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.

Acknowledgment. This work was supported by the National Science Foundation through Grant No. CHE-9007607.

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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Concerted Regulation of Intermolecular C–N Bond Formation of α-Aminomalonate with *trans*-[CoCl$_2$(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*-[CoCl$_2$(3,2,3-tet)]$^+$ (1^+).[5]

Table I. Crystallographic Data for [Co(*N*-(10-amino-4,7-diazadecanyl)-α,α-diaminomalonato)]NO$_3$·H$_2$O (**2b**)

$C_{11}H_{25}N_6O_8Co$ (fw 428.29)	T = 23 °C
monoclinic, $P2_1/c$	λ = 0.71069 Å
a = 11.906 (2) Å	μ(Mo Kα) = 10.45 cm^{-1}
b = 9.514 (1) Å	6.0° < 2θ < 64.9°
c = 16.248 (2) Å	R_{int} = 0.016
β = 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. NEt$_3$ was dried on P$_2$O$_5$ and distilled before use. *trans*-[CoCl$_2$(3,2,3-tet)]ClO$_4$ (**1a**), *trans*-[CoCl$_2$(3,2,3-tet)]Cl (**1b**),[8] and NH$_4$(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 D$_2$O as an internal reference for ^{1}H NMR spectra (400 and 270 MHz) and dioxane (δ = 67.4 ppm) in D$_2$O for ^{13}C NMR spectra (100 and 67.5 MHz). ^{1}H NMR spectra were measured at room temperature, and low-power broad-band proton-decoupled ^{13}C NMR spectra were measured at 34 °C.

Synthesis and Separation of Complexes: [Co(*N*-(10-amino-4,7-diazadecanyl)-α,α-diaminomalonato)]Br·H$_2$O ([Co(p-3,2,3-tet-AM)]Br·H$_2$O, 2a). NEt$_3$ (3.03 g) was slowly added to a suspension of **1a** or **1b** and NH$_4$(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 NEt$_3$. 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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Table II. Final Positional Parameters (Estimated Standard Deviations in Parentheses) and Equivalent Isotropic Thermal Parameters (B_{eq}, Å^2) for Non-Hydrogen Atoms of [Co(*N*-(10-amino-4,7-diazadecanyl)-α,α-diaminomalonato)]$NO_3 \cdot H_2O$ (**2b**)

atom	*x*	*y*	*z*	B_{eq}[a]
Co	0.29310 (2)	0.17943 (2)	0.32033 (1)	1.49
O(1)	0.4575 (1)	0.2027 (1)	0.39705 (8)	2.14
O(2)	0.6026 (1)	0.3651 (2)	0.42436 (9)	3.13
O(3)	0.3410 (1)	0.2116 (1)	0.22012 (7)	1.96
O(4)	0.4414 (1)	0.3744 (1)	0.17404 (8)	2.64
N(1)	0.1255 (1)	0.1652 (2)	0.2406 (1)	2.08
N(2)	0.3229 (1)	−0.0234 (1)	0.3177 (1)	2.08
N(3)	0.2920 (1)	0.3855 (1)	0.3244 (1)	1.84
N(4)	0.2499 (1)	0.1384 (1)	0.42354 (9)	1.92
N(5)	0.4391 (2)	0.5553 (2)	0.3106 (1)	2.94
C(1)	0.1024 (2)	0.0739 (2)	0.1613 (1)	2.84
C(2)	0.1378 (2)	−0.0763 (2)	0.1871 (1)	3.11
C(3)	0.2720 (2)	−0.0979 (2)	0.2323 (1)	2.78
C(4)	0.2955 (2)	−0.0956 (2)	0.3900 (1)	2.86
C(5)	0.3153 (2)	0.0081 (2)	0.4640 (1)	2.62
C(6)	0.3971 (1)	0.3294 (2)	0.2264 (1)	1.84
C(7)	0.4097 (1)	0.4103 (2)	0.3115 (1)	1.92
C(8)	0.5006 (1)	0.3221 (2)	0.3851 (1)	2.08
C(9)	0.2829 (2)	0.4635 (2)	0.4013 (1)	2.67
C(10)	0.2075 (2)	0.3875 (2)	0.4457 (1)	2.60
C(11)	0.2643 (2)	0.2521 (2)	0.4890 (1)	2.67
O(11)	0.9952 (1)	0.1177 (2)	0.4155 (1)	4.39
O(12)	0.8302 (2)	0.0018 (3)	0.3665 (1)	6.4
O(13)	0.9582 (1)	−0.0166 (2)	0.3022 (1)	4.51
N(11)	0.9276 (1)	0.0345 (2)	0.3622 (1)	3.01
O(5)[b]	0.8555 (2)	0.2296 (2)	0.0137 (1)	4.91

