Synthesis and X-Ray Crystal Structure of $[NMe_4][Cd_3(SC_6H_2Pr^i{}_3)_7]\cdot C_5H_{12}$

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The core of the cluster anion $[Cd_3(SC_6H_2Pr^i{}_3)_7]^-$ is formed by a defective cubane unit with three cadmium and four sulphur atoms at its vertices; each cadmium atom exhibits tetrahedral coordination with one terminal sulphur, two doubly bridging sulphur and one triply bridging sulphur atoms.

The chemistry of cadmium thiolates is relevant to the metallothioneins (MTs). The crystal structure determination of Cd and Zn metallothioneins has proved that there are two metal clusters $[M_3(Cys\text{-}S)_9]^{3-}$ and $[M_4(Cys\text{-}S)_{11}]^{4-}$ in MTs.[1] Several crystal structures of Cd^{II}–SR cluster complexes have been reported: $[Cd_4(SC_6H_5)_{10}]^{2-}$,[2] $Cd_4(SC_6H_4Me\text{-}4)_8$,[3] $Cd_8(SC_6H_4Br\text{-}4)_{16}(DMF)_3$,[2] $Cd_7(SC_6H_4Me\text{-}2)_{14}(DMF)_2$,[4] $[S_4Cd_{10}(SPh)_{16}]^{4-}$,[5] $[S_4Cd_{17}(SPh)_{28}]^{2-}$[6] *etc.* Also some mono- and di-meric Cd thiolates with high steric hindrance have been known: $[PPh_4][Cd(SC_6H_5Pr^i{}_3)_3]$[7] $[Cd(SC_6H_2Pr^i{}_3)_2(1\text{-}Me\text{-}imid)_8]$,[8] and $Cd_2(SC_6H_2Bu^t{}_3)_4$.[9] However, no report on trinuclear Cd^{II}–SR species has been found. As part of a systematic investigation on transition metal thiolates, we present the synthesis and crystal structure of the first trinuclear Cd^{II}–SR complex $[NMe_4][Cd_3(SC_6H_2Pr^i{}_3)_7]\cdot C_5H_{12}$ in this paper. This cluster complex provides a pertinent strucutre for the Cd^{II}–cysteinate aggregate in MTs.

The complex was prepared by stirring $Cd(NO_3)_2\cdot 4H_2O$ (308 mg) with 3.2 equiv. of 2,4,6-triisopropylthiophenol(TIPT, 710 mg)[10] and Et_3N (0.49 ml) in MeOH (7.5 ml) in the presence of Me_4NCl (134 mg) under a nitrogen atmosphere at room temperature for 12 h. The white precipitate formed was filtered off and washed with MeOH. Recrystallization from pentane–benzene (2 : 1) gave colourless bulky crystals; m.p. 270–272 °C. The crystals are not stable in the air by losing the solvent pentane molecules.

The crystal structure determination indicates that the complex consists of $[Me_4N]^+$ cation and trinuclear cluster anion $[Cd_3(SC_6H_2Pr^i{}_3)_7]^-$.† The core and the structure of the anion are shown in Figs. 1 and 2, respectively. The principal structural features of $[Cd_3(SC_6H_2Pr^i{}_3)_7]^-$ are summarized as follows. (*i*) The anion contains a defective cubane-like Cd_3S_4 cage, composed of a Cd_3-trigonal and a distorted S_4-tetra-

