Figure 2. ¹H-decoupled ³¹P NMR spectrum of [Mo₃Pt₂S₄Cl₄(PEt₃)₆]· 0.5THF in 25% toluene-*d₈* (109.25 MHz; reference, 85% H₃PO₄). Numbers in the figure are observed coupling constants in hertz.

reported for several carbonyl cluster complexes.[6] The two μ_3-sulfido ligands S(1) and S(2) capping the Mo₂Pt triangle are on the same side of the Mo₃Pt₂ plane while S(3) capping the Mo₃ is on the other. The fourth sulfido ligand, S(4), is bridging the unique unshared edge of the Mo₃ triangle. Both of the platinum atoms are slightly shifted (0.12 Å) from the plane determined by the three molybdenum atoms to the side where S(3) exists. All of the molybdenum atoms have five coordinating ligands ("Cl₂S₃" for Mo(1), and "ClS₃P" for Mo(2) and Mo(3)). The platinum atoms have a μ_3-sulfido ligand and two terminal phosphine ligands.

The configuration of the starting Mo₃ complex is kept in the central part of **1**. Three μ_2-sulfido ligands in the Mo₃ complex correspond to S(1), S(2), and S(4) in **1**. In both the starting Mo₃ complex and **1**, all phosphine ligands bonded to the molybdenum atoms are approximately trans to the μ_3-sulfido ligand on the Mo₃ triangle.

The Mo–Mo distances are in the range 2.68–2.73 Å, which shows bonding interaction between the molybdenum atoms (calculated bond order: 0.73).[7] On the other hand, the Mo–Pt distances (2.86–2.98 Å) indicate that the Mo–Pt bonds are weak (calculated bond order: 0.29). The Mo₃ triangle in **1** is not regular: the distance Mo(2)–Mo(3) is longer by 0.04–0.05 Å than the distances Mo(1)–Mo(2) and Mo(1)–Mo(3). Similar deformation of the Mo₃ triangle has been observed in [Mo₃Ni₂S₄Cl₄(PEt₃)₅] where the basal Mo–Mo distance is longer by 0.04–0.06 Å than other Mo–Mo distances.[1] These deformations may be attributed to the larger electron donation from the two d¹⁰ metal atoms to the central molybdenum atom than from the other two molybdenum atoms.

The number of the cluster valence electrons in this cluster complex is 68, which is 6 electrons fewer than that of the square-pyramidal nickel derivative that has five phosphine ligands.[1] The small number is due to the bonding mode of the chloro ligands,

which are all terminal, and may be ascribed to the general trend in the cluster compounds that platinum derivatives have fewer valence electrons than would be expected on the basis of the polyhedral skeletal electron pair theory.[8]

NMR Spectra. The ³¹P NMR spectrum of **1** measured in 25% toluene-*d₈* is shown in Figure 2. There are three resonances at 15.1 (A), 20.3 (B), and 53.2 ppm (C). This is consistent with the X-ray structure showing three pairs of equivalent phosphines {P(1),P(3)}, {P(2),P(4)}, and {P(5),P(6)}. Peak A, which shows no coupling with ¹⁹⁵Pt, is assigned to the triethylphosphines coordinated to the molybdenum atoms, {P(5),P(6)}. Peaks B and C accompany satellite peaks due to ³¹P–¹⁹⁵Pt couplings of 3092 and 4414 Hz, respectively, and they are assigned to the phosphorus atoms bonded with the platinum atoms.[9] The splittings of the main peaks originate from ³¹P–³¹P couplings; $J(AB)$ = 4.0 Hz, $J(AC)$ = 10.0 Hz, and $J(BC)$ = 23.0 Hz. The fine couplings between the equivalent nuclei further modify the spectrum since the six phosphorus atoms constitute an AA′MM′XX′ spin system. They were, however, too small to be determined unequivocally.

Supplementary Material Available: Tables of full crystallographic details, anisotropic thermal parameters, hydrogen atom parameters, and complete bond distances and angles (7 pages); a table of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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(9) Further unambiguous assignments of peaks B and C are not possible at present. We can, however, tentatively assign peak B with a smaller coupling with ¹⁹⁵Pt (J_{P-Pt} = 3092 Hz) to {P(1),P(3)} which has a longer P–Pt bond distance (2.33 Å on the average), and peak C (J_{P-Pt} = 4414 Hz) to {P(2),P(4)}, (P–Pt distance: 2.26 Å on the average).

