

## Synthesis of Apparently Covalent Double Alkoxides of Rubidium & Caesium

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A number of volatile double metal isopropoxides of rubidium and caesium of the formulae  $M[Al(OPr^i)_4]$ ,  $M[Zr_2(OPr^i)_8]$ ,  $M[Ta(OPr^i)_5]$  (where  $M = Rb$  or  $Cs$ ),  $Cs_2[Zr_3(OPr^i)_{14}]$ ,  $Cs[Hf_2(OPr^i)_6]$ ,  $Cs_2[Hf_3(OPr^i)_{14}]$  and  $Cs[Nb(OPr^i)_5]$  have been synthesized by the reaction of the respective metal alkoxides in different stoichiometric proportions in isopropanol. Tentative structures based on NMR data have been suggested.

**S**YNTHESIS of apparently covalent volatile double alkoxy derivatives of electropositive metals lithium, sodium and potassium<sup>1-4</sup> has generated an interest regarding the synthesis of compounds of even more strongly electropositive elements rubidium and caesium. Here we report a number of apparently covalent double isopropoxides of Cs and Rb with Al, Zr, Ta, Hf and Nb.

### Materials and Methods

All the preparations were carried out under anhydrous conditions.

Aluminium isopropoxide was procured from NCL, Poona. Benzene (BDH) and isopropanol (BDH) were dried as usual.

Zirconium, hafnium, niobium and tantalum isopropoxides were prepared by the ammonia method<sup>5-7</sup> using the corresponding chlorides (Fluka AG).

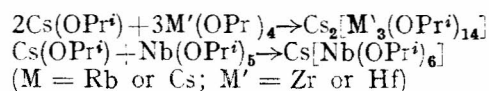
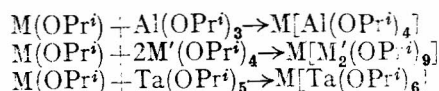
Zirconium, hafnium, niobium and tantalum were estimated as oxides. Aluminium was estimated as oxinate.

The alkoxy groups were estimated by oxidation with potassium dichromate<sup>8</sup>.

*Preparation of double alkoxides of Rb and Cs*—Rubidium or caesium isopropoxide was prepared by dissolving the corresponding metal in isopropanol. The resultant reaction was exothermic. The solution obtained was cooled to the room temperature and stoichiometric quantities of  $Al(OPr^i)_3$ ,  $Zr(OPr^i)_4$ ,  $Hf(OPr^i)_4$ ,  $Nb(OPr^i)_5$  or  $Ta(OPr^i)_5$  were added. The reaction mixture was refluxed for 1-2 hr. Excess of the solvent was removed by distillation and the product was dried *in vacuo*. The products could be sublimed under reduced pressure. Analytical results are summarized in Table 1.

### Results and Discussion

These reactions are facile and can be represented by following equations:



The products are white crystalline solids, sparingly soluble in isopropanol and benzene. The compounds were purified either by recrystallization from isopropanol or by sublimation/distillation under reduced pressure in yields between 40 and 75% (Table 1). Ebullioscopic determination of molecular weights of some of the present double alkoxides soluble in benzene showed them to be monomeric.

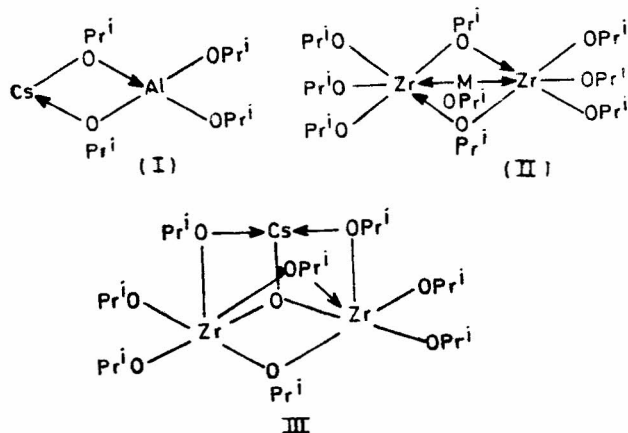
In the present series of the double isopropoxides, the solubility goes on increasing from lithium to

