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LIGAND-TO-GUEST CONVERSION OF p-TOLUIDINE MOLECULE IN METAL COMPLEX BIS(p-TOLUIDINE)-1,6-DIAMINOHEXANECADMIUM(II) TETRACYANONICKELATE(II) AND FORMATION OF CLATHRATE COMPOUND 1,6-DIAMINOHEXANECADMIUM(II) TETRACYANONICKELATE(II)-p-TOLUIDINE(1/1)

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Bis(p-toluidine)-1,6-diaminohexanecadmium(II) tetracyanonickelate(II) is thermally converted to a clathrate compound 1,6-diaminohexanecadmium(II) tetracyanonickelate(II)-p-toluidine(1/1) in the intermediate stage of the thermal decomposition under ambient atmosphere. The clathrate is prepared in another way by the method similar to those applied to the o- and the m-isomer clathrates but using more dilute guest-diluent mixture.

As we have recently reported,[1,2] the o- and the m-isomers of toluidine give the clathrate compounds in the three-dimensional metal complex host 1,6-diaminohexanecadmium(II) tetracyanonickelate(II) with a general formula $Cd[NH_2(CH_2)_6NH_2]Ni(CN)_4 \cdot G$ (G = o-$CH_3C_6H_4NH_2$, **1**; m-$CH_3C_6H_4NH_2$, **2**) but the p-isomer gives a coordination complex bis(p-toluidine)-1,6-diaminohexanecadmium(II) tetracyanonickelate(II), $Cd(p\text{-}CH_3C_6H_4NH_2)_2[NH_2(CH_2)_6NH_2]Ni(CN)_4$, **3**, under the preparation conditions similar to one another. In the course of thermal analyses of these three toluidine compounds we have discovered that the p-toluidine complex **3** is converted to a p-toluidine clathrate with the structure similar to those of the o- and the m-isomer clathrates.

The clathrates **1** and **2** lost the respective guest molecules up to 520 K on heating under ambient atmosphere. The complex **3** decomposed thermally by releasing the two molecules of the p-toluidine ligands stepwise: at the first stage (up to 445 K) ca. 1 mol of the ligand was released from the complex, the rest 1 mol being liberated at the second stage (up to 470 K), as exemplified in Fig. 1. The residual product left after the fisrt stage, **4'**, gave the composition similar to that of the clathrate **1** or **2**: the ratio of the metal complex moiety, $Cd[NH_2(CH_2)_6NH_2]Ni(CN)_4$, to the toluidine isomer was ca. 1:1. Found: C, 38.90; H, 5.07; N, 19.23%. Its IR and Raman spectra showed the features similar to those observed for **1** and **2**; the powder X-ray diffraction pattern gave the lines attributable to the basal spacing of 9.36 Å, the distance being comparable with those observed for **1** (9.54 Å) and **2** (9.73 Å). From these observations we concluded that the product **4'** obtained after the first stage of the thermal decomposition of **3** should be the clathrate of p-toluidine molecule in the three-dimensional metal complex host

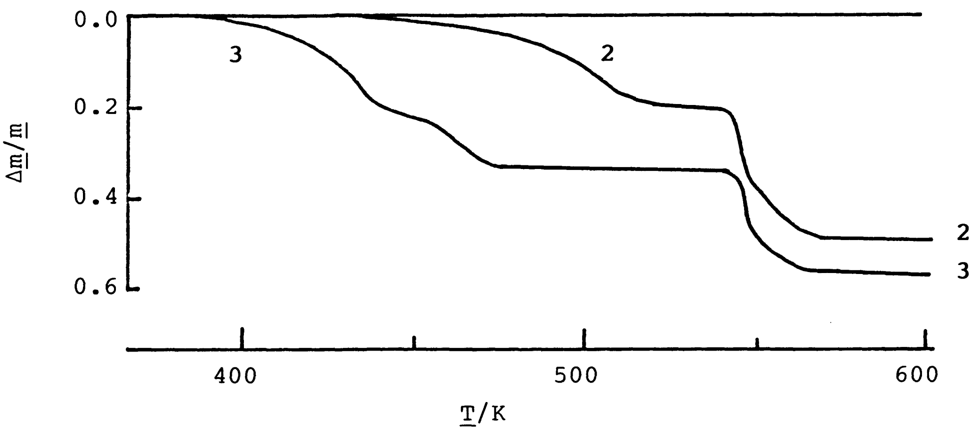

Fig. 1. Thermogravimetric curves of **2** and **3** recorded on a Seiko Electronics SSC560GH with the heating rate of 10 K min^{-1} for ca. 10 mg each sample; $\Delta m/m$ is the ratio of mass loss to the mass of sample.

similar to those of **1** and **2**.