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

Barium Binding to Carboxylate Residues: Synthesis and Structure of a New Form of Barium Malonate

Derek J. Hodgson* and R. Owen Asplund

It has been suggested that the presence of the modified amino acid residue γ-carboxyglutamate (Gla) in place of glutamate (Glu) in prothrombin and other blood coagulation proteins is due to the the availability of a dicarboxylate in Gla rather than a simple carboxylate function; the dicarboxylate would bind preferentially to calcium rather than magnesium, thereby allowing the protein to discriminate between the two metals.[1] The binding of these metal ions to carboxylates has been extensively studied by Einspahr and Bugg,[2] who note that a simple carboxylate (e.g. Glu) can bind the calcium (or, by extension, barium) in either a unidentate or a bidentate manner. In a dicarboxylate (e.g. mal, Gla) there is an additional mode in which the barium binds to two oxygen atoms from the two different carboxylate groups. This mode, which is only available to a dicarboxylate like malonate (mal), is sometimes

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Table I. Crystallographic Data

$C_9H_{10}O_{12}Ba$	$\lambda = 0.71073$ Å
fw = 447.5	$T = 294$ K
space group = $C2/c$ (No. 15)	$\rho_{obsd} = 2.25$ g cm^{-3}; $\rho_c = 2.277$ g cm^{-3}
$a = 17.593$ (7) Å	NO = 1850 $[I \geq 3\sigma(I)]$
$b = 8.975$ (4) Å	$\mu = 31.05$ cm^{-1}
$c = 8.449$ (2) Å	transm coeff = 0.09–0.31
$\beta = 101.93$ (3)°	$R(F_o) = 0.0482$
$V = 1305.3$ (9) Å^3	$R_w(F_o) = 0.0654$
$Z = 4$	

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for [Ba(mal)(malH$_2$)$_2$]

	x	y	z	U(eq)^a
Ba	0	6298 (1)	2500	15 (1)
O(1A)	−275 (3)	3574 (5)	706 (6)	28 (1)
O(2A)	602 (2)	1999 (5)	274 (4)	29 (1)
C(1A)	126 (3)	2426 (6)	1081 (5)	20 (1)
C(2A)	0	1614 (7)	2500	36 (3)
O(1B)	1469 (3)	5008 (6)	2340 (7)	44 (2)
O(2B)	1724 (3)	3101 (6)	4031 (6)	45 (2)
O(3B)	3924 (3)	3500 (5)	2955 (7)	36 (1)
O(4B)	3251 (2)	5280 (5)	3920 (5)	32 (1)
C(1B)	1869 (3)	3979 (7)	2858 (8)	27 (1)
C(2B)	2551 (3)	3426 (7)	2236 (8)	30 (2)
C(3B)	3314 (3)	4075 (6)	3079 (6)	22 (1)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

known as the "malonate" mode.

Although we[3-5] and others[6-9] have investigated the binding of calcium to malonate and its derivatives, much less is known concerning the binding of barium(II) to carboxylates. No diffraction study of barium malonate has appeared, but recently we reported the synthesis and structures of several barium complexes of α-substituted malonate derivatives and demonstrated the existence of all three types of binding in these complexes.[10]

We have now isolated a new complex in the barium–malonic acid system and have succeeded in crystallizing this complex. Here we report the synthesis and characterization of this new complex, which is a 1:3 complex of formulation Ba(mal)(malH$_2$)$_2$, where mal is malonate dianion and malH$_2$ is the acid.

