

## Preparation and Physico-chemical Studies of some Chloride and Alkoxide Isopropoxymetallates of Cobalt(II) Containing $\{Al(OPr^i)_4\}^-$ , $\{Zr_2(OPr^i)_9\}^-$ and $\{M(OPr^i)_6\}^-$ Units (M = Nb or Ta)

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### Abstract

Chloride isopropoxymetallates of cobalt(II),  $[ClCo\{Al(OPr^i)_4\}]$ ,  $[ClCo\{Zr_2(OPr^i)_9\}]$  and  $[ClCo\{M(OPr^i)_6\}]$  (M = Nb or Ta) have been synthesized by reactions of  $CoCl_2$  with  $Li\{Al(OPr^i)_4\}$ ,  $K\{Zr_2(OPr^i)_9\}$  and  $K\{M(OPr^i)_6\}$  in equimolar ratio. The chlorine in these chloride bimetallic isopropoxides has been replaced with alkoxide groups by their reactions with potassium alkoxides yielding products of the types,  $[(OR)Co\{Ta(OPr^i)_6\}]$  and  $[(OR)Co\{Zr_2(OPr^i)_9\}]$  (R = Me, Pr<sup>n</sup>, Pr<sup>i</sup>, Bu<sup>n</sup>, Bu<sup>s</sup> or Bu<sup>t</sup>). Alcohol interchange reactions of the above derivatives have been studied. All these new bimetallic alkoxides of cobalt(II) have been characterized by elemental analyses, IR, electronic spectral (visible) and magnetic susceptibility measurements.

### Introduction

A survey of the literature reveals that only limited attention has been paid to the chemistry of halide alkoxides of later transition metals. Brubaker and Wicholas [1] followed by Winter *et al.* [2, 3] have reported the synthesis of insoluble, non-volatile and polymeric halide alkoxides of later \*3d\* transition metals and their characterization by magnetic and electronic spectral studies.

The synthesis and chemistry of bisisopropoxymetallates of cobalt(II) and copper(II) have been described in our earlier publications [4–6]. These were found to be soluble and monomeric in organic solvents and could be volatilized in most of the cases. However, the halide alkoxymetallates of later transition metals have not been reported in the literature so far.

In this paper, we report the synthesis, reactions and characterization of some novel chloride and alkoxide isopropoxymetallates of cobalt(II), which have proved to be useful precursors for the synthesis of a new class of metals alkoxides, *i.e.* termetallic isopropoxides [7] of transition metals.

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### Experimental

#### General

All the reactions were carried out under anhydrous conditions [4]. Anhydrous cobalt(II) chloride was prepared and analysed as reported earlier [4]. Zirconium [8], tantalum [9] and aluminium [10] isopropoxides were prepared by literature procedures.

Zirconium [11] was estimated as oxide after precipitation as mandelate. Niobium and tantalum were precipitated as hydroxides and estimated as oxides. Cobalt was estimated as oxide in the niobium (tantalum) derivatives, whereas in the zirconium derivatives it was estimated as mixed oxide. Chlorine was estimated by Vohlar's method [11]. Isopropanol was estimated by an oxidimetric method [12].

Infra-red and electronic spectra and magnetic susceptibilities were determined as described earlier [4].

#### Synthesis and Reactions

##### Preparation of $[ClCo\{Al(OPr^i)_4\}]$

A freshly prepared solution of  $Li\{Al(OPr^i)_4\}$  (prepared by reaction of lithium metal (0.07 g) dissolved in ~20 ml of  $Pr^iOH$  and  $Al(OPr^i)_3$  (2.61 g) in ~30 ml  $C_6H_6$ ) was added to a suspension of  $CoCl_2$  (1.34 g) in ~20 ml  $Pr^iOH$ . The reaction mixture was refluxed/stirred (5–7 h) to ensure the completion of reaction. The solvent from the reaction mixture was evaporated off under reduced pressure and the isolated product was dissolved in excess of benzene (~40 ml). This solution was filtered to remove the LiCl residue (as it is insoluble in  $C_6H_6$ ). The dark blue solid product (3.50 g; 98%) was isolated after removing the solvent from the filtrate under reduced pressure.

