

The Preparation and Crystal Structures of the Sterically Hindered Lithium Alkylchlorocadmiate $[\text{Li}(\text{thf})_4][\text{Li}(\text{thf})_2(\mu\text{-Cl})_4\{\text{CdC}(\text{SiMe}_3)_3\}_2]\cdot\text{thf}$ (thf = tetrahydrofuran), the Alkylcadmium Halides $[\{\text{Cd}[\text{C}(\text{SiMe}_3)_3]\text{Cl}\}_4]$ and $[\{\text{Cd}[\text{C}(\text{SiMe}_2\text{Ph})_3]\text{Br}\}_2]$, and the Hydrate $[\{\text{Cd}[\text{C}(\text{SiMe}_2\text{Ph})_3]\text{Br}(\text{H}_2\text{O})\}_2]\cdot(\text{thf})$

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Tris(trimethylsilyl)methyl-lithium reacts with cadmium(II) chloride in tetrahydrofuran (thf) to give the lithium salt $[\text{Li}(\text{thf})_4][\text{Li}(\text{thf})_2(\mu\text{-Cl})_4\{\text{CdC}(\text{SiMe}_3)_3\}_2]\cdot\text{thf}$, which has a chloride-bridged anion and on heating gives tetrameric chloro[tris(trimethylsilyl)methyl]cadmium; bromo[tris(dimethylphenylsilyl)methyl]cadmium is dimeric in the solid, and, on recrystallisation from wet thf forms the hydrate $[\{\text{Cd}[\text{C}(\text{SiMe}_2\text{Ph})_3]\text{Br}(\text{H}_2\text{O})\}_2]\cdot\text{thf}$.

Alkylcadmium halides obtained by reactions between dialkylcadmiums and cadmium(II) halides are rather insoluble in organic solvents.¹ They have been shown by cryoscopic measurements to be monomeric in Me_2SO ,² but both monomeric 'solvated RCdX ' ($\text{R} = \text{Me}$ or Et , $\text{X} = \text{Cl}$, Br , or I)^{3,4} and dimeric species⁵ have been postulated from i.r. data for solutions in tetrahydrofuran (thf) or Et_2O . Methylcadmium bromide has been detected by n.m.r. spectroscopy,⁶ but its structure is not known. As far as we are aware, no alkylcadmium halide has previously been characterised by X-ray diffraction. Alkylzinc halides EtZnX ($\text{X} = \text{Cl}$ or Br) are tetrameric in benzene,⁷ but EtZnI is polymeric in the solid.⁸

The initial product of the reaction between tris(trimethylsilyl)methyl-lithium and cadmium(II) chloride was recently formulated as $\text{Li}(\text{thf})\text{CdCl}_2\text{R}$ [$\text{R} = \text{C}(\text{SiMe}_3)_3$].⁹ Crystals were obtained from light petroleum (b.p. $60\text{--}80^\circ\text{C}$)–thf, and it was

possible to collect limited X-ray diffraction data† which show that the compound is ionic. The unambiguously characterized anion (Figure 1) is, unexpectedly, a halogen-bridged lithium-dicadmiate cage (1), similar to the previously described trimanganate (2). The identity of the cation is uncertain because thf molecules in it are disordered, but it is probably $[\text{Li}(\text{thf})_4]^+$. The ^7Li n.m.r. spectrum at -80°C shows two peaks, indicating the presence of two distinct lithium-containing species. On purely crystallographic grounds we cannot rule

