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DUAL COORDINATION BEHAVIOR OF MONOETHANOLAMINE IN HOFMANN-MEA-TYPE CLATHRATES $Cd(NH_2CH_2CH_2OH)_2Ni(CN)_4.C_4H_5N$ AND $Cd(NH_2CH_2CH_2OH)Ni(CN)_4.2C_6H_6$

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In the host structures of the novel clathrates $Cd(mea)_2Ni(CN)_4.C_4H_5N$ and $Cd(mea)Ni(CN)_4.2C_6H_6$ the mea (= $NH_2CH_2CH_2OH$) behaves as a unidentate ligand in the former and as an ambident one in the latter.

Monoethanolamine (mea = $NH_2CH_2CH_2OH$) may behave as either a bidentate ligand like ethylenediamine (en) or a unidentate one like ammonia. Bothe the cases of mea coordination were demonstrated in the host structures of the novel clathrates containing mea as the host constituent.

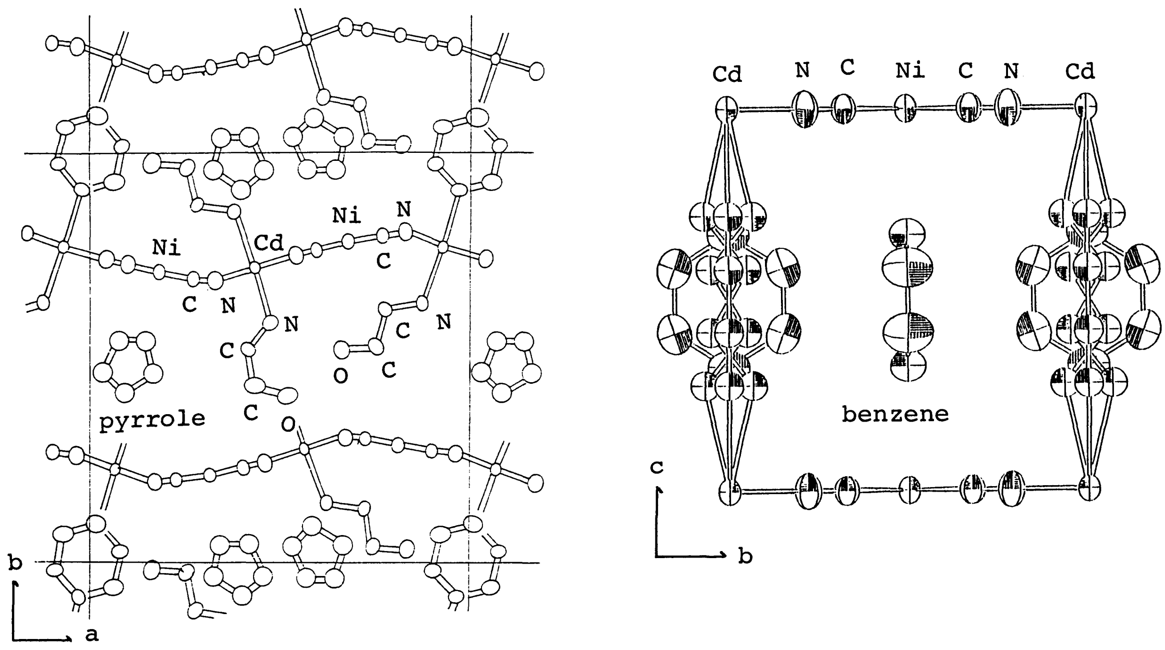
In the series of the clathrates analogous to Hofmann-type we have developed Hofmann-en-type $Cd(en)Ni(CN)_4.2G$ (G = C_4H_5N, C_4H_4S, or C_6H_6) from Hofmann-type $Cd(NH_3)_2Ni(CN)_4.2G$ by replacing the two unidentate NH_3 ligands by an ambident en which makes a span between the Cd atoms in adjacent $[Cd(NC)_4Ni]_\infty$ sheets.[1,2] Accoridng to the procedure similar to that for Hofmann-en-type but using mea in place of en, we obtained two kinds of novel clathrates for pyrrole and benzene as the respective guest: $Cd(mea)_2Ni(CN)_4.C_4H_5N$, I, and $Cd(mea)Ni(CN)_4.2C_6H_6$, II. The composition of I resembles that of Hofmann-type except for the number of guest molecules in the formula, and that of II is similar to that of Hofmann-en-type. The crystal structures of I and II were analyzed by the X-ray diffraction method.