Experimental Section

Synthesis. A 10.4-g (0.10-mol) amount of malonic acid was dissolved in 250 mL of membrane-filtered, deionized water. A 9.85-g (0.051-mol) amount of barium carbonate was added in approximately 250-mg portions with stirring. Between additions, the cloudy solution was allowed to become clear. The final solution has a permanent cloudiness and was clarified by filtration through paper ($H = 3.5$). This was then allowed to air-evaporate at room temperature. Crystallization began when about 80% of original volume was reached. The first crystals took the form of white rosettes consisting of very small needles that were markedly dendritic. Crystals were harvested with increasing frequency (every 72 h at first, every 12 h toward and end), and the filtrate subjected to further evaporation. At about 5% of original volume, the form of crystallization changed. This was signaled by the formation of a surface crust on the solution. Crystals now formed were much larger, colorless transparent prisms. The largest of these were 3 mm in their longest dimension. The
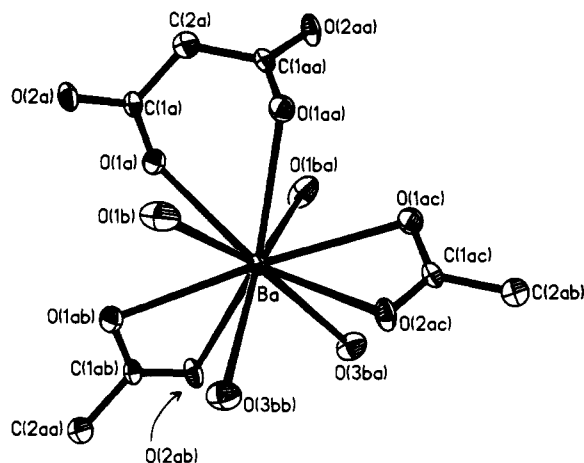
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Figure 1. View of the coordination around a single barium center in [Ba(mal)(malH$_2$)$_2$]. Hydrogen atoms are omitted for clarity. Symmetry labels are as in Table III, with the right-hand half of the molecule related to the left-hand half by the two-fold axis passing through Ba and C(2a).

Table III. Bond Lengths (Å) in [Ba(mal)(malH$_2$)$_2$]^a

Ba–O(1A)	2.864 (4)	Ba–O(1B)	2.860 (5)
Ba–O(1Ab)^1	2.851 (5)	Ba–O(2Ab)^1	2.816 (4)
Ba–O(3Ba)^2	2.818 (5)	O(1A)–C(1A)	1.252 (6)
O(2A)–C(1A)	1.246 (7)	C(1A)–C(2A)	1.458 (6)
O(1B)–C(1B)	1.189 (7)	O(2B)–C(1B)	1.331 (9)
C(1B)–C(2B)	1.491 (9)	C(2B)–C(3B)	1.501 (8)
O(3B)–C(3B)	1.214 (7)	O(4B)–C(4B)	1.311 (7)

^{a} Symmetry operations: (1) $-x$, $1 - y$, $-z$; (2) $-^1/_2 + x$, $^1/_2 + y$, z.

