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# Synthesis and Characterization of Cobalt(III) Complexes Containing $\alpha$-Diamine and Carbinolamine Derived from $\alpha$-Aminomalonate and Ethylenediamine

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The $\alpha$-aminomalonate anion ($AM^{2-}$) undergoes a C–N bond formation reaction with *trans*-$[CoCl_2(en)_2]^+$ (en = ethylenediamine) in the presence of triethylamine ($Et_3N$) to produce $\alpha$-diamine and carbinolamine complexes. The reaction in water under air gives the carbinolamine complex **3** predominantly whereas the reaction under $N_2$ yields the $\alpha$-diamine complex **2** preferentially. These complexes were characterized by absorption and $^1H$ and $^{13}C$ NMR spectroscopy and elemental analysis. The X-ray crystal structure of the $\alpha$-diamine complex **2b** ([Co(*N*-(2-aminoethyl)-$\alpha$,$\alpha$-diaminomalonato)(en)]Cl·0.5$H_2O$) has been determined: formula $C_7H_{17}N_5O_4CoCl\cdot0.5H_2O$, space group $P\bar{1}$ (triclinic); $a$ = 13.196 (4) Å, $b$ = 13.212 (5) Å, $c$ = 7.259 (3) Å, $\alpha$ = 93.78 (3)°, $\beta$ = 89.00 (3)°, $\gamma$ = 92.80 (3)°, $Z$ = 4, $R$ = 0.056. The free OH group of the carbinolamine complex **3** ([Co(*N*-(2-aminoethyl)-$\alpha$-amino-$\alpha$-hydroxymalonato)(en)]$ClO_4\cdot H_2O$) was confirmed by $^1H$ NMR in DMSO-$d_6$ with the addition of $D_2O$. Of great interest is that the C–N bond formation reaction occurs on the $sp^3$ carbon of the $AM^{2-}$ ion.

## Introduction

Much attention has been given to the intermolecular and intramolecular C–N bond formation on transition-metal complexes.[2] Some of the attractive properties of metal complexes are the activation of coordinated molecules and the enhancement of their reactivity. For instance, so-called "template" reactions, i.e., the condensation between amines and carbonyl compounds on substitution-labile metal ions such as Co(II)[3] and Ni(II),[4] appear to have a great synthetic utility. In contrast, reactions between the nitrogen atom of the polyamine ligands in substitution-inert cobalt(III) complexes and the carbon of carbonyl or nitrile groups give Schiff bases (imines),[5] $\alpha$-iminoamines,[6] and carbinolamines,[7] the last of which are assumed to be an intermediate in the reaction of carbonyl groups with amines.[8]

Previously, we investigated the reactions of $\alpha$-alkyl-$\alpha$-aminomalonate anions ($ARM^{2-}$) with Co(III)–polyamine complexes.[9] The complexes obtained, in which $ARM^{2-}$ was coordinated to the central metal ion through the amino group and one of the carboxyl groups as a bidentate ligand, were used for the asymmetric synthesis of $\alpha$-amino acids. However, reaction of the $\alpha$-aminomalonate anion ($AM^{2-}$) and 3,7-diaza-1,9-diaminononane (2,3,2-tet) gives a noval compound containing an $\alpha$-diamine linkage. This arose from the unexpected C–N bond formation between the $\alpha$-carbon of $AM^{2-}$ and one of the coordinated amino groups of 2,3,2-tet.[10] In light of this observation, we focused our attention on whether such a C–N bond formation occurs generally in Co(III)–polyamine complexes. Here we report on an examination of the reaction of the $AM^{2-}$ ion with a Co(III) complex of ethylenediamine (en), including an X-ray crystal structure determination for one of the complexes.

## Experimental Section

Analytical reagents were used without further purification. Commercial $Et_3N$ was distilled before use. *trans*-$[CoCl_2(en)_2]Cl\cdot HCl\cdot 2H_2O$ was synthesized by a standard procedure.[11]

Monoammonium $\alpha$-aminomalonate was synthesized by the method of Thanassi[12] and purified by Dowex 2-X8 (200–400 mesh, $CH_3COO^-$ form) anion-exchange column chromatography eluted with 2 M $CH_3COONH_4$. The $^1H$ NMR spectrum of this compound in $D_2O$ did not show any other resonances except that for $\alpha$-proton of the $AM^{2-}$ ion at 4.16 ppm.

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 (DSS) in $D_2O$ and tetramethylsilane ($Me_4Si$) in DMSO-$d_6$ as references for $^1H$ NMR spectra (400 MHz) and dioxane in $D_2O$ for $^{13}C$ NMR spectra (100 MHz). $^1H$ NMR spectra were measured at room temperature and low-power broad-band proton-decoupled $^{13}C$ NMR spectra and proton-decoupled INEPT $^{13}C$ NMR spectra were measured at 34 °C. $^{13}C$ NMR spectra of complexes were measured after exchanging $ClO_4^-$ for $Cl^-$ with anion-exchange resin Dowex 2-X8 by stirring in 0.7 mL of $D_2O$ overnight. Absorption spectra were measured with a Shimazu UV-240 UV–visible spectrophotometer.

