Supplementary Material (ESI) for Chemical Communications

$[Pb_9CdCdPb_9]^{6-}$: A Zintl cluster anion with an unsupported cadmium-cadmium bond.

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Computational details

All calculations described in this paper were performed using the Amsterdam Density Functional package (ADF2007.01).[1] A triple-ζ Slater-type basis set, extended with a single polarization function, was used to describe Cd and Pb. Electrons in orbitals up to and including 3d {Cd} and 4d {Pb} were considered part of the core and treated in accordance with the frozen core approximation. The local density approximation was employed for the optimizations,[2] along with the local exchange-correlation potential of Vosko, Wilk and Nusair[3] and gradient corrections to exchange and correlation proposed by Becke and Perdew (BP86).[4] Relativistic effects were incorporated using the Zeroth Order Relativistic Approximation (ZORA).[5] The presence of cations in the crystal lattice was modeled by surrounding the anion with a continuum dielectric using COSMO.[6] The chosen dielectric constant $\varepsilon = 16.9$ corresponds to that of ammonia, although structural parameters are not strongly dependent on this choice. All structures were optimized using the gradient algorithm of Versluis and Ziegler.[7]

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[3] S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys*., 1980, **58**, 1200.

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Optimised Cartesian coordinates [Å]

atom	*x*	*y*	*z*
1. Pb	0.000000	0.000000	8.105330
2. Pb	2.416232	0.000000	6.066439
3. Pb	0.000000	2.416232	6.066439
4. Pb	−2.416232	0.000000	6.066439
5. Pb	0.000000	−2.416232	6.066439
6. Pb	1.660925	1.660925	3.465424
7. Pb	−1.660925	1.660925	3.465424
8. Pb	−1.660925	−1.660925	3.465424
9. Pb	1.660925	−1.660925	3.465424
10. Cd	0.000000	0.000000	1.385967
11. Pb	0.000000	0.000000	−8.105330
12. Pb	−2.416232	0.000000	−6.066439
13. Pb	0.000000	−2.416232	−6.066439
14. Pb	2.416232	0.000000	−6.066439
15. Pb	0.000000	2.416232	−6.066439
16. Pb	−1.660925	−1.660925	−3.465424
17. Pb	1.660925	−1.660925	−3.465424
18. Pb	1.660925	1.660925	−3.465424
19. Pb	−1.660925	1.660925	−3.465424
20. Cd	0.000000	0.000000	−1.385967

Synthesis of $Cd(C_9H_{11})_2$

25 mL of $Mg(C_9H_{11})Br$ (1.0 M THF) was added drop-wise to a solution of anhydrous $CdBr_2$ (3.2 g, 0.012 mol) in THF (100 mL) over two hours at −78°C. The reaction mixture was allowed to warm to room temperature and stirred for 24 hours in the dark. The residue was subsequently pumped to dryness and the solid washed with cold diethylether. The insoluble fraction was dried under vacuum and redissolved in THF (60 mL). The resulting solution was filtered and then stirred for 1 hour in the presence of dry 1, 4-dioxane (10 mL). The mixture was filtered and the filtrate concentrated *in vacuo* yielding white feather-like crystals of $Cd(C_9H_{11})_2$ which were isolated and dried under vacuum. Yield: 2.04 g (48%). ^{1}H NMR (300.2 MHz, d_8-THF): δ (ppm) 6.76 (s), 2.46 (s), 2.23 (br, s). $^{13}C\{^1H\}$ NMR (75.4 MHz, d_8-THF): δ (ppm) 21.5, 28.2, 126.6, 136.6, 145.3.