Table IV. Bond Angles (deg) in [Ba(mal)(malH$_2$)$_2$]^a

O(1a)–Ba–O(1B)	71.7 (1)	O(1A)–Ba–O(1Ab)	64.8 (2)
O(1B)–Ba–O(1Ab)	68.8 (1)	O(1A)–Ba–O(1Aa)	62.8 (2)
O(1B)–Ba–O(1Aa)	67.9 (2)	O(1Ab)–Ba–O(1Aa)	119.6 (1)
O(1A)–Ba–O(1Ac)	119.6 (1)	O(1B)–Ba–O(1Ac)	113.2 (1)
O(1Ab)–Ba–O(1Ac)	175.4 (2)	O(1AB)–Ba–O(1Ac)	64.8 (2)
O(1A)–Ba–O(2Ab)	91.7 (1)	O(1B)–Ba–O(2Ab)	111.7 (1)
O(1Ab)–Ba–O(2Ab)	45.2 (1)	O(1Aa)–Ba–O(2Ab)	153.8 (1)
O(1Ac)–Ba–O(2Ab)	131.3 (1)	O(1A)–Ba–O(2Ac)	153.8 (1)
O(1B)–Ba–O(2Ac)	94.1 (1)	O(1Ab)–Ba–O(2Ac)	131.3 (1)
O(1Aa)–Ba–O(2Ac)	91.7 (1)	O(1Ac)–Ba–O(2Ac)	45.2 (1)
O(2Ab)–Ba–O(2Ac)	114.2 (2)	O(1A)–Ba–O(1Ba)	67.9 (2)
O(1B)–Ba–O(1Ba)	132.2 (2)	O(1Ab)–Ba–O(1Ba)	113.2 (1)
O(1Aa)–Ba–O(1Ba)	71.7 (1)	O(1Ac)–Ba–O(1Ba)	68.8 (1)
O(2Ab)–Ba–O(1Ba)	94.1 (1)	O(2Ac)–Ba–O(1Ba)	111.7 (1)
O(1A)–Ba–O(3Ba)	128.8 (1)	O(1B)–Ba–O(3Ba)	158.3 (1)
O(1Ab)–Ba–O(3Ba)	110.6 (1)	O(1Ab)–Ba–O(3Ba)	124.8 (2)
O(1Ac)–Ba–O(3Ba)	65.9 (1)	O(2Ab)–Ba–O(3Ba)	65.5 (1)
O(2Ac)–Ba–O(3Ba)	69.7 (1)	O(1Ba)–Ba–O(3Ba)	68.8 (1)
O(1A)–Ba–O(3Bb)	124.8 (2)	O(1B)–Ba–O(3Bb)	68.8 (1)
O(1Ab)–Ba–O(3Bb)	65.9 (1)	O(1Aa)–Ba–O(3Bb)	128.8 (1)
O(1Ac)–Ba–O(3Bb)	110.6 (1)	O(2Ab)–Ba–O(3Bb)	69.7 (1)
O(2Ac)–Ba–O(3Bb)	65.5 (1)	O(1Ba)–Ba–O(3Bb)	158.3 (1)
O(3Ba)–Ba–O(3Bb)	90.9 (2)	Ba–O(1A)–C(1A)	122.9 (3)
Ba–O(1A)–BaC	115.2 (2)	C(1A)–O(1A)–BaC	94.4 (3)
C(1A)–O(2A)–BaC	96.2 (3)	O(1A)–C(1A)–O(2A)	121.5 (5)
O(1A)–C(1A)–C(2A)	116.5 (5)	O(2A)–C(1A)–C(2A)	122.0 (4)
C(1A)–C(2A)–C(1Ab)	120.0 (6)	Ba–O(1B)–C(1B)	140.3 (5)
C(3B)–O(3B)–BaA	160.1 (4)	O(1B)–C(1B)–O(2B)	122.9 (6)
O(1B)–C(1B)–C(2B)	126.0 (6)	O(2B)–C(1B)–C(2B)	110.9 (5)
C(1B)–C(2B)–C(3B)	114.2 (5)	O(3B)–C(3B)–O(4B)	125.0 (5)
O(3B)–C(3B)–C(2B)	120.9 (5)	O(4B)–C(3B)–C(2B)	114.1 (5)

^{a} Symmetry operations are as given in footnote a of Table III and in Figure 1.

yield of the latter crystals was less than 3% of theoretical based on barium recovery. Elemental analysis confirms that both crystal forms are the same material. Anal. Calcd for $C_9H_{10}O_{12}$Ba: Ba, 30.69; C, 25.16; H, 2.25. Found:[11] Ba, 30.65; C, 24.39; H, 2.30.

(11) Barium analyses were performed by Wyoming Analytical Laboratories, Laramie, WY 82070. Carbon and hydrogen analyses were by Atlantic Microlabs, Inc., Norcross, GA.

Table V. Coordination Geometries of Barium Complexes of Malonate and Substituted Malonate Derivatives

complex	coordin no.	coordn mode	Ba–O, Å	ref
[Ba(bz(mal)H)$_2$]·H$_2$O	10	bidentate (2)	2.88	15
		malonate (2)	2.79	
[Ba(bz(mal))]·3H$_2$O	10	unidentate (1)	2.866 (5)	15
		bidentate (1)	2.95	
		malonate (2)	2.87	
[Ba(dmal)]$_2$·5H$_2$O^a	8	unidentate (3)	2.73	15
		malonate (1)	2.82	
[Ba(dmal)]$_2$·5H$_2$O^a	9	unidentate (2)	2.77	15
		bidentate (1)	2.99	
		malonate (1)	2.83	
[Ba(et(mal)H)$_2$]·H$_2$O	10	unidentate (4)	2.86	15
		malonate (2)	2.87	
[Ba(mal)(malH$_2$)$_2$]	10	unidentate (4)	2.84	this
		bidentate (2)	2.83	work
		malonate (1)	2.864 (4)	

^{a} There are two crystallographically independent barium ions in this structure.

