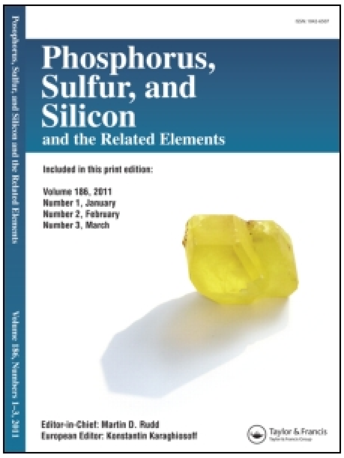

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A Sr(II)-Zr(IV)-Cd(II) ALKOXIDE CLUSTER: SYNTHESIS AND X-RAY STRUCTURE OF $[\{Cd(OPr^i)_3\}Sr\{Zr_2(OPr^i)_9\}]_2$

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New hetero*tri*metallic alkoxide $[\{Cd(OPr^i)_3\}Sr\{Zr_2(OPr^i)_9\}]_2$ (1) is obtained quantitatively in an anion-exchange reaction involving well-characterised iodide heterobimetallic alkoxide $ICd\{Zr_2(OPr^i)_9\}$ and the alkali metal reagent $KSr(OPr^i)_3$. The formation of **1** is accompanied with an exchange of metals (Cd(II) and Sr(II)) between the constituting fragments ('$Cd\{Zr_2(OPr^i)_9\}^+$' and '$Sr(OPr^i)_3^-$') and the chelating $Zr_2(OPr^i)_9^-$ anion, in **1**, coordinates to Sr^{2+} in contrast to the precursor $ICdZr_2(OPr^i)_9$ where it is bound to Cd^{2+}. The heterotrimetallic nature of **1** is unambiguously established by multinuclear (^1H, ^{13}C and ^{113}Cd) NMR spectral data and a single crystal X-ray diffraction analysis.

Keywords: Heterotrimetallic frameworks; halide heterobimetallic alkoxides; anion-exchange reaction

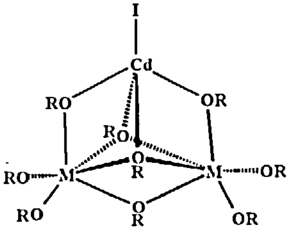
INTRODUCTION

While the examples of stable and isolable heterobimetallic alkoxides are extensively known[1], the unambiguous existence of discrete hetero*tri*metallic species in solution and the solid-state has only recently been established. Using coordinatively unsaturated $Ba(OPr^i)_3^-$ species, we have described a facile pathway for the rational construction of heterotrimetallic derivatives, $[\{Cd(OPr^i)_3\}Ba\{M_2(OPr^i)_9\}]_2$.[2-4]

We now report the synthesis and characterisation of a Sr(II)-Zr(IV)-Cd(II) alkoxide cluster.

RESULTS AND DISCUSSION

The halide heterobimetallic isopropoxides $ICdM_2(OPr^i)_9$ (M(IV) = Sn, Ti, Zr, Hf) (I) react with equimolar amount of alkali-metal reagent $KBa(OPr^i)_3$ to form the isostructural heterotermetallic isopropoxides $[\{Cd(OPr^i)_3\}Ba\{M_2(OPr^i)_9\}]_2$.[2-4]



I

The formation of Cd(II)-M(IV)-Ba(II) heterotrimetallic frameworks has revealed an unprecedented phenomenon of the rearrangement of metal atoms, taking place in the solution of metal alkoxides. Curiously, the switching of metal atoms is quantitative and no 'breakdown' in the constituent alkoxides or formation of other possible heterometal species is observed. The driving force for the switching of metals which offers barium a higher coordination number is possibly the larger size and greater oxophilic nature of Ba(II) in comparison to Cd(II) (Ba^{2+} = 1.35 Å; Cd^{2+} = 0.99 Å). In view of the above, we were interested in examining if a similar rearrangement is induced by the much smaller Sr^{2+} ion (1.18 Å). Indeed, the reaction (1:1) of $ICdZr_2(OPr^i)_9$ with $KSr(OPr^i)_3$ in toluene at room temperature, offers $[\{Cd(OPr^i)_3\}Sr\{Zr_2(OPr^i)_9\}]_2$ (1) in high yield. The work-up of the reaction mixture was similar to that described for analogous compounds.[2-4] Microanalytical data conforms the formulation of 1.

1 is stereochemically rigid and the ^{1}H NMR spectrum[5] at 20 °C exhibits six methyl signals in integration ratio 4:4:2:4:6:4 which corresponds to the solid-state structure (Fig. 1); the methine signals are observed as three overlapping septets with integrals of 10:6:4. This observation is corroborated by the ^{13}C NMR spectrum[5] displaying six methine resonances in intensity ratio 4:4:2:4:6:4; the methyl region exhibits seven signals. The ^{113}Cd NMR chemical shift (δ 225.43) is comparable to those observed among $[\{Cd(OPr^{i})_3\}Ba\{M_2(OPr^{i})_9\}]_2$ derivatives for a four-coordinate Cd(II) centre.[2-4] Cryoscopy indicates the tendency of 1 to retain a dimeric structure in solution.

