cell lines. The complexes discussed here may represent a further example of this effect.

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Registry No. Ic, 136844-76-3; IIc, 112198-62-6; IIt, 114532-23-9; IIIc, 110321-22-7; IIIt, 121350-06-9; $K[PtCl_3(NH_3)]$, 13820-91-2.

Supplementary Material Available: Anisotropic temperature factors (Table S1), fixed coordinates of the hydrogen atoms (Table S2), weighted least-squares planes (Table S3), distances and angles of possible hydrogen bonds (Table S4), and a stereoscopic view of packing in the crystal *cis*-$[PtCl_2(NH_3)$(1-{(((2-hydroxyethyl)amino)carbonyl)methyl}-2-nitroimidazole] (Figure S1) (5 pages); observed and calculated structure factor amplitudes (Table S5) (15 pages). Ordering information is given on any current masthead page.

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Syntheses and Characterization of Complexes Derived from α-Aminomalonate and *trans*-$[CoCl_2(2,3,2\text{-tet})]^+$ (2,3,2-tet = 1,9-Diamino-3,7-diazanonane)

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The reaction of α-aminomalonate (AM^{2-}) with *trans*-$[CoCl_2(2,3,2\text{-tet})]ClO_4$ (2,3,2-tet = 1,9-diamino-3,7-diazanonane) (**1**) in MeOH in the presence of Et_3N under aerobic conditions gave an AM^{2-} complex (**2**), unusually stabilized α-diamine complexes (**3**, **4**), and a carbinolamine complex (**5**). The X-ray crystallographic study was undertaken on $[Co(AM)(2,3,2\text{-tet})]ClO_4{\cdot}H_2O$ (**2**) and the α-diamine complexes [Co(*N*-(2-aminoethyl)-*N*-(6-amino-4-azahexyl)-α,α-diaminomalonato)]ClO_4 (**3**) and [Co(*N*-(9-amino-3,7-diazanonyl)-α,α-diaminomalonato)]$ClO_4{\cdot}H_2O$ (**4**), and the following data were obtained. For compound **2**: $C_{10}H_{23}N_5O_4CoClO_4{\cdot}H_2O$, monoclinic, space group *Cc*, $a = 13.856$ (2) Å, $b = 11.466$ (2) Å, $c = 11.898$ (3) Å, $\beta = 107.32$ (1)°, $Z = 4$, $R = 0.057$, $R_w = 0.066$. For compound **3**: $C_{10}H_{21}N_5O_4CoClO_4$, monoclinic, space group $P2_1/c$, $a = 7.399$ (5) Å, $b = 23.199$ (5) Å, $c = 9.452$ (4) Å, $\beta = 92.02$ (5)°, $Z = 4$, $R = 0.050$, $R_w = 0.052$. For compound **4**: $C_{10}H_{21}N_5O_4CoClO_4{\cdot}H_2O$, space group $P2_1/c$, $a = 7.360$ (2) Å, $b = 13.571$ (3) Å, $c = 17.370$ (6) Å, $\beta = 91.02$ (2)°, $Z = 4$, $R = 0.067$, $R_w = 0.070$. The C–N bond formation between AM^{2-} and the amine ligand was promoted by dioxygen, Co(III) ion, heat, and MeOH and was enhanced photoinductively. The carbinolamine complex **5** was also obtained from the reaction of ketomalonate anion (KM^{2-}) with **1** in MeOH in the presence of NEt_3. X-ray crystallographic study on the carbinolamine complex, [Co(*N*-(9-amino-3,7-diazanonyl)-α-amino-α-hydroxylmalonato)]$ClO_4{\cdot}H_2O$ (**5**) was also performed: $C_{10}H_{20}N_4O_5CoClO_4{\cdot}H_2O$, orthorhombic, space group $P2_12_12_1$, $a = 7.291$ (1) Å, $b = 13.408$ (2) Å, $c = 17.143$ (3) Å, $Z = 4$, $R = 0.061$, $R_w = 0.066$. The results of X-ray crystallography and pK_a measurements indicated that the uncoordinated NH_2 or OH groups of **3**, **4**, and **5** had some properties which were similar to those of an anilinic amino group or a phenolic hydroxy group in spite of being bound to the sp^3 carbon atoms.

Introduction

Recently, much attention has been focused on the reactivities of bioactive molecules toward transition-metal complexes in the light of the chemistry of metalloenzymes.

α-Aminomalonic acid (AMH_2) has not been found in nature; however, it is known that AMH_2 can act as an inhibitor of enzymes which include pyridoxal phosphate (PLP) as a cofactor and for which glycine can be a substrate.[1] Especially, it inhibits δ-aminolaevulate synthetase in the biosynthesis of porphyrin of heme proteins.[2] In those reactions, AMH_2 becomes tightly bound to PLP in the enzymes. In contrast, AMH_2 is converted to a chiral glycine, (*S*)-[2-^{3}H]glycine, by L-aspartate β-decarboxylase (PLP as the cofactor) in ^3H_2O.[3] Thus the reactivities of AMH_2 have been intensively investigated in biology; however, those toward transition-metal complexes have not been interpreted.

In the course of our research of the asymmetric syntheses of α-amino acids from the thermal decarboxylation of prochiral α-amino-α-alkylmalonate anion (ARM^{2-}) with cobalt(III)–tetraamine complexes under acidic conditions,[4,5] we adopted AM^{2-} as a precursor for the synthesis of chiral glycine in which one of the methylene protons is substituted by a deuterium. Contrary to our expectation, the reaction of AM^{2-} did not lead to chiral induction. However, it gave a variety of interesting complexes.

It is well-known that high-valent transition-metal complexes are capable of stabilizing unstable organic compounds with substantial electron-withdrawing effects of the metal ions, so that they can be available as reaction probes for ligand reactions. Previously, Sargeson and co-workers developed the inter- and intramolecular C–N bond formation between substrates containing unsaturated bonds, such as $>C{=}O$,[6] $-C{\equiv}N$,[7] and $>C{=}C<$,[8] and

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amine or ammine ligands in the coordination sphere of Co(III) ions. These substrates undergo nucleophilic attack by conjugated bases generated from the deprotonation of coordinated amino groups in basic media.[9]

Recently, we have reported on the C–N bond formation between AM^{2-} and *trans*-$[CoCl_2(en)_2]^+$.[10,11] The reaction occurred in MeOH in the presence of NEt_3 under both aerobic and anaerobic conditions. The complexes obtained had unusually stable α-diamine (N–C–N) and carbinolamine (N–C–O) linkages. The reaction probably proceeds via an iminomalonato intermediate for the α-diamine formation[12,13] and the ketomalonato intermediate for carbinolamine formation.[14] It is noteworthy that the C–N bond formation took place on the sp^3 α-carbon of AM^{2-}, in contrast to the reactions described by Sargeson and co-workers.[6–8]

In a previous communication,[12] we reported the C–N bond formation between α-aminomalonate anion (AM^{2-}) and *trans*-$[CoCl_2(2,3,2\text{-tet})]^+$ (**1**).[10] In this paper we describe syntheses and characterization of X-ray analysis of four new complexes obtained from the reaction of AM^{2-} with **1**, including the X-ray crystallographic study on the four complexes. We also discuss the effects of reaction conditions on the C–N bond formation between AM^{2-} and the amine ligand.

