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# A Novel Transamination Induced by Terpyridine Ligand Coordinated on Cobalt(III) Ion

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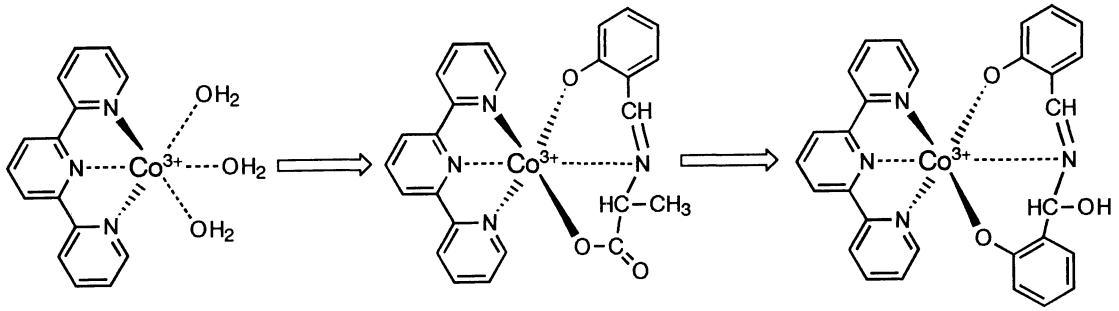
The reaction of salicylidene-L-alanine with the Co(III) complex involving 2,2':6',2"-terpyridine (terpy) in aqueous ethanol solution afforded a peculiar transamination to form the complex, [Co(α-hydroxy salicylidene-o-hydroxybenzylamine)(terpy)]$^{+}$, whose structure has been confirmed by X-ray structure analysis and positive FAB mass spectrometry.

Biomimetic reactions for amino acid transformation in pyridoxal enzyme are usually performed on metal complexes with Schiff base ligands that consist of pyridoxal and amino acids.[1,2] Recently we have discovered the α-hydroxylation of amino acids mediated on the substitutionally inert Co(III) ion, which was a new type of oxygenation of amino acid in the vitamin $B_6$ model reaction.[3] This reaction was characteristic of pyridoxal, but was not promoted in the presence of salicylaldehyde, a coordination analogue of pyridoxal. The former can activate the α-position of amino acid through the conjugation between the aldimine and ketimine forms of the Schiff base, but the latter being unable to take such a conjugation system can not activate it. In order to cause to proceed the transformation of amino acid for the latter system, we introduced 2,2':6',2"-terpyridine (terpy) to serve an electronic effect. Polypyridine compounds, such as terpy, demonstrate very attractive features of electron-transfer, photochemical, and related reactions[4] and sometimes exhibit the activation of the trans position through the central metal. For instance, in osmium complex involving terpy the reaction of trans-$[OsCl_2(terpy)N]^{+}$ with triphenylphosphine have been found to cause the nitrogen atom transfer to trans-$[OsCl_2(terpy)(NPPh_3)]^{+}$, accompanied by the redox reaction of Os(VI) to Os(IV).[5,6] In this reaction,




Starting Complex  Possible Intermediate (1)  Transamination Product (2)

terpy served not only to activate the nitrogen atom of trans position but also to stabilize the intermediate oxidation states. Here we describe a novel type of transamination, i.e., a nitrogen-atom-transfer reaction from amino acid to salicylaldehyde, promoted by the π-bond character of terpy, which is of special interest from a viewpoint of the transformation of amino acid.