[a] $B_{eq} = (4/3)\sum_i\sum_j B_{ij}(\mathbf{a}_i \cdot \mathbf{a}_j)$. [b] A water molecule of crystallization.

water gave microcrystals of compound **2a**. Anal. Calcd for $CoC_{11}H_{23}N_5O_4Br \cdot H_2O$: C, 29,61; H, 5.65; N, 15.70. Found: C, 29.76; H, 5.26; N, 15.90.

The same complex was also obtained dominantly in the yield of 19% as an anhydride salt from the reaction of **1a** with NH_4(AM)H in MeOH/NEt_3 upon reflux for 3 h under an inert atmosphere.

Synthesis of [Co(*N*-(3-aminopropyl)-*N*-(6-amino-3-azahexyl)-α,α-diaminomalonato)]Br·$^1/_2$H$_2$O ([Co(s-3,2,3-tet-AM)]Br·$^1/_2$H$_2$O, 3). Complex **3** was synthesized by a similar procedure under N_2 using **1b** as a starting complex. Complex **3** was separated with a SP-Sephadex C-25 column eluted with 0.02 M NaBr(aq) and purified by a Sephadex G-15 column under air. Crude yield, ca. 20%. Anal. Calcd for $C_{11}H_{23}N_5O_4CoBr \cdot {}^1/_2H_2O$: C, 30.22; H, 5.53; N, 16.02. Found: C, 30.30; H, 5.16; N, 15.84.

X-ray Diffraction Data Collection and Structure Refinement for [Co(*N*-(10-amino-4,7-diazadecanyl)-α,α-diaminomalonato)]NO$_3$·H$_2$O ([Co(p-3,2,3-tet-AM)]NO$_3$·H$_2$O, 2b). Br^- in **2a** was exchanged to NO_3^- with a SP-Sephadex C-25 cation-exchange column (3-cm o.d. × 5 cm) eluted with $NaNO_3$(aq) (0.5 M) to obtain **2b**. Block-shaped red-organe crystals suitable for X-ray analysis were obtained by recrystallization from water. X-ray diffraction data were collected on a Rigaku AFC-5s four-circle diffractometer at 23 °C. The lattice constants were determined by using 25 independent reflections in the range of $39.6° < 2\theta < 39.9°$. Empirical absorption and Lorenz-polarization corrections were made. The crystallographic data are summarized in Table I. Structure solution and refinement were made by direct-method and full-matrix least-squares techniques, respectively. The effects of anomalous dispersion were corrected in structure factor calculations for all non-hydrogen atoms. The differential Fourier map showed all of the hydrogen atoms, which were refined with isotropic temperature factors. All the calculations were performed on a Vax Workstation 3300 by using the TEXSAN program system (Molecular Structure Corp., TX, 1987). The final $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum_w(|F_o| - |F_c|)^2/w\sum|F_o|^2]^{1/2}$ were 0.030 and 0.036, respectively. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.30 and −0.44 e/Å^3. The final positional parameters for non-hydrogen atoms are listed in Table II.