Experimental Section

Analytical reagents were used without further purification. Commercial Et_3N was distilled before use. *trans*-$[CoCl_2(2,3,2\text{-tet})]ClO_4$ (**1**) was synthesized by a modified method of a reported procedure.[15] Ammonium α-aminomalonate was synthesized as described previously.[11] The experimental procedures were performed in air, unless otherwise noted.

SP-Sephadex C-25 (Na^+ form) and Dowex 50W-X2 (200–400 mesh, Na^+ form) cation exchange resins were both used for the separation of the complexes studied.

NMR spectroscopy was carried out on a JEOL GX-400 instrument using sodium trimethylsilylpentanesulfonate (TSP) in D_2O as a reference for ^1H NMR spectra (400 MHz) and 1,4-dioxane in D_2O for ^{13}C NMR spectra (100 MHz). ^1H NMR spectra were measured at room temperature and ^{13}C NMR spectra at 34 °C. The ^{13}C NMR spectra of the complexes were measured after ClO_4^- was exchanged for Cl^- with anion exchange resin Dowex 2-X8 (Cl^- form) by stirring in 0.7 mL of D_2O overnight. Absorption spectra were measured in H_2O with a Shimazu UV-240 UV–visible spectrophotometer.

1. Syntheses of [Co(α-aminomalonato)(2,3,2-tet)]$ClO_4\cdot H_2O$ (2), [Co(*N*-(2-aminoethyl)-*N*-(6-amino-4-azahexyl)-α,α-diaminomalonato)]ClO_4 (3), [Co(*N*-(9-amino-3,7-diazanonyl)-α,α-diaminomalonato)]$ClO_4\cdot H_2O$ (4), and [Co(*N*-(9-amino-3,7-diazanonyl)-α-amino-α-hydroxymalonato)]$ClO_4\cdot H_2O$ (5). Et_3N (3.03 g, 30 mmol) was slowly added to a suspension of $NH_4(AM)H$ (0.50 g, 3.7 mmol) and *trans*-$[CoCl_2(2,3,2\text{-tet})]ClO_4$ (1.60 g, 4.1 mmol) in methanol and refluxed for 3 h. After the mixture was evaporated to dryness, water was added and subsequently evaporated in order to remove Et_3N. The residue was dissolved in water and adsorbed on a SP-Sephadex C-25 (Na^+ form) cation-exchange-resin column. The column was washed well with water (ca. 2 L) and eluted with 0.02 M $NaClO_4$ to reveal three components. In addition, a large amount of a red-brownish highly charged band remained at the top of the SP-Sephadex column.

The first eluate was a well-known compound $[Co(CO_3)(2,3,2\text{-tet})]^+$.

The third eluate was collected and desalted by filtration and Sephadex G-15 gel chromatography. The crystals of compound **2** were obtained by recrystallization from water and washed with ethanol and ether. Anal. Calcd for $C_{10}H_{23}N_5O_4CoClO_4\cdot H_2O$: C, 26.47; H, 5.55; N, 15.44; Cl, 7.81. Found: C, 26.17; H, 5.40; N, 15.47; Cl, 7.70. Absorption spectrum, in H_2O: log ϵ_{494} = 2.13; log ϵ_{352} = 2.18.

The second eluate of the SP-Sephadex C-25 column was collected and partially desalted by filtration and adsorbed on the Dowex 50W-X2 cation-exchange column. The column was washed well with water and eluted by 0.2 M $NaClO_4$, revealing five components.

The first eluate from the Dowex column was collected and condensed by a rotatory evaporator. Filtration and Sephadex G-15 gel chromatography were performed, and recrystallization from water gave orange crystals of α-diamine complex **3**: yield, 14%. Anal. Calcd for $C_{10}H_{21}N_5O_4CoClO_4$: C, 27.69; H, 4.88; N, 16.15; Cl, 8.17. Found: C, 27.39; H, 4.74; N, 16.15; Cl, 8.40. Absorption spectrum, in H_2O: log ϵ_{481} = 2.07; log ϵ_{352} = 2.06.

The second eluate from the Dowex column was collected, reduced to a small volume, and desalted by filtration. After Sephadex G-15 gel chromatography, the eluate was reduced to a small volume and orange crystals of compound **4** were obtained. They were filtered and washed well with ethanol and ether. Yield, 21%. Anal. Calcd for $C_{10}H_{21}N_5O_4CoClO_4\cdot H_2O$: C, 26.59; H, 5.13; N, 15.50; Cl, 7.85. Found: C, 26.42; H, 5.04; N, 15.88; Cl, 7.91. Absorption spectrum, in H_2O: log ϵ_{475} = 2.25; log ϵ_{351} = 2.11.

The third eluate from the Dowex column was collected, reduced to a small volume, and desalted by filtration. After Sephadex G-15 gel chromatography, the eluate was reduced to a small volume to obtain orange crystals of carbinolamine complex **5**. They were washed well with ethanol and ether. Yield, 2%. Anal. Calcd for $C_{10}H_{20}N_4O_5CoClO_4\cdot H_2O$: C, 26.53; H, 4.90; N, 12.38; Cl, 7.83. Found: C, 26.49; H, 4.88; N, 12.44; Cl, 7.81. Absorption spectrum, in H_2O: log ϵ_{476} = 2.30; log ϵ_{353} = 2.20.

The fourth and fifth components will be reported elsewhere.

Improved Syntheses of Complex 2. (1) An aqueous solution (125 mL) of *trans*-$[CoCl_2(2,3,2\text{-tet})]ClO_4$ (1.60 g, 4.1 mmol) was adjusted to pH 6–7 by 0.1 M NaOH. To the solution, $NH_4(AM)H$ (0.53 g, 3.9 mmol) was added, and pH was maintained at 8 by 1 M NaOH and 1 M HCl. After the addition of charcoal, the temperature of the solution was raised to 50 °C and maintained for 2 h. After the charcoal was filtered off, the solution was diluted and adsorbed on a SP-Sephadex C-25 cation-exchange column. The column was washed well with water and eluted with 0.02 M $NaClO_4$. The reddish orange band was collected and desalted by filtration and Sephadex G-15 gel chromatography. Complex **2** was obtained as an orange powder from the reduced aqueous solution. Yield, 60%. (2) To a stirred suspension of **1** and $NH_4(AM)H$ in MeOH, NEt_3 was added slowly under anaerobic conditions. After the mixture was refluxed for 3h, an orange suspension was obtained and the volatile components were removed by evaporation. The orange powder was dissolved in ~2 L of water in air, and the reaction mixture was adsorbed onto an SP-Sephadex C-25 cation-exchange-resin column. The column was washed well with water and eluted with 0.02 M $NaClO_4$ to reveal a single orange band as a cationic (+1) fraction. The band was collected and purified by SP-Sephadex G-15 gel chromatography. The recrystallization from aqueous solution gave orange crystals of **2** in the yield of ca. 40–50%.