Since the crystals of these clathrates were unstable under ambient condition, they were coated with epoxy resin prior to being subjected to the single crystal experiments. The refinement of the unit cell dimensions and the collection of intensity data were carried out on a four-circle automated diffractometer wih MoKα radiation. The structures were solved by the heavy-atom method and refined by successive Fourier syntheses and least-squares calculations to the conventional R values of 0.047 with 575 reflections for I and of 0.053 with 3050 reflections for II. The crystal data are:

I, $Cd(NH_2CH_2CH_2OH)_2Ni(CN)_4.C_4H_4N$, F.W. = 440.43, orthorhombic, space group $Pna2_1$, $a/\mathrm{\AA} = 14.691(1)$, $b/\mathrm{\AA} = 15.881(1)$, and $c/\mathrm{\AA} = 7.575(1)$, Z = 4.

II, $Cd(NH_2CH_2CH_2OH)Ni(CN)_4.2C_6H_6$, F.W. = 492.48, tetragonal, space group $P4/mmm$, $a/\mathrm{\AA} = 7.529(1)$ and $c/\mathrm{\AA} = 8.094(1)$, Z = 1.

As Fig. 1 shows, the mea is unidentate in I, but ambident in II. The mea in II bridges the coplanar $[Cd(NC)_4Ni]_\infty$ sheets similarly to the en in Hofmann-en-type benzene clathrate $Cd(en)Ni(CN)_4.2C_6H_6$[3], III, leading to the structure of II essentially similar to that of III. Similar to the en in III, the mea in II is statistically distributed about the fourfold axis of the unit cell, and additionally one cannot make difference between the nitrogen-end and the oxygen-end of



(a) (b)

Figure 1. (a) Projection along c-axis of $Cd(mea)_2Ni(CN)_4.C_4H_5N$: the metal cyanide network of the upper layer is shifted by c/2 from that of the lower layer, and two of the four CN linkages are shown from each Cd and Ni. (b) Projection along a-axis of $Cd(mea)Ni(CN)_4.2C_6H_6$: three of the four orientations of mea related to the fourfold axis are shown.

the mea with the applied space group P4/mmm which is the most plausible among the five space groups predicted by the 4/mmm Laue group in the Weissenberg photographs. On the other hand, there are two crystallographically-independent unidentate mea's in I. Each mea coordinates at the nitrogen-end to the Cd atom in $[Cd(NC)_4Ni]_\infty$ network which is considerably distorted from the coplanar structures observed for Hofmann-type, Hofmann-en-type, and II. One mea has the N-C-C-O skeletal configuration approximated to a trans-form, which bends its skeletal chain to snake into a cavity instead of the guest pyrrole molecule. The other mea in a cis-form appears to behave as a column along the b-axis of crystal dividing each cavity for the guest pyrrole molecule or the tail of the trans-mea.

Although each series of Hofmann-type and the analogous clathrates so far have been known has the host structures essentially similar to each other with the same host constituents, the novel "Hofmann-mea-type" are divided into two sub-groups. One is Hofmann-mea-type(1) $Cd(mea)_2Ni(CN)_4.C_4H_5N$ with the unidentate mea, and the other is Hofmann-mea-type(2) $Cd(mea)Ni(CN)_4.2C_6H_6$ with the ambident mea.

References

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