TABLE 1—REACTIONS OF RUBIDIUM AND CAESIUM ISOPROPOXIDES WITH AL, Zr, Hf, Nb AND Ta ISOPROPOXIDES

Reaction of Rb or Cs isopropoxide with	Molar* ratio (M:M' isopropoxide)	b.p. (°C/mm), yield (%)	Found % (calc.)	
			Isopropoxy	Metal (M')
DOUBLE ISOPROPOXIDES OF Rb				
$Al(OPr^i)_3$	1:1	180-82°/0.2 45	67.69 (67.76)	7.74 (7.73)
$Zr(OPr^i)_4 \cdot Pr^iOH$	1:2	160-63°/0.1 75	66.48 (66.51)	22.65 (22.80)
$Ta(OPr^i)_5$	1:1	150-60°/0.2 80	56.49 (57.10)	28.95 (29.13)
DOUBLE ISOPROPOXIDES OF Cs				
$Al(OPr^i)_3$	1:1	300-305°/0.2 40	59.74 (59.50)	6.84 (6.81)
$Zr(OPr^i)_4 \cdot Pr^iOH$	1:2	190-93°/0.1 70	21.44 (21.53)	62.76 (62.79)
$Zr(OPr^i)_4 \cdot Pr^iOH$	2:3	220-22°/0.1 50	60.84 (60.61)	18.88 (20.04)
$Hf(OPr^i)_4 \cdot Pr^iOH$	1:2	230-33°/0.1 58	51.83 (50.43)	34.88 (34.93)
$Hf(OPr^i)_4 \cdot Pr^iOH$	2:3	160-63°/0.1 67	50.82 (50.79)	32.25 (32.88)
$Nb(OPr^i)_5$	1:1	180-85°/0.1 58	61.75 (61.09)	16.52 (16.29)
$Ta(OPr^i)_5$	1:1	210-12°/0.1 70	52.66 (53.01)	28.79 (27.04)

\*M = Rb or Cs; M' = Al, Zr, Ta, Hf or Nb.

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caesium. This is unlike the other series where the coordination compounds of potassium exhibit anomalous stability and solubility behaviour<sup>3</sup>.

*NMR spectra* — PMR spectra of only two products,  $\text{Cs}[\text{Al}(\text{OPr}^i)_4]$  and  $\text{Cs}[\text{Zr}_2(\text{OPr}^i)_9]$ , could be scanned due to the low solubilities of other products in  $\text{CCl}_4$  and  $\text{CDCl}_3$ . The spectrum of  $\text{Cs}[\text{Al}(\text{OPr}^i)_4]$  shows two types of doublets centred at 8.82 and 8.88  $\tau$  due to the *gem*-dimethyl protons of bridging and terminal isopropoxy groups. The intensities of these doublets are in 1:1 ratio suggesting the presence of two bridging and two terminal isopropoxy groups as shown in the probable structure (I). Mehrotra *et al.*<sup>3</sup> have suggested structure (II) for the products,  $\text{M}[\text{M}'_2(\text{OPr}^i)_9]$  (where  $\text{M} = \text{Li}, \text{Na}, \text{K}$  and

$\text{M}' = \text{Zr}$  or  $\text{Hf}$ ), in which nine isopropoxy groups are arranged around the two zirconium or hafnium atoms by sharing the faces of two octahedra. This structure has been supported by the NMR spectra of the compounds  $\text{K}[\text{Hf}_2(\text{OPr}^i)_9]$  and  $\text{Li}[\text{Hf}_2(\text{OPr}^i)_9]$  which give two types of isopropoxy groups (bridging and terminal) having the intensity ratio 1:2.

However, NMR spectrum of  $\text{Cs}[\text{Zr}_2(\text{OPr}^i)_9]$  shows two types of doublets centred at 8.71 and 8.75  $\tau$  in 5:4 ratio suggesting the presence of bridging and terminal isopropoxy groups in the ratio of 5:4. For  $\text{Cs}[\text{Zr}_2(\text{OPr}^i)_9]$ , the five bridging and four terminal isopropoxy groups can be arranged as shown in structure (III).

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