A Hydrogen-Bond Bridged Layer Host: Crystal Structure of 2-Phenylethylammonium Tetracyanonickelate(II)-(*N,N*-Dimethylaniline) (1/1)

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The ammonio group of 2-phenylethylammonium cation links tetracyanonickelate(II) anions at the N atoms of square-planar $Ni(CN)_4$ moieties through hydrogen bonds to form a layer of doubly-CN-bridged one dimensional extensions of $[(PhCH_2CH_2NH_3)_2Ni(CN)_4]_n$ with protrusion of the 2-phenylethyl groups into the interlayer space; these groups act as the spacers to produce the cavities for the guest *N,N*-dimethylaniline molecules.

Replacement of the cationic $[M(NH_3)_2]^{2+}$ moiety in the Hofmann-type $[M(NH_3)_2M'(CN)_4]$ host with 2-phenylethylammonium $PhCH_2CH_2NH_3^+$ (β-peaH$^+$) produces a novel host structure. The Hofmann-type structure was first determined by Powell and Rayner[1] for Hofmann's benzene clathrate $[Ni(NH_3)_2Ni(CN)_4]\cdot 2C_6H_6$;[2] and later for various metal ions.[3] The Hofmann-type host has a layer structure of a $[M(NH_3)_2M'(CN)_4]_n$ network in which the $[M(NH_3)_2]^{2+}$ moiety connects four $[M'(CN)_4]^{2-}$ moieties to extend the two dimensional (2D) network. The NH_3 ligands, coordinated to the octahedral M, protrude from the network up and down into the interlayer spaces. The guest molecule G is accommodated in the interlayer cavity spaced by the NH_3 ligands.

The clathrate $[(\beta\text{-peaH})_2Ni(CN)_4]\cdot PhNMe_2$ was prepared as single crystals. $PhCH_2CH_2NH_2$ (16 mmol) was added to $K_2[Ni(CN)_4]$ (aq. 8 mmol in 100 cm^3) and the pH was adjusted to 6.5 (citric acid and 2-hydroxyethylamine). The solution was covered with a layer of $PhNMe_2$ at *ca.* 5 °C for a few days. Pale-yellow crystals were obtained at the aqueous–organic interface; satisfactory elemental analyses were obtained. Unidentified fine particles adsorbed on the surface of single crystals were rather difficult to remove by washing and mechanical removal resulted in the disintegration of the crystals with liberation of the guest molecules.

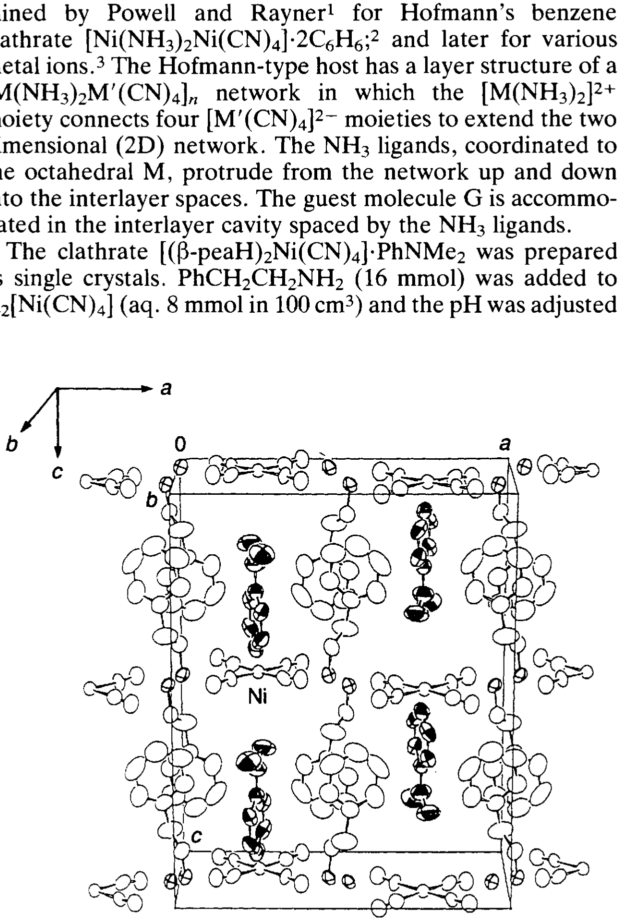

Fig. 1 A perspective view of the structure: anisotropic sections are shown for the atoms of the guest and anisotropic peripheries for the N of β-peaH$^+$

