A Novel Three-Dimensional Cyano-Linked Metal-Complex Host Clathrate [{Cd(imH)}{Cd(CN)$_3$(imH)}{Cd(CN)$_3$}]·C_6H_6 (imH = imidazole): X-Ray Single Crystal Structure and Solid State ^{113}Cd and ^{2}H NMR

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The title clathrate involves imidazole-ligated octahedral and tetrahedral Cd atoms along with CN-only-ligated tetrahedral Cd linked by CN bridges to one another to give a three-dimensional host framework in which the guest benzene molecule takes a uniaxial reorientational motion about the molecular sixfold axis.

Our synthetic investigations of $Cd(CN)_2$, and the isopolycyanopolycadmate $[Cd_x(CN)_y]^{2x-y}$ supramolecular systems that are built of octahedral and tetrahedral Cd atoms linked by CN groups, have revealed a number of host structures variegated in topology.[1] This communication reports the novel three-dimensional (3D) host structure of $3Cd(CN)_2{\cdot}2imH{\cdot}C_6H_6$ containing imidazole (imH) ligands at the octahedral Cd atom and one of the two tetrahedral Cd atoms, all of the Cd atoms being linked by the CN groups to give a cage cavity to the guest C_6H_6 molecule, as has been demonstrated in the single crystal X-ray structure. This structure is the first example of the isopolycyanopolycadmate host with the unidentate ligand at the tetrahedral Cd atom. The coordination environments about the Cd atoms are interpreted in terms of the CP/MAS ^{113}Cd NMR and the motional behaviour of the C_6D_6 guest in terms of the solid state ^{2}H NMR.

Into an aqueous solution containing an equimolar mixture of $CdCl_2$ and $K_2[Cd(CN)_4]$ (5 mmol each in 100 cm^3 H_2O) 10 mmol of imH was added in stirring. The solution was covered with a layer of neat benzene at ambient temperature for a few days; colourless crystals were formed at the interface between the organic and the aqueous phases and the bottom of the latter phase. The composition $3Cd(CN)_2{\cdot}2(C_3H_4N_2){\cdot}C_6H_6$ was identified by elemental analyses, IR spectroscopy and gas chromatography. The product is unstable under ambient conditions to release the guest molecule gradually. Crystals for ^{2}H NMR measurements were prepared using C_6D_6 as the guest.

The single crystal subjected to the X-ray experiment[2,3] on a Rigaku AFC 5R diffractometer was coated with epoxy-resin. The solved structure is shown in Figure 1. The 3D host has a pillared layer structure constructed of the CN-linkages among the octahedral Cd(o) and tetrahedral Cd(t1) and Cd(t2). Cd(o) ligated by an imH is linked to three Cd(t2) and two Cd(t1); Cd(t1) is ligated by another imH and linked to two Cd(o) and one Cd(t2); Cd(t2) is linked to three Cd(o) and one Cd(t1), respectively.[4] The bond distances and angles observed about the Cd coordination environments as well as the ring structures of the imH ligands are not unusual.

A one-dimensional (1D) chain with a repeating unit of -NC-Cd(t1)-CN-Cd(t2)-CN-Cd(o)- runs in parallel to the *c* axis of the unit cell. According to the symmetry requirements of the $P2_1/n$ space group, the 1D chain is successively linked to adjacent chains running in almost parallel along the *bc* plane to extend a two-dimensional (2D) network with pentagonal meshes through the CN-linkages between Cd(t1) and Cd(o), and between Cd(o) and Cd(t2). The networks stacked along the *a* axis are pillared by

