

Structural Characterisation of Infinite Three-dimensional $[\text{Cd}_4(\text{CN})_9]^-$ Ion

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Single crystal X-ray determination reveals the first example of a mineralomimetic $[\text{Cd}_4(\text{CN})_9]^-$ open framework consisting of interconnected tetrahedral and octahedral cadmium centres in the ratio 3:1, while solid state ^{113}Cd NMR spectroscopy indicates that some of the bridged cyano groups between the Cd atoms are disordered.

Although cadmium cyanide is well known, its ability to form cristobalite-like clathrates and various types of polycyanopolycadmiate frameworks were found only recently.¹⁻⁶ Since tetrahedral, trigonal-bipyramidal and octahedral coordinations of cadmium can coexist in the poly-

cyanopolycadmiate systems,^{1,3-6} we can mimic the silicate structures containing octahedral cations such as Mg^{2+} and Al^{3+} .

Polycyanopolycadmiate host frameworks containing tetrahedral and octahedral cadmium atoms in a ratio of 2:1 have

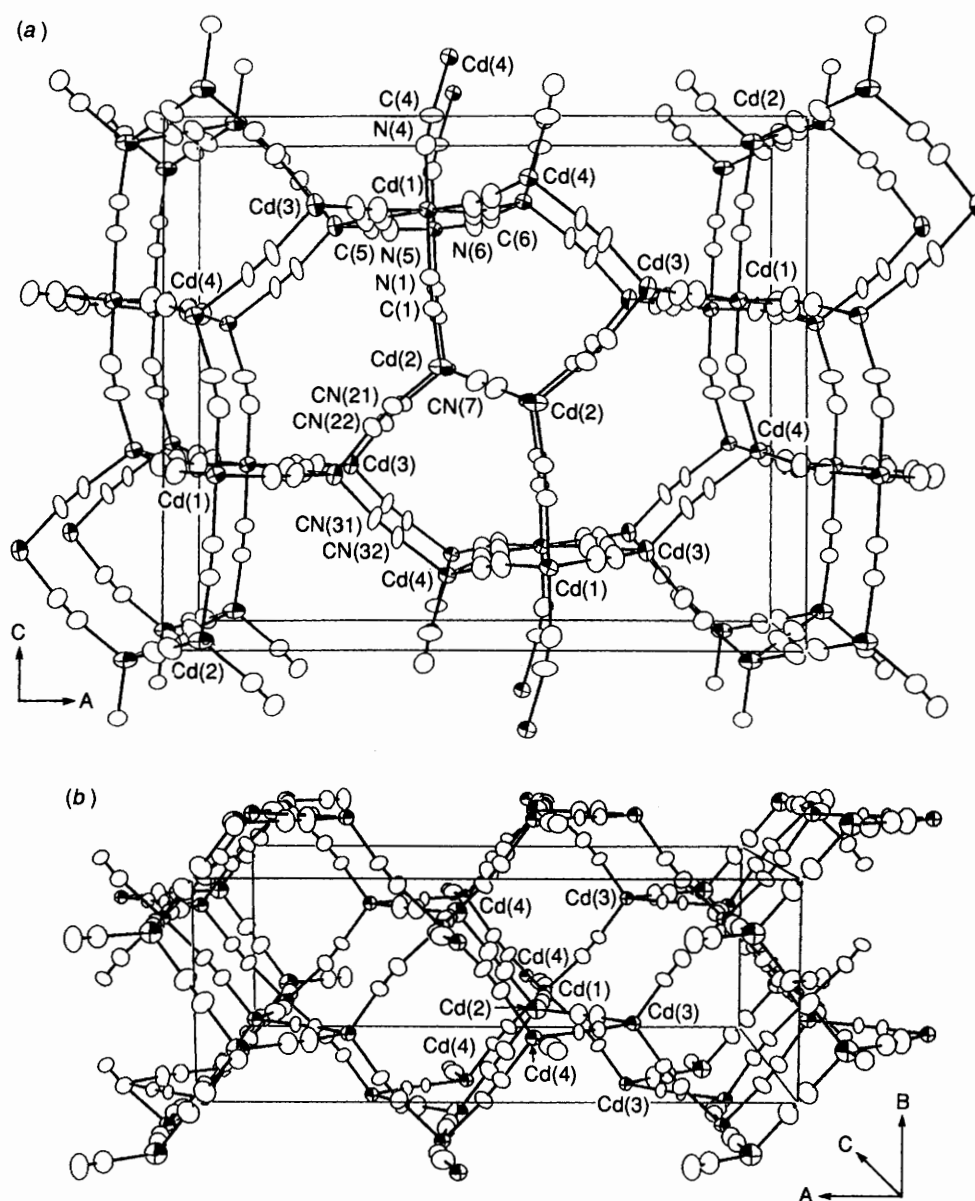


Fig. 1 Open framework structure of the $[\text{Cd}_4(\text{CN})_9]^-$ - $[\text{K}]_4\text{EtCN}$ complex. Anisotropic sections are shown for the Cd atoms. Potassium ions and propionitrile are omitted. (a) The view approximately normal to the crystallographically mirror plane. All Cd atoms and the cyano groups of CN(1), CN(2), CN(3) and CN(4) are located on the mirror plane. The sequences of $-\text{Cd}(1)-\text{CN}(1)-\text{Cd}(2)-\text{CN}(2)-\text{Cd}(3)-\text{CN}(3)-\text{Cd}(4)-\text{CN}(4)-$ is found running on the mirror plane periodically. The cyano groups out of the mirror plane [CN(5), CN(6), CN(7)] bridge between the sequences respectively on the plane and the adjacent planes. The atoms of CN(21), CN(22), CN(31), CN(32) and CN(7) are 50/50 mixtures of disordered C and N atoms. (b) The view approximately along the mirror plane. The mirror planes are on $b = 0.25$ and 0.75 .

