CHEMISTRY LETTERS, pp. 1129-1130, 1983.

CRYSTAL STRUCTURES OF THE o-, THE m-, AND THE p-TOLUIDINE CLATHRATES IN BISDIMETHYLAMINECADMIUM(II) TETRACYANONICKELATE(II) HOST

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The crystal structures of three clathrates $Cd(NH(CH_3)_2)_2Ni(CN)_4.G$ (G = o-$CH_3C_6H_4NH_2$, m-$CH_3C_6H_4NH_2$, and p-$CH_3C_6H_4NH_2$) have been analyzed by single crystal X-ray diffraction method. The structures are substantially similar to one another, although the way of puckering in the two-dimensional metal cyanide network in the host structure of the o-isomer clathrate is different from the two others.

As has been reported in the previous communication,$^{1)}$ the layered host of bisdimethylaminecadmium(II) tetracyanonickelate(II) can enclathrate the aromatic molecules with bulky substituent group(s) such as toluene, xylenes, toluidines, xylidines, halo- and dihalobenzenes, etc., those molecules which have never been enclathrated in Hofmann-type and the analogous hosts previously developed.$^{2)}$ Among the novel clathrates with a general formula $Cd(NH(CH_3)_2)_2Ni(CN)_4.G$, we have obtained single crystals of three clathrates with the o-, the m-, and the p-isomer of toluidine as the guest G, respectively, and their structures were analyzed by X-ray diffraction method. The crystal data are listed in Table 1 and the structures are compared in Fig. 1. Although the space groups are different to one another, the essential similarities are observed in the host structures for the stacking of two-dimensionally extended metal cyanide network $[CdNi(CN)_4]_\infty$ and the protrusion of dimethylamine ligands coordinate to the Cd atom in a trans configuration; the feature is also similar to that of the host structures of Hofmann-type and the analogous clathrates containing the $[CdNi(CN)_4]_\infty$ moieties, as has been suggested in the previous communication.$^{1)}$ A remarkable difference between the present structures and those of Hofmann-type and the analogous ones is the puckering of the metal cyanide network in the formers, although such a puckering has been observed for Hofmann-mea-type(1) pyrrole clathrate $Cd(NH_2CH_2CH_2OH)_2$-$Ni(CN)_4.C_4H_5N$.$^{3)}$ Among these three structures the o-isomer clathrate is different in the way of puckering

Table 1. Crystal Data

Host	$Cd(NH(CH_3)_2)_2Ni(CN)_4$		
Guest	o-$CH_3C_6H_4NH_2$	m-$CH_3C_6H_4NH_2$	p-$CH_3C_6H_4NH_2$
Space group	Pmma	P2/m	$P\bar{1}$
a/Å	26.32(1)	14.667(7)	14.61(2)
b/Å	7.614(9)	7.61(1)	7.61(2)
c/Å	10.364(1)	10.369(8)	10.63(1)
α/deg.	90	90	94.2(1)
β/deg.	90	115.52(6)	118.2(1)
γ/deg.	90	90	89.9(1)
Z	4	2	2
R	0.053	0.074	0.053

from the two others. The puckering occurs along the a-axis at the joints between the every other Cd atom ($\underline{\mathrm{Cd}}$ in Fig. 1) and the N-ends of the tetracyanonickelate(II) moieties. The way in the *o*-isomer clathrate is mirror-symmetric with respect to the mirror plane vertical to the a-axis, whereas that in the *m*- and the *p*-isomer ones is centrosymmetric with respect to the Cd atom ($\underline{\mathrm{Cd}}$ in Fig. 1) located at the center of symmetry with the bent joints with the N-ends of the tetracyanonickelate(II).

There are two kinds of cavities for the guest toluidine molecules in these three clathrates. One is surrounded mainly by eight methyl groups of four dimethylamine ligands protruded from the $\underline{\mathrm{Cd}}$ atoms. The guest molecule appears to be enclathrated tightly in this cage-like cavity. Another has a tunnel structure extended along the b-axis. The tunnel is mainly walled by the methyl groups of dimethylamine ligands protruded from the Cd atoms approximately coplanar to the tetracyanonickelate(II) moieties. The methyl and amino groups of toluidine molecules are statistically distributed about the phenyl rings in these cavities for all the three clathrates. In the Fourier maps and the block-diagonal least-squares calculations, it has been impossible to discriminate between the amino and the methyl groups for each of the toluidine molecules. For the *o*-isomer, the ortho substituent group is distributed with an equal probability to both sides each of the mirror planes required from the Pmma space group. For the *m*-isomer, the space group P2/m requires to have a center of symmetry at the center of the phenyl ring so as to make the molecular shape as if it were a 1,2,4,5-tetrasubstituted benzene. In Fig. 1, one of the possible orientations is shown for each molecule. Full details of the structure refinements will be reported elsewhere.

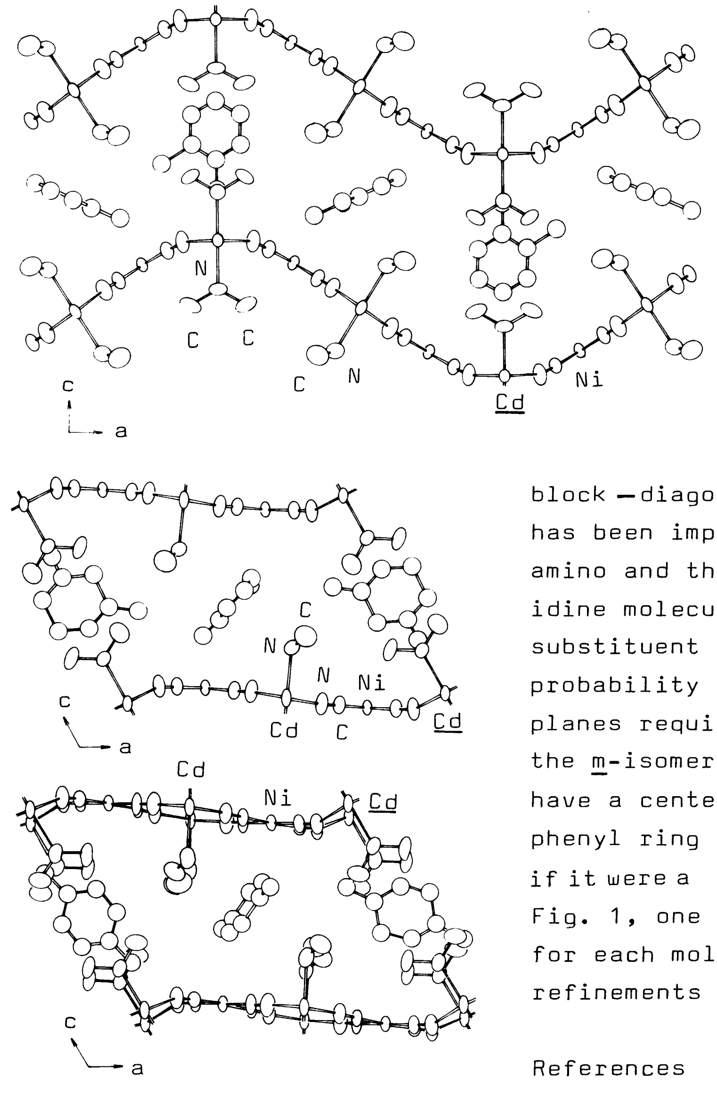

Fig. 1. Projections along the b-axis.
Top: the *o*-isomer clathrate; middle: the *m*-isomer one; and bottom: the *p*-isomer one.

References

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(Received May 6, 1983)