Another Synthetic Method of Complexes 3 and 4. To a stirred suspension of **1** (1.60 g, 4.1 mmol), $NH_4(AM)H$ (0.54 g, 4 mmol), and *p*-benzoquinone (0.54 g, 5 mmol) in methanol (250 mL), NEt_3 (4.2 mL, 30 mmol) was added under N_2. The mixture was refluxed for 3 h and then reduced to dryness. The reaction mixture was dissolved in ca. 2 L of water and adsorbed on the SP-Sephadex C-25 cation-exchange-resin column under air. The column was washed well with water and eluted with 0.02 M $NaClO_4(aq)$ to obtain an orange cationic (+1) fraction. The main band was collected and purified by SP-Sephadex G-15 gel chromatography. Recrystallization from water gave orange powder of a mixture of **3** and **4** (410 mg; yield, 24% as **3**).

Synthetic Procedure of Complex 5 Using Ketomalonic Acid or Tartlonic Acid. Et_3N (3.63 g) was slowly added to a suspension of ketomalonic acid (0.53 g) and **1** (1.75 g) in methanol and refluxed for 4 h. After the mixture was evaporated to dryness, water was added and subsequently evaporated to remove Et_3N. The reaction mixture was dissolved in water and adsorbed onto a SP-Sephadex C-25 (Na^+ form) cation-exchange column. The column was washed well with water and eluted with 0.02 M $NaClO_4$ to give an orange band as the major fraction. The band was collected and condensed by evaporation to obtain the block-shaped orange crystals of compound **5**: yield, 9%. Anal. Calcd for $C_{10}H_{20}N_4O_5CoClO_4\cdot H_2O$: C, 26.53; H, 4.90; N, 12.38; Cl, 7.83. Found: C, 26.79; H, 4.80; N, 12.22; Cl, 7.95.

Complex **5** was also obtained from the reaction of tartlonic acid (α-hydroxymalonic acid, $(HM)H_2$) with **1** in methanol in the presence of NEt_3. To a suspension of $(HM)H_2$ (0.44 g, 3.7 mmol) and **1** (1.67 g, 4.1 mmol) in MeOH (250 mL), NEt_3 (30 mmol) was added slowly. The reaction mixture was refluxed for 3 h and evaporated to dryness in order to remove MeOH and NEt_3. The mixture was dissolved in ca. 2 L of

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

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Table I. Crystallographic Data and Experimental Conditions for Complex Cations **2–5**

compd	**2**	**3**	**4**	**5**
formula	$C_{10}H_{23}N_5O_4CoClO_4H_2O$	$C_{10}H_{21}N_5O_4CoClO_4$	$C_{10}H_{21}N_5O_4CoClO_4H_2O$	$C_{10}H_{20}N_4O_5CoClO_4H_2O$
formula wt	453.72	433.69	451.71	452.69
cryst size, mm³	0.5 × 0.4 × 0.5	0.65 × 0.4 × 0.2	0.30 × 0.25 × 0.08	0.25 × 0.23 × 0.39
cryst system	monoclinic	monoclinic	monoclinic	orthorhombic
space group	*Cc*	$P2_1/c$	$P2_1/c$	$P2_12_12_1$
a, Å	13.856 (2)	7.399 (5)	7.360 (2)	7.291 (1)
b, Å	11.466 (2)	23.199 (5)	13.571 (3)	13.408 (2)
c, Å	11.898 (3)	9.452 (4)	17.730 (6)	17.143 (3)
β, deg	107.32 (1)	92.02 (5)	91.02 (2)	
V, Å³	1804.4 (5)	1621 (1)	1734 (1)	1675.9 (5)
Z	4	4	4	4
d(calcd), g·cm⁻³	1.67	1.78	1.730	1.79
d(obsd), g·cm⁻³	1.67	1.78	1.738	1.72
μ, mm⁻¹	1.150	1.319	1.196	1.24
no. of data	2401 ($\|F_o\| > 5\sigma(F_o)$)	3712 ($\|F_o\| > 3\sigma(F_o)$)	2483 ($\|F_o\| > 3\sigma(F_o)$)	3122 ($\|F_o\| > 3\sigma(F_o)$)
R	0.057	0.050	0.067	0.061
R_w	0.066	0.052	0.070	0.066

Table II. Change of Yields of Complexes under Various Conditions[a]

reaction conditions	**2**	**3**	**4**	**5**
in MeOH/NEt at reflux under air (daylight)	6	14	21	2
in MeOH/NEt_3 at reflux under air in the dark	*b*	12		*b*
in MeOH/NEt at reflux under N_2 (daylight)	40	0	0	0
in MeOH/NEt_3/*p*-benzoquinone at reflux under N_2	0	24		*c*
in H_2O (pH 8–9) at 50 °C under air	60	*c*		

[a] Isolated yields (%). [b] Not determined. [c] Not detected.

water and adsorbed onto a SP-Sephadex C-25 (Na^+ form) cation-exchange column. The column was washed well with water and eluted with 0.02 M $NaClO_4$ to reveal a minor orange band as the third fraction. This fraction was collected and purified by filtration and SP-Sephadex G-15 gel chromatography. The identity was confirmed by ^{13}C NMR spectroscopy.

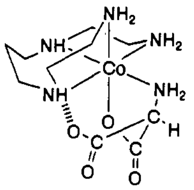
2. Collection of Diffraction Data and Structure Refinements. Diffraction data were collected on Rigaku AFC-5 (for **2** at Nara Women's University and **3** at the Institute of Physical and Chemical Research). Rigaku AFC-4 (for **4** at the Institute of Physical and Chemical Research), and AFC-6A (for **5** at The University of Tokyo) four-cycle automated diffractometers with Mo Kα (λ = 0.7107 Å) radiation and a graphite monochromator. In each case, data were collected at room temperature. Empirical absorption and Lorentz–polarization absorption corrections were made. The crystallographic and experimental data are summarized in Table I. All calculations for **2** and **5** were carried out on a HITACM-M680H(C) computer at the University of Tokyo and were also carried out on a FACOM M380 (for **3**) and FACOM M-780 (for **4**) at the Institute of Physical and Chemical Research, with universal program UNICS III.[16] Atomic scattering factors were taken from ref 17, and both Δ*f*′ and Δ*f*″ for non-hydrogen atoms were taken from ref 18. The structures were resolved by Patterson and Fourier methods and refined by block-diagonal least-squares techniques. In each case, the final difference map did not reveal any chemically significant electron density. The most intense residual peaks are as follows: **2**, 1.48 e/Å³, close to a Co ion; **3**, 0.73 e/Å³, close to a Cl atom; **4**, 0.96 e/Å³, near a perchlorate anion; **5**, 1.11 e/Å³, close to a Co ion. Final positional and thermal parameters are listed in Table S-I–S-VIII as supplementary material.

3. pK_a Titration for Complexes. The pK_a titrations were carried out at 25 °C. Titrations were performed with 0.1 M HCl for **3** and **4** in aqueous solutions and 0.1 M NaOH for **5**.