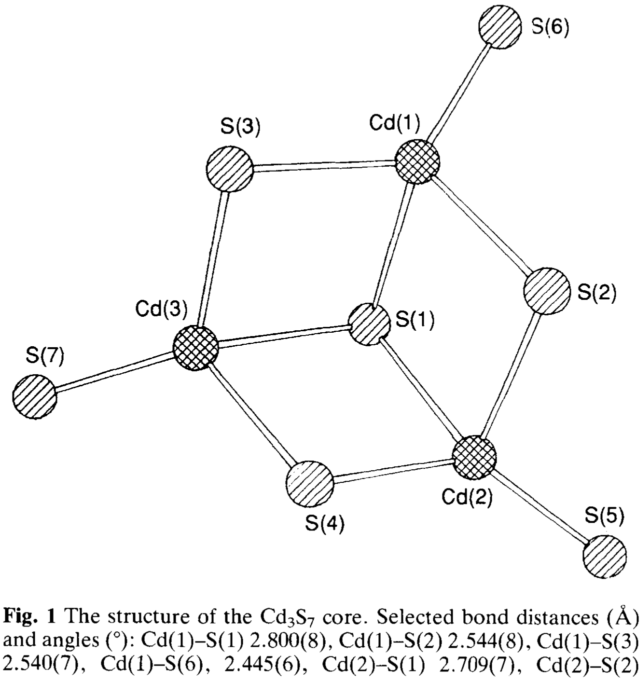

Fig. 1 The structure of the Cd_3S_7 core. Selected bond distances (Å) and angles (°): Cd(1)–S(1) 2.800(8), Cd(1)–S(2) 2.544(8), Cd(1)–S(3) 2.540(7), Cd(1)–S(6), 2.445(6), Cd(2)–S(1) 2.709(7), Cd(2)–S(2) 2.613(8), Cd(2)–S(4) 2.488(9), Cd(2)–S(5) 2.421(9), Cd(3)–S(1) 2.787(7), Cd(3)–S(3) 2.552(8), Cd(3)–S(4) 2.560(10), Cd(3)–S(7) 2.434(8); S(1)–Cd(1)–S(2) 80.5(2), S(1)–Cd(1)–S(3) 86.1(2), S(2)–Cd(1)–S(3) 116.6(2), S(1)–Cd(1)–S(6) 120.5(2), S(2)–Cd(1)–S(6) 110.5(2), S(3)–Cd(1)–S(6) 129.1(3), S(1)–Cd(2)–S(2) 81.1(2), S(1)–Cd(2)–S(4) 82.7(3), S(2)–Cd(2)–S(4) 100.4(3), S(1)–Cd(2)–S(5) 128.4(2), S(2)–Cd(2)–S(5) 110.9(3), S(4)–Cd(2)–S(5) 137.9(3), S(1)–Cd(3)–S(3) 86.2(2), S(1)–Cd(3)–S(4) 79.8(2), S(3)–Cd(3)–S(4) 107.8(3), S(1)–Cd(3)–S(7) 131.8(3), S(8)–Cd(3)–S(7) 123.0(8), S(4)–Cd(3)–S(7) 118.2(3).

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† The data collection was completed on a Siemens R3 diffractometer. The SHELXTL PLUS program was used to solve and refine the structure. *Crystal data*: $C_{114}H_{185}NS_7Cd_3$, M = 2131.25, space group $P2_1/n$, a = 19.629(6), b = 25.608(9), c = 25.450(9) Å, β = 107.54(3)°, V = 12 203(7) $Å^3$, D_c = 1.16 g cm^{-3}, Z = 4. With anisotropic thermal parameters for Cd, S atoms and isotropic thermal parameters for C atoms, the refinement yielded the final discrepancy R = 0.076 for 3839 reflections [$F > 6.0(F)$]. The 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.

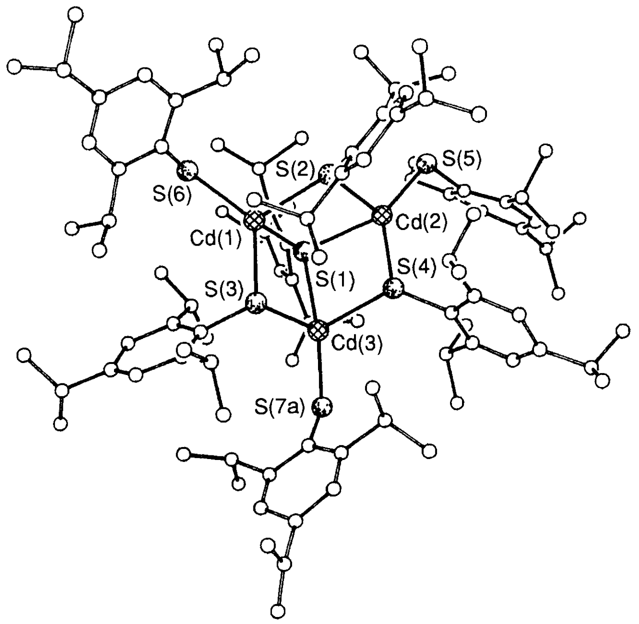

Fig. 2 The structure of the anion $[Cd_3(SC_6H_2Pr^i_3)_7]^-$

hedron. The cage closely approaches the C_{3v} symmetry. This is the first example of Cd_3S_4 cage structure in cadmium thiolate clusters. (*ii*) There are three types of coordination in the seven thiolate ligands: three terminal, three doubly bridging and one triply bridging thiolates. The last type exists neither in the metal aggregates of MTs nor in other cadmium thiolates. The mean values of three types of Cd–S bond lengths are respectively: Cd–Sdb 2.550 (2.488–2.613), Cd–Stb 2.765 (2.709–2.800), Cd–St 2.433 (2.421–2.445) Å. The bond lengths of Cd–Stb are much longer than those of the other two types. The bond lengths of Cd–St and Cd–Sdb are similar to those in $[Cd_4(SPh)_{10}]^{2-}$,[2] in which Cd–St (mean) 2.467 and Cd–Sdb (mean) 2.56 Å. (*iii*) Each Cd^{II} atom has one terminal, two doubly bridging and one triply bridging thiolate ligands forming a distorted tetrahedral CdS_4 unit, which is similar to the metal coordinations in MTs.[1] Substantial deviations from local C_{3v} symmetry are apparent from large variations in Sdb–Cd–St, Stb–Cd–St, Sdb–Cd–Sdb and Sdb–Cd–Stb angles of each unit. (*iv*) In this anion, there is one chairlike $Cd_3(\mu\text{-}S)_3$ ring which occurs in the two aggregates of metal–cysteinate in MTs. Such a ring can also be found in the adamantane-like tetranuclear cluster $[Cd_4(SC_6H_5)_{10}]^{2-}$.[2]

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