To ascertain this conclusion we attempted to prepare the *p*-toluidine clathrate by the method similar to those applied to the cases of the *o*- and the *m*-isomers. The clathrates **1** and **2** were prepared by keeping the aqueous solution of the host components with ca. 0.1 mol/dm^3 each concentration of metal-containing species ($CdCl_2$ and $K_2[Ni(CN)_4]$) in contact with the organic phase of the respective toluidine-mesitylene mixture (1:10 in volume). When the *p*-toluidine-mesitylene (1:10) mixture was used, the product was the metal complex **3**.[2] Our idea to prepare the clathrate of *p*-toluidine isomer, **4**, was to use a more dilute *p*-toluidine-mesitylene mixture. Fine crystals of the clathrate were obtained by leaving the aqueous solution of the host-components in contact with a dilute (1:200) mixture for 2 months. Anal. Found: C, 39.13; H, 5.00; N, 19.59; Cd, 22.79; Ni 12.12%. Calcd for $Cd(C_6H_{16}N_2)Ni(CN)_4 \cdot C_7H_9N$: C, 40.95(40.13); H, 5.05(4.98); N, 19.66(19.81); Cd, 22.54(23.04); Ni, 11.77(12.03)%. The values in the parentheses are those calculated for the specimen of a 90% occupancy of the guest molecule. Although the deviation is considerably large for the C value, the results, which are similar to those obtained for **4'**, can be interpreted in terms of sub-stoichiometric enclathration of the guest (ca. 90% occupancy) in the metal complex host structure similar to those of **1** and **2**. In the course of the systematic investigations of the Hofmann-α,ω-diaminoalkane-type clathrates, we have obtained lots of the clathrates with non-stoichiometric composition of the guests, non-stoichiometry being usually thought of a common character among clathrate compounds;[3] the stoichiometries which have been observed for the Hofmann-type and analogous series are rather unusual.[4]

The features in the IR and Raman spectra and in the powder X-ray diffraction pattern observed for the fine crystals of **4** showed close resemblances to those for the thermal decomposition product **4'**. One of the characteristic features in the IR and Raman spectra is compared in the region of the CN stretch modes of cyanide group (2100 to 2200 cm^{-1}), as shown in Fig. 2. The IR band at the lower frequency side (2120 cm^{-1}) of the doublet observed in **3**[2] disappeared in **4** and **4'**; the wave