**Synthesis and Separation of Complexes: ($\alpha$-Aminomalonato)bis(ethylenediamine)cobalt(III) Perchlorate Dihydrate ([Co(AM)(en)$_2$]$ClO_4\cdot 2H_2O$, 1), (*N*-(2-Aminoethyl)-$\alpha$,$\alpha$-diaminomalonato)(ethylenediamine)cobalt(III) Perchlorate ([Co(am-en)(en)]$ClO_4$, 2a), (*N*-(2-Aminoethyl)-$\alpha$-amino-$\alpha$-hydroxymalonato)(ethylendiamine)cobalt(III) Perchlorate Hydrate ([Co(ta-en)(en)]$ClO_4\cdot H_2O$, 3). The Reaction in Methanol.** $Et_3N$ (3.03 g) was slowly added to a stirred suspension of $NH_4AMH$ (0.50 g) and *trans*-$[CoCl_2(en)_2]Cl\cdot HCl\cdot 2H_2O$ (1.47 g) in methanol (250 mL) 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 reaction mixture 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 and eluted with 0.02 M $NaClO_4$ to reveal three components. On the top of the SP-Sephadex column, a large amount of a red-brown highly charged band was adsorbed.

The third minor orange eluate was collected, and after elimination of $NaClO_4$ by filtration and SP-Sephadex G-15 gel chromatography, compound **1** was obtained by recrystallization from water. Crystals were

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**Table I.** Crystal Data and Experimental Conditions for (*N*-(2-Aminoethyl)-$\alpha$,$\alpha$-diaminomalonato)(ethylenediamine)cobalt(III) Chloride Hemihydrate (**2b**)

| | | | |
|---|---|---|---|
| formula | $C_7H_{17}N_5O_4CoCl\cdot0.5H_2O$ | mol wt | 338.64 |
| cryst size, mm$^3$ | 0.25 × 0.15 × 0.10 | cryst system | triclinic |
| space group | $P\bar{1}$ | $a$, Å | 13.196 (4) |
| $b$, Å | 13.212 (5) | $c$, Å | 7.259 (3) |
| $\alpha$, deg | 93.78 (3) | $\beta$, deg | 89.00 (3) |
| $\gamma$, deg | 92.80 (3) | $V$, Å$^3$ | 1261.3 (8) |
| $Z$ | 4 | $d$(obsd), g cm$^{-3}$ | 1.81 |
| $d$(calcd), g cm$^{-3}$ | 1.78 | monochromator | graphite |
| $\lambda$, Å | 0.7107 (Mo K$\alpha$) | abs coeff, mm$^{-1}$ | 1.59 |
| scan method | $\omega(2° \le 2\theta \le 30°)$,<br>$\theta$–$2\theta$ $(30° \le 2\theta \le 60°)$ | | |
| scan speed, deg min$^{-1}$ | 4 | stds | 3 every 100 reflections |
| no. of intens measd | 3049 | no. of data | 2624 ($\lvert F_o\rvert \ge 5\sigma(F_o)$) |
| $R$ | 0.056 | $R_w$ | 0.067 |

collected, washed with ethanol and ether, and dried (yield 0.8%). Anal. Calcd for $CoC_7H_{19}N_5O_4ClO_4\cdot2H_2O$: C, 19.48; H, 5.37; N, 16.22. Found: C, 19.21; H, 4.96; N, 15.97 (compound **1**). The maxima of absorption spectrum (in $H_2O$) of **1** were $\epsilon_{487}$ = 103 M$^{-1}$ cm$^{-1}$ and $\epsilon_{347}$ = 117 M$^{-1}$ cm$^{-1}$.

The second major orange eluate was collected, desalted by filtration and SP-Sephadex G-15 gel chromatography, and adsorbed on Dowex 50W-X2 cation-exchange resin column ($Na^+$ form). The column was washed well with water and eluted with 0.2 M $NaClO_4$ to reveal three components.[13]

The first eluate from the Dowex column was collected and desalted by filtration and SP-Sephadex G-15 gel chromatography. After reduction in solvent volume, orange crystals deposited, were filtered off, and washed with ethanol and ether, and dried (yield 0.8%). Anal. Calcd for $CoC_7H_{17}N_5O_4ClO_4$: C, 21.36; H, 4.35; N, 17.79. Found: C, 21.16; H, 4.35; N, 17.42 (compound **2a**). The maxima of absorption spectrum (in $H_2O$) of **2** were $\epsilon_{477}$ = 134 M$^{-1}$ cm$^{-1}$ and $\epsilon_{353}$ = 102 M$^{-1}$ cm$^{-1}$.

The second eluate from the Dowex column was collected and desalted by filtration and SP-Sephadex G-15 gel chromatography. After reduction in volume, ethanol was added and an orange powder deposited. This was filtered off and suspended in a small volume of water. Orange solid was filtered off, washed with ethanol and ether, and dried (yield 0.8%). This complex, **3**, was identified by $^1H$ and $^{13}C$ NMR spectroscopy to be the same compound obtained from the reaction in water in the presence of $Et_3N$.

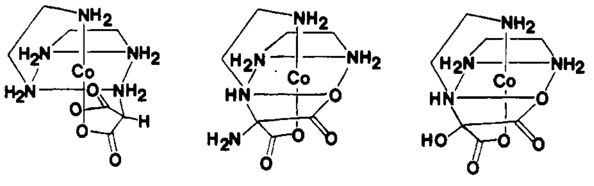
The first pink eluant from the Sephadex column contained $[Co(CO_3)(en)_2]^+$.

