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Template Synthesis of Copper(II) Complex with Tetraaza Macrocycle in Solid Phase

Manabu FUJIWARA,* Setsuko KINOSHITA, Hisanobu WAKITA,
Takayuki MATSUSHITA,† and Toshiyuki SHONO†
Department of Chemistry, Faculty of Science, Fukuoka University,
Nanakuma, Jonan-ku, Fukuoka 814-01
† Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Yamadaoka 2-1, Suita, Osaka 565

The ethylenediamine adduct of bis(3-nitro-2,4-pentanedionato)copper(II) was prepared in ethanol, and characterized by spectroscopic and elemental analyses. The thermal reaction of the adduct in the solid phase resulted in the formation of a tetraaza macrocyclic copper(II) complex by the intramolecular condensation.

Reactions of coordinated ligands have been shown to be potentially very useful, not only for their synthetic applications to organic chemistry but also for their reactions to life processes. For example, the metal chelates of acetylacetone derivatives with electron-withdrawing substituents have been known to possess high reactivity toward amines, producing Schiff base compounds.[1,2]

In a previous paper,[3] we have reported the preparation of a novel 14-membered tetraaza macrocycle by the template reaction of $Cu(3-NO_2\ acac)_2$ and ethylenediamine in xylene.

However, no example of a solid-state template synthesis has been reported so far. In this paper, we describe the preparation and characterization of the ethylenediamine adduct of bis(3-nitro-2,4-pentanedionato)copper(II), $Cu(3-NO_2\ acac)_2{\cdot}en_2$, which can be converted thermally to the copper(II) complex of the tetraaza macrocyclic Schiff base, $Cu(NO_2-N_4[14])$, by the intramolecular

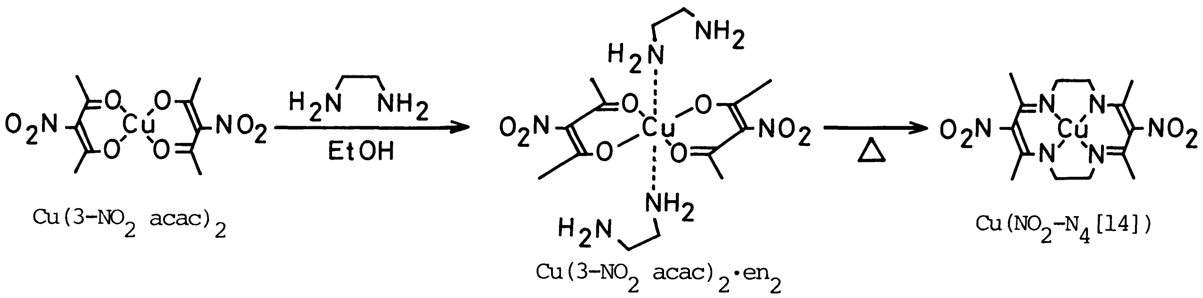

Fig. 1. Preparative scheme of copper(II) complexes.

condensation in the solid phase.

Figure 1 shows the preparative scheme for the copper(II) complexes, Cu(3-NO$_2$ acac)$_2$•en$_2$ and Cu(NO$_2$-N$_4$[14]). Cu(3-NO$_2$ acac)$_2$•en$_2$ was prepared by the following method. To a suspension of Cu(3-NO$_2$ acac)$_2$ (5 g, 1.4×10^{-2} mol) in ethanol (200 cm^3) was added excess ethylenediamine (2 g, 3.3×10^{-2} mol), and the green suspension changed to a gray precipitate. The mixture was stirred at room temperature for 3 h, and cooled in an ice bath. The precipitate was collected on a glass filter, washed with cold ethanol, and dried *in vacuo*. The analytical data for this adduct agreed with the calculated values for the formula, Cu(3-NO$_2$ acac)$_2$•en$_2$. Found: C, 35.67; H, 5.98; N, 17.70%. Calcd for $CuC_{14}H_{28}N_6O_8$: C, 35.62; H, 5.99; N, 17.81%. The infrared spectrum of the adduct has new absorption bands at 3250, 1660, 1310, 1280, 1115, and 1045 cm^{-1}, not present in the spectrum of Cu(3-NO$_2$ acac)$_2$. These absorption bands can be assigned to vibrations due to the ethylenediamine molecules. Other absorption bands at 1590, 1520, 1400, 1345, and 830 cm^{-1} are similar to those of Cu(3-NO$_2$ acac)$_2$. In the far infrared region, the spectrum of the adduct exhibits strong absorption bands at 580, 536, 476, 420, and 380 cm^{-1}. The bands at 580 and 420 cm^{-1} can be assigned to the combination of the Cu-O stretching vibration and ring deformation modes,4) which are shifted to lower frequencies about 30 cm^{-1} compared with those of Cu(3-NO$_2$ acac)$_2$. This may be caused by the coordination of ethylenediamine. A new band at 380 cm^{-1} can be assigned to the Cu-N stretching vibration mode.5) Previously, Kurauchi *et al.*6) have reported that bis(acetylacetonato)copper(II) reacted with ethylenediamine to give a six-coordinate copper(II) complex, Cu(en)$_2$(acac)$_2$, in which the copper(II) ion is surrounded tetragonally by four nitrogen atoms of two ethylenediamine molecules and axially by two oxygen atoms of two acetylacetone molecules, which act as a unidentate ligand. However, in their case, the infrared spectrum of $Cu(en)_2(acac)_2$ is significantly different from that of $Cu(acac)_2$. These results indicate that the complex obtained from the reaction of $Cu(3\text{-}NO_2\ acac)_2$ with ethylenediamine is the ethylenediamine adduct of $Cu(3\text{-}NO_2\ acac)_2$ in which the copper(II) ion is surrounded by a donor set of N_2O_4 as shown in Fig. 1.

