Urea- and Thiourea-like Host Structures of *catena*-[(1,2-Diaminopropane)cadmium(II) Tetra-μ-cyanonickelate(II)] Accommodating Aliphatic Guests

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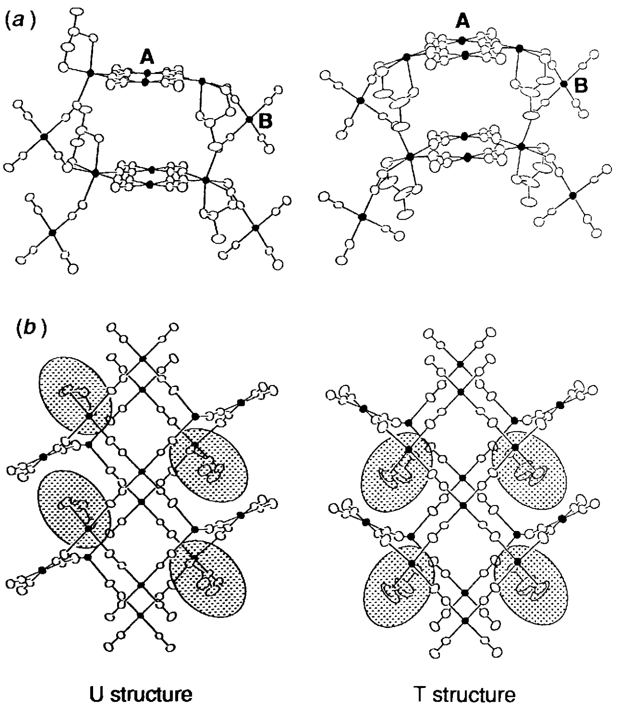
The three-dimensional framework of *catena*-[(1,2-diaminopropane)cadmium(II) tetra-μ-cyanonickelate(II)] gives a snake-like channel similar to that in the urea-host inclusion compound for straight chain aliphatic guests such as pentane, hexane, heptane and diethyl ether, but a nodal channel like that in the thiourea-host one for the branched aliphatic guests such as tetrachloroethane, 2-chlorobutane, 1,2-dichloropropane and isopropanol, respectively, by changing the arrangement of the 1,2-diaminopropane (= pn) chelate ring coordinated to the Cd atom as revealed in the single crystal structures of $Cd(pn)Ni(CN)_4{\cdot}xG$ ($x = 0.5$) inclusion compounds (G = aliphatic guest molecules).

So-called urea- and thioruea-adducts are typical examples of inclusion compounds with channel-like cavities accommodating organic guest molecules.[1–4] According to the shape of the channel, the urea host shows guest-selectivity for straight chain alkane derivatives in the spiral channel, but the nodal channel of the thiourea host prefers branched alkanes because the channel diameter is greater than that in the urea-host. Both types of channels have been materialised in the host structures of the metal–complex host inclusion compounds $Cd(pn)Ni(CN)_4{\cdot}xG$ ($x = 0.5$) of aliphatic guest G molecules (pn = 1,2-diaminopropane).

As has been reported previously,[5] the metal complex $Cd(pn)Ni(CN)_4$ adopts a host structure quite different from that of the Hofmann-pn-type clathrate $Cd(pn)Ni(CN)_4{\cdot}1.5G$

Table 1 Crystallographic data† of Cd(pn)Ni(CN)$_4$·xG (x = 0.5)

Cavity structure	U				T			
Crystal system	monoclinic				orthorhombic			
Space group	*A*2/*a* (No. 14; unique axis: *c*)				*Pnma* (No. 62)			
G	C_5H_{12}	C_6H_{14}	C_7H_{16}	$(C_2H_5)_2O$	$Cl_2CHCHCl_2$	$CH_3CHClC_2H_5$	$ClCH_2CHClCH_3$	$CH_3CHOHCH_3$
a/Å	14.083(1)	13.987(2)	14.014(5)	13.961(3)	14.061(1)	14.183(1)	14.104(3)	14.157(3)
b/Å	27.047(2)	26.971(2)	26.963(5)	26.998(3)	27.192(3)	26.983(2)	26.799(1)	26.699(2)
c/Å	7.616(1)	7.595(2)	7.576(4)	7.589(3)	7.590(1)	7.615(1)	7.657(1)	7.586(2)
γ/°	90.16(1)	91.74(1)	91.74(2)	90.84(1)	90	90	90	90
V/Å^3	2900.7(5)	2863.6(7)	2862(2)	2860(1)	2901.9(5)	2914(1)	2893.8(6)	2867.5(9)
Z	8	8	8	8	8	8	8	8
Used reflections	3485	3177	3344	2911	2373	2680	2379	2820
R	0.033	0.042	0.039	0.049	0.071	0.057	0.060	0.050