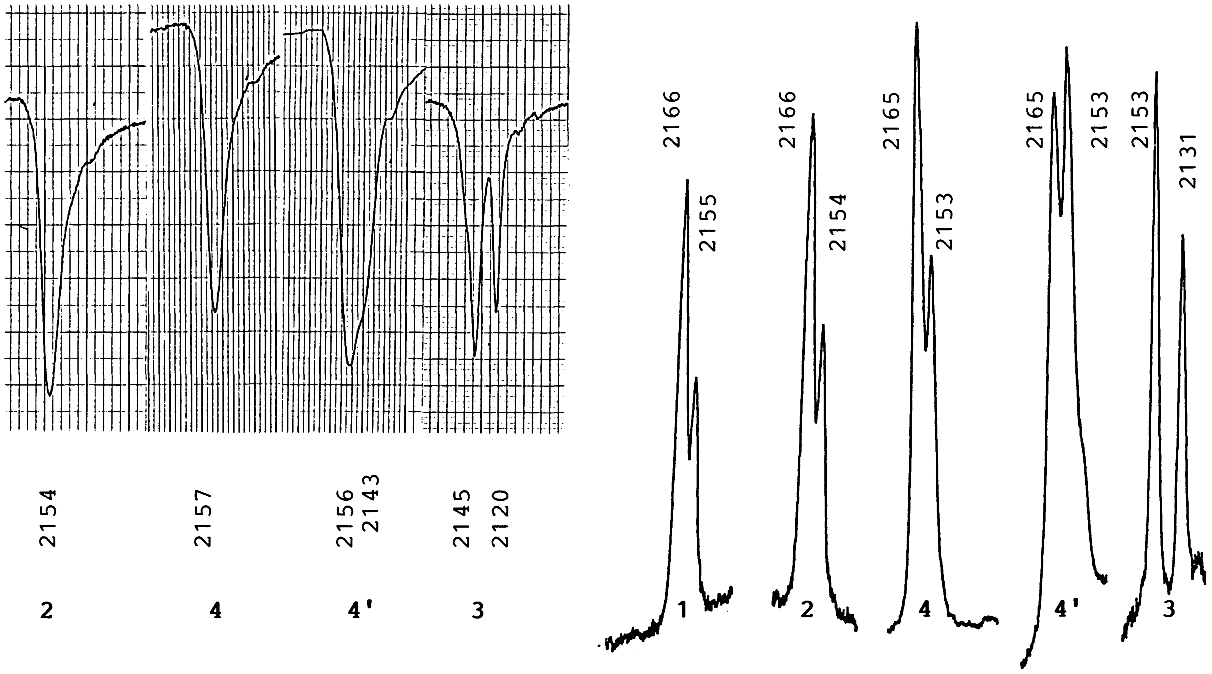

Fig. 2. Infrared (left) and Raman bands (right) of the CN stretch modes. See text for the numbering of compound.

number of the remaining singlet is similar to each other in **4** (2157 cm^{-1}) and **4'** (2156 cm^{-1}) as well as to those in **1** (2153 cm^{-1}) and **2** (2154 cm^{-1}), although a shoulder at ca. 2143 cm^{-1}, the wave number being similar to the higher twin of the doublet in **3**, remained in **4'**. Since the higher twin was assinged to the cyanide group of the one-dimensional catena-μ-linkage in the crystal structure of **3**, the shoulder is seen to reflect an intermediate character of **4'** between **3** and **4** with respect to the structure of two-dimensional cyanometal complex, i.e., the tetracyanonickelate(II) moiety in **4'** is not completely recovered to that of the D_{4h} symmetry in **4** in the process of thermal decomposition but distortion remains in a considerable extent. In either case, the disappearance of the band at 2120 cm^{-1}, which was assigned to the cyanide with free N-end in **3**, supports that all the cyanide groups of the metal complex moiety participate in the catena-μ-linkage in **4** and **4'**. The Raman bands with a doublet structure at 2166 cm^{-1} and 2154 cm^{-1} in **4** are similar in shape and wave number to those observed for **1** and **2**: the split is narrower and the wave numbers are higher than those in **3**. Those in **4'** give the wave numbers same to those observed for **4**, but the relative intensity is reversed. Since the wave number of the band at lower frequency side in **4'** happens to coincide with that of the band at higher frequency side in **3**, the line shape observed for **4'** is seen to reflect the intermediate character of **4'** between **3** and **4** as well as the observation in the IR spectra.

The powder X-ray diffraction patterns of **4** and **4'** supported the presence of a layered structure with a basal spacing of 9.36 Å, although the diffraction lines were rather broadened for **4'** owing to the partial degradation of cyrstal lattice in the thermal decomposition reaction. The 9.36 Å-distance shorter than those of

9.54 Å in **1** and 9.73 Å in **2** is reasonable assuming that the 1,6-diaminohexane column bridging between adjacent cyanometal complex networks is more reclined than those in **1** and **2** in order to accommodate the p-isomer longer than the o- and the m-isomers.

These observations are enough for us to ascertain the formation, both through the thermal decompositon of **3** and the crystallization from the liquid media, of a clathrate compound of the 1,6-diaminohexanecadmium(II) tetracyanonickelate(II) host and p-toluidine guest similar to those formed between the same host and the o- and the m-isomer guest, respectively. The limiting composition of the p-isomer clathrate should be $Cd[NH_2(CH_2)_6NH_2]Ni(CN)_4 \cdot p\text{-}CH_3C_6H_4NH_2$ when all the cavities are occupied by the guest molecules. Although the structural analysis is highly desired, it is still impossible owing to the difficulty in growing well-developed single crystals suitable for diffraction experiments.

Usually the clathrate compound is thermally unstable; it is a general tendency of clathrate compounds to liberate their guests easily on heating. The Hofmann-type and analogous clathrates themselves also liberate their guest molecules more or less spontaneously under ambient conditions, and the liberation of guest molecules precedes, or is accompanied with, the liberation of the ammine or amine ligands in the host during the thermal decomposition processes under ambient atmosphere. Furthermore, a coordination bond in a metal complex may be stronger than an intermolecular interaction in a clathrate compound. It appears unnatural that the direction of conversion is from ligand to guest in the present case. We do not know any other examples of the conversion in which a ligand in a metal complex turns to a guest molecule in the resulting metal complex host during a thermal decomposition reaction of the metal complex.

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