Results

I. Preparation of the Complexes. The yields of cationic (+1) products obtained from the reaction of AM^{2-} with **1** under various conditions are shown in Table II, and the structures of the complexes are described in Figure 1. In all the reactions, a large amount of an unidentified and highly charged reddish brown species was observed, which was strongly adsorbed onto the SP-Sephadex C-25 cation-exchange-resin column in the workup of the reaction mixture.

The reaction of AM^{2-} with **1** in MeOH/NEt_3 under reflux in air and in daylight gave complexes **2–5**. These reaction conditions were favorable for the formation of α-diamine complexes **3** and **4**. In addition, when the reaction was performed in air and in the dark, the yields of **3** and **4** were reduced. However, no C–N bond formation was observed when the reaction was photoirradiated by a high-pressure Hg lamp or in daylight at ambient temperature.



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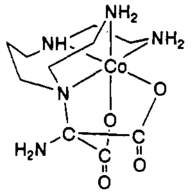

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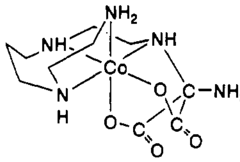

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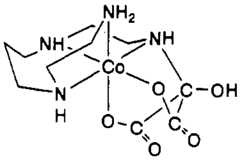

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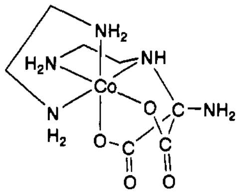

6

Figure 1. Structures of complexes discussed in the text.

Conversely, under anaerobic conditions, condensation was not observed and **2** was obtained as the main product. This is in sharp contrast with the results in the Co(III)–en system in which an α-diamine complex was obtained even in the absence of O_2.[11] However, addition of *p*-benzoquinone allowed the generation of **3** and **4** under N_2, although the yields were low.

When **1** and AM^{2-} were reacted in H_2O at pH 8–9, adjusted with the addition of 1 M NaOH at 50 °C in air, **2** was obtained as the major product without C–N bond formation. When NEt_3 was used as a base, no carbinolamine complexes were obtained, whereas the carbinolamine formation occurred selectively in the Co(III)–en system under similar reaction conditions.[11]

Carbinolamine complex **5** was isolated as a minor product of the α-diamine formation in air. The same complex was also obtained as a main product from the reaction of ketomalonic acid

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(16) Sakurai, T.; Kobayashi, K. *Rikagaku Kenkyusho Hokoku* **1979**, *55*, 69.
(17) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1962; Vol. III, pp 270–276.
(18) Cromer, D. T. *Acta Crystallogr.* **1965**, *18*, 17.

Table III. ^1H and Low-Power Broad-Band Proton Decoupled ^{13}C NMR Spectroscopic Data of Complexes **2–5** in D_2O (ppm)[a]

compound	α-proton	α-carbon	$-COO^-$	2,3,2-tet part
2	4.12, 4.15	64.8	172.8, 183.4	24.3, 45.3, 45.6, 46.7, 51.0, 51.6, 57.2
3		95.0	174.9, 177.3	27.8, 42.4, 48.5, 48.7, 55.9, 56.5, 58.0
4		85.0	175.7, 176.5	24.2, 44.3, 44.7, 46.5, 48.4, 50.7, 57.0
5		93.1	175.1, 175.9	24.2, 44.3, 44.9, 46.5, 48.4, 50.9, 57.2

[a] Sodium trimethylpentanesulfonate (TSP) as a reference for ^1H NMR chemical shift; dioxane (67.4 ppm) for ^{13}C NMR chemical shift.

((KM)H_2) with **1** in MeOH/NEt_3. Interestingly, the reaction of tartlonic acid (α-hydroxymalonic acid, (HM)H_2) with **1** gave **5** as a minor product.

II. Characterization of Complexes. The ^1H and ^{13}C NMR spectroscopic data in D_2O of complexes **2–5** are cited in Table III.

AM Complex (2). The absorption spectrum of complex **2** in H_2O indicated a typical $Co^{III}N_5O$ chromophore. The ^1H NMR spectrum of this complex exhibited two resonances at 4.15 and 4.12 ppm ascribed to the α-proton of the AM^{2-} ligand in Pro-R and Pro-S isomers of **2** for the prochirality of the α-carbon as described below. These peaks diminished gradually even in a neutral D_2O solution, with the peak at 4.15 ppm decreasing faster than the other. This observation indicates that the α-proton is more acidic than those of coordinated α-amino acids, which are known to be deprotonated in alkaline aqueous solutions.[19] The ^{13}C NMR spectrum of **2** in D_2O showed the resonance of the α-carbon at 64.8 ppm, a downfield shift of 5.0 ppm from that of a free NH_4(AM)H in D_2O. We assigned the signal at 183.4 ppm to the coordinated carboxyl group and that at 172.8 ppm to the uncoordinated one.[20]

In addition, the decarboxylation of complex **2** in 1 M HCl at 70 °C readily gave $[Co(gly)(2,3,2\text{-tet})]^{2+}$ (gly = glycinato).

Complexes Derived from the C–N Bond Formation. The absorption spectra of α-diamine and carbinolamine complexes in H_2O (absorption maxima: **3**, 481 and 352 nm; **4**, 475 and 351 nm; **5**, 476 and 353 nm) exhibited those of $Co^{III}N_5O$ chromophores in spite of the fact that they had *cis*-(*O*,*O*)-$Co^{III}N_4O_2$ geometries. The ^{13}C NMR spectra of complexes **3** and **4** showed downfield shifts for the resonance of the α-carbon in the AM^{2-} moiety compared with that of complex **2**. This is the general feature for the AM–amine condensed ligands on Co(III) ions. The downfield shift of the signal of the α-carbon for complex **4** is smaller than that of complex **3**. The α-carbon is bound to a primary amino group of the 2,3,2-tet ligand in complex **4**, whereas it is bound to a secondary amino group in **3**. Generally a carbon adjacent to amino groups tends to shift to lower field with the order of $-NR_2 > -NHR > -NH_2$.[21] This tendency is reflected in the chemical shifts of α-carbons in α-diamine linkages. The similar α-diamine complex [Co(*N*-(2-aminoethyl)-α,α-diaminomalonato)(ethylenediamine)]$^+$ ([Co(AM–en)(en)]$^+$, **6**)[11] showed the chemical shift of the α-carbon at 85.9 ppm, which was near that of **4**.

For a carbinolamine complex **5**, the chemical shift of the α-carbon of AM^{2-} showed a similar downfield shift toward 93.1 ppm. Moreover, elemental analysis of **5** showed good correspondence with the formula of the proposed structure, i.e. compound **5** has an uncoordinated hydroxy group.