##### Preparation of $[ClCo\{Zr_2(OPr^i)_9\}]$

To a suspension of  $CoCl_2$  (0.74 g; 5.75 mmol) in ~5 ml  $Pr^iOH$  was added a solution of  $K\{Zr_2(OPr^i)_9\}$  (4.33 g; 5.75 mmol) in ~40 ml of benzene. It was refluxed for 3–4 h, during which time the colour changed from light to dark blue. The precipitated KCl

TABLE I. Synthetic Details of Chloride and Alkoxide Isopropoxymetallates of Cobalt(II)

Reactants (g)	Product Found (calc.) (g)	Physical State	Volatility <sup>a</sup> (°C/mm) (% yield)	Analysis, Found (calc.) (%)			
				Co	Zr/M/Al (M = Nb or Ta)		
CoCl <sub>2</sub> + K{Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> } 0.74 4.33	[ClCo{Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> }] 4.47(4.68)	royal blue crystalline solid		7.29 (7.33)	22.40 (22.56)	65.80 (65.77)	4.38 (4.44)
[ClCo{Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> }] + KOMe 2.00 0.17	[(OMe)Co{Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> }] 1.67(1.98)	violet crystalline solid	180/0.4* (30)	7.46 (7.33)	22.99 (22.69)	65.95 (66.13)	
[ClCo{Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> }] + KOPr <sup>i</sup> 3.46 0.42	[(OPr <sup>i</sup> )Co{Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> }] 3.48(3.56)	violet crystalline solid	175/0.2* (42)	6.98 (7.08)	22.63 (21.92)	63.45 (63.84)	
[ClCo{Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> }] + KOBu <sup>s</sup> 1.38 0.19	[(OBu <sup>s</sup> )Co{Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> }] 1.35(1.44)	violet blue solid	D	7.15 (6.96)	22.85 (21.56)	61.80 (62.84)	
[ClCo{Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> }] + KOBu <sup>n</sup> 1.49 0.21	[(OBu <sup>n</sup> )Co{Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> }] 1.48(1.56)	violet solid	185/0.5* (50)	7.05 (6.96)	22.85 (21.56)	61.55 (62.84)	
[ClCo{Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> }] + KOBu <sup>t</sup> 1.58 0.22	[(OBu <sup>t</sup> )Co{Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> }] 1.45(1.65)	violet crystalline solid	(D) 190/0.4	7.91 (6.96)	22.25 (21.56)	62.20 (62.84)	
CoCl <sub>2</sub> + K{Nb(OPr <sup>i</sup> ) <sub>6</sub> } 0.72 2.69	[ClCo{Nb(OPr <sup>i</sup> ) <sub>6</sub> }] 2.56(3.00)	blue crystalline solid		11.68 (10.88)	18.77 (17.15)	65.21 (65.43)	6.70 (6.54)
CoCl <sub>2</sub> + K{Ta(OPr <sup>i</sup> ) <sub>6</sub> } 0.61 2.70	[ClCo{Ta(OPr <sup>i</sup> ) <sub>6</sub> }] 2.84(2.96)	blue crystalline solid		9.28 (9.36)	29.17 (28.73)	56.05 (56.29)	5.47 (5.63)
[ClCo{Ta(OPr <sup>i</sup> ) <sub>6</sub> }] + KOMe 1.32 0.15	[(OMe)Co{Ta(OPr <sup>i</sup> ) <sub>6</sub> }] 1.29(1.31)	violet crystalline solid		9.35 (9.42)	29.26 (28.93)	56.24 (56.68)	
[ClCo{Ta(OPr <sup>i</sup> ) <sub>6</sub> }] + KOPr <sup>i</sup> 1.45 0.23	[(OPr <sup>i</sup> )Co{Ta(OPr <sup>i</sup> ) <sub>6</sub> }] 1.48(1.50)	violet crystalline solid		9.81 (9.01)	28.38 (27.68)	62.99 (63.31)	
[ClCo{Ta(OPr <sup>i</sup> ) <sub>6</sub> }] + KOBu <sup>n</sup> 1.38 0.24	[(OBu <sup>n</sup> )Co{Ta(OPr <sup>i</sup> ) <sub>6</sub> }] 1.40(1.46)	violet crystalline solid		8.78 (8.82)	27.82 (27.11)	53.20 (53.12)	
CoCl <sub>2</sub> + Li{Al(OPr <sup>i</sup> ) <sub>4</sub> } 1.34 2.78	[ClCo{Al(OPr <sup>i</sup> ) <sub>4</sub> }] 3.50(3.54)	royal blue		16.90 (16.47)	7.50 (7.54)	56.98 (66.07)	10.00 (9.91)
[ClCo{Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> }] + MeOH 1.21 ~35 ml	[ClCo{Zr <sub>2</sub> (OMe) <sub>9</sub> }] <sup>b</sup> 0.81(0.83)	blue powdery solid		10.52 (10.60)	33.06 (32.81)		6.25 (6.38)
[ClCo{Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> }] + Bu <sup>s</sup> OH 0.38 ~40 ml	[ClCo{Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>4</sub> (OBu <sup>s</sup> ) <sub>5</sub> }] <sup>c</sup> 0.41(0.41)	blue crystalline solid		6.62 (6.71)	20.82 (20.78)		(4.04)