**The Reaction in Water.** To the aqueous solution (250 mL) of $NH_4AMH$ (0.50 g) and *trans*-$[CoCl_2(en)_2]Cl\cdot HCl\cdot2H_2O$ (1.47 g) was added $Et_3N$ immediately to achieve a neutral pH. Then $Et_3N$ was added without exceeding pH 10 and the temperature kept in the range 50–60 °C; a stationary state in pH (<8) was regarded as the end of the reaction. The solution was evaporated to dryness to remove $Et_3N$ and the residue dissolved in water. The reaction mixture was adsorbed on SP-Sephadex C-25 cation-exchange column and washed well with water. The column was eluted with 0.02 M $NaClO_4$ to reveal three components. The first pink eluate was $[Co(CO_3)(en)_2]^+$; the third orange fraction was compound **1** as obtained in methanol.

The second orange eluate was collected, desalted by filtration and SP-Sephadex G-15 gel chromatography, and adsorbed on Dowex 50W-X2 cation-exchange column. The column was washed well with water and eluted with 0.2 M $NaClO_4$ to reveal three trace bands and one main band. The eluate from the main band was collected and desalted. After concentration of the desalted solution, ethanol was added to obtain an orange powder. This was suspended in a small volume of water, filtered, washed with ethanol and ether, and dried (yield 12.0%). Anal. Calcd for $CoC_7H_{16}N_4O_5ClO_4\cdot H_2O$: C, 20.38; H, 4.40; N, 13.58; Cl, 8.59. Found: C, 20.60; H, 4.03; N, 13.91; Cl, 8.94 (compound **3**). The maxima of absorption spectrum (in $H_2O$) of **3** were $\epsilon_{481}$ = 134 M$^{-1}$ cm$^{-1}$ and $\epsilon_{355}$ = 118 M$^{-1}$ cm$^{-1}$.

**$^1H$ NMR Spectrum of Carbinolamine Complex 3 in DMSO-$d_6$.** A 9.2-mg sample of **3** was dissolved in 0.72 mL of DMSO-$d_6$ (the concentration of the complex was 3.10 × 10$^{-2}$ M). The $^1H$ NMR spectra at room temperature were measured immediately after the addition of $D_2O$ (0.02-mL aliquots).

**X-ray Diffraction Data Collection for (*N*-(2-Aminoethyl)-$\alpha$,$\alpha$-diaminomalonato)(ethylenediamine)cobalt(III) Chloride Hemihydrate (2b).** The perchlorate (**2a**) obtained above (90 mg) was stirred in a small volume of water (1 mL) with anion-exchange resin Dowex 2-X8 (120 mg) overnight. Crystals of this compound were obtained from the filtrate, and a block-shaped orange crystal was used in the reflection data collection. Anal. Calcd for $C_7H_{17}N_5O_4CoCl\cdot0.5H_2O$: C, 24.82; H, 5.36; N, 20.68. Found: C, 25.71; H, 5.27; N, 20.10. Cell dimensions and space group data were obtained from Weissenberg photographs. Diffraction data were collected at room temperature on a Rigaku AFC-5 four-circle automated diffractometer controlled by a FACOM U-100 computer and Rigaku FOS program system. The crystal parameters and experimental procedure are listed in Table I. Three standard reflections were monitored every 100 reflections, and their intensities showed random variation within 3.1% for which no correction was made. The density was measured by flotation in a dichloroethane–dibromoethane mixture.



1 2 3

**Figure 1.** Plausible structures of complexes.

**Structure Solution and Refinement.** All calculations were carried out on a HITACM-M680H(C) computer at the computer center of the University of Tokyo with universal program UNICS III.[14] The structure was solved by direct methods and the coordinates of two Co atoms were determined from the initial *E* map. The positions of the other non-hydrogen atoms were refined by means of mutual cycles of Fourier synthesis and block-diagonal least-squares techniques. Scattering factors for non-hydrogen atoms were taken from ref 15a and for hydrogen atoms from ref 15b. The effects of anomalous dispersion were corrected for in structure factor calculations, and values of $\Delta f'$ and $\Delta f''$ for nonhydrogen atoms were taken from ref 16. Least-squares refinement of the positional and individual anisotropic thermal parameters of non-hydrogen atoms gave convergence at $R$ = 6.58%. At this stage, a difference Fourier synthesis showed a water molecule of crystallization and the hydrogen atoms that are connected to carbon atoms. The positional and isotropic thermal parameters of these atoms were refined. The final $R = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$ and $R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/w\sum\lvert F_o\rvert^2]^{1/2}$ ($w$ = 1) factors were 5.6% and 6.7%, respectively. The final difference Fourier synthesis revealed no unusual features with the highest residual peak being 0.75 e Å$^{-3}$. The final positional parameters are cited in Table II.