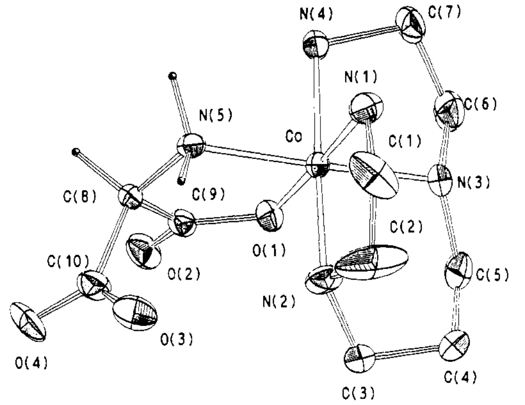

Figure 2. ORTEP drawing of the complex cation of **2** with the numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

Table IV. Selected Bond Lengths and Angles of **2** (Estimated Standard Deviations Cited in Parentheses)

	(a) Bond Lengths (Å)		
Co–O(1)	1.846 (6)	Co–N(1)	1.991 (8)
Co–N(2)	1.958 (7)	Co–N(3)	1.981 (8)
Co–N(4)	1.980 (7)	Co–N(5)	1.979 (6)
O(1)–C(9)	1.300 (8)	O(2)–C(9)	1.222 (10)
O(3)–C(10)	1.256 (13)	O(4)–C(10)	1.258 (11)
N(5)–C(8)	1.496 (9)	C(8)–C(9)	1.522 (12)
C(8)–C(10)	1.569 (11)		
	(b) Bond Angles (deg)		
O(1)–Co–N(1)	178.2 (3)	O(1)–Co–N(5)	86.2 (3)
N(1)–Co–N(2)	86.1 (3)	N(2)–Co–N(3)	93.1 (3)
N(2)–Co–N(4)	175.2 (3)	N(3)–Co–N(4)	87.0 (3)
N(3)–Co–N(5)	173.8 (3)	O(1)–C(9)–C(8)	115.4 (6)
O(2)–C(9)–C(8)	121.7 (7)	O(3)–C(10)–C(8)	117.3 (7)
O(4)–C(10)–C(8)	114.7 (9)	N(5)–C(8)–C(9)	109.7 (5)
N(5)–C(8)–C(10)	111.0 (6)	C(9)–C(8)–C(10)	109.1 (6)

III. Molecular Structure of [Co(α-aminomalonato)(2,3,2-tet)]$ClO_4 \cdot H_2O$ (2). An ORTEP drawing of the Λ-isomer of complex **2** is shown in Figure 2. Selected bond lengths and bond angles are cited in Table IV. The geometry around the central cobalt ion is essentially octahedral, with four coordination sites being occupied by the 2,3,2-tet ligand and the remaining two sites chelated by a bidentate AM^{2-} ligand through an amino group and one of the carboxyl groups. The 2,3,2-tet ligand coordinates to the Co(III) ion in a cis-β_2 fashion, which is typical, as observed in the (α-amino-α-alkylmalonato)- (ARM^{2-}) or (α-amino acidato)cobalt(III) complexes with 2,3,2-tet derivatives.[4,5]

All Co–N bond lengths are in the range from 1.958 (7) Å (Co–N(2)) to 1.991 (8) Å (Co–N(4)) [average 1.978 Å], which are longer than those of other complexes containing AM^{2-}, described below. The distance between the nitrogen atom (N(5)) of the amino group and the α-carbon (C(8)) of the AM^{2-} moiety is 1.496 (9) Å, which is normal for those of aliphatic amino compounds such as 2,3,2-tet. The α-carbon of the AM^{2-} ligand is prochiral. Its chirality was determined to be R in the Λ-isomer and S in the Δ-isomer. Intramolecular hydrogen bonding was observed between the uncoordinated carboxyl group of AM^{2-} and the secondary amino group of the 2,3,2-tet ligand (O(3)---N(2); 2.973 (11) Å) which was slightly longer than those between AMM^{2-} and 2,3,2-tet derivatives of Co(III) complexes.[5] These intramolecular hydrogen bondings play an important role in a three-point recognition of ARM^{2-} with cobalt(III)–polyamine complexes, which led to the asymmetric syntheses of α-amino acids via their decarboxylation reactions.[5] The decarboxylation of **2** in 1 M ^{2}HCl gave $[Co([^2H_2]gly)(2,3,2\text{-tet})]^{2+}$. Therefore, it seems impossible to synthesize a chiral [^{2}H]glycine as in the asymmetric induction of alanine observed in the decarboxylation of [Co(AMM)(5*R*,7*R*-Me_2-2,3,2-tet)]$^+$ (AMM = α-amino-α-methylmalonate). As described above, the α-proton of AM^{2-} can exchange too fast to be retained.

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(19) (a) Buckingham, D. A.; Marzilli, L. G.; Sargeson, A. M. *J. Am. Chem. Soc.* **1967**, *89*, 5133. (b) Buckingham, D. A.; Stewart, I.; Sutton, P. A. *J. Am. Chem. Soc.* **1990**, *112*, 845.

(20) Previously we reported on the assignment of two carboxyl groups of the coordinated AM^{2-} for $[Co(AM)(en)_2]^+$ in the ^{13}C NMR spectrum in ref 11. Correction was made as follows: A signal at 172.9 ppm was assigned to an uncoordinated carboxyl group and a coordinated one at 183.3 ppm.

(21) Yashiro, M.; Yano, S.; Yoshikawa, S. *J. Am. Chem. Soc.* **1986**, *108*, 1096.

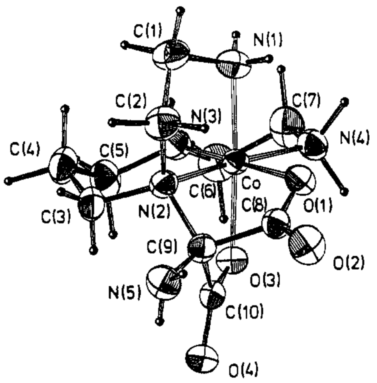

Figure 3. ORTEP representation of the complex cation of **3** with the numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

Table V. Selected Bond Lengths and Angles of **3** (Estimated Standard Deviations Cited in Parentheses)

	(a) Bond Lengths (Å)		
Co–O(1)	1.910 (2)	Co–O(3)	1.923 (2)
Co–N(1)	1.938 (3)	Co–N(2)	1.954 (3)
Co–N(3)	1.952 (3)	Co–N(4)	1.950 (3)
O(1)–C(8)	1.283 (4)	O(2)–C(8)	1.218 (4)
O(3)–C(10)	1.282 (4)	O(4)–C(10)	1.222 (4)
N(2)–C(2)	1.509 (5)	N(2)–C(3)	1.498 (4)
N(2)–C(9)	1.528 (4)	N(5)–C(9)	1.422 (5)
C(8)–C(9)	1.541 (4)	C(9)–C(10)	1.550 (4)
	(b) Bond Angles (deg)		
O(1)–Co–O(3)	89.37 (9)	O(1)–Co–N(2)	84.8 (1)
O(3)–Co–N(2)	84.2 (2)	N(1)–Co–N(2)	88.8 (1)
N(2)–Co–N(3)	99.9 (1)	N(3)–Co–N(4)	85.0 (1)
O(1)–Co–N(3)	174.9 (1)	O(3)–Co–N(1)	172.5 (1)
N(2)–Co–N(4)	174.5 (1)	N(2)–C(9)–N(5)	113.5 (3)
N(2)–C(9)–C(8)	105.8 (2)	N(2)–C(9)–C(10)	102.7 (2)
N(5)–C(9)–C(8)	115.6 (3)	N(5)–C(9)–C(10)	113.9 (3)
C(8)–C(9)–C(10)	104.1 (2)		

IV. Molecular Structure of [Co(*N*-(2-aminoethyl)-*N*-(6-amino-4-azahexyl)-α,α-diaminomalonato)]ClO_4 (3). An ORTEP representation of the Δ-isomer of complex **3** is shown in Figure 3. Selected bond lengths and bond angles are cited in Table V. The coordination at the central cobalt ion is essentially octahedral, with six coordination sites being occupied by a condensed ligand, *N*-(2-aminoethyl)-*N*-(6-amino-4-azahexyl)-α,α-diaminomalonato (s-AM–2,3,2-tet). The 2,3,2-tet moiety of the condensed ligand binds to the Co(III) ion in a typical cis-β fashion. The conformations of the chelate rings are λ for (N(1)–C(1)–C(2)–N(2) (out of plane), δ for N(3)–C(6)–C(7)–N(4) (in plane), and a chair form for the six-membered ring of N(2)–C(3)–C(4)–C(5)–N(3).

