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ON THE THERMOCHROMISM OF A Cu-$(N)_4$-TYPE COPPER(II) CHELATE, BIS(1,5-DIAZACYCLOOCTANE)COPPER(II) NITRATE

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The title complex, $[Cu(daco)_2](NO_3)_2$, was newly obtained, and found to show a characteristic reversible thermochromism. Its color changes from orange to violet on heating at 90°C, and becomes orange again on cooling. The mechanism of this thermochromism is suggested on the basis of the UV-visible reflectance spectra, and IR and TG-DTA data.

Recently, we prepared the chelate, $[Cu(daco)_2](NO_3)_2$, by dehydrating $Cu(NO_3)_2 \cdot 3H_2O$ with 2,2-dimethoxypropane, adding ethanol to the resulting solution, and then an ether solution of daco (daco=1,5-diazacyclooctane). The precipitate obtained was washed with an ethanol-ether mixture and recrystallized from an ethanol-methanol mixture(1:1). [Analytical data: C 34.44, H 6.77, N 20.16%; calcd. for $Cu(daco)_2(NO_3)_2(CuC_{12}H_{28}N_6O_6)$: C 34.64, H 6.80, N 20.21%].

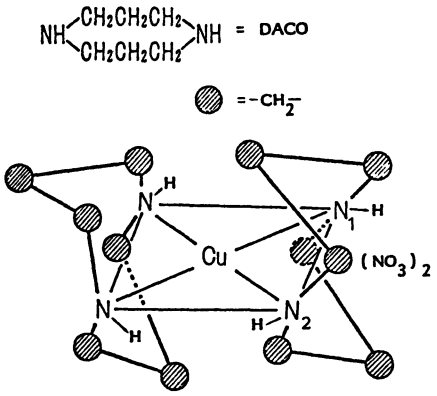

Fig. 1. $[Cu(daco)_2](NO_3)_2$

Tanaka et al. carried out an X-ray study of its orange crystal, confirming that the cation $[Cu(daco)_2]^{2+}$ in its crystal has the conformation shown in Fig. 1 (Cu-N_1: 1.995(2) and Cu-N_2: 2.034(2)Å, the angle of N_1-Cu-N_2: 85.92°),[2] which was expected earlier by Musker and Hussain for the same cation in $[Cu(daco)_2](ClO_4)_2$.[1] Thus the coordination sphere of Cu(II) is highly square planar, with very little axial influence.

Now we found that the chelate, $[Cu(daco)_2](NO_3)_2$ shows a peculiar thermochromism, when heated above ca. 90°C. The color of the compound changes quite abruptly from orange to violet. On the other hand, on cooling, it gradually becomes orange again. It ia interesting to note that for the perchlorate, $[Cu(daco)_2](ClO_4)_2$, no such thermochromism was observed.

Figure 2 shows the change of the solid reflectance spectrum of this chelate by heating, followed up to ca. 100°C with a Hitachi 340 Recording Spectrophotometer with a reflectance attachment containing temperature-controlled sample holder.[3] A new broad absorption band could be observed to appear at ca. 700 nm with the temperature increase. The change was also followed by TG-DTA technique, which showed a simple endothermic DTA peak at 105°C without any weight decrease.

It was also found by temperature dependent IR spectral measurements that the thermochromic change causes a splitting of the IR band of NO_3^- at 1747 cm^{-1} into two (1742 and 1763 cm^{-1} at 90°C), indicating that the NO_3^- ions act as monodentate ligands in the high-temperature(violet) form.[4] Unfortunately, we have not any X-ray information on the violet form because of the pulverization of the crystals which accompanies the thermochromic change.

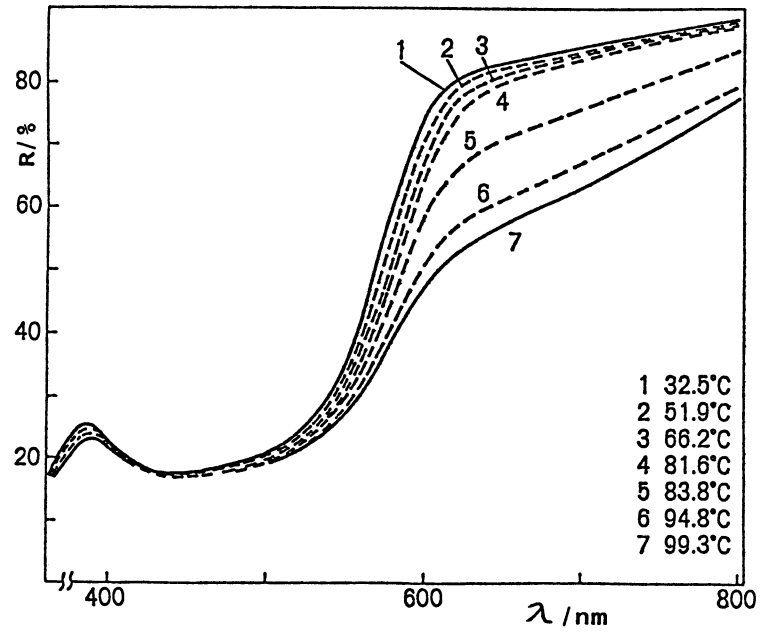

Fig. 2. Temperature dependent solid reflectance spectra of the chelate $[Cu(daco)_2](NO_3)_2$

These results show that this thermochromic change is truly a drastic phenomenon, involving extensive change of the coordination geometry around Cu(II), probably from a nearly square planar structure to the tetragonal one with axial coordinated NO_3^- ions.

This is in contrast to the well-known thermochromism of $[Cu(N,N-Et_2en)_2](ClO_4)_2$, observed at ca. 45°C, which was recently explained by Grenthe et al.[5] as the result of the thermal flapping of the ethylenediamine chelate rings(N,N-Et_2en=N,N-diethylethylenediamine).

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