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Facile and Selective Conversion of Ethylenediaminetetraacetate to Ethylenediamine-*N,N,N'*-triacetate on a Cobalt Complex

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Ethylenediaminetetraacetatocobaltate(III) is converted to aqua(ethylenediamine-*N,N,N'*-triacetato)cobalt(III) selectively in a 1 mol dm^{-3} K_2CO_3 aqueous solution at room temperature in the presence of PbO_2. This reaction could be a simple and versatile procedure to obtain ed3a-type ligands.

Selective oxidation using transition metal complexes has been attracting much interest. We wish to report on oxidation of edta-type (edta = ethylenediaminetetraacetate) ligands on a cobalt complex to give ed3a-type (ed3a = ethylenediamine-*N,N,N'*-triacetate) ligands selectively in a basic aqueous solution in the presence of PbO_2.

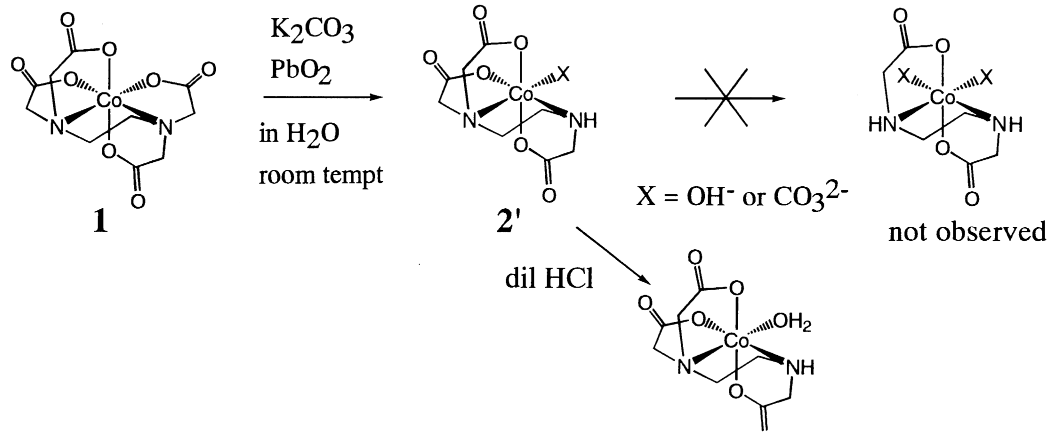
A great number of metal complexes of edta or edta-type ligands have been isolated and characterized.1) It has been reported that electronic spectrum of Na[Co(edta)] in a basic aqueous solution is different from those in a neutral or an acidic solutions.2) It has been also reported that K[Co(edta)]3) and $[Co(ed3a)(NO_2)]$4c) generate cobalt(II) in basic aqueous solutions. These observations suggest that oxidation of the ligand could occur in basic conditions. However, attention concerning these compounds is mainly focused on stable chelation of the ligands and their stereochemistry,1) and characterization of species after treatment of these complexes in basic conditions has not been reported to our knowledge. We tried to characterize the species in the mixture thus obtained.

$K[Co(edta)]\cdot 2H_2O$ (**1**)5) (0.5 g) was dissolved in 0.1 mol dm^{-3} K_2CO_3 (10 ml) and stirred at room temperature for 12 h. The resulting solution was subjected to a column of Dowex 2X-8 (100-200 mesh, Cl^- form) and a column of SP-Sephadex C-25 (Na^+ form). The mixture was separated into two major components, one of which retained on the anion exchange column, and another passed through both the anion and cation exchange column. The complex retained on the anion exchange column was eluted with 0.1 mol dm^{-3} NaCl, and UV-vis absorption and ^{13}C NMR spectroscopies indicated recovery of **1** in 44%. Concentration of the fraction which passed through both columns gave violet microcrystals (**2**). Elemental analysis and ^{13}C NMR spectroscopy indicated that **2** is *cis-eq*-[Co(ed3a)(H_2O)]·H_2O (10%).[4c,e] One of four acetate arms of edta is replaced by hydrogen.

Then, we made an effort to improve the yield of **2**, and finally found that the high conversion can be achieved when PbO_2 was used. To an aqueous solution of K_2CO_3 (1 mol dm^{-3}, 10 ml), **1** (0.5 g) and PbO_2 (0.5 g) were added and stirred overnight at room temperature.6) After filtration, the filtrate was neutralized with diluted HCl. Column chromatographic separation as described above yielded **2** in 81%, along with the recovery of **1** in 10%. Other colored species were of trace amount.

