Crystal and Molecular Structure of the Dimeric Complex $[\{Cd[Zr_2(OPr^i)_9](\mu\text{-}Cl)\}_2]$

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The product of the (1 : 1) reaction between $CdCl_2$ and $K[Zr_2(OPr^i)_9]$ in benzene is the dimeric species $[\{Cd[Zr_2(OPr^i)_9](\mu\text{-}Cl)\}_2]$, the first (chloro)alkoxometallate derivative to be characterized by X-ray crystallography.

The structures of a few homoleptic alkoxometallates, the evidence for the existence of which as unique entities was based[1–4] mainly on spectroscopic and other physicochemical evidence, have been determined[5–7] only recently. Compared to homoleptic derivatives, the (chloro)alkoxometallates synthesized[2] since 1985, $[ClM(\mu\text{-}OPr^i)_2Al(OPr^i)_2]_x$ ($M = Zn^{II}$, Cd^{II} or Hg^{II}), would be expected to be less stable as discrete molecular species. Hence, the simple chloride bridged structure of the thermally stable and hydrocarbon-soluble complex $[\{Cd[Zr_2(OPr^i)_9](\mu\text{-}Cl)\}_2]$ **1**, which we have now synthesized[8a] by the reaction of $CdCl_2$ with $K[Zr_2(OPr^i)_9]$ in equimolar proportions in benzene should be of considerable interest,

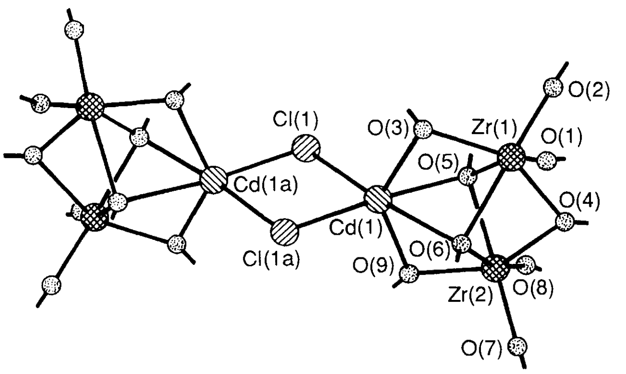

Fig. 1 Crystal structure of **1**, with the isopropyl groups omitted for clarity. Selected bond lengths (Å): Cd(1)–Cl(1) 2.561(2), Cd(1)–Cl(1a) 2.554(2) [mean Cd–Cl 2.557(2)]; Cd(1)–O(3) 2.361(4), Cd(1)–O(6) 2.444(4), Cd(1)–O(9)···2.352(4), Cd(1)–O(5) 2.360(4) (mean Cd–O 2.379(4)]; Zr(1)···Zr(2) 3.313(1); Cd(1)···Zr(1) 3.354(1), Cd(1)···Zr(2) 3.351(1) [mean Cd···Zr separation 3.353(1)]. Selected bond angles (°): O(3)–Cd(1)–O(5) 71.4(1), O(5)–Cd(1)–O(9) 71.0(1), O(9)–Cd(1)–Cl(1a) 107.7(1), Cl(1a)–Cd(1)–O(3) 105.2(1), Cl(1)–Cd(1)–O(6) 171.3(1), Cl(1a)–Cd(1)–O(5) 170.6(1), O(9)–Cd(1)–O(3) 134.3(1).

particularly in view of the use of heterobimetallic chloride alkoxides in synthesizing a variety of heterometallic products, which we are currently studying.[3,4,8b,9] The structure **1** is believed to be the first crystallographic characterization of a six-coordinate cadmium alkoxide, wherein an alkoxometallate ligand is bonded to the central metal atom in a tetradentate manner, providing a derivative **1** with remarkable thermal stability, subliming unchanged at 162 °C and 0.01 mmHg.

Colourless crystalline needles of compound **1** suitable for X-ray diffraction studies were obtained from toluene–n-hexane at −10 °C.†

Complex **1** (Fig. 1) is a centrosymmetric dimer composed of two triangular $CdZr_2(\mu_3\text{-}OPr^i)_2(\mu\text{-}OPr^i)_3(OPr^i)_4{}^+$ units linked by two chloride bridges. In each of these units cadmium interacts with a face-shared bioctahedral $Zr_2(OPr^i)_9{}^-$ moiety *via* two terminal and two bridging OPr^i groups of the $Zr_2(OPr^i)_9{}^-$ unit. This leads to octahedral geometry at both cadmium and zirconium, with substantial departures from an ideal octahedral geometry around cadmium tending to approach a bicapped tetrahedral arrangement.

The chelate bite angles vary from 71.0(1) to 82.6(1)°. The axial ligating sites, Cl(1), O(6); Cl(1a), O(5); O(9), O(3), are distorted from linearity with angles of 171.3(1), 170.6(1) and 134.3(1)° respectively at cadmium. This distortion is due mostly to the constraints imposed by the positions of the isopropoxy oxygens in the $Zr_2(OPr^i)_9{}^-$ framework.

The Cd–O bond lengths range from 2.352(4) to 2.444(4) Å [average 2.379(4) Å]. These values are in good agreement with the range found in other six-coordinated derivatives of cadmium[11] (2.240–2.535 Å), which are significantly shorter than those observed in the octahedral K[Cd(chloropropamide)$_3$] complex, $\{K[Cd(ClC_6H_4SO_2NCONHPr^n)_3]\}$.[12] For comparison, Cd–O bond distance of 2.058(4) Å for the aryl oxide ligands and 2.498(5) Å for the tetrahydrofuran (thf) ligands have been observed for the square planar complex[13] $[Cd(2,6\text{-}Bu^t{}_2C_6H_3O)_2(thf)_2]$.

