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Novel Carbinolamine Complex Derived from Ketomalonate and trans-[$CoCl_2$(3,7-Diaza-1,9-diaminononane)]$^+$. Synthesis and Characterization of [Co(N-(3,7-Diaza-9-aminononyl)-α-amino-α-hydroxymalonato)]$ClO_4 \cdot H_2O$

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A novel carbinolamine complex, [Co(N-(3,7-diaza-9-aminononyl)-α-amino-α-hydroxymalonato)]$^+$, was obtained from the reaction of ketomalonic acid and trans-[$CoCl_2$(2,3,2-tet)]$^+$ and the molecular structure was determined by X-ray analysis. A free OH group in the carbinolamine linkage had aromatic properties despie it binds to an sp^3 carbon.

Unstable intermediates have often been proposed in many organic reactions, however, the direct determination of those structures is generally difficult. The stable high-valent metal complexes are substitution-inert in many cases and they can be available as reaction probes because they stabilize unstable molecules by coordination.

A carbinolamine is a plausible intermediate for the reaction between an amine and a ketone or an aldehyde to generate an imine.(1) The molecular structures of several Co(III)-carbinolamine(2) and imine(3) complexes have been determined, however, no X-ray crystal structures of the complexes having a condensed ligand formed from an amine and ketomalonate anion (KM^{2-}), have been reported.(2c)

Previously we reported the synthesis and characterization of α-diamine and carbinolamine complexes derived from α-aminomalonate anion (AM^{2-}) and Co(III)-polyamine complexes which contained ethylenediamine (en)(4a) and 3,7-diaza-1,9-diaminononane (2,3,2-tet)(4b) as polyamine ligands. In this communication, we wish to report the successful isolation and X-ray crystal structure of a novel carbinolamine complex derived from the reaction of KM^{2-} with trans-[$CoCl_2$(2,3,2-tet)]ClO_4 (**1**).

To a suspension of the mixture of **1** (4.5 mmol) and H_2KM (4.5 mmol) in methanol (250 mL), triethylamine (30 mmol) was added slowly. After refluxing for 4 h, the reaction mixture was evaporated to dryness. The mixture was dissolved in water and SP-Sephadex C-25 cation exchange column chromatography⁵⁾ was performed to reveal one orange main band. The band was collected and the solution was concentrated to obtain block-shaped orange crystals of the carbinolamine complex, $[Co(HM\text{-}2,3,2\text{-}tet)]ClO_4\cdot H_2O$ (**2**) (yield, 9%).$^{6)}$ The compounds were spontaneously resolved as crystals in the space group $P2_12_12_1$.$^{7)}$

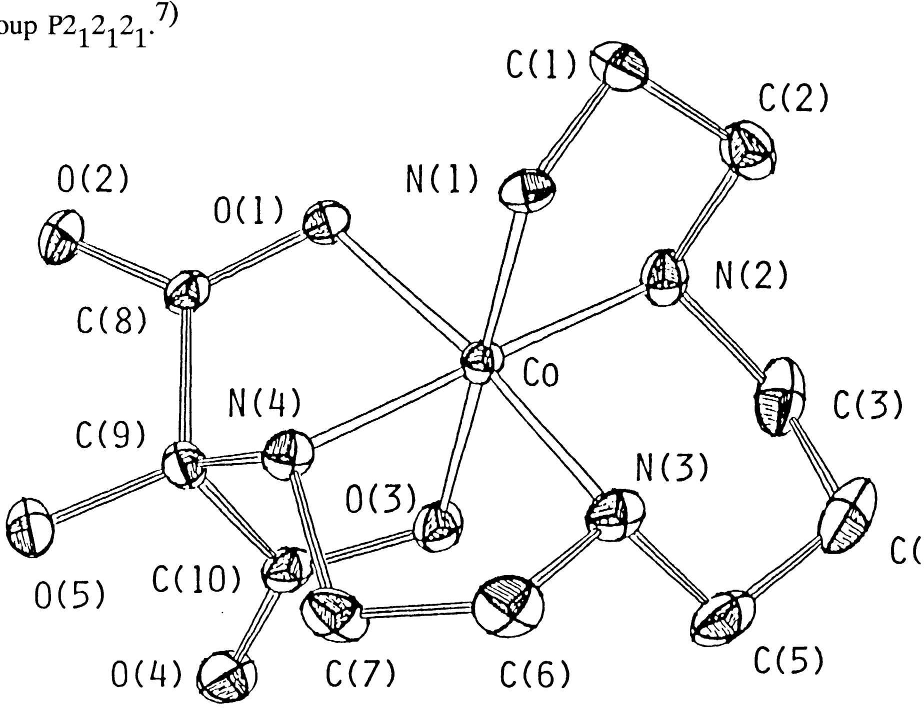


Fig. 1. ORTEP representation of complex cation of **2**.