The transamination was proceeded on the basis of the following procedure. The cobalt(III) complex with a terpy ligand was firstly prepared in aqueous ethanol solution. To $K_3[Co(CO_3)_3]$ (15 mmol) in a mixture of water (40 mL) and ethanol (20 mL) was added dropwise 0.23 g of terpy (10 mmol) in 30 mL of an ethanol solution at 40℃ for 2 h. and appropriately several portions of an aqueous $K_3[Co(CO_3)_3]$ solution in order to avoid the formation of $[Co(terpy)_2]^{3+}$. The resulting mixture was stirred for 16 h at room temperature. After the removal of the precipitate of unreacted $[Co(CO_3)_3]^{3-}$, crude $[Co(terpy)(H_2O)_3]^{3+}$ containing the $[Co(terpy)_2]^{3+}$ complex as a by-product was obtained. To 100 mL of an aqueous ethanol solution of the $[Co(terpy)(H_2O)_3]^{3+}$ was added 0.89 g of L-alanine (10 mmol) and 1.22 g of salicylaldehyde (10 mmol), and the resulting solution was stirred for 5 h at 35 ℃ and then filtered. After evaporation the resulting residue was diluted with 200 mL of water, and then passed through a cation exchange column of SP Sephadex C-25 resin (3.6 cm $\phi$ x 25 cm). The dark brown band adsorbed was firstly eluted with a 0.5 M NaCl solution to give the ternary cobalt(III) complex (23% yield based on the amount of added terpy). Single crystal suitable for X-ray structure analysis was available from the solution within several days. Although the main product of the present reaction was $[Co(terpy)_2]^{3+}$ eluted thirdly (over 50% yield based on the terpy), it was no relation to the present transamination.

The crystal structure established (Fig. 1)[7] demonstrates that the cobalt(III) ion is coordinated with two terdentate ligands of terpy and α-hydroxy salicylidene-o-hydroxy-benzylamine (shbs) in meridional form, which reveals the very surprising three aspects. Firstly, the methyl group of L-alanine presented in the starting compound of the reaction was absent in the product complex, whereas the nitrogen atom originating from L-alanine remained as the azomethine nitrogen of shbs. Presence of imine moiety was supported from the typical C=N bond lengths of 1.27(1) and 1.29(1) Å and the shoulder peak of absorption spectrum at 24 x $10^3$ $cm^{-1}$ of the characteristic azomethine bond. It is apparent that the nitrogen atom of L-alanine has been uptaken into salicylaldehyde to give the shbs ligand.

Secondly, this transamination has occurred in the ternary cobalt(III) complex containing salicylaldehyde. In biomimetic studies for the pyridoxal model reaction in the presence of metal ions, early workers reported that pyridoxal was essential for the transformation of amino acid, whereas salicylaldehyde did not carry out such a transformation[1,8,9] because salicylaldehyde cannot form a quinoide-type Schiff base intermediate that may be indispensable in the course of the transformation of amino acid. This is the first report to our knowledge that transamination including salicylidene-amino acid does proceed on the metal complex that is different from the previous transamination involving the aldimine-ketimine equilibrium.

Thirdly, the present reaction was accompanied by the hydroxylation of the Schiff base at the α-position, which was identified by the electron density of the located atoms and the bond lengths in the X-ray analysis and by the positive FAB mass spectrum giving the parent peak at $m/z$ = 533 assignable to $[Co(shbs)(terpy)] + H]^+$. Presumably, the oxygen atom of hydroxy group in shbs is expected to originate from the carbonyl oxygen of salicylaldehyde, because the absorption of molecular oxygen,