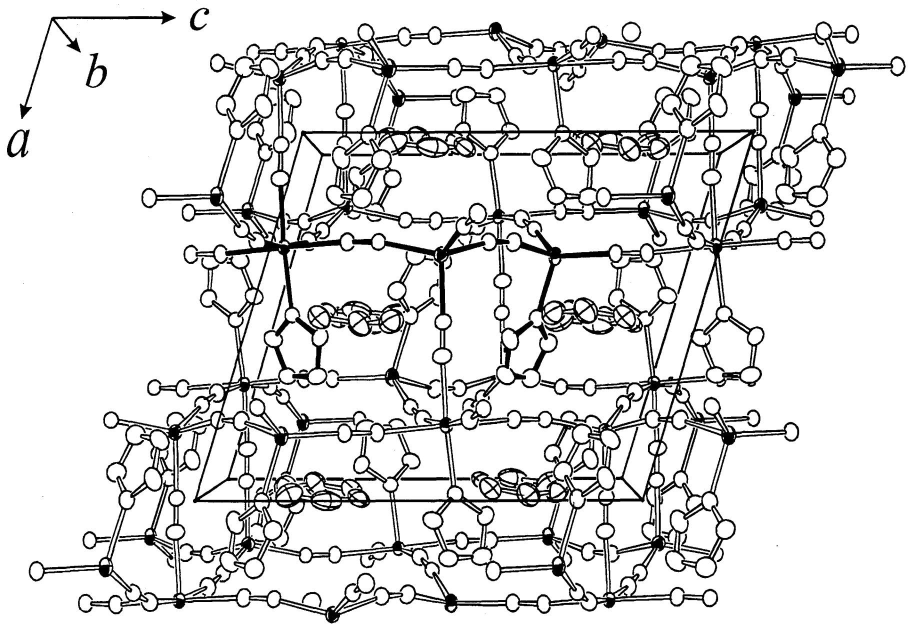

Figure 1. Structure of [{Cd(o)(imH)}{Cd(t1)(CN)$_3$(imH)}{Cd(t2)(CN)$_3$}] · C_6H_6: projection along the *b* axis. A unit of the 1D chain along with the imH rings is shown with solid bonds.

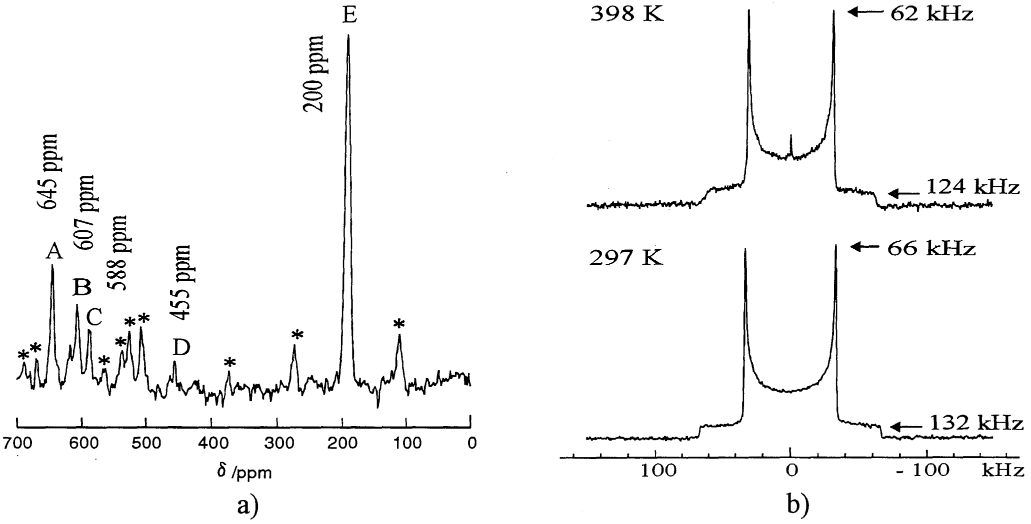

Figure 2. a) CP/MAS ^{113}Cd NMR spectrum; side bands are asterisked. b) Solid state ^{2}H NMR spectra at 297 and 398 K.

the CN-linkage between Cd(t2) and Cd(o) to build up the 3D host framework. The cavity for the guest has the shape of a pentagonal box; the top and the bottom are the pentagonal meshes of the 2D networks pillared by a couple of Cd(t2)-CN-Cd(o) linkages. The imH ligands protruding from the networks cover the sides of the cavity. The guest C_6H_6 molecule is accommodated in the cavity with its aromatic plane almost in parallel to the top and the bottom, viz., to the 2D network of the host.