## Results

### 1. Synthesis of Cobalt(III) $\alpha$-Diamine and Carbinolamine Complexes.

Previously we reported the C–N bond formation between $AM^{2-}$ and *trans*-$[CoCl_2(2,3,2\text{-tet})]^+$ in methanol in the presence of $Et_3N$ to obtain an $\alpha$-diamine complex.[10] In this study of the cobalt(III)–en system, we obtained the similar $\alpha$-diamine complex **2** and the novel carbinolamine complex **3** in low yields (0.8% each) with no selectivity, in addition to the $AM^{2-}$ complex **1** (yield 0.8%) from the reaction in methanol. The major loss is due to the formation of a large amount of a highly-charged

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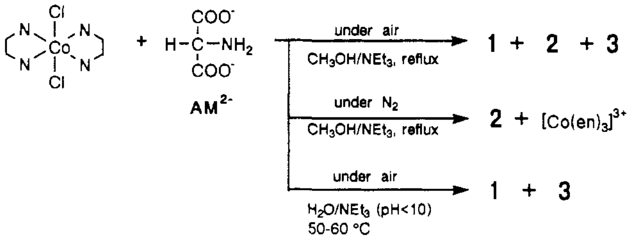
**Table II.** Final Positional Parameters and Their Established Standard Deviations (in Parentheses) for (*N*-(2-Aminoethyl)-$\alpha$,$\alpha$-diaminomalonato)(ethylenediamine)cobalt-(III) Chloride Hemihydrate (**2b**)

| atom | *x* | *y* | *z* | $\beta_{eq}$,[b] Å$^2$ |
|---|---|---|---|---|
| Co(1) | 0.286 14 (9) | −0.158 52 (9) | 0.033 46 (17) | 1.3 |
| Co(2) | 0.191 90 (9) | 0.339 14 (9) | 0.502 92 (17) | 1.3 |
| Cl(1) | 0.200 28 (22) | 0.144 83 (19) | 0.008 93 (34) | 2.5 |
| Cl(2) | 0.086 09 (21) | −0.155 45 (24) | −0.423 35 (38) | 3.1 |
| O(1) | 0.302 14 (49) | −0.252 32 (50) | 0.225 44 (90) | 1.9 |
| O(2) | 0.428 97 (57) | −0.340 98 (62) | 0.324 27 (104) | 3.1 |
| O(3) | 0.394 42 (57) | −0.073 04 (48) | 0.138 07 (87) | 1.7 |
| O(4) | 0.556 46 (58) | −0.088 76 (58) | 0.211 63 (110) | 3.1 |
| O(5) | 0.282 01 (52) | 0.373 27 (53) | 0.709 49 (91) | 2.2 |
| O(6) | 0.349 59 (64) | 0.514 95 (65) | 0.852 92 (113) | 3.7 |
| O(7) | 0.087 84 (45) | 0.415 55 (48) | 0.626 68 (90) | 1.7 |
| O(8) | 0.076 91 (50) | 0.571 61 (55) | 0.762 34 (108) | 2.7 |
| N(1) | 0.286 75 (57) | −0.075 68 (58) | −0.178 00 (115) | 1.9 |
| N(2) | 0.393 95 (59) | −0.231 13 (58) | −0.089 09 (101) | 1.7 |
| N(3) | 0.171 15 (59) | −0.243 60 (62) | −0.055 60 (109) | 1.9 |
| N(4) | 0.187 40 (60) | −0.080 67 (56) | 0.175 88 (104) | 1.7 |
| N(5) | 0.555 79 (67) | −0.281 52 (69) | 0.033 96 (118) | 2.5 |
| N(6) | 0.111 10 (55) | 0.324 50 (55) | 0.280 47 (98) | 1.4 |
| N(7) | 0.241 20 (60) | 0.468 59 (58) | 0.421 91 (101) | 1.7 |
| N(8) | 0.296 38 (70) | 0.255 93 (70) | 0.390 38 (129) | 1.6 |
| N(9) | 0.136 15 (62) | 0.215 13 (60) | 0.603 05 (112) | 2.0 |
| N(10) | 0.258 72 (70) | 0.634 64 (61) | 0.604 62 (120) | 2.4 |
| C(1) | 0.348 69 (78) | −0.122 93 (78) | −0.329 07 (139) | 2.2 |
| C(2) | 0.435 39 (78) | −0.173 95 (82) | −0.246 72 (132) | 2.2 |
| C(3) | 0.082 92 (76) | −0.225 82 (87) | 0.071 27 (141) | 2.4 |
| C(4) | 0.081 95 (70) | −0.112 78 (76) | 0.112 05 (136) | 2.0 |
| C(5) | 0.395 26 (73) | −0.282 73 (78) | 0.219 66 (132) | 2.0 |
| C(6) | 0.462 28 (68) | −0.234 16 (70) | 0.073 79 (129) | 1.7 |
| C(7) | 0.476 11 (71) | −0.120 98 (74) | 0.143 58 (125) | 1.9 |
| C(8) | 0.149 35 (71) | 0.401 54 (70) | 0.155 61 (108) | 1.5 |
| C(9) | 0.177 43 (77) | 0.497 53 (66) | 0.267 72 (137) | 1.9 |
| C(10) | 0.294 41 (88) | 0.159 63 (88) | 0.481 74 (156) | 3.0 |
| C(11) | 0.186 78 (90) | 0.128 79 (76) | 0.511 65 (155) | 2.7 |
| C(12) | 0.296 67 (70) | 0.470 72 (76) | 0.734 49 (132) | 1.9 |
| C(13) | 0.231 96 (69) | 0.528 60 (68) | 0.604 50 (120) | 1.6 |
| C(14) | 0.121 31 (71) | 0.506 84 (71) | 0.675 14 (126) | 1.7 |
| O′[a] | 0.443 48 (71) | 0.426 29 (82) | 0.300 62 (182) | 6.3 |

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

**Scheme I**



brownish species that is strongly adsorbed on SP-Sephadex C-25 resin. Under nitrogen, however, the $\alpha$-diamine complex **2** was obtained selectively as a main product (crude yield, 29.0%), another product being $[Co(en)_3]^{3+}$.