The geometry around the α-carbon of the AM^{2-} moiety is of a normal tetrahedral. The bond length of the newly formed C–N bond (N(2)–C(9)) was 1.528 (4) Å, which is normal for aliphatic amino compounds. In contrast, the bond length between the α-carbon (C(9)) and the nitrogen atom (N(5)) of a free amino group is 1.422 (5) Å, which is shorter than those of the uncondensed AM^{2-} ligand in **2** and aliphatic amino compounds such as 2,3,2-tet (in complex **3**, the bond lengths of C–N bonds of the 2,3,2-tet moiety are in the range of 1.48–1.50 Å) and similar to those of aniline derivatives.[22]

V. Molecular Structure of [Co(*N*-(9-amino-3,7-diazanonyl)-α,α-diaminomalonato)]ClO_4·H_2O (4). A perspective view of the Δ-isomer of **4** is shown in Figure 4. The coordination at the central cobalt ion is essentially octahedral, with all six coordination sites being occupied by the condensed ligand, *N*-(9-amino-3,7-diazanonyl)-α,α-diaminomalonato (p-AM–2,3,2-tet). Selected bond lengths and bond angles, together with their estimated standard deviations, are cited in Table VI.

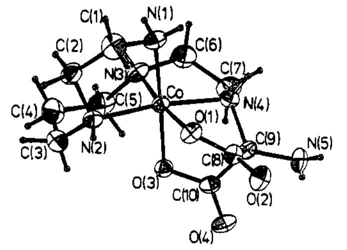

Figure 4. ORTEP plot of the complex cation of **4** with the numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

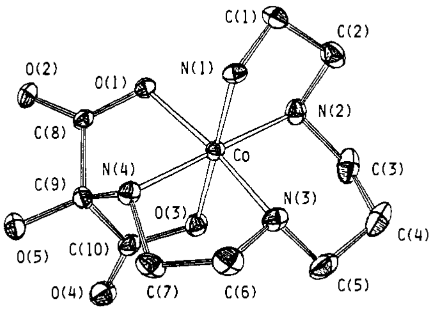

Figure 5. ORTEP representation of the complex cation of **5** with the numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

Table VI. Selected Bond Lengths and Angles of **4** (Estimated Standard Deviations Cited in Parentheses)

	(a) Bond Lengths (Å)		
Co–O(1)	1.930 (5)	Co–O(3)	1.926 (3)
Co–N(1)	1.947 (6)	Co–N(2)	1.936 (6)
Co–N(3)	1.941 (6)	Co–N(4)	1.932 (5)
O(1)–C(8)	1.279 (8)	O(2)–C(8)	1.229 (8)
O(3)–C(10)	1.290 (8)	O(4)–C(10)	1.224 (8)
N(4)–C(9)	1.490 (8)	N(5)–C(9)	1.427 (9)
C(8)–C(9)	1.559 (9)	C(9)–C(10)	1.532 (9)
	(b) Bond Angles (deg)		
O(1)–Co–O(3)	89.7 (2)	O(1)–Co–N(3)	172.8 (2)
O(1)–Co–N(4)	83.7 (2)	O(3)–Co–N(1)	176.4 (3)
O(3)–Co–N(4)	83.3 (2)	N(1)–Co–N(2)	87.5 (3)
N(2)–Co–N(3)	94.5 (3)	N(2)–Co–N(4)	172.5 (3)
N(3)–Co–N(4)	89.2 (2)	N(4)–C(9)–N(5)	115.0 (6)
N(4)–C(9)–C(8)	104.1 (5)	N(4)–C(9)–C(10)	103.7 (5)
N(5)–C(9)–C(8)	113.6 (6)	N(5)–C(9)–C(10)	115.1 (6)
C(8)–C(9)–C(10)	104.0 (5)	C(7)–N(4)–C(9)	115.3 (5)

The conformations of the chelate rings are δ for N(1)–C(1)–C(2)–N(2) (out of plane), λ for N(3)–C(6)–C(7)–N(4) (in plane), and a chair form for the six-membered chelate ring of N(2)–C(3)–C(4)–C(5)–N(3). The conformations of two five-membered chelate rings in the Δ-isomers in **4** are inverted when compared with those in **2**, whereas those in **2** and **3** are consistent with each other. Conversely, in α-diamine complex **6**,[11] the conformations of the two ethylenediamine chelates are both δ in the Δ-isomer.

The Co–N lengths range from 1.932 (5) Å [Co–N(4)] to 1.947 (6) Å [Co–N(1)] and average 1.939 Å, which is similar to that of **6** (average 1.937 Å) but shorter than that of **3** (average 1.949 Å).

The bond length of the newly formed C–N bond, N(4)–C(9), was 1.490 (8) Å, which is standard for a saturated aliphatic C–N bond but shorter than that of complex **3** (1.528 (4) Å) and that of **6** (1.503 (12) Å). The distance between the α-carbon of AM^{2-} and the free amino group, C(9)–N(5), is 1.427 (9) Å, which is also shorter than the standard length of C(sp^3)–N bonds as observed in complex **3**. This is a general feature for the α-diamine linkages derived from AM^{2-} and cobalt(III)–polyamine complexes.

The nitrogen atom (N(4)) of the condensed amino group for complex **4** is chiral, its chirality determined to be R in the Δ-isomer. On the contrary, an S chirality was found in the Δ-isomer for complex **3**.

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[22] *Kagaku Bin-ran, Kiso-hen II*; The Chemical Society of Japan: Maruzen, Tokyo, 1975; p 1379.