X-ray Crystallography. Intensity data were collected on a Nicolet R3m/V diffractometer equipped with molybdenum tube [λ(Kα$_1$) = 0.709 26 Å; λ(Kα$_2$) = 0.713 54 Å] and a graphite monochromator. Data were corrected for Lorentz–polarization effects and for absorption. Additional experimental details are presented in Table I. Programs were from the SHELXTL system.

The structure was solved by direct methods and refined by full-matrix least-squares techniques. All hydrogen atoms were located unambiguously in a difference Fourier map, but attempts to refine them were unsuccessful. Consequently, in the final least-squares cycles the hydrogen atoms were included in fixed positions, as determined from the difference Fourier summation, while other atoms were refined anisotropically. The final atomic positional parameters are presented in Table II; lists of hydrogen atom parameters, atomic thermal parameters, and observed and calculated structure amplitudes are available as supplementary material.

Discussion

The structure consists of [Ba(mal)(malH$_2$)$_2$] molecules that are extensively hydrogen bonded to each other to form a polymeric aggregate. A view of the coordination around a single barium center is shown in Figure 1. Significant bond lengths and angles in the complex are compiled in Tables III and IV, respectively.

The barium atom lies on a crystallographic 2-fold (C_2) axis that also passes through the central carbon atom [C(2A)] of the malonate dianion. As can be seen from an examination of Figure 1, the barium ion is ten-coordinate in the complex, the coordination sites being occupied by six oxygen atoms from three different malonate dianions and four oxygen atoms from four different malonic acid molecules. The geometry at barium does not approximate either of the idealized polyhedra, the bicapped square antiprism, or the bicapped dodecahedron; this observation is not surprising in view of the steric requirements of the malonate ligands in the structure.

Each barium ion binds to three different malonate dianions, forming two bidentate interactions and one malonate interaction. In addition, it binds to four different malonic acid residues, forming four unidentate interactions. Hence, in the present complex, all three possible forms of binding between barium and dicarboxylate or dicarboxylic acid are present. The modes of binding observed in barium complexes of malonic acid and its derivatives are compared in Table V. As is the case for the more extensively studied calcium(II) complexes, the barium(II) ions in these complexes show considerable coordinative flexibility.

The Ba–O bond lengths in the complex are in the range 2.816 (4)–2.864 (4) Å; these values are consistent with the range observed in our earlier studies.[15] The anticipated trends in Ba–O
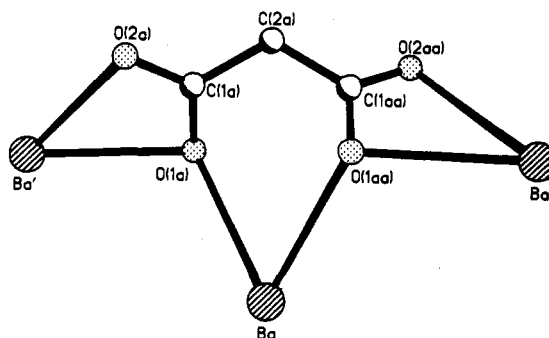

Figure 2. View of the bonding of a single malonate dianion in [Ba(mal)(malH$_2$)$_2$], showing three different barium atoms and the malonate and bidentate binding modes.
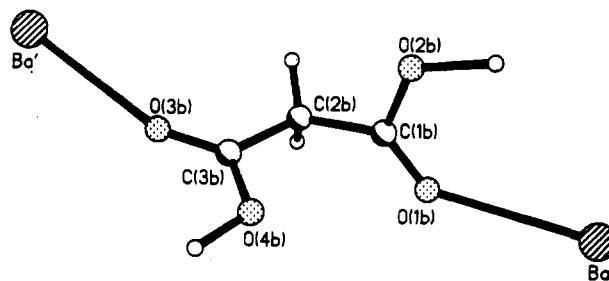

Figure 3. View of the bonding of a malonic acid molecule in [Ba(mal)(malH$_2$)$_2$], showing the unidentate interaction with two different barium atoms.

bond lengths are not strictly observed. Thus, while the Ba–O(1A) bonds of 2.864 (4) Å involved in the malonate mode are the longest in the structure, the Ba–O(2A) bonds of 2.816 (4) Å, which are part of the bidentate binding, are the shortest.