been reported previously, for example $\text{Cd}_3(\text{CN})_6(\text{H}_2\text{O})_2 \cdot 3\text{Bu}^+\text{OH}$ with a honeycomb-like framework,⁴ clay-like layered clathrates of general formula $\text{Cd}_3(\text{CN})_6\text{L}_2\text{G}$, where L is a unidentate ligand^{1,5} and zeolite-like clathrates of the general formula $[\text{Cd}_3(\text{CN})_7]\cdot[\text{onium}]\text{G}$ according to the host $[\text{Cd}_3(\text{CN})_7]$ and the guest components of [onium] and neutral G.^{1,3}

We have prepared a novel polycyanopolycadmate framework consisting essentially of interconnected tetrahedral and octahedral centres in a ratio of 3:1. An equimolar aqueous solution of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ and $\text{K}_2[\text{Cd}(\text{CN})_4]$ was treated with neat propionitrile and after leaving at room temp. for several days, yielded colourless crystals with composition $[\text{Cd}_4(\text{CN})_9]\cdot[\text{K}]\text{4EtCN}$.

The X-ray crystal structure† of this complex (Fig. 1) shows that the host framework contains four crystallographically independent Cd atoms: Cd(1) is octahedral and, Cd(2), Cd(3) and Cd(4) are tetrahedral. In the host framework there are seven crystallographically independent bridged cyano groups. The C and N of the cyano group were assigned on the basis of the ^{113}Cd NMR spectrum. The centre of the CN(7) link is an inversion centre, so that, based on the X-ray result alone, this group must be in the 1:1 disorder state.

^{113}Cd NMR spectroscopy is a powerful tool for assigning the C and N atoms of the cyano groups which link two Cd atoms in the polycyanopolycadmate systems.⁶ The spectrum obtained for $[\text{Cd}_4(\text{CN})_9]\cdot[\text{K}]\text{4EtCN}$ is shown in Fig. 2. The signals due to octahedrally coordinated Cd atoms usually appear at much lower frequency than the lines due to tetrahedrally coordinated atoms, and hence the single line at δ 167.1 can be assigned to an ordered, octahedrally coordinated Cd atom. Seven distinct tetrahedral Cd lines were identified, rather than the three lines which would be expected for the cyano groups completely ordered between tetrahedral Cd atoms. Comparison with the previous work⁶ leads to the following assignments of the lines: δ 650.6, Cd(4)C₄; 627.7, Cd(3)C₄; 601.5,