Table VII. Selected Bond Lengths and Angles of **5** (Estimated Standard Deviations Cited in Parentheses)

(a) Bond Lengths (Å)			
Co–O(1)	1.930 (4)	Co–O(3)	1.906 (4)
Co–N(1)	1.938 (5)	Co–N(2)	1.949 (6)
Co–N(3)	1.929 (6)	Co–N(4)	1.939 (5)
N(4)–C(9)	1.482 (8)	C(8)–C(9)	1.547 (8)
C(9)–C(10)	1.543 (9)	O(5)–C(9)	1.369 (8)
O(1)–C(8)	1.275 (7)	O(2)–C(8)	1.216 (7)
O(3)–C(10)	1.278 (7)	O(4)–C(10)	1.217 (8)
(b) Bond Angles (deg)			
O(1)–Co–O(3)	89.8 (2)	O(1)–Co–N(3)	173.1 (2)
O(1)–Co–N(4)	84.2 (2)	O(3)–Co–N(1)	176.7 (2)
O(3)–Co–N(4)	83.3 (2)	N(1)–Co–N(2)	86.7 (2)
N(2)–Co–N(3)	94.7 (2)	N(2)–Co–N(4)	173.3 (2)
N(3)–Co–N(4)	88.9 (2)	N(4)–C(9)–O(5)	114.4 (5)
N(4)–C(9)–C(8)	105.1 (5)	N(4)–C(9)–C(10)	105.5 (5)
O(5)–C(9)–C(8)	114.2 (5)	O(5)–C(9)–C(10)	113.1 (5)
C(7)–N(4)–C(9)	115.1 (5)		

The unit cell contains two molecules, each of Δ-isomer and Λ-isomer. The uncoordinated amino group binds to a water molecule of crystallization by hydrogen bonding, as in the crystal of **6**$Cl\cdot O.5H_2O$. In contrast to **4** and **6**, the uncoordinated amino group of **3** formed a hydrogen bond toward the ClO_4^- ion.

VI. Molecular Structure of [Co(*N*-(9-amino-3,7-diazanonyl)-α-amino-α-hydroxymalonato)]$ClO_4\cdot H_2O$ (5). A perspective view of the Λ-isomer of **5** is shown in Figure 5. In the unit cell of this compound, preferential crystallization was observed. The molecule of this compound contained a hexadentate ligand, *N*-(9-amino-3,7-diazanonyl)-α-amino-α-hydroxylmalonato (p-HM–2,3,2-tet). Selected bond lengths and bond angles, together with their estimated standard deviations, are cited in Table VII.

Similar to the structure of complex **4**, the primary amino group of 2,3,2-tet condensed with the carbonyl carbon of the ketomalonate anion. This complex has a free hydroxyl group and maintained a carbinolamine linkage expectedly. The length of the newly formed C–N bond (1.482 (8) Å) was shorter than those of α-diamine linkages, and the distance (1.369 (8) Å) between the oxygen of the free OH group (O(5)) and the α-carbon (C(9)) of the newly formed hydroxymalonato moiety was shorter than those of sp^3 carbon–oxygen single bonds. Sargeson et al.[6b] reported the intramolecular carbinolamine formation between aminoacetoaldehyde and the trien (1,8-diamino-3,6-diazaoctane) ligand; they found the complex obtained had a free OH group, and the distance of the newly formed C–N bond and the distance between the OH group and the central carbon of the carbinolamine linkage were 1.502 (9) and 1.416 (10) Å, respectively. These bond lengths are longer than those of complex **5**.

The intramolecular imine formation reactions of 2-keto acids with cobalt(III)–ammine complexes have already been reported;[6a] however, the reaction of KM^{2-} with **1** gave no imine complexes, and **5** was obtained selectively.

Discussion

I. Structures of Complexes. The striking feature of complexes **3–5** is that they stabilize unstable intermediate compounds in their coordination spheres. The α-diamine linkage is postulated as an intermediate in the reaction between an amine and an imine.[23] The carbinolamine structure is also assumed to be an intermediate of the reaction of an amine with a ketone or an aldehyde.[23] The high-valent and substitution-inert Co(III) contributes to the stabilization of those transient skeletons with an electron-withdrawing effect. For complexes **3–5**, they have noncoordinated free amino or hydroxyl groups on the molecular surfaces.

Table VIII. Comparison of the Bond Lengths (Å) and pK_a Values among Related Compounds

compound	α-C–N(amine)	α-C-uncoordinated functional group	pK_a[a]
2		1.496 (9)[b]	
3	1.528 (4)	1.422 (5)	*c*
4	1.490 (8)	1.427 (9)	1.6
6	1.503 (12)	1.427 (13)	*d*
AM^{2-}			9.83
aniline		1.431[e]	4.596[f]
5	1.482 (8)	1.369 (8)	9.1
phenol		1.364[e]	9.7

[a] Titration was performed at 25 °C. [b] The distance between a coordinated amino group and the α-carbon. [c] Indeterminable. [d] Not determined. [e] *Kagaku Bin-ran*; Maruzen: Tokyo, 1975; pp 1379. [f] Korton, G., Vogel, W., Andrussov, K., Eds. *Dissociation Constants of Organic Acids in Aqueous Solution*; Butterworth: London, 1961.

Regarding the α-diamine and carbinolamine linkages, surprisingly, their free functional groups showed different chemical behavior from aliphatic amines or alcohols despite the fact they are bound to sp^3 carbon atoms. In Table VIII, some properties of the linkages are summarized and compared with related compounds. The bond lengths between the α-carbon of the AM^{2-} moieties and the free NH_2 groups are shortened to 1.422 (5) Å (for **3**), 1.427 (9) Å (for **4**) and 1.427 (13) Å (for **6**), which are similar to that of aniline. In α-diamine skeletons found in the "cage" complexes $[Co(sep)]^{2+}$[24] and $[Co(azacapten)]^{3+}$,[25] one of the C–N bonds was shortened to 1.419 (15) and 1.37 (6) Å, respectively. On the other hand, in the reported carbinolamine linkage in $[CoCl(trenenol)]^{2+}$, the bond length between the oxygen atom of the free OH group and the carbon bound to the OH group is 1.416 (10) Å, which is normal for an aliphatic carbon–oxygen single bond.[6b] However, the carbinolamine complex **5** had a shorter distance of 1.369 (8) Å between the condensed carbon and the oxygen atom of a free OH group, and this is close to that of phenol.

The pK_a values of **3** was not measurable, but that of **4** was determined to be 1.6. The basicity of the amino group of the AM moiety was considerably reduced in comparison with the free AM^{2-} (pK_a = 9.83). On the other hand, the pK_a of **5** was determined to be 9.1 which was similar to that of phenol (pK_a = 9.7). These data are consistent with the short C–N and C–O bonds described above. The source of the properties of these complexes is still ambiguous.

II. Occurrence of C–N Bond Formation. The C–N bond formation between AM^{2-} and **1** occurred between a coordinated amino group and the α-carbon having sp^3 character. It is reasonable to consider the existence of an imine intermediate derived from the oxidation of AM^{2-} prior to the C–N bond formation. The possibility of the existence of an imine intermediate was supported by the isolation of an imido-bridged binuclear Co(III) complex, *p*-$[Co_2(\mu\text{-}(\mu_2\text{-}N;\ \eta^1\text{-}O,O')\text{-imidomalonato})(tren)_2]^{3+}$ when tren[10] was used as a polyamine ligand.[13] As described above, the oxidation of AM^{2-} toward the imine intermediate is mediated by the cobalt(III) ion and O_2 in the 2,3,2-tet system, whereas the α-diamine formation is observed even under anaerobic conditions with en as the amine component.[11] Dioxygen plays a role as the hydrogen or electron and proton acceptor in the 2,3,2-tet system, but *p*-benzoquinone can act as an alternative. The ESR measurements of the reaction mixture of **1** and AM^{2-} in $MeOH/NEt_3$ in the presence of *p*-benzoquinone under N_2 showed a semiquinone radical which had some interaction with the cobalt center. This shows that the oxidation of AM^{2-} takes place through a radical mechanism.[26] The oxidation mechanism will be discussed in detail elsewhere.