Results and Discussion

In the daylight under air the reaction of AM^{2-} with *trans*-[$CoCl_2$(3,2,3-tet)]ClO_4 (**1a**) or *trans*-[$CoCl_2$(3,2,3-tet)]Cl (**1b**) in MeOH/NEt_3 upon reflux gave an α-diamine complex, **2**$^+$, in a moderate yield (from **1a**, 17%; from **1b**, ca. 50%) in which a new C–N bond was formed between a primary amino group of the 3,2,3-tet and the α-carbon of AM^{2-}. Conversely, under an inert atmosphere the same reaction of **1b** gave another α-diamine complex, **3**$^+$, in a lower yield (ca. 20%) that has a new C–N bond with a secondary amino group of the ligand. The counteranion probably affects the regioselectivity; when **1b** (*chloride* salt) was used as a starting complex for the reaction under an inert atmosphere, **3**$^+$ was obtained selectively, whereas **2**$^+$ (yield, 19%) was obtained from the reaction of **1a** (*perchlorate* salt).

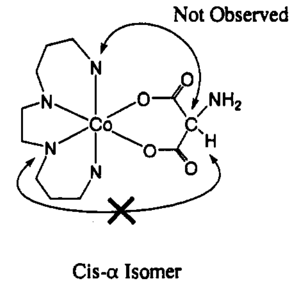
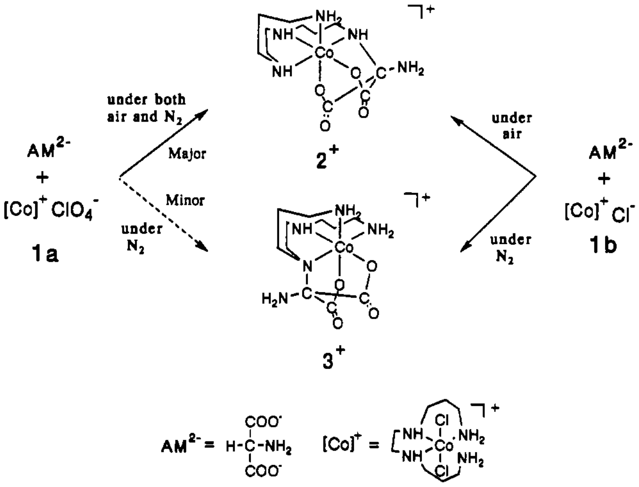


Figure 1. Cis-α isomer, excluded for the reasons described in the text.

Scheme I. Summary of Reactions in the 3,2,3-tet System



The yield of **2**$^+$ from the reaction of **1b** with AM^{2-} under air was drastically improved from 7% in the dark to 50% in the daylight. This phenomenon was also observed in the 2,3,2-tet system.[7b]

The complexes obtained from the reaction as main products under aerobic and anaerobic conditions are summarized in Scheme I. The C–N bond formation in the 3,2,3-tet system could take place even under an inert atmosphere, as observed in the en system,[6] whereas no C–N bond formations occurred in the 2,3,2-tet system.[7] On the other hand, when the chloride salt **1b** was reacted with AM^{2-} under air, the yield of α-diamine complex improved in the 3,2,3-tet system under photolytic conditions, as observed in the 2,3,2-tet system,[7b] whereas such photochemical effects were not detected in the en system.[9]

In the ^{13}C NMR spectrum of **2**$^+$,[10] a signal assigned to the α-carbon of the AM^2-moiety in the condensed ligand was observed at 86.1 ppm similar to those of related α-diamine complexes, [Co(*N*-(2-aminoethyl)-α,α-diaminomalonato)(en)]$^+$ (**4**$^+$) (85.9 ppm)[6] and [Co(*N*-9-amino-3,7-diazanonyl)-α,α-diaminomalonato)]$^+$ (**5**$^+$) (85.0 ppm).[7b] The structures of the latter two compounds include, as determined X-ray crystallography, the new C–N bond formed between the α-carbon of AM^{2-} and a primary amino group of the amine ligands. On the other hand, the ^{13}C NMR spectrum[10] of **3**$^+$ exhibited the resonance of the α-carbon of the AM^{2-} moiety in the condensed ligand at 93.9 ppm. The value is close to that of an α-diamine complex, [Co(*N*-(2-