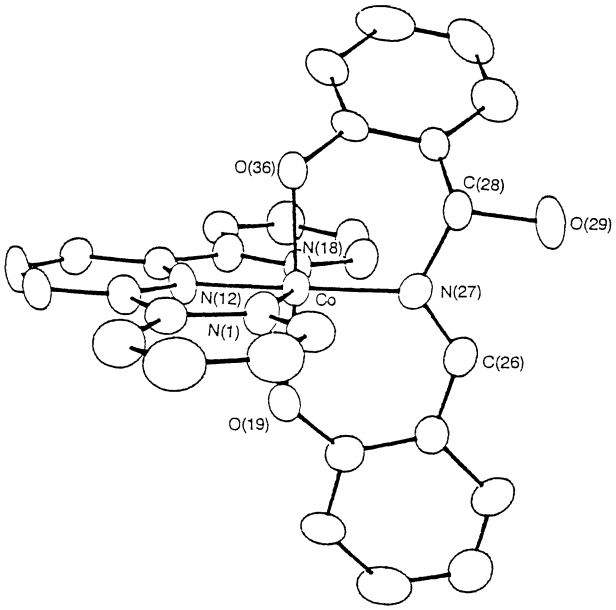



Fig. 1. An ORTEP drawing of one of the two $[Co(shbs)(terpy)]^+$ cations in the asymmetric unit of **2**.[7] Selected bond lengths (Å): Co-N(1) 1.949(9) and 1.921(7), Co-N(12) 1.859(7) and 1.832(8), Co-N(18) 1.945(9) and 1.972(8), Co-N(27) 1.942(7) and 1.914(8), Co-O(19) 1.871(7) and 1.870(7), Co-O(36) 1.897(1) and 1.881(7), N(27)-C(26) 1.27(1) and 1.29(1), N(27)-C(28) 1.53(1) and 1.52(1), and O(29)-C(28) 1.42(1) and 1.39(1).

previously noticed in the α-hydroxylation of pyridoxylidene-amino acid mediated on the Co(III) ion,[3] was not observed during the reaction.

The present nitrogen-atom-transfer reaction from salicylidene-alanine to shbs was peculiarly observed in the ternary Co(III) complex containing terpy ligand, whereas such a reaction was detected neither in the bis(salicylidene-amino carboxylato) cobalt(III) complex nor in the ternary Co(III) complex containing salicylidene-L-alanine and N,N,N',N",N"-pentamethyl-diethylenetriamine ligand with σ-coordinating character. This fact indicates that the terpy ligand having π-bonding character importantly contributes to the reaction. The activation of the nitrogen atom of azomethine group was observed as the trans influence due to the strong π-bonding character of terpy; rather short Co-N(12) bonds, 1.859(7) and 1.832(8) Å, compared with other two Co-N ones, 1.949(9) and 1.972(7) Å for Co-N(1) and 1.945(9) and 1.914(8) Å for Co-N(18), and smaller N(1)-Co-N(18) angle of 164.5(3) and 164.8(4)° compared with normal angle of 180°

On the basis of the above results, the following mechanism is presumed for this transamination. In the first step, the aldimine-type Schiff base ligand consisting of salicylaldehyde and L-alanine coordinates to the Co(III)-terpy complex to form the intermediate complex, [Co(salicylidene-alaninato)(terpy)]$^+$ (**1**), whose isolation is under investigation. In the next step, aldehyde carbon of another salicylaldehyde in the reaction media immediately attacks the nitrogen atom of the Schiff base of **1** activated by the trans influence of terpyridine through the Co(III) ion. Through another intermediate complex with a plausible ligand such as N,N-bis(salicylidene)-alanine, the ternary Co(III) complex (**2**) with shbs and terpy ligands is formed as the thermodynamically stable product. In this reaction, the use

of β-alanine in place of L-alanine resulted in the formation of the Co(III) ternary complex coordinated by salicylidene-β-alanine Schiff base with no transamination of this type. The present work describes a new type of transamination of salicylidene-amino acid mediated on Co(III) complex; a detailed comprehension of the mechanism will be reported elsewhere.

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7) Crystal data : $C_{58}H_{46}Cl_2Co_2N_8O_6 \cdot 7H_2O$, $M = 1265.92$, triclinic, $P\bar{1}$, $a = 9.844(4)$ Å, $b = 13.738(3)$ Å, $c = 22.290(8)$ Å, $\alpha = 92.51(2)^\circ$, $\beta = 96.34(3)^\circ$, $\gamma = 109.14(2)^\circ$, $Z = 2$, $V = 2820.1$ Å$^3$, $D_c = 1.502$ g cm$^{-3}$, $\mu(\mathrm{MoK}_\alpha) = 7.50$ cm$^{-1}$, and 4228 independent reflections with $I_0 > 3\sigma(I_0)$ were used in the refinement to $R = 0.078$, $R_w = 0.088$. There are two molecules in the asymmetric unit, whose corresponding bond parameters are essentially the same to each other.
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