Although it was impossible to discriminate between C and N in the Cd(t1)-CN-Cd(t2) linkage in the X-ray structure refinement, the CP/MAS ^{113}Cd NMR spectrum,[5a] as shown in Figure 2a, supports the random orientation of the CN group from the bands observed at 645, 607, 588, 455 and 200 ppm assignable respectively to the Cd atoms in the ligations of Cd(t2)C_4, Cd(t2)C_3N, Cd(t1)C_3N(imH), Cd(t1)C_2NN(imH) and Cd(o)N_5N(imH) with the reasonable intensities.[6]

The ^{2}H NMR powder patterns observed for the C_6D_6 guest (Figure 2b)[5b] are typical of the C_6D_6 molecule taking reorientational motion about its sixfold molecular axis similar to those observed for the Hofmann-type $[Cd(NH_3)_2Ni(CN)_4]\cdot 2C_6D_6$ and Hofmann-en-type $[Cd(en)Ni(CN)_4]\cdot 2C_6D_6$ clathrates at similar temperature regions.[7] The spectral feature being unchanged upon increase of the temperature from 297 to 373 K, slight narrowing of the line widths was observed at 398 K, nearly to the thermal decomposition point: from 132 to 124 kHz for the $\Delta\nu_{zz}$ and from 66 to 62 kHz for the $\Delta\nu_{xx} = \Delta\nu_{yy}$, probably due to rattling of the rotational axis. The central small sharp peak at 398 K is attributable to partial decomposition of the specimen.

Similar clathrates $3Cd(CN)_2\cdot 2imH\cdot G$ have been obtained for such guest G as toluene, cyclohexanone, *m*-xylene, *p*-xylene, ethylbenzene; the present imH-ligated host appears not to be rigid but flexible enough to accommodate various guests different in size and functionality. Details on these clathrates will be reported later.

References and Note

1 a) T. Kitazawa, S. Nishikiori, R. Kuroda, and T. Iwamoto, *Chem. Lett.*, **1988**, 459; *J. Chem. Soc., Dalton Trans.*, **1994**, 1029; b) T. Kitazawa, S, Nishikiori, and T. Iwamoto, *J. Chem. Soc., Dalton Trans.*, **1994**, 3695; c) T. Kitazawa, T. Kikuyama, M. Takahashi, and M. Takeda, *J. Chem. Soc., Dalton Trans.*, **1994**, 2933.

2 Crystal data. $C_{18}H_{14}N_{10}Cd_3$, M = 707.61, monoclinic, $P2_1/n$, a = 12.369(2), b = 14.117(2), c = 14.423(2) Å, β = 106.58(1)°, U = 2413.6(6) Å^3, Z = 4, Dx = 1.95 and Dm = 1.95(1) g cm^{-3}, μ(Mo Kα) = 26.37 cm^{-1}, 7790 reflections observed by 2θ-ω scan, 5023 used, R = 0.037 and Rw = 0.035 by SHELX76,[3] *GOF* = 1.45. Details of the crystal structure determination will be reported elsewhere along with those for the analogous clathrates.

3 G. M. Sheldrick, SHELX 76, Program for crystal structure determinations. University of Cambridge, 1976.

4 The atomic notations Cd(o), Cd(t1) and Cd(t2) have been applied for those given by symmetry operations.

5 a) a Chemagnetics CMX-300 NMR spectrometer, 66.61 MHz Larmor frequency for ^{113}Cd, cross polarization pulse sequence with 5 μs ^{1}H 90° pulse width, 4 ms contact time and 10 s recycle delay time, 5 kHz spinning rate, at 296 K, $Cd(NO_3)_2\cdot 4H_2O$ external standard; b) 46.09 MHz Larmor frequency, quadrupole echo pulse sequence with 2μs 90° pulse width and 35 μs pulse spacing time and 4 s recycle delay time, at 297, 323, 348, 373, and 398 K.

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