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(10) ^{13}C NMR data in D$_2$O: for **2**$^+$, 177.1, 175.4 (COO$^-$), 86.5 (α-*C* of AM moiety), 52.7, 48.8, 48.0, 46.0, 44.2, 38.0, 28.1, 22.3 (–*C*H$_2$– of 3,2,3-tet); for **3**$^+$, 175.8, 174.4 (–*C*OO$^-$), 93.9 (α-*C* of AM moiety), 53.2, 49.2, 48.6, 46.3, 44.1, 38.6, 28.1, 22.4 (–*C*H$_2$– of 3,2,3-tet).

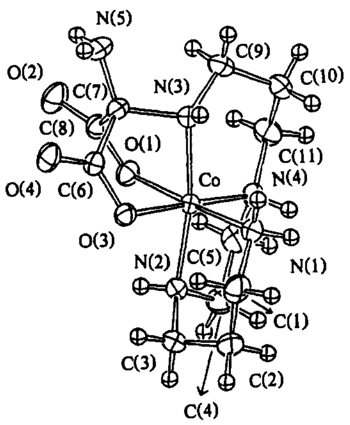

Figure 2. ORTEP representation of a Δ-isomer of $\mathbf{2}^+$. Thermal ellipsoids are drawn at the 50% probability level.

Table III. Selected Bond Lengths (Å) and Angles (deg) for $[\mathrm{Co(p\text{-}3,2,3\text{-}tet\text{-}AM)}]\mathrm{NO_3{\cdot}H_2O}$ (**2b**)

(a) Bond Lengths			
Co–O(1)	1.928 (1)	Co–O(3)	1.929 (1)
Co–N(1)	1.965 (1)	Co–N(2)	1.965 (1)
Co–N(3)	1.962 (1)	Co–N(4)	1.959 (1)
O(1)–C(8)	1.289 (2)	O(2)–C(8)	1.226 (2)
O(3)–C(6)	1.291 (2)	O(4)–C(6)	1.225 (2)
N(3)–C(7)	1.507 (2)	N(5)–C(7)	1.424 (2)
C(6)–C(7)	1.543 (2)	C(7)–C(8)	1.548 (2)
(b) Bond Angles			
O(1)–Co–O(3)	89.63 (5)	O(1)–Co–N(1)	177.28 (6)
O(1)–Co–N(2)	88.68 (6)	O(1)–Co–N(3)	83.15 (5)
O(3)–Co–N(1)	89.26 (1)	O(3)–Co–N(2)	91.64 (5)
O(3)–Co–N(3)	82.97 (5)	O(3)–Co–N(4)	177.08 (5)
N(1)–Co–N(2)	93.84 (6)	N(2)–Co–N(3)	170.22 (6)
N(2)–Co–N(4)	85.77 (6)	N(3)–Co–N(4)	99.40 (6)
N(3)–C(7)–N(5)	113.4 (1)	N(3)–C(7)–C(6)	104.2 (1)
N(3)–C(7)–C(8)	103.9 (1)	N(5)–C(7)–C(6)	114.9 (1)
N(5)–C(7)–C(8)	115.1 (1)	C(6)–C(7)–C(8)	104.1 (1)

aminoethyl)-*N*-(6-amino-4-azahexyl)-α,α-diaminomalonato)]$^+$ (95.2 ppm),[7] which contains the new C–N bond between the α-carbon and a secondary amino group of the 2,3,2-tet ligand. The configuration of the 3,2,3-tet moiety of the hexadentate ligand in $\mathbf{3}^+$ is expected to be cis-β since in a cis-α configuration the AM^{2-} moiety in the condensed ligand should be inevitably located in the opposite position of the secondary amino groups in the 3,2,3-tet, as shown in Figure 1, thus making the formation of the new C–N bond impossible.