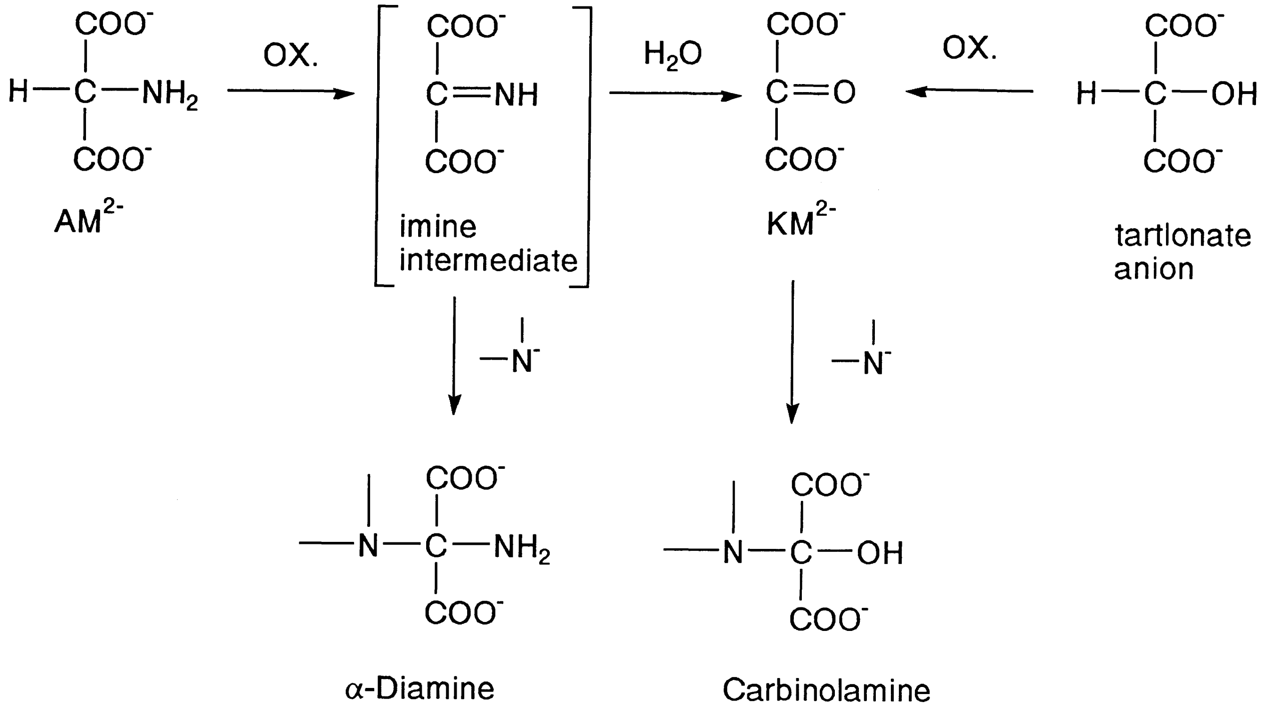
The molecular structure of the Λ-isomer of **2** is shown in Fig. 1. It was revealed that the central carbonyl carbon of KM^{2-} was bound to a primary amino group of 2,3,2-tet ligand to form a carbinolamine linkage (N(4)-C(9)-O(5)). The 2,3,2-tet moiety possesses a cis-β fashion, which is typical for the ligand.