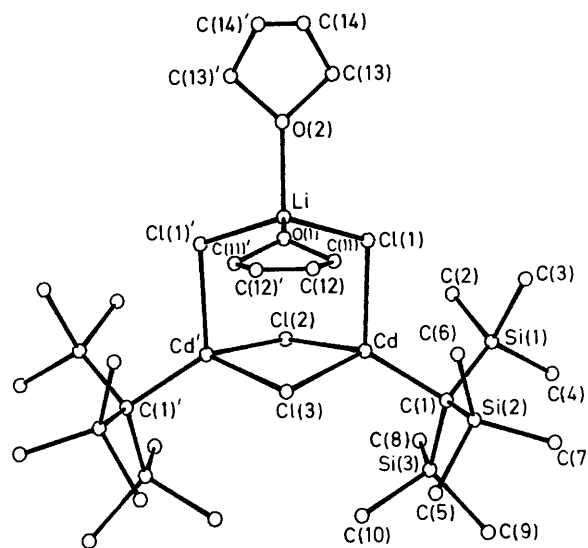
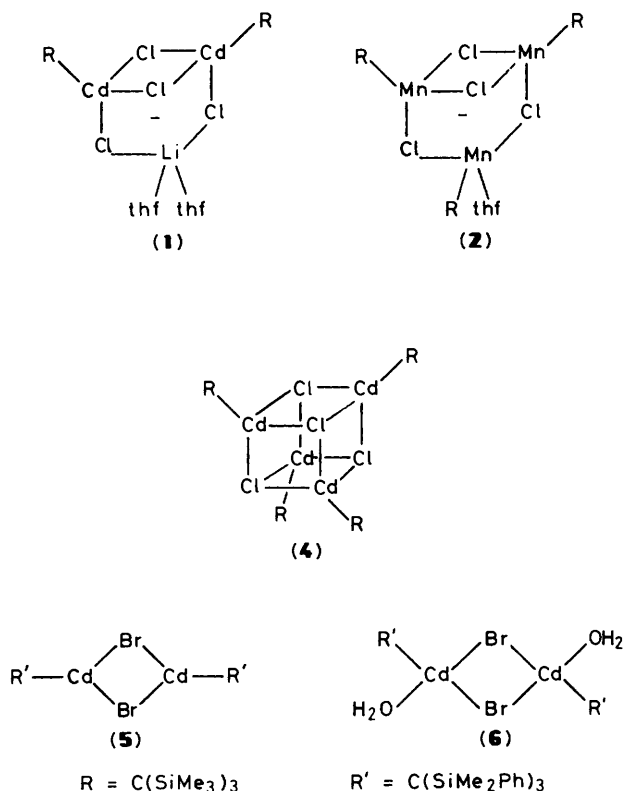


Figure 1. The structure of the anion (1). Selected mean bond lengths (Å) and angles ($^\circ$): Cd–Cl(1) 2.526(6), Cd–Cl(2) 2.576(6), Cd–Cl(3) 2.582(6), Li–Cl 2.40(4), Cd–C 2.21(2), Si–C 1.86(3), Si–Me 1.94(2), Li–O 1.90(8); Cl(1)–Cd–Cl 98.1(3), Cl(2)–Cd–Cl(3) 88.1(2), C–Cd–Cl 121.8(6), Cd–Cl–Cd 90.4(3), Cd–Cl–Li 112(2), Si–C–Si 113(1), Me–Si–Me 105(2).

† Crystal data for $[\text{Li}(\text{thf})_4][\text{Li}(\text{thf})_2(\mu\text{-Cl})_4\{\text{CdC}(\text{SiMe}_3)_3\}_2]\cdot\text{thf}$ (3): $M = 1348.4$, monoclinic, space group $P2_1/m$; $a = 12.691(2)$, $b = 19.656(3)$, $c = 14.154(3)$ Å, $\beta = 99.36(1)^\circ$, $U = 3483.4$ Å³, $Z = 2$, $D_c = 1.29$ g cm⁻³. Monochromated Mo- K_α radiation, $\lambda = 0.71069$ Å, $\mu = 9.0$ cm⁻¹, 1997 reflections ($2 < \theta < 20^\circ$) with $|F|^2 > \sigma(F^2)$. Cd and Cl atoms found from MULTAN¹⁰ and remaining atoms from difference maps. Full matrix least squares refinement with temperature factors anisotropic except for thf atoms. H atoms omitted. $R = 8.3$, $R' = 11.5\%$. Atomic co-ordinates, and bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

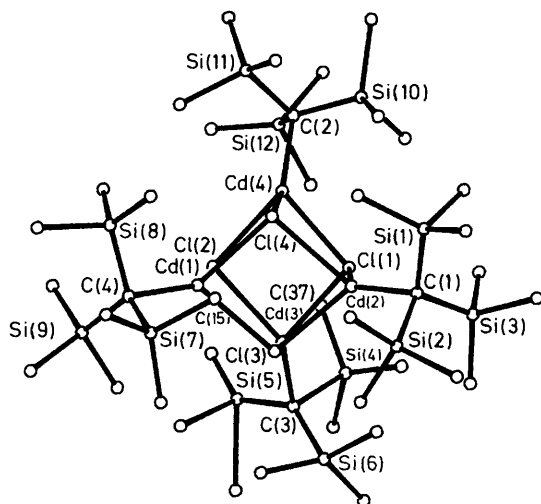


Figure 2. The cubane structure of (4). Selected mean bond lengths (Å) and angles (°): Cd–Cl 2.626(7), Cd–C 2.19(2), C–Si 1.89(3), Si–Me 1.93(6); Cl–Cd–Cl 83.5(2), Cd–Cl–Cd, 96.1(2), Cl–Cd–C 129.6(7), Si–C–Si 113(2), Me–Si–Me 110(2).

