid[27] and those found in both the barium complex[12] and the methylguanidinium salt[28] of this ion. As is usually the case in substituted malonate structures, in molecule B the two carboxyl groups are nearly orthogonal. The dihedral angle between the planes O(1b)–C(1b)–O(2b) and O(3b)–C(3b)–O(4b) is 92°, the group at C(1b) being 14° out of the central atom plane [C(1b)–C(2b)–C(3b)] while that at C(3b) forms an angle of 82° with this plane. In molecule A, however, the two carboxyl groups are almost coplanar, the dihedral angle between them being only 5°. This result is very surprising, but it is noteworthy that in the methylguanidinium salt of the related hydrogen ethylmalonate ion, the corresponding dihedral angle of 21° is also relatively small.[28] The present value of 5° is, however, the smallest such angle reported to date. The approximate coplanarity of the carboxyl groups of molecule A is clearly seen in both Figures 1 and 3.

The present structural study, in conjunction with previous related work, serves to underscore our contention that a major reason for the presence of Gla rather than Glu in calcium-binding proteins is the ability of Gla to provide extra carboxylate moieties that are used to form extensive polymeric arrays linking several calcium centers to each other. This aggregation, along with the extraordinary flexibility of calcium in adapting to a wide variety of binding sites, clearly allows the protein to discriminate between calcium and magnesium since the stereochemical requirements of magnesium are very rigid[10] and this precludes the formation of polymeric networks involving magnesium.

Registry No. $Ca(bzmalH)_2$, 114058-41-2.

Supplementary Material Available: Tables of hydrogen atom parameters and anisotropic thermal parameters (U_{ij}) (3 pages); a table of observed and calculated structure amplitudes (12 pages). Ordering information is given on any current masthead page.

(27) Lepore, U.; Lepore, G. C.; Ganis, P. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1975**, *B31*, 2874–2876.
(28) Yokomori, Y.; Hodgson, D. J. *Int. J. Pept. Protein Res.* **1988**, *31*, 289–298.

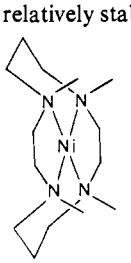
Contribution from Ames Laboratory
and the Department of Chemistry,
Iowa State University, Ames, Iowa 50011

Cyclopentane Formation in the Reduction of 1,5-Dihaloalkanes with a Nickel(I) Macrocycle

M. S. Ram, Andreja Bakac,* and James H. Espenson*

Received November 4, 1987

Alkyl halides are known[1,2] to react with the nickel(I) macrocycle[3] $Ni(tmc)^+$ to yield a relatively stable organometallic entity.



R, S, R, S-[$Ni(tmc)^+$]

With 1,5-dihalopentanes, $X(CH_2)_5X$ (X = Br, I), however, cyclopentane is produced in nearly quantitative yield. We report here how this rare[4–7] transformation occurs, since mechanistic precedents are few indeed, and synthetic applications of this easily accessible[8] nickel reagent may be considerable.

Table I. Rate Constants[a] for Reactions of Bromoalkyl Compounds with $Ni(tmc)^+$

dihalide	$10^{-3}k/M^{-1}\ s^{-1}$	monohalide	$10^{-3}K/M^{-1}\ s^{-1}$
$Br(CH_2)_4Br$	4.5[b]	$(tmc)Ni(CH_2)_4Br^+$	1.6
$Br(CH_2)_5Br$	4.2[b]	$(tmc)Ni(CH_2)_5Br^+$	3.2
$Br(CH_2)_4Cl$	3.6	1-bromobutane	1.5
		1-bromopentane	1.0

[a] 25.0 °C, 0.020 M NaOH, μ = 0.10 M. [b] Statistically corrected; values are $k/2$.