In contrast, the reaction of $AM^{2-}$ and *trans*-$[CoCl_2(en)_2]^+$ in water in the presence of $Et_3N$ gave the carbinolamine complex **3** in moderate yield (12.0%), although the $AM^{2-}$ complex **1** was also formed in low yield (0.8%). This was a specific phenomenon for the cobalt(III)–en system, not observed in the 2,3,2-tet system. Three other products were observed on the Dowex 50W-X2 column, but their yields were too small to be identified.

The distribution of reaction products under various conditions are summarized in Scheme I.

**2. Characterization of Isolated Complexes.** The absorption spectra of isolated compounds are shown in Figure 2. The $^1H$ and the low-power broad-band proton-decoupled $^{13}C$ NMR spectroscopic data are cited in Table III.

The absorption spectrum of compound **1** indicated a typical $Co^{III}N_5O$ chromophore[17] as shown in Figure 2. The $^1H$ NMR spectrum of **1** exhibited a resonance at 4.1 ppm ascribed to the $\alpha$-proton of the $AM^{2-}$ ligand. This peak completely disappeared after dissolution in $D_2O$ for 130 h.

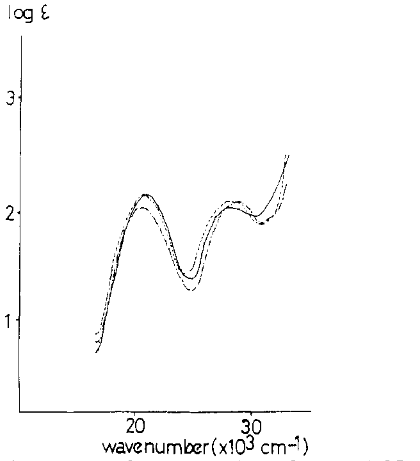


**Figure 2.** Absorption spectra of complexes in $H_2O$: (‒ ‒ ‒) $[Co(AM)(en)_2]^+$ ($1^+$): (—) $[Co(am-en)(en)]^+$ ($2^+$); (‐ ‐) $[Co(ta-en)(en)]^+$ ($3^+$).

**Table III.** $^1H$ NMR and Low-Power Broad-Band Proton-Decoupled $^{13}C$ NMR Spectroscopic Data for the $AM^{2-}$ Ion and the Cobalt(III) Complexes in $D_2O$ (ppm)

| compd | $\alpha$-proton[a] | $\alpha$-carbon[b] | $-COO^-$[b] | en[b] |
|---|---|---|---|---|
| $AM^{2-}$ | 4.2 | 59.8 | 170.8 | |
| **1** | 4.1 | 63.1 | 172.9, 183.3 | 43.9, 44.9, 45.5, 45.9 |
| **2** ($\alpha$-diamine) | | 85.9 | 175.8, 176.5 | 44.1, 45.9, 46.7, 48.8 |
| **3** (carbinolamine) | | 93.8 | 175.1, 175.7 | 44.2, 45.7, 46.8, 49.0 |

[a] DSS as a reference. [b] 1,4-Dioxane as a reference.

As shown in Table III, the chemical shifts of resonances of the $\alpha$-proton and the $\alpha$-carbon of the $AM^{2-}$ ligand in compound **1** were nearly equal to those of the free $AM^{2-}$ ion. The proton-decoupled INEPT $^{13}C$ NMR spectrum of **1** indicated that the resonance at 63 ppm can be assigned to a methine carbon.[18] Two resonances due to carboxyl groups of the $AM^{2-}$ ligand were observed, one of which at 172.9 ppm could be assigned to the coordinated carboxyl group and the other at 183.3 ppm to the uncoordinated carboxyl group.[9c] These results indicated that compound **1** contained the $AM^{2-}$ ligand coordinated through the amino group and one carboxyl group in the manner of $\alpha$-amino-$\alpha$-methylmalonato ($AMM^{2-}$) complexes[9c] as shown in Figure 1.

The $^{13}C$ NMR spectrum of **2** exhibited a resonance, assigned to the $\alpha$-carbon of the AM moiety, at 85.9 ppm, a downfield shift of 22.8 ppm from that of **1**. Furthermore, one of the resonances of en showed a small downfield shift compared with the same resonance for **1** (Table III). These results indicated that a C–N bond was formed between the $\alpha$-carbon of $AM^{2-}$ and one of the coordinated nitrogens of one of the en ligands, which was confirmed by X-ray crystallography.

In the $^{13}C$ NMR spectrum of **3**, the $\alpha$-carbon resonance was observed at 93.8 ppm, a downfield shift of 30.7 ppm from that of **1**; this is a greater downfield shift than that observed in **2**. These results indicated that a new C–N bond was formed between the $\alpha$-carbon of $AM^{2-}$ and one of the coordinated nitrogens of the en ligands. From the elemental analysis results, it was suggested that a free amino group in **2** was changed to a free hydroxyl group to form a carbinolamine linkage. The $^1H$ NMR spectrum of this compound in DMSO-$d_6$ showed a singlet peak corresponding to one proton at 7.35 ppm. This peak was assigned to the free hydroxyl group, drastically diminished with the addition of $D_2O$

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(18) $\Delta = {}^3/_4J$ (s) ($J$ = 140 Hz).