A single-crystal X-ray analysis confirmed the molecular structure of **2b**. A perspective view of a Δ-isomer of complex cation $\mathbf{2}^+$ is shown in Figure 2. Selected bond lengths and angles are cited in Table III. The 3,2,3-tet moiety in the condensed ligand of **2b** was found to be a cis-β configuration, as observed in the 2,3,2-tet system: the conformation of both of the two six-membered chelate rings is the chair form; that of the five-membered ring is δ in the Δ-isomer. The geometry around the α-carbon of the AM moiety is approximately tetrahedral and the bond length of the newly formed C–N bond (N(3)–C(7)) is 1.507 (2) Å, which lies in the normal range for those of C(sp^3)–N bonds.[11] Conversely, the bond length between the α-carbon (C(7)) and a nitrogen (N(5)) of an uncoordinated amino group is shortened to 1.427 (2) Å, similar to those of C–N bonds for aniline derivatives. This feature is common for α-diamine complexes derived from AM^{2-} and Co(III)–polyamine complexes.[7b] The newly formed α-diamine linkage imposes severe distortion on the octahedral geometry around the cobalt center (N(2)–Co–N(3), 170.22 (6)°). In addition, unlike $\mathbf{4}^+$ and $\mathbf{5}^+$, no hydrogen bonding around the nitrogen atom N(5) of the uncoordinated amino group was found in the unit cell of **2b**.[6,7b]

The regioselective C–N bond formation has been reported in the reaction of aminoacetaldehyde with Co(III)–tetraamine complexes such as $[\mathrm{CoCl_2(tren)}]^+$.[5,12] In those cases, the regioselectivity was attributed to the trans effect of the chloride ligand in a starting complex. Although, the reason for the regioselectivity regulated by the counteranion of $\mathbf{1}^+$ and dioxygen in our system is still under investigation, the reactions under air and an inert atmosphere appear to proceed via different pathways regarding the reaction of **1b**. Apparently, under an inert atmosphere, an electron transfer from AM^{2-} to the Co(III) ion should occur to form a putative cobalt–iminomalonato intermediate.[7,9,13,14] In contrast, under air a photochemical dioxygen activation probably occurs for the oxidation of AM^{2-}.

Thus the present observations suggest to us the importance of selection of counterions, ligands, and reaction conditions when we use metal complexes as catalyst or mediators to regulate reactions.

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Supplementary Material Available: Tables listing experimental details for X-ray crystallography, anisotropic thermal parameters, positional parameters of hydrogen atoms, and complete bond lengths and angles of $[\mathrm{Co(p\text{-}3,2,3\text{-}tet\text{-}AM)}]\mathrm{NO_3{\cdot}H_2O}$ (**2b**) and a figure showing a PLUTO drawing with the complete atom-labeling scheme (9 pages); a table of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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Laser Flash Photolysis and Pulse Radiolysis of Aqueous Solutions of the Fluoroxysulfate Ion, SO_4F^-

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The fluoroxysulfate ion, SO_4F^-, is the only known ionic hypofluorite.[1] It is a very strong oxidant capable of oxidizing water, but the rate of its reaction with water is sufficiently low to allow studies of its chemistry in aqueous solution.[2] Aqueous fluoroxysulfate appears to react primarily as a 1-electron oxidant, and an F atom transfer mechanism has been proposed to account for many of its reactions.[2] The present work is a study of the laser flash photolysis and pulse radiolysis of aqueous solutions of SO_4F^-.

Results and Discussion

Solutions containing SO_4F^- in concentrations between 6×10^{-4} and 3.6×10^{-3} M and $HClO_4$ in concentrations up to 1 M were laser-flash-irradiated with light of wavelength 193 nm. Upon irradiation, an instantaneous increase of transient absorbance was observed in the wavelength region 290–550 nm. Figure 1 shows a plot of the optical absorbance 30 ns after the laser pulse as a

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