The reaction is photoinductively enhanced so that when the reaction was performed in the dark, the yields of the α-diamine complexes were reduced. However, no α-diamine complexes were obtained at room temperature in daylight or by irradiation by Hg lamp. These observations show that the C–N bond formation is essentially thermal and photoinductively enhanced. In the 2,3,2-tet system, the condensation reaction occurred only in MeOH. The

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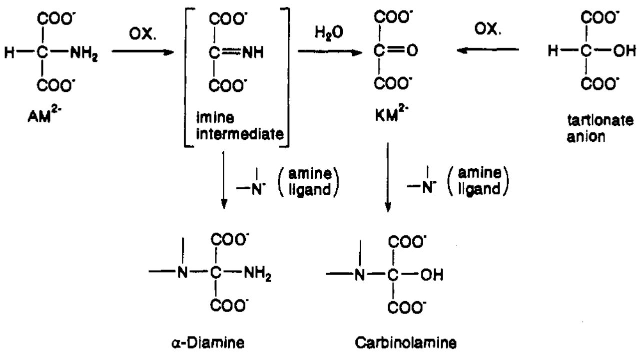
Scheme I



same reaction was not observed in water, EtOH, or acetone under both aerobic and basic conditions. This indicates that MeOH plays some important role in the reaction, especially in the oxidation of AM^{2-}.

In contrast, in the en system, the α-diamine formation was not influenced by the existence of O_2 and daylight. In addition, the carbinolamine formation was dominant in H_2O/NEt_3 in air in the en system,[11] whereas the reaction of AM^{2-} with **1** gave no complexes containing the new C–N bonds under similar conditions. It is obvious that the reaction mechanism is different in each amine system.

The existence of a ketomalonato intermediate was confirmed when $(KM)H_2$ reacted with **1** to afford **5**. As it is likely that the ketomalonato intermediate is formed via the hydrolysis of the imine intermediate, this observation would provide evidence for the formation of the imine intermediate. A schematic description of the conversion of AM^{2-} to the α-diamine and the carbinolamine linkages is shown in Scheme I. The conversion of AM^{2-} toward ketomalonate via iminomalonate can be compared to reactions performed by amino acid oxidases containing flavin adenine dinucleotide (FAD) as a cofactor.[27]

Summary

We have described the reaction of AM^{2-} with *trans*-$[CoCl_2(2,3,2\text{-tet})]^+$ to give α-diamine and carbinolamine complexes. Those reactions are essentially *thermal*, are enhanced photochemically, and need *MeOH* as a solvent. The oxidation of AM^{2-} to form the imine intermediate is conducted by Co(III) ion and *dioxygen*. Because of various discrepancies between the observations in the en and 2,3,2-tet systems, the oxidation mechanisms seem to depend on the polyamine systems employed.[28]

The remarkable properties of α-diamine and carbinolamine complexes are as follows: (1) New C–N bonds are formed between a coordinated amino group and a saturated sp^3 α-carbon of AM^{2-}. (2) The complexes have uncoordinated functional groups on the molecular surfaces and these functional groups show some properties similar to those attached to aromatics.

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Registry No. **1**, 20631-56-5; **2**, 136847-03-5; **3**, 96760-21-3; **4**, 136847-06-8; **5**, 132879-49-3; 2,3,2-tet, 4741-99-5; ammonium α-aminomalonate, 25624-92-4; $[Co(AM)(en)_2]ClO_4$, 125108-72-7.

Supplementary Material Available: Tables of anisotropic thermal parameters and positional parameters of **2**–**5**, mean-square displacement, tensor values, and full details of X-ray crystallography (17 pages); tables of observed and calculated structure factors for **2**–**5** (50 pages). Ordering information is given on any current masthead page.

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X-ray Structural and NMR Characterization of the Copper(I) Dimer $[Cu(dmpe)_2]_2(BF_4)_2$, Where Dmpe is 1,2-Bis(dimethylphosphino)ethane

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The reaction of $[Cu(CH_3CN)_4]BF_4$ with dmpe (where dmpe is 1,2-bis(dimethylphosphino)ethane) in methanol yields the air-stable, white solid $[Cu(dmpe)_2]_2(BF_4)_2$. This dimeric Cu(I) complex has been characterized by single-crystal X-ray crystallography, variable-temperature ^{31}P and ^{63}Cu NMR spectroscopy in solution, and solid-state CPMAS ^{31}P NMR spectroscopy. The complex crystallizes in the triclinic space group $P\bar{1}$ with unit cell parameters $a = 8.8390$ (10) Å, $b = 10.0080$ (10) Å, $c = 12.479$ (2) Å, $\alpha = 99.300$ (10)°, $\beta = 95.640$ (10)°, $\gamma = 93.940$ (10)°, $V = 1080.1$ (2) Å³, and $Z = 2$; $R_w = 4.20\%$ for 5126 observed reflections [$F > 6.0\sigma(F)$]. The structure consists of a centrosymmetric $[Cu(dmpe)_2]_2^{2+}$ dimer and two disordered BF_4^- anions. The two copper atoms in the cation are bridged by two dmpe ligands to form a ten-membered $Cu_2P_4C_4$ ring. Tetrahedral coordination around each copper atom is completed by a bidentate dmpe ligand. Cu–P bond lengths range from 2.263 (1) to 2.293 (1) Å. The P–Cu–P bond angle for the chelating dmpe ligand is 89.2 (1)°, while the P–Cu–P angles linking different dmpe ligands range from 110.3 (1) to 116.9 (1)°. The solution ^{31}P NMR spectrum at ambient temperature shows a well-resolved quartet centered at −14.6 ppm (relative to 85% H_3PO_4), while the ^{63}Cu NMR spectrum at room temperature consists of a quintet centered at 186.7 ppm (relative to $[Cu(CH_3CN)_4]BF_4$ in CH_3CN). The line spacings due to Cu–P coupling amount to 800 Hz in both spectra. Lowering the temperature causes line broadening; both the ^{31}P and the ^{63}Cu spectra start to collapse at −33 °C due to quadrupolar relaxation of the copper atoms. The CPMAS ^{31}P solid-state spectrum shows a quartet centered at −22 ppm relative to solid ammonium phosphate; the asymmetry of the line spacings within this quartet is consistent with the distorted tetrahedral coordination observed in the crystal structure.

Introduction

Detailed investigations of Cu(I) diphosphine complexes have been reported for only a few diphosphine ligands. The best defined systems involve dppe (1,2-bis(diphenylphosphino)ethane) and dppm (1,2-bis(diphenylphosphino)methane) for which Cu(I) complexes with P:Cu ratios of 4:1, 3:1, 2:1, 1:1, 3:2, and 4:3 have been isolated.[3-8] These complexes are mostly polynuclear species

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