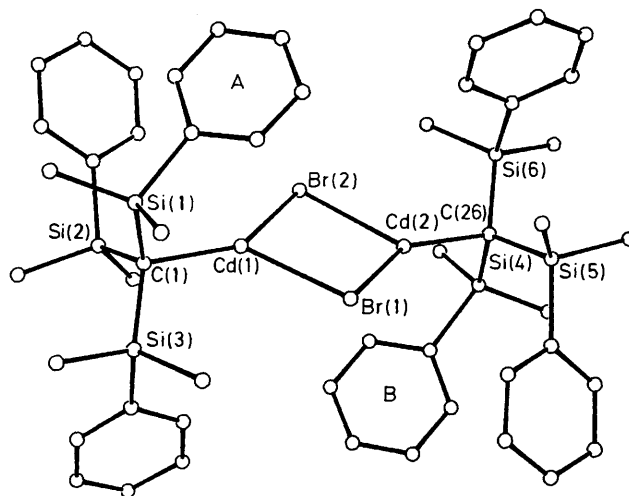


Figure 3. The dimeric structure of (5). Selected mean bond lengths (Å) and angles (°): Cd–Br 2.667(1) and 2.605(1), Cd–C 2.19(1), Si–C 1.886(7), Si–Me 1.87(1), Si–Ph 1.89(1); Cd–Br–Cd 92.71(4), Br–Cd–Br 87.15(4), Br–Cd–C 128.6(2)—144.0(2), Si–C–Si 113.8(4), Me–Si–Me 106.1(4).

out the possibility that it is $[(\text{thf})\text{Li}(\mu\text{-OH})(\mu\text{-thf})_2\text{Li}(\text{thf})]^+$, but this would require a Li : Cd atom ratio of 1.5 whereas the experimental value is 0.91. The crystalline compound is thus formulated as $[\text{Li}(\text{thf})_4][\text{Li}(\text{thf})_2(\mu\text{-Cl})_4\{\text{CdC}(\text{SiMe}_3)_3\}_2]\cdot\text{thf}$ (3). Tetrahydrofuran is lost rapidly from the crystal as mother liquor is removed by evaporation or washing with hydrocarbon solvents.

When heated compound (3) decomposes to LiCl, thf, and chloro[tris(trimethylsilyl)methyl]cadmium (4). Dimeric molecules of this compound were detected in the gas phase by mass spectroscopy,⁹ but an X-ray study[‡] shows that the solid consists of tetramers (Figure 2). In contrast, bromo[tris(dimethylphenylsilyl)methyl]cadmium (5) is dimeric in the solid (Fig. 3).§ On recrystallisation from moist thf, this compound forms a hydrate (6). Centrosymmetric dimers are

linked by hydrogen bonds (Figure 4) to thf molecules that are disordered equally between two orientations.¶

The low quality of the X-ray data for (3), (4), and (6) (a result of deterioration of the crystals during mounting, largely because of loss of thf) precludes detailed comparison of bond lengths and angles, but all are consistent with those obtained previously.⁹ In (5), for which the data are better, the $\text{Cd}_2\text{Br}_2\text{C}_2$ system is planar, the Cd–Br(1) and Cd–Br(2) bond lengths are significantly different, and the molecule as a whole is almost centrosymmetric. Co-ordination of water to give (6) equalises the Cd–Br bond lengths and increases the Br–Cd–Br angles, but otherwise results in no significant change in molecular parameters.

The different molecular complexities of (4) and (5) may arise from the fact that a RCdBr_3 unit is more crowded than a RCdCl_3 unit. For the conformation adopted by (5) in the crystal, tetramer formation is prevented by the phenyl groups A and B, but the formation of the hydrate (6) shows that these can be bent away from the Cd_2Br_2 -ring to allow cadmium to increase its co-ordination from three to four. The insoluble alkylcadmium halides previously described¹ are probably polymeric; the present work suggests that oligomers are formed when alkyl groups are large or donor solvents are present.

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‡ *Crystal data* for $\text{C}_{40}\text{H}_{108}\text{Cd}_4\text{Cl}_4\text{Si}_{12}$ (4): $M = 1517.75$, monoclinic, space group $P2_1/c$, $a = 22.269(3)$, $b = 14.969(3)$, $c = 22.918(4)$ Å, $\beta = 102.90(1)^\circ$, $U = 7446.7$ Å³, $Z = 4$, $D_c = 1.35$ g cm⁻³, $F(000) = 3104$, $\lambda(\text{Mo-K}\alpha) = 0.71069$ Å, $\mu = 14.8$ cm⁻¹, 4254 reflections ($2 < \theta < 20^\circ$) with $|F|^2 > \sigma(F^2)$. Enraf-Nonius CAD4 diffractometer. Cd and Cl were found by direct methods; Si and C from difference maps. Alternative Si sites, as found previously,⁹ in three $\text{C}(\text{SiMe}_3)_3$ groups. Full matrix least squares refinement with Cd and Cl anisotropic, Si and C isotropic, H not included, $R = 9.8$, $R' = 11.5\%$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ *Crystal data* for $\text{C}_{50}\text{H}_{66}\text{Br}_2\text{Cd}_2\text{Si}_6$ (5): $M = 1220.22$, monoclinic, space group $P2_1/n$, $a = 14.996(4)$, $b = 18.274(2)$, $c = 20.993(2)$ Å, $\beta = 109.15(2)^\circ$, $U = 5434.4$ Å³, $Z = 4$, $D_c = 1.49$ g cm⁻³, $F(000) = 2464$, $\lambda = 0.71069$ Å, $\mu = 24.0$ cm⁻¹, 3955 reflections ($2 < \theta < 22^\circ$) with $|F| > \sigma(F^2)$. Routine heavy atom methods. Full matrix least squares refinement with non hydrogen atoms anisotropic and H atoms at calculated positions. $R = 4.3$, $R' = 4.5\%$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