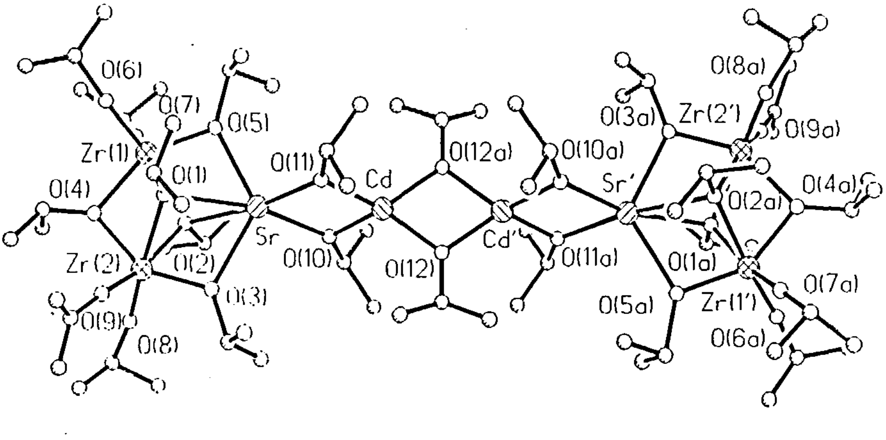


FIGURE 1 Molecular structure of 1. Selected bond distances (Å) and angles (°): Cd-O(11), 2.170(11); Cd-O(12), 2.164(12); Cd-O(12') 2.178(12); Cd-O(10), 2.186(11); Sr-O(10), 2.433(11); Sr-O(11), 2.398(12); Sr-O(3), 2.560(11), Sr-O(5), 2.591(14), Zr-O 1.920 - 2.246; O(11)-Cd-O(10) 86.1(4), O(12)-Cd-O(12') 79.2(5), O(10)-Sr-O(11) 76.0(4), O(2)-Sr-O(11) 172.5(4), O(3)-Sr-O(5) 123.0(4).

Single crystals of 1 suitable for an X-ray diffraction study[6] were grown from a cold (-8 °C) toluene solution. The solid-state structure

(Fig. 1) reveals a centrosymmetric dimer formed by spirocyclic linking of two triangular $Sr\{Zr_2(OPr^i)_9\}^+$ units to a $[(Pr^iO)_2Cd(\mu_2\text{-}OPr^i)_2Cd(OPr^i)_2]^{2-}$ unit, the dissection in charged fragments being purely formal. The one-dimensional array of Sr...Cd...Cd...Sr lying on a 2-fold axis in the metal-oxygen framework of the central $Sr(\mu_2\text{-}OPr^i)_2Cd(\mu_2\text{-}OPr^i)_2Cd'(\mu_2\text{-}OPr^i)Sr'$ unit is similar to the solid-state structures of divalent transition metal alkoxy-germanates(II) (-stannates(II) or -plumbates(II)) of general formula $M_2M'_2(OR)_8$.[1] Each Zr and Sr atom displays a strained octahedral geometry whereas Cd is present in a quasi-tetrahedral environment. The overall bonding parameters are comparable with analogous barium derivatives.

Acknowledgements

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[5.] Spectral data for **1**: ^1H NMR (C_6D_6, 20 °C): δ 1.34 (d, 24H), 1.37 (d, 24H), 1.42 (d, 12H), 1.48 (d, 24H), 1.51 (d, 36H), 1.63 (d, 24H) (CH_3); δ 4.48, 4.53 and 4.64(CH). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C): δ 26.16, 26.57, 26.74, 26.85, 27.46, 29.71, 30.54 (CH_3), 65.58, 68.02, 68.64, 69.61, 71.03 (CH). $^{113}Cd\{^1H\}$ NMR (C_6D_6, 20 °C): δ 225.43.

[6.] Crystal data for **1** $C_{72}H_{168}Cd_2O_{24}Sr_2Zr_4$, M = 2182.98, monoclinic, space group $P2_1/c$, a = 22.720(5) Å, b = 12.838(3) Å, c = 19.320(4) Å, V = 5598(2) $Å^3$, Z = 2, Dcal = 1.295, λ(MoKα) = 0.71073 Å, T = 293(2) K, μ = 1.728 mm^{-1}, R1 = 0.0956. Some of the isopropyl groups suffered from disorder problems and could not be refined satisfactorily. A toluene molecule fills the void in the crystal lattice of **1**.