

Synthesis and Structural Characterization of a New Mineralomimetic Ion, $[\text{Cd}_2(\text{CN})_7]^{3-}$

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$[\text{PPh}_4]_3[\text{Cd}_2(\text{CN})_7]$ contains a novel mineralomimetic discrete $[\text{Cd}_2(\text{CN})_7]^{3-}$ anion which is topologically similar to the pyrosilicate anion, $\text{Si}_2\text{O}_7^{6-}$.

We and others have been developing a new family of mineralomimetic inclusion structures similar to natural silica and silicates such as cristobalite, clays and zeolite, using cadmium cyanide and polycyanopolycadmiate systems.¹⁻⁴ For example, in cristobalite the SiO_4^{4-} tetrahedra are linked so that every oxygen atom is shared between two tetrahedra, giving the composition SiO_2 . Likewise the three-dimensional framework structure of $\text{Cd}(\text{CN})_2$ in the $\text{Cd}(\text{CN})_2$ -guest clathrate compounds is isostructural with the high temperature phase of cristobalite and the cubic I_c phase of ice.^{1,3} Similarly, the parent structural unit in polycyanopolycadmates is $[\text{Cd}(\text{CN})_4]^{2-}$, where the cadmium atom is tetrahedral; the highest degree of polymerisation results in a three-dimensional infinite framework structure of stoichiometry $\text{Cd}(\text{CN})_2$.

The pyrosilicate anion, $\text{Si}_2\text{O}_7^{6-}$, in which one oxygen atom is shared between two SiO_4^{4-} tetrahedra, is known in nature.^{5,6} We therefore attempted to obtain the new $[\text{Cd}_2(\text{CN})_7]^{3-}$ ion which is topologically similar to the pyrosilicate anion. 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 a warm aqueous solution of PPh_4Br : a precipitate formed immediately. This was dissolved by adding citric acid, 2-aminoethanol and acetonitrile and the solution kept standing in a refrigerator for a week to obtain colourless hexagonal crystals, $[\text{PPh}_4]_3[\text{Cd}_2(\text{CN})_7]$.[†] Crystal growth occurred only over a very narrow range of pH (7.7–8.3).

The X-ray crystal structure[‡] of this complex (Fig. 1) shows

that one cyanide ligand from each tetrahedrally-coordinated cadmium centre is shared through development of a linear bridge, so resulting in the formation of the new discrete $[\text{Cd}_2(\text{CN})_7]^{3-}$ anion. The conformation of the two tetrahedra is staggered (D_{3d}) rather than eclipsed (C_{2v}). To our knowledge, this is the first example of a compound containing the discrete $[\text{Cd}_2(\text{CN})_7]^{3-}$, in which one CN group links two Cd atoms. The topological and structural features of the $(\text{NC})_3\text{Cd}-\text{CN}-\text{Cd}(\text{CN})_3$ are similar to $\text{O}_3-\text{Si}-\text{O}-\text{Si}-\text{O}_3$ though the Cd–CN–Cd grouping is essentially linear, whereas the Si–O–Si bond angle varies from 180 to 133° in various minerals depending on the cation.^{5,6}

These preliminary results indicate that the use of a large lipophilic cation, such as PPh_4^+ , allows the easy preparation of a new compound containing non-polymeric $[\text{Cd}_2(\text{CN})_7]^{3-}$ anions. The structural dimension in cadmium cyanide and polycyanopolycadmiate systems is dictated by the size, shape

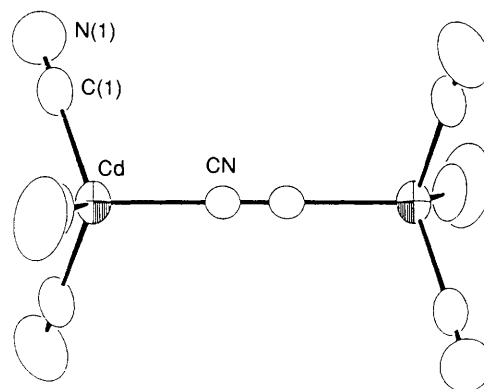


Fig. 1 View of the $[\text{Cd}_2(\text{CN})_7]^{3-}$ in $[\text{PPh}_4]_3[\text{Cd}_2(\text{CN})_7]$. It is impossible to discriminate between C and N atoms of the bridged cyanide in the $R\bar{3}c$ space group. The CN units are effectively a 50:50 mixture of disordered C and N atoms. Disorder in the orientation of the cyanide group has been found by solid state Cd NMR spectroscopy in $\text{Cd}(\text{CN})_2$ host-guest materials.⁸ Anisotropic sections are shown for the Cd atoms. Selected bond lengths (Å) and angles (°): Cd–C(1) 2.26(1), Cd–CN 2.26(1), C(1)–N(1) 1.07(1), C–N (bridging) 1.15(2), Cd···Cd' 5.685(2), CN–Cd–C(1) 106.6(3), C(1)–Cd–C(1') 112.2(2), Cd–C(1)–N(1) 177(1).

[†] Satisfactory elemental analyses were obtained.

[‡] *Crystal data:* $[\text{PPh}_4]_3[\text{Cd}_2(\text{CN})_7]$, $M = 1425.13$; rhombohedral, $R\bar{3}c$ (No. 167), $a = 18.990(4)$, $c = 34.301(4)$ Å, $U = 10713(4)$ Å³, $Z = 6$, $D_m = 1.34(2)$, $D_x = 1.33$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 7.04$ cm⁻¹, Rigaku AFC5S diffractometer. 5823 Reflections observed, 1113 used; 138 parameters refined; $R = 0.055$, $R_w = 0.056$, goodness of fit (gof) = 2.71. The structure was solved using the TEXSAN software package installed on the diffractometer system. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were not inserted in the refinement. The cations are oriented with the crystallographic C_2 axis of the coordination tetrahedron perpendicular to the z axis of the cell. 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.

and packing requirements of the cations and/or the neutral guest molecules.¹⁻⁴ With relatively small cations, such as NMe_4^+ and SMe_3^+ , these anion complexes possess polymeric structures based on the bridging behaviour of the cyanide groups,^{2,3} but with a large organic cation, the anion structure loses its polymeric nature⁷ and dinuclear clusters consist of two tetrahedra sharing one corner.

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