**Figure 3.** Change in the $^1$H NMR spectrum of [Co(ta-en)(en)]$^+$ ($3^+$) in DMSO-$d_6$ with the addition of $D_2O$ (0.02-mL aliquots): (a) DMSO-$d_6$ only; (b) solution plus one $D_2O$ aliquot; (c) solution plus two $D_2O$ aliquots.

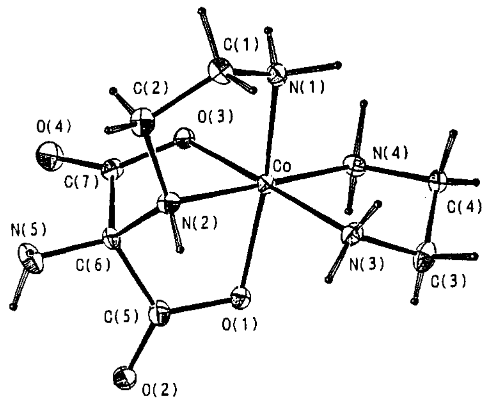

**Figure 4.** ORTEP drawing of Δ-[Co(am-en)(en)]$^+$ ($2^+$).

**Table IV.** Selected Bond Lengths (Å)[a]

| | | | |
|---|---|---|---|
| Co(1)-O(1) | 1.946 (7) | Co(1)-O(3) | 1.913 (6) |
| Co(1)-N(1) | 1.943 (8) | Co(1)-N(2) | 1.927 (8) |
| Co(1)-N(3) | 1.938 (8) | Co(1)-N(4) | 1.941 (8) |
| N(1)-C(1) | 1.479 (13) | C(1)-C(2) | 1.508 (15) |
| C(2)-N(2) | 1.494 (13) | N(3)-C(3) | 1.490 (13) |
| C(3)-C(4) | 1.504 (15) | C(4)-N(4) | 1.507 (13) |
| N(2)-C(6) | 1.503 (12) | C(6)-N(5) | 1.427 (13) |
| C(6)-C(5) | 1.522 (14) | C(6)-C(7) | 1.550 (14) |
| O(1)-C(5) | 1.311 (12) | O(2)-C(5) | 1.220 (13) |
| O(3)-C(7) | 1.279 (12) | O(4)-C(7) | 1.223 (13) |

[a] Established standard deviations are cited in parentheses.

without correlation with other resonances as shown in Figure 3. This result indicated the existence of the free hydroxyl group in compound **3**, the plausible structure of which is shown in Figure 1.

**3. Molecular Structure of (*N*-(2-Aminoethyl)-α,α-diaminomalonato)(ethylenediamine)cobalt(III) Chloride Hemihydrate (2b).** The unit cell in the crystal of this compound contained two asymmetric units, in which two molecules each of the Δ- and Λ-isomers were included. Since the structures of those isomers were essentially equivalent, we will discuss the structure of the Δ-isomer.

The coordination at the central cobalt ion is essentially octahedral, with four coordination sites being occupied by the condensed am-en ligand, the *N*-(2-aminoethyl)-α,α-diaminomalonato ligand, and two sites being occupied by the en ligand. A perspective view of the Δ-isomer is shown in Figure 4 in which the thermal ellipsoids have been drawn to include 50% probability distribution. Pertinent *selected* bond lengths and interbond angles, together with their estimated standard deviations, are shown in Tables IV and V, respectively. Hydrogen bonds in the unit cell and torsion angles are cited in Tables VI and VII, respectively.

**Table V.** Selected Interbond Angles (deg)[a]

| | | | |
|---|---|---|---|
| O(1)-Co(1)-O(3) | 89.5 (3) | Co(1)-N(2)-C(6) | 98.0 (5) |
| O(1)-Co(1)-N(1) | 171.2 (3) | Co(1)-N(3)-C(3) | 108.7 (6) |
| O(1)-Co(1)-N(2) | 84.0 (3) | Co(1)-N(4)-C(4) | 109.7 (6) |
| O(1)-Co(1)-N(3) | 88.4 (3) | N(1)-C(1)-C(2) | 109.0 (8) |
| O(1)-Co(1)-N(4) | 93.6 (3) | C(1)-C(2)-N(2) | 107.8 (8) |
| O(3)-Co(1)-N(1) | 89.6 (3) | N(3)-C(3)-C(4) | 106.1 (9) |
| O(3)-Co(1)-N(2) | 84.2 (3) | C(3)-C(4)-N(4) | 105.5 (8) |
| O(3)-Co(1)-N(3) | 175.8 (3) | N(2)-C(6)-N(5) | 114.7 (8) |
| O(3)-Co(1)-N(4) | 90.5 (3) | N(2)-C(6)-C(5) | 104.1 (7) |
| N(1)-Co(1)-N(2) | 87.2 (3) | N(2)-C(6)-C(7) | 103.3 (7) |
| N(1)-Co(1)-N(3) | 93.0 (4) | N(5)-C(6)-C(5) | 115.2 (8) |
| N(1)-Co(1)-N(4) | 95.1 (3) | N(5)-C(6)-C(7) | 113.5 (8) |
| N(2)-Co(1)-N(3) | 99.2 (3) | C(5)-C(6)-C(7) | 104.8 (7) |
| N(2)-Co(1)-N(4) | 174.2 (3) | O(1)-C(5)-O(2) | 124.8 (10) |
| N(3)-Co(1)-N(4) | 86.0 (3) | O(1)-C(5)-C(6) | 113.7 (8) |
| Co(1)-O(1)-C(5) | 109.3 (6) | O(2)-C(5)-C(6) | 121.4 (9) |
| Co(1)-O(3)-C(7) | 111.2 (6) | O(3)-C(7)-O(4) | 126.6 (9) |
| Co(1)-N(1)-C(1) | 109.5 (6) | O(3)-C(7)-C(6) | 113.1 (8) |
| Co(1)-N(2)-C(2) | 109.9 (6) | O(4)-C(7)-C(6) | 120.0 (9) |