The average Cd–Cl bond length [2.556(2) Å] is significantly shorter than the sum of the ionic radii[14] (2.780 Å) and shows that these bonds are essentially covalent. This Cd–Cl distance is considerably shorter than those found in octahedrally coordinated cadmium complexes such as $CdCl_2{\cdot}2.5H_2O$[15] [Cd–Cl(bridge) = 2.680 and 2.710 Å], $[CdCl_2(imidazole)]$[16] [Cd–Cl(bridge) = 2.670 Å], bis(thiocarbonohydrazide-N,S)cadmium dichloride[17] [Cd–Cl(terminal) = 2.730 Å] and $[Cd(bpa)Cl_2]$[18] [Cd–Cl(bridge) = 2.760(1) and 2.670(1) Å] [bpa = bis(3-aminopropyl)amine].

For four-coordinated tetrahedral compounds[19] the typical terminal Cd–Cl distance is 2.460 Å. Significantly longer distances are found in six-coordinated anionic species,[20] $CdCl_6{}^{4-}$ (2.588, 2.617 and 2.765 Å). Thus the Cd–Cl bond length observed in the complex **1** is consistent with highly distorted octahedral geometry.[21]

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† *Crystal data* for **1**: $C_{54}H_{126}Cd_2Cl_2O_{18}Zr_4$, crystal size 0.3 × 0.3 × 1.0 mm, monoclinic, a = 12.5120(10), b = 19.462(3), c = 16.4250(10) Å, β = 93.250(10)°, U = 3993.3(7) Å^3, space group $P2_1/n$, Z = 2, $F(000)$ = 1768, D_c = 1.434 Mg m^{-3}, μ(Mo-Kα) = 1.136 mm^{-1}, 5390 reflections collected with $7 < 2\theta < 45°$ at 293 K; of these 5182 were unique and 4483 which had $F > 3\sigma(F)$ were used in structural analysis. The data were collected on a Siemens-Stoe AED2 diffractometer using Mo-Kα (λ = 0.71069 Å) radiation; ω–2θ scans with online profile fitting[10] and variable scan speeds were used. A semi-empirical absorption correction was applied. The structure was solved by routine heavy atom methods and refined by full-matrix least-squares techniques using SHELXTL PLUS (PC version). All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms (riding model) with fixed isotropic thermal parameters. 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.

References

1 R. C. Mehrotra, *Adv. Inorg. Chem. Radiochem.*, 1983, **26**, 269.
2 M. Aggrawal and R. C. Mehrotra, *Polyhedron,* 1985, **4**, 845.
3 R. K. Dubey, A. Singh and R. C. Mehrotra, *J. Organomet. Chem.*, 1988, **341**, 569.
4 R. K. Dubey, A. Shah, A. Singh and R. C. Mehrotra, *Recl. Trav. Chim. Pays-Bas*, 1988, **107**, 237.
5 F. A. Cotton, D. O. Marler and W. Schwotzer, *Inorg. Chem.*, 1984, **23**, 4211.
6 J. L. Stewart and R. A. Andersen, *J. Chem. Soc., Chem. Commun.*, 1987, 1846.
7 K. G. Caulton and L. G. Hubert-Pfalzgraf, *Chem. Rev.*, 1990, **90**, 969.
8 S. Sogani, A. Singh and R. C. Mehrotra, (*a*) *Main Group Metal Chemistry*, 1991, in the press; (*b*) unpublished results.
9 R. C. Mehrotra, *J. Non-Cryst. Solids*, 1988, **100**, 1; 1990, **121**, 1.
10 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.
11 T. M. Greaney, C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1975, 876; L. G. Purnell, E. D. Estes and D. J. Hodgson, *J. Am. Chem. Soc.*, 1976, **98**, 740; W. Harrison and J. Trotter, *J. Chem. Soc., Dalton Trans.*, 1972, 956; A. Mitschler, J. Fischer and R. Weiss, *Acta Crystallogr.*, 1967, **22**, 236; P. Knuuttila, *Polyhedron*, 1984, **3**, 303.
12 D. P. Kessissoglou, G. E. Manoussakis, A. G. Hatzidimitriou and M. G. Kanatzidis, *Inorg. Chem.*, 1987, **26**, 1395.
13 S. C. Goel, M. Y. Chiang and W. E. Buhro, personal communication; A. Haaland, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 992.
14 L. Pauling, *The Nature of the Chemical Bond*, 2nd edn., Cornell University Press, Ithaca, NY, 1945.
15 H. Leligny and J. C. Monier, *Acta Crystallogr., Sect. B*, 1975, **31**, 728.
16 L. R. Nassimbeni and A. C. Rodgers, *Acta Crystallogr., Sect. B*, 1976, **32**, 257.
17 F. Bigoli, A. Braibanti, A. M. M. Lanfredi, A. Tiripicchio and M. T. Camellini, *Inorg. Chim. Acta*, 1971, **5**, 392.
18 M. Cannas, G. Marongui and S. Saba, *J. Chem. Soc., Dalton Trans.*, 1980, 2090.
19 M. F. Richarson, K. Franklin and D. M. Thompson, *J. Am. Chem. Soc.*, 1975, **97**, 3204; A. F. Cameron, K. P. Forrest and G. Ferguson, *J. Chem. Soc. A*, 1971, 1286.
20 J. T. Veal and D. J. Hodgson, *Inorg. Chem.*, 1972, **11**, 597.
21 C. Gagnon and A. L. Beauchamp, *Can. J. Chem.*, 1979, 57, **1372.**