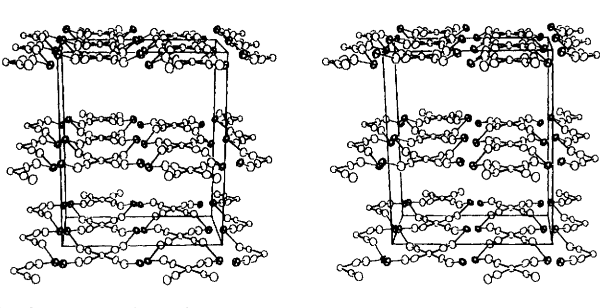

Fig. 2 A stereoview of the double-1D extensions bridged through the hydrogen bonds between β-peaH$^+$ and $[Ni(CN)_4]^{2-}$ moieties: only the N atoms of β-peaH$^+$ are shown with the $[Ni(CN)_4]^{2-}$ moieties, guest molecules and 2-phenylethyl skeletons of β-peaH$^+$ having been omitted

The host has a layer structure analogous to the Hofmann-type.† A pair of X-shaped $[Ni(CN)_4]^{2-}$ moieties are connected at their N atoms by the ammonio groups of two β-peaH$^+$ cations through N–H···NC hydrogen bonds with the N···N distances of 2.847(15) and 2.926(14) Å, to make distorted squares cornered by the Ni atoms and the ammonio-N atoms alternately, with the edges of the CN groups. The squares are connected successively to form a doubly-bridged one-dimensional (double-1D) extension running along the *b* axis at *c* = *ca.* 0 and 0.5 (Fig. 2). The double-1D extensions are arrayed side by side to form a sheet parallel to the *ab* plane without direct chemical bonds. The $PhCH_2CH_2$-group protruding from each of the diagonal corners of the square stands up or hangs down in parallel from the double-1D extension to which its phenyl ring is almost vertical with the *trans* conformation about the $PhH_2C\text{–}CH_2NH_3^+$ bond. The phenyl rings behave as spacers between the layers and as walls of the interlayer cavities, which are topped and bottomed with the double-1D layers. The guest $PhNMe_2$ molecule keeps its aromatic plane almost vertical to the double-1D layer as well as the phenyl ring of β-peaH$^+$; both aromatic planes of the host and the guest are arrayed almost vertical to each other. With this respect the cavity has a resemblance with that of the Hofmann-type, being topped and bottomed with the square meshes of $[MM'(CN)_4]_n$ networks and walled with the amine ligands protruding into the interlayer space. The polar guest molecules are arranged in parallel along the *c* axis but in antiparallel between those along the glide planes at *a* = 0.25 and 0.75 as well as the couple of the $PhCH_2CH_2$-groups sandwiching the guest.

A remarkable difference from the Hofmann-type is the array of the cavities separated by the β-peaH$^+$ spacers; the 2D network on the *ab* plane in the Hofmann-type is split into the double-1D extensions arrayed in parallel to one another. The rather high *R* value in the final refinement may be due to two reasons: (*i*) from the tough contamination on the crystal surface and (*ii*) from the loose packing of this split structure so as to give considerably large thermal amplitudes for both of those atoms comprising the host and guest moieties.

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Footnote

† The structure was solved by the heavy-atom method using 1343 reflections; 165 atomic parameters were refined anisotropically by the full-matrix least-squares procedure to *R* = 0.0789. The crystal data are: the orthorhombic space group *Pccn*, *a* = 16.329(1), *b* = 8.785(1), *c* = 20.378(3) Å, *U* = 2923.5(7) Å^3, *Z* = 4. The solved structure is shown in Figs. 1 and 2. Atomic coordinates, bond lengths and angles,

and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

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