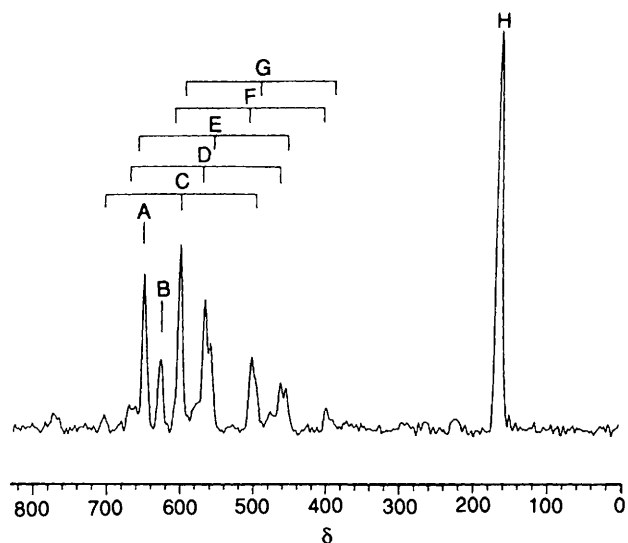


Fig. 2 ^{113}Cd CP MAS NMR spectrum of $[\text{Cd}_4(\text{CN})_9]\cdot[\text{K}]\text{4EtCN}$, spinning at 6.2 kHz. Spectra were recorded at 59.79 MHz on JEOL EX270 NMR spectrometer with a solid high resolution NMR unit. Samples were contained in zirconia tubes (6 mm od). Contact times were 10 ms, delay times 5 s. Chemical shifts are given relative to $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. A = Cd(4)C₄, B = Cd(3)C₄, C = Cd(4)C₃N, D = Cd(2)C₃N, E = Cd(3)C₃N, F = Cd(2)C₂N₂, G = Cd(3)C₂N₂, H = Cd(1)N₆.

Cd(4)C₃N; 566.2, Cd(2)C₃N; 559.1, Cd(3)C₃N; 501.4, Cd(2)C₂N₂; 496.7 Cd(3)C₂N₂; implying CN(2) and CN(3) are disordered.

The novel $[\text{Cd}_4(\text{CN})_9]^-$ framework provides a structural link between cristobalite-like $\text{Cd}(\text{CN})_2$ and zeolite-like $[\text{Cd}_3(\text{CN})_7]^-$ frameworks.¹⁻³ The novel framework is also based on the dimeric anion $[\text{Cd}_2(\text{CN})_7]^{3-}$ and the infinite chain-like anion $\text{Cd}(\text{CN})_3^-$.^{7,8}

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† Crystal data: $[\text{Cd}_4(\text{CN})_9]\cdot[\text{K}]\text{4EtCN}$, single crystal $0.40 \times 0.35 \times 0.30$ mm, $M = 943.22$; orthorhombic, *Pnma* (No. 62), $a = 22.773(5)$, $b = 8.549(1)$, $c = 18.850(9)$ Å, $V = 3670(3)$ Å³, $Z = 4$, $D_m = 1.73(2)$ g cm⁻³, $D_x = 1.71$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 22.23$ cm⁻¹, Rigaku AFC5S diffractometer, 6099 reflections observed, 2077 used; 188 parameters refined, $R = 0.056$, $R_w = 0.042$, goodness of fit = 2.20. The structure was solved using the TEXSAN software package with Ψ -scan absorption correction. After refinement of the host framework $[\text{Cd}_4(\text{CN})_9]^-$, difference maps indicated that the EtCN molecules displayed positional disorder due to the large thermal motion and the pseudosymmetry of the structure. Anisotropic thermal parameters were applied to all non-hydrogen atoms except those of the EtCN molecules. The atoms of the disordered EtCN molecules were refined with isotropic thermal parameters. The four kinds of EtCN molecules and the K⁺ ion are situated in distinct cavities. The X-ray results suggest the EtCN molecules weakly interact with the K⁺ ions in the cavities and have van der Waals contacts with the host $[\text{Cd}_4(\text{CN})_9]^-$ framework. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors Issue No. 1.