The reaction between $Ni(tmc)^+$ and $X(CH_2)_5X$ (eq 1) actually occurs in steps. Initially, the reaction proceeds by the accepted[1,2]

$$2Ni(tmc)^+ + X(CH_2)_5X \rightarrow 2XNi(tmc)^+ + c\text{-}C_5H_{10} \quad (1)$$

atom-transfer (i.e., inner-sphere electron-transfer) mechanism, first to yield $X(CH_2)_4CH_2^\bullet$ and thence (when this radical reacts with a second $Ni(tmc)^+$) the organometallic complex $(tmc)Ni(CH_2)_4CH_2X^+$. Cyclopentane is formed by the $Ni(tmc)^+$-catalyzed decomposition of $(tmc)Ni(CH_2)_5X^+$ (eq 2).

$$(tmc)Ni(CH_2)_5X^+ \xrightarrow{Ni(tmc)^+} XNi(tmc)^+ + c\text{-}C_5H_{10} \quad (2)$$

The following observations pertain to the reaction of 1,5-dibromopentane and related compounds: (1) Spectrophotometric titrations established that $Ni(tmc)^+$ and $Br(CH_2)_5Br$ react in a 2:1 ratio, the same as when monohaloalkanes react with $Ni(tmc)^+$. (2) Cyclopentane is the major product (80–98% by vapor-phase chromatography), accompanied by minor (2–20%) but variable amounts of 1-bromopentane, 5-bromo-1-pentene, and *n*-pentane, depending on the reaction conditions. The highest yields of cyclopentane are observed when excess $Ni(tmc)^+$ is used. (3) 1-Bromopentane and 5-bromo-1-pentene are completely absent when the nickel(I) reagent is used in excess. (4) With even the slightest excess of $Ni(tmc)^+$, the characteristic absorption spectrum of an organonickel complex was not seen. (5) With excess 1,5-dibromopentane, however, the visible absorption spectrum of an organonickel complex[6,7] was observed. This intermediate shows an absorption maximum at 405 nm ($\epsilon \sim 2 \times 10^3\ M^{-1}\ cm^{-1}$). It was identified as $(tmc)Ni(CH_2)_5Br^+$, because it hydrolyzes[9] to 1-bromopentane upon standing or when H_3O^+ is added. The unimolecular rate constant for hydrolysis is $1.7 \times 10^{-2}\ s^{-1}$, which lies in the same narrow range found for almost all other $RNi(tmc)^+$ complexes.[9] (6) Addition of $Ni(tmc)^+$ to the organometallic intermediate causes its "immediate" decomposition, accompanied by cyclopentane formation. This reaction is catalytic, requiring but a trace of excess $Ni(tmc)^+$. (7) The rate constants for the reaction of $Ni(tmc)^+$ with $Br(CH_2)_4Br$, $Br(CH_2)_5Br$, $Br(CH_2)_4Cl$, $Br(CH_2)_4OH$, $Br(CH_2)_4OTs$, and $(tmc)Ni(CH_2)_4Br^+$ are all very similar and are close to those for primary monobromoalkanes, as the values[10] given in Table I show. This provides additional evidence upon which we base our conclusion that the initial reaction of $Ni(tmc)^+$ with $X(CH_2)_5X$, like that

(1) Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1986**, *108*, 713.
(2) Ram, M. S.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1986**, *25*, 3267.
(3) The complex[4] depicted is (1*R*,4*S*,8*R*,11*S*)-(1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)nickel(I), which we abbreviate as *R,S,R,S*-[$Ni(tmc)^+$] or, when not confusing, simply as $Ni(tmc)^+$.
(4) Radical-induced reactions of 1,5-diiodopentane with peroxides form cyclopentane in only 4–8% yields: Kaplan, L. *J. Am. Chem. Soc.* **1967**, *89*, 4059.
(5) An unsuccessful attempt to observed ϵ-elimination has been reported: Trahanovsky, W. S.; Doyle, M. P. *J. Org. Chem.* **1967**, *32*, 146.
(6) Cyclopentane results in reactions of 1,5-dihaloalkanes with sodium naphthalenide (Garst, J. F.; Barbas, J. T. *J. Am Chem. Soc.* **1974**, *96*, 3329) and with *tert*-butyllithium (Bailey, W. F.; Gagnier, R. P.; Patricia, J. J. *J. Org. Chem.* **1984**, *49*, 2098).
(7) The reaction of $Co(CN)_5^{3-}$ with 1,5-diiodopentane yields 1-pentane (94%) and *cis*-2-pentene (6%); no cyclopentane is formed: Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1969**, *91*, 582.
(8) Barefield, E. K.; Wagner, F. *Inorg. Chem.* **1973**, *12*, 2435.
(9) Ram, M. S.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1986**, *25*, 4115.
(10) At 25.0 °C and 0.010 M NaOH. Values cited for the dibromides are $k/2$, corrected statistically for comparison purposes.

0020-1669/88/1327-2011$01.50/0