In spite of the fact that the coordination around cobalt(III) is cis-(O, O)-$Co^{III}N_4O_2$, the absorption spectrum of **2** in H_2O showed the absorption maxima at 476 and 353 nm which is typical for $Co^{III}N_5O$ chromophore. This is the common feature for the α-diamine and carbinolamine complexes derived from AM^{2-}.$^{4)}$ The conformation of the two five-membered chelate rings of the 2,3,2-tet moiety is δ for N(1)-C(1)-C(2)-N(2) and λ for N(3)-C(6)-C(7)-N(4). The six-membered chelate ring, N(2)-C(3)-C(4)-C(5)-N(3), has a chair form which is similar to the conformation observed for the α-diamine complex previously reported.$^{4b)}$

The newly generated tertiary carbon possessed normal tetrahedral geometry, and the length of the newly generated C-N bond was 1.482(8) Å which is shorter than those of α-diamine complexes.$^{4)}$ The complex has a free hydroxy group which is directed toward the outer coordination sphere, and in the crystal, a water molecule of crystallization was bound to the OH group through a hydrogen bond. A similar hydrogen bond was observed between water and the free NH_2 moiety in the case of the α-diamine complex, [Co(N-(2-aminoethyl)-α, α -diaminomalonato)(en)]$^{+}$.$^{4a)}$ Of our interest, the distance between the α-carbon

(C(9)) and the oxygen of the OH group (O(5)) was 1.369(8) Å. The C–O bond length in complex **2** is near to that of phenol (1.364 Å) rather than those of alcoholic C–OH groups (1.42–1.43 Å) or chloral hydrate which has α-diol structure (1.47 and 1.48 Å).8) This indicates that the free OH group of **2** has properties similar to those of phenolic OH. Actually, the pKa value of complex **2** obtained by titration was 9.1, which was near to that of phenolic OH (phenol; pKa = 9.7).9)

Previously we obtained the identical carbinolamine complex from the reaction of **1** with AM^{2-} 10,11) This indicates that the carbinolamine formation from AM^{2-} and **1** proceeds via the formation of the ketomalonate intermediate which is derived from the hydrolysis of an imine intermediate.



Scheme 1.

Scheme 1 shows the schematic description of the conversion of AM^{2-} into α-diamine and carbinolamine on Co(III)-polyamine complexes. The carbinolamine is formed by a nucleophilic attack of a deprotonated amino group of 2,3,2-tet ligand on the carbonyl carbon of coordinated KM^{2-}. Interestingly compound **2** was also obtained from the reaction of tartolonic acid (α-hydroxymalonic acid) with **1** under the same conditions.12) The reaction must include the oxidation of the tartolonic acid to KM^{2-}. This observation suggests that the α-diamine linkage is generated through the formation of an imine intermediate.

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5) The eluent was 0.02 M aqueous solution of $NaClO_4$.

6) Anal. Found: C, 26.79; H, 4.80; N, 12.22; Cl, 7.95 %. Calcd for $[Co(HM\text{-}2,3,2\text{-}tet)]ClO_4 \cdot H_2O$, $CoC_{10}H_{20}N_4O_5 \cdot ClO_4 \cdot H_2O$ (**2**): C, 26.53; H, 4.90; N, 12.38; Cl, 7.83 %.

7) Crystal data for **2**: space group, $P2_12_12_1$; a = 7.291(1) Å, b = 13.408(2) Å, c = 17.453(3) Å, V = 1675.9(5) $Å^3$; Z = 4; d(calcd) = 1.79 g/cm^3, d(obs) = 1.72 g/cm^3; μ(Mo Kα) = 1.24 mm^{-1}; No. of intensities measd, 4190; No. of data, 3122($|Fo|>3\sigma(Fo)$); R(Rw) = 0.061(0.067).

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9) Titration was performed by 0.10 M NaOHaq at 25 °C.

10) T. Kojima, T. Usui, M. Yashiro, T. Tanase, K. Kobayashi, T. Sakurai, S. Yoshikawa, S. Yano,and M. Hidai, unpublished results.

11) ^{13}C-NMR spectroscopic data for **2** (measured in D_2O, 1,4-dioxane as a reference): 24.1, 44.2, 44.8, 46.5, 48.2, 50.8, 57.2 (2,3,2-tet moiety), 93.0, 175.2, 175.9 (condensed hydroxymalonato moiety). These data were identical to those of a complex afforded from the reaction of **1** with AM^{2-}. Anal. Found: C, 26.49; H, 4.88; N, 12.44; Cl, 7.81 %. Calcd for $C_{10}H_{20}N_4O_5Co \cdot ClO_4 \cdot H_2O$: C, 26.53; H, 4.90; N, 12.38; Cl, 7.83 %.

12) When a suspension of **1** and H_2HM in MeOH in the presence of NEt_3 was refluxed for 3 h under air, **2** was obtained as a minor product.

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