¶ *Crystal data* for $\text{C}_{50}\text{H}_{70}\text{Br}_2\text{Cd}_2\text{O}_2\text{Si}_6 \cdot \text{C}_4\text{H}_8\text{O}$ (6): $M = 1328.3$, triclinic, space group $P1$, $a = 11.074(6)$, $b = 11.876(7)$, $c = 12.246(5)$ Å, $\alpha = 82.86(2)$, $\beta = 84.64(2)$, $\gamma = 71.07(2)^\circ$, $U = 1509.2$ Å³, $Z = 1$, $D_c = 1.41$ g cm⁻³, $F(000) = 676$, $\lambda = 0.71069$ Å, $\mu = 21.7$ cm⁻¹, 2529 reflections with $|F^2| > \sigma(F^2)$. Routine heavy atom methods. C atoms of thf fixed at positions estimated from electron density map. Full matrix least squares refinement with anisotropic temperature factors. H atoms omitted. $R = 8.7$, $R' = 12.3\%$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

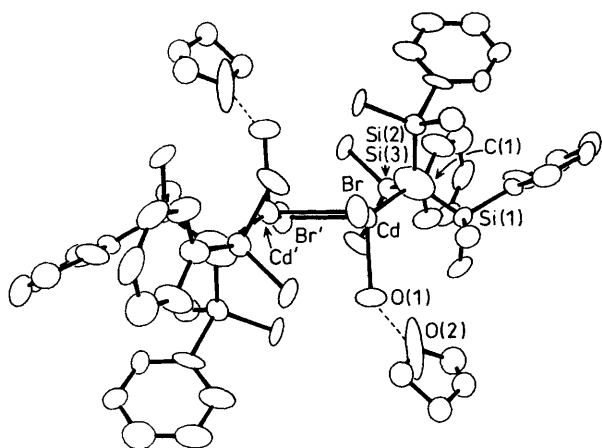


Figure 4. The dimeric structure of (6). Selected mean bond lengths (Å) and angles (°): Cd-Br 2.676(3) and 2.651(3), Cd-C 2.22(2), Cd-O 2.38(2), Si-C 1.88(2), Si-Me 1.90(2), Si-Ph 1.88(2); Br-Cd-Br 91.5(1), Cd-Br-Cd 88.5(1), C-Cd-O 116.7(7), Br-Cd-C 127.3(7), Br-Cd-O 92.1(6), Si-C-Si 116(1), Me-Si-Me 105(1).

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References

- 1 N. I. Sheverdina, I. E. Paleeva, E. D. Delinskaya, and K. A. Kocheshkov, *Dokl. Akad. Nauk SSSR*, 1959, **125**, 348.
- 2 I. E. Paleeva, N. I. Sheverdina, and K. A. Kocheshkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1967, 1263.
- 3 K. Cavanagh and D. F. Evans, *J. Chem. Soc., A.*, 1969, 2890.
- 4 A. N. Rodionov, I. E. Paleeva, D. N. Shigorin, N. I. Sheverdina, and K. A. Kocheshkov, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1967, 1031.
- 5 J. R. Sanders and E. C. Ashby, *J. Organomet. Chem.*, 1970, **25**, 277.
- 6 W. Bremser, M. Winokur, and J. D. Roberts, *J. Am. Chem. Soc.*, 1970, **92**, 1080.
- 7 J. Boersma and J. G. Noltes, *Tetrahedron Lett.*, 1966, 1521.
- 8 P. T. Moseley and H. M. M. Shearer, *J. Chem. Soc., Dalton Trans.*, 1973, 64.
- 9 N. H. Buttrus, C. Eaborn, M. N. A. El-Kheli, P. B. Hitchcock, J. D. Smith, A. C. Sullivan, and K. Tavakkoli, *J. Chem. Soc., Dalton Trans.*, 1988, 381.
- 10 G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A.*, 1971, **27**, 368.