U structure T structure

Fig. 1 Structures of the snake-like channel in U (left) and the nodal channel in T (right). Projections along the *c*-axis (*a*) and perspective views along the *a*-axis of the respective channels (*b*) are shown. In (*a*) about half of each of the unit cells is shown; in (*b*) each channel is shown for *ca.* 2.5*c* extension with the approximate van der Waals spaces shadowed for the respective pn chelate rings.

(G = C_4H_5N, C_4H_4S, or C_6H_6),[6] when the guest is an aliphatic molecule such as 1,2-dichloroethane. The 1,2-dichloroethane is accommodated in the channel-like cavity formed in the three-dimensional host framework; the cage-like cavity in the Hofmann-pn-type host is substantially similar to that in the Hofmann-type $Cd(NH_3)_2Ni(CN)_4·2C_6H_6$,[7] which is isostructural to the original Hofmann's benzene clathrate $Ni(CN)_2·NH_3·C_6H_6$ [= $Ni(NH_3)_2Ni(CN)_4·2C_6H_6$].[8] We attempted to accommodate a number of aliphatic guests in the channel-like cavity of the novel host by the method similar to that previously reported.[5] Eventually we obtained two kinds of host structures, U and T, for the straight chain and the branched aliphatic guest molecules, respectively.

As the crystallographic data listed in Table 1 show, the alkanes from pentane to heptane, and diethyl ether give crystals of the monoclinic system with the space group *A*2/*a*, whereas the branched haloalkane- and isopropanol-guest compounds crystallise in the orthorhombic space group *Pnma*; the monoclinic space group *A*2/*a* has been chosen for the sake of comparison between the two structures. The unit cell dimensions for each structure, including the very small monoclinic distortion angle γ from the rectangle, are similar to one another, suggesting that they are isostructural. As shown in Fig. 1, the three-dimensional host frameworks are topologically similar to one another. The difference is seen in the arrangement of the pn chelate ring.

The framework is built of the pn-chelated Cd atoms and the two kinds of square planar tetracyanonickelates(II), **A** and **B**, linking the Cd atoms, respectively. **A** links two of the Cd atoms along the *c*-axis to form a doubly bridged one-dimensional X-membered frame, which separates the channels extending along the *c*-axis. **B** crosslinks the top and bottom frames at two of the Cd atoms to make the side-wall of the channel.

As is illustrated in Fig. 1, the pn chelate ring at the octahedral Cd is arranged point-symmetrically in the monoclinic unit cell of the U structure but mirror-symmetrically in the orthorhombic unit cell of the T structure. The former, U, gives a snake-like extension to the channel analogous to the spiral channel in the urea host with the alternate array of the pn chelate rings related to the inversion centre 1/2, 1/2, 1/2. In the latter, T, the pn chelate rings arranged at both sides of the mirror plane (400) makes a node in the channel similar to that of the thiourea host. These structural features of the channels are reflected in the respective guest-selectivities of U for the straight chain molecules and of T for the branched ones. In fact, the guest selects the host structure. When the guest is a straight chain aliphatic molecule, the host takes the U structure, and when the guest is a branched aliphatic molecule, the host takes the T structure. As for the U structure, the inclusion abilities for the short-chain pentane and diethyl ether of the five-membered skeletons are specific to the metal complex host $Cd(pn)Ni(CN)_4$, but different from the urea-host inclusion compound. In contrast with the case between the urea and the thiourea hosts, the host of T has the same chemical composition as that of U with little difference in the lattice parameters. Including the Hofmann-pn-type host, these metal complex structures with the common composition $Cd(pn)Ni(CN)_4$ exemplify a kind of structural isomerism in the polymeric coordination compounds.

In the refined crystal structures the guest molecules are in general disordered with extremely large thermal parameters. Despite the expectation of a non-stoichiometric composition of the guest for these inclusion compounds with the channel-like cavities, the analytical results have supported x = 0.5 for all of the guests. A problem is that the straight chain

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† Atomic coordinates and thermal parameters for the compounds in Table 1 have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

haloalkane 1,2-dichloroethane is accommodated in the T structure.[5] Details of the respective crystal structures and this problem will be discussed elsewhere.[9]

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