The thermal properties of this adduct were investigated in the solid phase. The TG-DSC curves for $Cu(3\text{-}NO_2\ acac)_2 \cdot en_2$ are shown in Fig. 2, together with the temperature profile of the reaction cell. The TG and DSC curves were recorded in a flowing nitrogen atmosphere at a heating rate of 2 °C/min. $Cu(3\text{-}NO_2\ acac)_2 \cdot en_2$ undergoes two exothermic changes. The change corresponding to the first DSC peak maximum (t = 60 min) is accompanied by a weight-loss of 7.4%, which is in good agreement with the calculated value of 7.64% for the elimination of two water molecules from one molecule of the adduct. The second DSC peak maximum appears at t = 78 min, and the total weight-loss reaches 15.3%, which agrees with the calculated value of 15.27% for the elimination of four moles of water from one mole of the adduct. The infrared spectrum of the resulting dark brown copper(II) complex was quite similar to that of the authentic copper(II) complex of the 14-membered tetraaza macrocycle, $Cu(NO_2\text{-}N_4[14])$.3) The resulting complex was recrystallized from a mixture of ethanol and chloroform (1:1) for the elemental analysis. Its analytical data also agreed with $Cu(NO_2\text{-}N_4[14])$. Found: C, 41.78; H, 5.38; N, 20.67%. Calcd for $CuC_{14}H_{20}N_6O_4$: C, 42.04; H, 5.05; N, 21.02%. The evolved water was condensed on a trap in liquid nitrogen and identified by gas chromatography. Kurauchi *et al.*6) have also reported the thermal properties of the

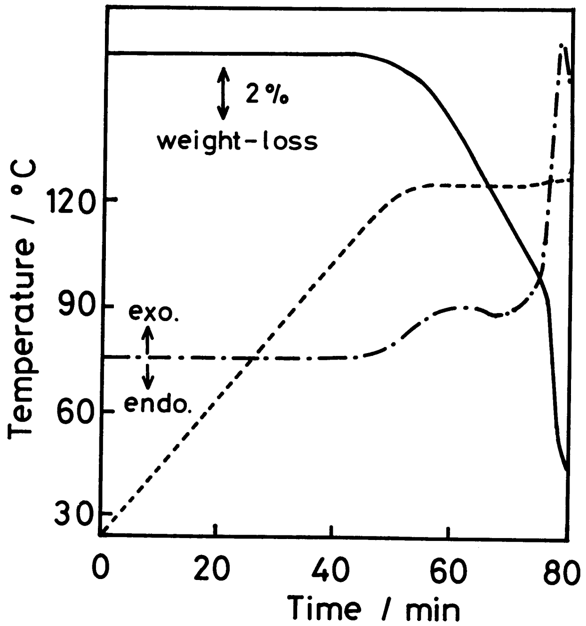

Fig. 2. TG and DSC curves of $Cu(3\text{-}NO_2\ acac)_2 \cdot en_2$.
(———):TG curve,
(—·—·—):DSC curve,
(-------):temperature.

ethylenediamine complex, Cu(en)$_2$(acac)$_2$, of which two molecules of ethylenediamine are eliminated by two steps to produce Cu(acac)$_2$. The difference in the thermal properties between Cu(3-NO$_2$ acac)$_2$•en$_2$ and Cu(en)$_2$(acac)$_2$ may be ascribed to the strong electron-withdrawing nitro groups, which enhance the reactivity of the coordinated carbonyl groups with ethylenediamine. Consequently, the thermal reaction of Cu(3-NO$_2$ acac)$_2$•en$_2$ produced Cu(NO$_2$-N$_4$[14]) intramolecularly without the elimination of ethylenediamine.

Further work is in progress to study the thermal and spectroscopic properties of the diamine adducts of Cu(3-NO$_2$ acac)$_2$ such as 1,3-diaminopropane and 1,4-diaminobutane.

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