The remarkable feature of the present reaction is that **2** is yielded selectively, and no further oxidation occurs under these experimental conditions (Scheme 1). Oxidation of edta by transition metal ions often give a mixture of decomposed products.7) The selective formation of **2** indicates that oxidation is highly regulated by coordination to cobalt. The result is surprising, because generation of cobalt(II) is also observed for an ed3a-cobalt(III) complex ([Co(ed3a)(NO_2)]) in a basic solution.4c) The reported relationships between redox potentials and ligand field energies of cobalt-(III) complexes10) also suggest that the reduction potential of cobalt(III) in **1** does not differ very much from that in **2'**. Therefore, the important factor for the selective oxidation is not the difference between the reduction potential of cobalt(III) in the edta complex and that in the ed3a complex, but selective activation of edta for oxidation. We recently reported selective oxidation of spermine on a cobalt complex, and the important factor is formation of an energetically unfavorable seven-membered ring.11) Thus, oxidation of the ligand could be highly dependent on the chelate structure. X-ray crystallographic studies of **1** suggest that the edta chelate is sterically distorted, because three five-membered chelate rings form a girdle about cobalt.12) Such strain is released in the ed3a chelate, in which one of the three five-membered rings in the girdle is absent.4) The steric strain in the edta chelate should be the important factor for the selective oxidation, which results in selective formation of **2**.13) Because the oxidation proceeds with transfer of two electrons, the cobalt complex without an oxidizing agent results in only low conversion. High conversion could be achieved when an appropiate oxidizing agent such as PbO_2 is used.

The reaction has been further applied to [Co(1,3-pdta)]$^-$ (**3**) (1,3-pdta =



Scheme 1.

1,3-propanediaminetetraacetate), for which similar steric strain has been indicated.14) By similar procedures described above, **3** could be converted into [Co(1,3-pd3a)(H_2O)]15) (**4**) (1,3-pd3a = 1,3-propanediamine-*N,N,N'*-triacetate) in 71%. Similarly, K[Co(cdta)] (**5**) (cdta = *trans*-cyclohexanediaminetetraacetate) gave [Co(cd3a)(H_2O)]8b) (**6**) (cd3a = *trans*-cyclohexanediamine-*N,N,N'*-triacetate) in 55%. Thus, the oxidation undergoes quite generally for cobalt complexes containing edta-type ligands.

Since selective preparation of ed3a-type compounds is difficult, they have been obtained as a mixture and used without isolation.4) The present reaction could be useful in obtaining pure ed3a-type compounds. Then, the following was conducted in order to isolate H_3ed3a from **2**. The aqueous solution of **2** was treated with excess ethylenediamine. The color of the solution gradually turned to orange. The solution was poured to the column of SP-Sephadex C-25 (Na^+ form), and washed with water. Almost all colored species were retained on the resin. Then the solution passed through the SP-Sephadex column was poured to the column of Dowex 2X-8 (100-200 mesh, Cl^- form). The resin was washed with water, and subsequently eluted with 1 mol dm^{-3} HCl. Concentration of the eluate and removal of the solvent gave hygroscopic H_3ed3a almost quantitatively. ^{13}C NMR spectrum (D_2O, dioxane δ 67.4): δ 44.64, 49.14, 49.73, 53.59, 56.63, 163.87, 168.02, and 172.23. Anal. Found: C, 32.13; H, 6.86; N, 9.80%. Calcd for $C_8H_{14}N_2O_6 \cdot 3.5H_2O$: C, 32.32; H, 7.12; N, 9.42%.

In conclusion, we have found that [Co(edta)]⁻ is converted to [Co(ed3a)(H_2O)] in a basic aqueous solution at room temperature in the presence of PbO_2. The oxidation is highly selective, and the resulting ed3a chelate can be isolated from the complex by simple procedures using ion exchange chromatographies. Thus, the present reaction will be useful for the facile and selective conversion from an edta-type compound to an ed3a-type one.

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6) pH of the solution at the final stage of the reaction was 11.0. When KOH (0.1 mol dm^{-3}) was used instead of K_2CO_3, **2** was obtained in 77%.

7) Oxidative decomposition of edta is reported for Co(III),[8a] Mn(III)[8b] (in solid states), Cu(II), or Fe(III)[8c] (in basic conditions) on heating above 100 °C. Similar decomposition is reported to proceed at room temperature in an aqueous solution on Mn(III)[8d] or Ag(III).[8e] Another study reported a selective oxidation of *N*-(phosphonomethyl)iminodiacetate on cobalt.[9]

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