[a] Established standard deviations are cited in parentheses.

**Table VI.** Hydrogen Bonds and Their Established Standard Deviations (in Parentheses)[a]

| D-H | A | D···A, Å | H···A, Å | sym transformn of A |
|---|---|---|---|---|
| N(9)-H(N9)2 | Cl(1) | 3.28 (1) | 2.39 (8) | *x*, *y*, *z* − 1 |
| N(4)-H(N4) | Cl(2) | 3.37 (1) | 2.47 (11) | *x*, *y* + 1, *z* |
| N(9)-H(N9)1 | Cl(2) | 3.27 (1) | 2.38 (9) | −*x*, −*y* + 1, −*z* + 1 |
| N(1)-H(N1) | O(4) | 2.95 (1) | 2.23 (8) | −*x* + 1, −*y* + 1, −*z* |
| N(3)-H(N3) | O(8) | 2.93 (1) | 2.28 (13) | *x*, *y* + 1, *z* + 1 |
| N(6)-H(N6) | O(8) | 2.92 (1) | 2.13 (9) | −*x*, −*y* + 1, −*z* + 1 |
| N(1)-H(N1) | O(4) | 2.95 (1) | 2.23 (8) | −*x* + 1, −*y* + 1, −*z* + 1 |
| N(5)-H(N5) | O′[b] | 2.99 (1) | 2.32 (16) | −*x* + 1, −*y*, −*z* |

[a] Hydrogen bonds are selected as follows: Cl–N, O bonds are less than 3.5 Å, N–O are less than 3.0 Å. [b] An oxygen atom of the water of crystallization.

**Table VII.** Selected Torsion Angles[a]

| atom 1 | atom 2 | atom 3 | atom 4 | torsion angles,[b] deg |
|---|---|---|---|---|
| N(1) | C(1) | C(2) | N(2) | 44.6 (10) |
| O(1) | C(5) | C(6) | N(2) | −39.8 (10) |
| N(2) | C(6) | C(7) | O(3) | 40.0 (10) |
| N(3) | C(3) | C(4) | N(4) | −52.3 (9) |

[a] Their established standard deviations in parentheses. [b] The torsion angle is positive if, when the structure is viewed from atom 2 to atom 3, a clockwise motion of atom 1 superimposes it on atom 4.

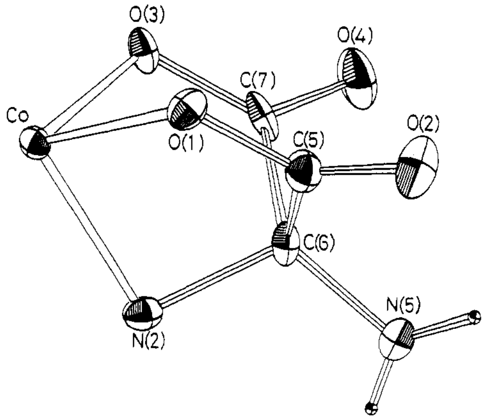

**Figure 5.** Structure of the AM moiety in complex **2**. N(2) is the nitrogen of the condensed en ligand.

The conformations of the two en ligands in Figure 4 are both δ. The AM moiety coordinates through the two carboxyl groups with the remaining free amino group located in the outer sphere of the complex as shown in Figure 5.

The Co–N lengths range from 1.927 (8) Å [Co–N(2)] to 1.943 (8) Å [Co–N(1)] and average 1.937 Å, which is shorter than the average for the previously reported $\alpha$-diamine complex in 2,3,2-tet system (1.949 Å).[10] The N–Co–N angles of the five-membered chelating en ligands are 87.2 (3)° [N(1)–Co–N(2)] and 86.0 (3)° [N(3)–Co–N(4)], the N–Co–O angles of the five-atom chelating rings are 84.0 (3)° [O(1)–Co–N(2)] and 84.2 (3)° [O(3)–Co–N(2)]; therefore, there is a slight distortion at the cobalt atom from the usual octahedral geometry.