The binding of a single malonate dianion is shown in Figure 2. As can be seen in that figure, each malonate ion binds to three different barium ions. Each oxygen atom is involved in a bidentate interaction, and in addition atoms O(1A) and O(1AA) form the malonate interaction. In most structures involving malonate and its derivatives, the two carboxyl groups are nearly orthogonal; in the present case, the dihedral angle between the planes O(1A)–C(1A)–O(2A) and O(1AA)–C(1AA)–O(2AA) is 66.7°.

The binding of malonic acid moieties is depicted in Figure 3. Each malonic acid molecule binds in a unidentate (1) manner to two barium centers, one through O(1B) and the other through O(3B). Atoms O(2B) and O(4B) are protonated. Consequently, the nominally double bonds C(1B)–O(1B) and C(3B)–O(3B) of 1.189 (7) and 1.214 (7) Å are significantly shorter than the nominally single bonds C(1B)–O(2B) and C(3B)–O(4B) of 1.311 (7) and 1.331 (9) Å. The corresponding C–O bond lengths of 1.246 (7) and 1.252 (6) Å in the dianion are, of course, approximately equal to each other and intermediate between these single- and double-bond values. The dihedral angle between the two carboxyl groups in the malonic acid moiety is 82.2°.

The malonic acid moiety forms two hydrogen bonds to the malonate ion. Atom O(1A) of the malonate ion accepts a hydrogen bond from O(2B)–H(2B), with O(2B)···O(1A) and H(2B)···O(1A) separations of 2.639 (7) and 1.51 Å and the associated O(2B)–H(2B)···O(1A) angle of 130°. Malonate oxygen atom O(2A) interacts with the other end of a different malonic acid molecule, forming an O(4B)–H(4B)···O(2A) hydrogen bonding interaction with O(4B)···O(2A) and H(4B)···O(2A) distances of 2.519 (8) and 1.49 Å and an O(4B)–H(4B)···O(2A) angle of 163°.

The present structural study underscores our earlier conclusions concerning the binding of barium to dicarboxylate residues like malonate and its derivatives, and by extension to Gla and Asa. The limited data available for the smaller alkaline-earth metals suggest that for Be^{2+} and Mg^{2+} the only binding mode may be the malonate mode, since this is the only one observed in Be(mal)$_2^{2-}$,[12] Mg(malH)$_2$·2H$_2$O,[13] and Mg(Me(Mal))(OH$_2$)$_4$.[3] For

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the larger members of the series, three coordination modes are possible and all three are observed in the present structure. More significant, however, is the distinction between the regular, *monomeric* structures observed for the smaller metals (Be^{2+}, Mg^{2+}) and the irregular, *polymeric* structures observed here and elsewhere for both barium and calcium. Hence, the present result again lends support to the contention that the ability of Gla to contribute additional carboxylate binding centers is a major reason for its presence in calcium proteins and may serve to discriminate between calcium and magnesium.[1] The present result supports our earlier suggestion[10] that barium could, in principle, bind in much the same way as calcium to such proteins, since both metals show high-coordination numbers and polymeric arrays in these model complexes. The observation that normal prothrombin absorbs onto barium citrate while abnormal prothrombin (which lacks the Gla residues) does not[14–16] is entirely consistent with the present observations.

Supplementary Material Available: Tables S1 (hydrogen atom coordinates) and S2 (anisotropic thermal parameters) (1 page); Table S3 (observed and calculated structure amplitudes) (7 pages). Ordering information is given on any current masthead page.

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(16) Nelsestuen, G. L.; Suttie, J. W. *J. Biol. Chem.* **1972,** *247,* 8176–8182.

