

$\text{Cd}(\text{CN})_3^-$: a Novel Mineralomimetic Infinite Chain-like Polycyanopolycadmte Anion

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$[\text{SbPh}_4]_2[\text{Cd}(\text{CN})_3]_2$ contains a novel mineralomimetic infinite chain-like $\text{Cd}(\text{CN})_3^-$ anion which is topologically similar to the linear single chain SiO_3^{2-} having a repeat unit after every second tetrahedron in the pyroxenes.

There is potentially a wide interest in polycyanopolycadmte systems.¹⁻³ The fact that polycyanopolycadmte can form open framework structures related to zeolites and clays has been reported previously;¹⁻⁶ the mineralomimetic behaviour of these systems has also been discussed.^{1,4-7} For example, in the pyrosilicate anion one oxygen atom is shared between two SiO_4^{4-} tetrahedra, giving the composition $\text{Si}_2\text{O}_7^{6-}$. Likewise $[\text{PPh}_4]_3[\text{Cd}_2(\text{CN})_7]$ contains a mineralomimetic discrete unit $[\text{Cd}_2(\text{CN})_7]^{3-}$, in which one CN group links two Cd atoms.⁷

In nature the most common conformation for single-chain type silicates $[\text{SiO}_3^{2-}]_\infty$ is a repeat unit after every second tetrahedron with the chains stacked parallel so as to give sites for the cations.⁸⁻¹⁰ Since the parent structural unit in

polycyanopolycadmte is tetrahedral $[\text{Cd}(\text{CN})_4]^{2-}$,¹¹ linear condensation of tetrahedra would lead to infinite single chains. Indeed such an anion $[\text{Cd}(\text{CN})_3^-]_\infty$ has been obtained by selecting the counter cation properties. An equimolar 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 an aqueous solution of SbPh_4OH . Citric acid, 2-aminoethanol and acetonitrile were added to the solution, which was kept standing at room temperature for a few days to obtain colourless crystals of $[\text{SbPh}_4]_2[\text{Cd}(\text{CN})_3]_2$.†

† Satisfactory elemental analyses were obtained.

The X-ray crystal structure \ddagger of this compound (Fig. 1) shows a new example of an infinite chain-like $\text{Cd}(\text{CN})_3^-$ ion. The structural features of $\text{Cd}(\text{CN})_3^-$ are topologically similar

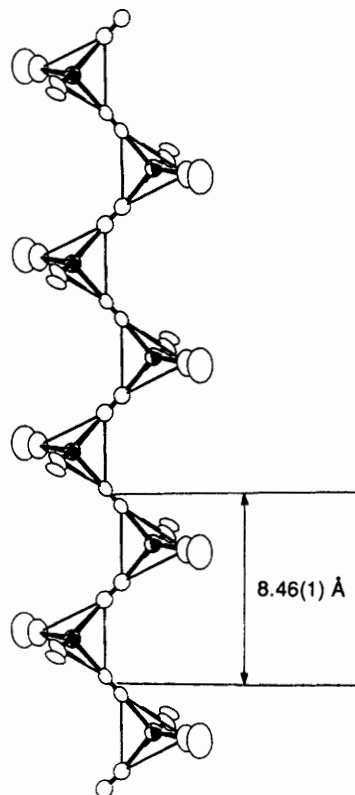


Fig. 1 View of one of the $\text{Cd}(\text{CN})_3^-$ anions in $[\text{SbPh}_4]_2[\text{Cd}(\text{CN})_3]_2$: infinite chain-like anion composed of Cd coordination tetrahedra linked by cyanide group. The chain has a period of 8.46(1) Å. Anisotropic sections are shown for the Cd atoms.

\ddagger *Crystal data*: $[\text{SbPh}_4]_2[\text{Cd}(\text{CN})_3]_2$, $M = 1241.28$; monoclinic, $P2_1/c$ (No. 14), $a = 19.807(5)$, $b = 8.46(1)$, $c = 31.079(7)$ Å, $\beta = 90.40(3)^\circ$, $V = 5208(9)$ Å³, $Z = 4$, $D_m = 1.60(2)$, $D_x = 1.58$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 18.75$ cm⁻¹, Rigaku AFC5S diffractometer, 13 086 reflections observed, 3108 used; 577 parameters refined; $R = 0.063$, $R_w = 0.059$, GOF = 2.25. The structure was solved using the TEXSAN software package installed on the diffractometer system. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms have not been located. Since 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 (ref. 3), CN(11), CN(12), CN(41) and CN(42) were refined by considering each site equally occupied with 50% carbon and 50% nitrogen. Atomic coordinate, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors Issue No. 1.

to *zweier* (zigzag)¹² single chains of SiO_3^{2-} found in pyroxenes $\text{M}_2\text{Si}_2\text{O}_6$, though the Cd–CN–Cd distance is *ca.* 5.5 Å and the Cd–CN–Cd grouping is nearly linear, whereas the Si–O–Si distance is *ca.* 3.2 Å and the Si–O–Si bond angle is more flexible. The anion structure consists of two crystallographically independent infinite zigzag chains parallel to the b axis. The topological features of two chains are essentially identical [average Cd–CN (bridging) 2.25(3) Å, Cd–C (terminal) 2.17(5) Å]. $\text{Cd}(\text{CN})_3^-$ chains have an identity period of 8.46(1) Å (cell dimension of b) though zigzag single chains in SiO_3^{2-} have a period of 5.2 to 5.3 Å.⁹

The present work has demonstrated that the primary building unit $\text{Cd}(\text{CN})_4^{2-}$ can condense to form a novel infinite chain-like ion. The new cyanide complex possesses no three-dimensional framework and infinite chains are the result of both bridged and unbridged behaviour of cyanide groups. The infinite chain anions and SbPh_4^+ cations are situated in a band parallel to the b axis. In contrast to PPh_4^+ , SbPh_4^+ has both trigonal bipyramidal and tetrahedral geometries depending upon the size and coordination ability of the counter anion.¹³ In the new complex SbPh_4^+ ions have weak interaction to N terminal of unbridged cyano groups [Sb(1)–N(5) 3.43(3), Sb(2)–N(2) 3.20(2) Å] and distorted tetrahedral symmetries [C(11)–Sb(1)–C(21) 99(1), C(51)–Sb(2)–C(71) 102(1)°]. The difference between the present compound and $[\text{PPh}_4]_3[\text{Cd}_2(\text{CN})_7]^-$ is associated with the larger size of SbPh_4^+ and weak $\text{Sb}\cdots\text{N}$ interactions, which cause distortions from tetrahedral.

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