The bond length of the newly formed C–N bond, N(2)–C(6), was 1.503 (12) Å, which was slightly longer than those of standard saturated aliphatic C–N bonds. Conversely, the distance between the free amino group and the $\alpha$-carbon, N(5)–C(6), was 1.427 (13) Å, which is much shorter than usual. C(5)–C(6) and C(6)–C(7) were 1.522 (14) and 1.550 (14) Å, respectively. Interbond angles of N(2)–C(6)–N(5), N(2)–C(6)–C(5), N(2)–C(6)–C(7), N(5)–C(6)–C(5), N(5)–C(6)–C(7), and C(5)–C(6)–C(7) were 114.7 (8), 104.1 (7), 103.3 (7), 115.2 (8), 113.5 (8), and 104.8 (7)°, respectively. These values indicated that the geometry around the $\alpha$-carbon was a normal tetrahedron. In the crystal, the free amino group binds to a water molecule of crystallization by a hydrogen bond [N(5)–H(N5)...O′] as shown in Table VI.

## Discussion

**1. Spectroscopic Features of Complexes.** For the $^1$H NMR spectrum of complex **1**, the resonance of the $\alpha$-proton diminishes faster in $D_2O$ than that in $[Co(AM)(2,3,2\text{-tet})]^+$. This result indicates that the cobalt(III)–en system provides a better opportunity toward $\alpha$-proton exchange in the $AM^{2-}$ ligand than does the cobalt(III)–2,3,2-tet system. It is known that $\alpha$-amino acids coordinated to cobalt(III) centers undergo base-catalyzed $\alpha$-proton exchange and mutarotation via a carbanion.[19] In complex **1**, even in a neutral aqueous solution, the $\alpha$-proton of the $AM^{2-}$ ligand is exchanged.

As one of the evidences for the C–N bond formation, we adopt the downfield shift of a signal assigned to a carbon of the en ligands. This assignment depends on the finding that the resonance of the vicinal carbon of a secondary amino group appears at a lower field compared with that of a primary amino group.[20] In the $[Co(\text{D-Rib-en})(en)]^+$ (D-Rib = D-ribose), the resonance of the vicinal carbon of the *N*-glycosidic amino group of the en ligand shows a downfield shift in the range of 7-8 ppm,[2] which is larger than ca. 3 ppm in compound **2**.

The absorption spectra of **2** and **3** in aqueous solution show the absorption maxima at lower wavelengths compared with the typical *cis*(*O*,*O*)-$Co^{III}N_4O_2$ chromophore.[17] This phenomenon is observed in the complex $[Co(N\text{-2-aminoethyl)aspartato)(en)}]^+$, which is formed by the reaction of the en and the maleato ion in $[Co(maleato)(en)_2]^+$.[21]

**2. Structural Features of Complexes.** In complex **1**, the $\alpha$-carbon of the $AM^{2-}$ ligand is a prochiral center. The $\Delta$-isomer is favored by a pro-*R* configuration whereas a $\Lambda$-isomer is favored by a pro-*S* configuration due to the intramolecular hydrogen bond between one amino group of en ligand and the free prochiral carboxyl group. Such a chiral recognition is observed in cobalt(III)-substituted 2,3,2-tet complexes of $AMM^{2-}$.[9c]

On the other hand, complex **2** contains the $\alpha$-diamine linkage, which is thought to be an intermediate of the reaction between amines and imines.[8,22] In spite of the fact that such a structure is usually assumed to be unstable, the electron-withdrawing effect of the cobalt(III) ion would stabilize it.[10] The $\alpha$-diamine structure can be found in cage complexes such as $[Co(sep)]^{3+}$ [23] and urotropin, each of which contain free tertiary amino groups. In addition, a complex having an $\alpha$-iminoamine group obtained from the reaction between $NH_2CH_2CN$ and en in a cobalt(III) complex was reported.[6a] The $\alpha$-diamine structure in which the $\alpha$-carbon is an sp$^2$ carbon such as an imino carbon and a keto carbon can be found in asparagine and urea. In contrast, in compound **2**, the $\alpha$-diamine linkage possesses a free primary amino group bound to an sp$^3$ carbon.

This complex (**2**) is slightly unstable compared with the previously reported $\alpha$-diamine complex in the 2,3,2-tet system. Though the condensed ligand is a hexadentate ligand in the 2,3,2-tet system, it is a tetradentate ligand in the en case. This difference in the number of chelate rings must exert an influence on the stability of these complexes.[24] The orange compound **2** decomposes in a neutral aqueous solution to a pink species that is thought to be a reduced cobalt(II) species but is not yet identified. This phenomenon is also observed for compounds **1** and **3**.

One nitrogen (N(2)) bound to the $\alpha$-carbon of $AM^{2-}$ is chiral: the crystallographic study showed that the *S* configuration is favored in the $\Delta$-isomer and the *R* in the $\Lambda$-isomer.

The carbinolamine complex **3** is assumed to have a structure similar to that of **2**, with a free hydroxyl group in place of the amino group.

## Summary

A Co(III)–en complex *trans*-$[CoCl_2(en)_2]^+$ undergoes C–N bond formation in its reaction with $AM^{2-}$, forming an $\alpha$-diamine or a novel carbinolamine complex. The latter reaction occurs selectively in water in the presence of $Et_3N$; this phenomenon is specific for this system. The results could indicate that the $\alpha$-diamine formation *generally* occurs in the reaction between Co(III)–polyamine (at least concerning linear polyamine ligands) complexes and $AM^{2-}$.

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**Supplementary Material Available:** Listings of anisotropic thermal parameters and atomic parameters of hydrogen atoms and a drawing showing the contents of the unit cell (5 pages); a listing of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

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