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Concerted Regulation of Intermolecular C–N Bond Formation of α-Aminomalonate with *trans*-[CoCl₂(1,10-diamino-4,7-diazadecane)]⁺ by Counteranion and Dioxygen

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Introduction

The regulation of reactions for selective synthesis of organic compounds has gathered sustained attention. For the rational synthesis of multidentate ligands, a template reaction within the coordination sphere in a metal ion is a useful strategy to control selectivity, to avoid polymerization, and to minimize stereochemical complexty.[1–3] Sargeson and co-workers have reported on the elegant entrapment species of metal ions called "sepluchrates".[4]

Recently, we have reported on the reactions of α-aminomalonate anion (AM^{2-}) with Co(III)–polyamine complexes having en[5] and 2,3,2-tet[5] as ligands to give α-diamine complexes.[6,7] In the 2,3,2-tet system, the C–N bond formation has occurred between the α-carbon of AM^{2-} and both a primary and a secondary amino groups without any selectivity. Here we wish to report on the regioselective intermolecular C–N bond formation between AM^{2-} and *trans*-[CoCl₂(3,2,3-tet)]⁺ (1⁺).[5]

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Table I. Crystallographic Data for [Co(*N*-(10-amino-4,7-diazadecanyl)-α,α-diaminomalonato)]NO₃·H₂O (**2b**)

C₁₁H₂₅N₆O₈Co (fw 428.29)	$T = 23\ °C$
monoclinic, $P2_1/c$	$\lambda = 0.71069\ Å$
$a = 11.906\ (2)\ Å$	$\mu(Mo\ K\alpha) = 10.45\ cm^{-1}$
$b = 9.514\ (1)\ Å$	$6.0° < 2\theta < 64.9°$
$c = 16.248\ (2)\ Å$	$R_{int} = 0.016$
$\beta = 110.579\ (9)°$	no. of unique reflcns measd = 6529
$V = 1723.0\ (4)\ Å^3$	no. of obsvd reflcns ($I > 3\sigma(I)$) = 4568
$Z = 4$	$R = 0.030$
$D_{calcd} = 1.651\ g/cm^3$	$R_w = 0.036$

Experimental Section

Analytical grade MeOH was used for the reaction under aerobic conditions. For the reaction under anaerobic conditions, MeOH was dried over Mg and distilled before use. NEt₃ was dried on P₂O₅ and distilled before use. *trans*-[CoCl₂(3,2,3-tet)]ClO₄ (**1a**), *trans*-[CoCl₂(3,2,3-tet)]Cl (**1b**),[8] and NH₄(AM)H[6] were synthesized by reported procedures. The separation of the complexes studied were performed with SP-Sephadex C-25 (Na⁺ form) cation-exchange column.

NMR spectroscopy was carried out on JEOL GX-400 and JEOL GSX-270 instruments using sodium trimethylsilylpentanesulfonate (TSP) in D₂O as an internal reference for ¹H NMR spectra (400 and 270 MHz) and dioxane ($\delta = 67.4$ ppm) in D₂O for ¹³C NMR spectra (100 and 67.5 MHz). ¹H NMR spectra were measured at room temperature, and low-power broad-band proton-decoupled ¹³C NMR spectra were measured at 34 °C.

Synthesis and Separation of Complexes: [Co(*N*-(10-amino-4,7-diazadecanyl)-α,α-diaminomalonato)]Br·H₂O ([Co(p-3,2,3-tet-AM)]Br·H₂O, **2a**). NEt₃ (3.03 g) was slowly added to a suspension of **1a** or **1b** and NH₄(AM)H in methanol (250 mL), and the mixture was refluxed for 3 h. After the mixture was evaporated to dryness, water was added and subsequently evaporated in order to remove NEt₃. The reaction mixture was dissolved in water and adsorbed on SP-Sephadex C-25 cation-exchange-resin column (Na⁺ form). The column was washed well with water and eluted with 0.02 M NaBr. On the top of the column, a large amount of red-brown highly charged band was adsorbed.

The main orange fraction was collected and desalted by Sephadex G-15 gel chromatography. The solution was reduced to a small volume to which EtOH was added to obtain the orange powder of **2a**. The powder was collected, washed well with EtOH and ether, and dried (yield, 17% from **1a**; crude yield, 50% from **1b**). Recrystallization from

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(5) Abbreviations: en = ethylenediamine; 2,3,2-tet = 1,9-diamino-3,7-diazanonane; 3,2,3-tet = 1,10-diamino-4,7-diazadecane; tren = tris(2-aminoethyl)amine.
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