[ClCo{Zr <sub>2</sub> (OPr <sup>t</sup> ) <sub>9</sub> }] + Bu <sup>s</sup> OH 1.26	[ClCo{Zr <sub>2</sub> (OPr <sup>t</sup> ) <sub>6</sub> (OBu <sup>s</sup> ) <sub>3</sub> }] <sup>b</sup> 1.30(1.32)	-do-	6.58 (6.93)	21.87 (21.46)	4.08 (4.17)
[ClCo{Zr <sub>2</sub> (OPr <sup>t</sup> ) <sub>9</sub> }] + Bu <sup>s</sup> OH 1.61	[ClCo{Zr <sub>2</sub> (OBu <sup>s</sup> ) <sub>9</sub> }] <sup>d</sup> 1.80(1.86)	-do-	6.25 (6.31)	19.82 (19.53)	3.84 (3.79)
[ClCo{Zr <sub>2</sub> (OPr <sup>t</sup> ) <sub>9</sub> }] + Bu <sup>t</sup> OH 0.74	[ClCo{Zr <sub>2</sub> (OPr <sup>t</sup> ) <sub>3</sub> (OBu <sup>t</sup> ) <sub>6</sub> }] <sup>d</sup> 0.80(0.82)	blue solid	6.62 (6.61)	20.91 (20.46)	3.89 (3.97)

a \*, sublimed; D, decomposed.  
removal of Pr<sup>t</sup>OH.

<sup>b</sup> Reaction carried out at room temperature.

<sup>c</sup> Carried out in refluxing benzene.

<sup>d</sup> Carried out in refluxing benzene with azeotropic

was removed by filtration and the filtrate was concentrated (~20 ml). After a few hours, the crystallized solid was filtered and dried under reduced pressure to yield a dark blue crystalline solid compound [ClCo{Zr<sub>2</sub>(OPr<sup>t</sup>)<sub>9</sub>}] (4.47 g; 95%).

The chlorides hexaisopropoxy niobate or tantalate [ClCo{M(OPr<sup>t</sup>)<sub>6</sub>}] (M = Nb or Ta) were prepared similarly (Table I).

#### Preparation of [(OR)Co{Zr<sub>2</sub>(OPr<sup>t</sup>)<sub>9</sub>}]

To a benzene (~35 ml) solution of [ClCo{Zr<sub>2</sub>(OPr<sup>t</sup>)<sub>9</sub>}] (3.46 g; 4.27 mmol) was added KOPr<sup>t</sup> (0.42 g; 4.28 mmol). It was refluxed for ~1 h during which the colour changed from dark blue to violet. The precipitate KCl was removed by filtration. The solvent was removed under reduced pressure to afford a violet crystalline solid (3.48 g; 97%). The product was further recrystallized from n-hexane.

Other alkoxide bimetallic isopropoxides were prepared similarly (Table I).

#### Alcoholysis Reactions of [ClCo{Zr<sub>2</sub>(OPr<sup>t</sup>)<sub>9</sub>}]

(i) Reactions with excess of MeOH: A mixture of [ClCo{Zr<sub>2</sub>(OPr<sup>t</sup>)<sub>9</sub>}] (1.21 g) solution in C<sub>6</sub>H<sub>6</sub> (~20 ml) and MeOH (~20 ml) was stirred for 4–5 h at room temperature. An insoluble light blue coloured solid product [ClCo{Zr<sub>2</sub>(OMe)<sub>9</sub>}] (0.81 g) was finally obtained.

(ii) With excess Bu<sup>s</sup>OH (at room temperature): A solution of [ClCo{Zr<sub>2</sub>(OPr<sup>t</sup>)<sub>9</sub>}] in C<sub>6</sub>H<sub>6</sub> with excess of Bu<sup>s</sup>OH was stirred at room temperature for ~5 h. The removal of the solvent under reduced pressure afforded a blue coloured crystalline solid of the composition, [ClCo{Zr<sub>2</sub>(OPr<sup>t</sup>)<sub>6</sub>(OBu<sup>s</sup>)<sub>3</sub>}].

(iii) With excess Bu<sup>s</sup>OH (in refluxing benzene): A benzene solution of [ClCo{Zr<sub>2</sub>(OPr<sup>t</sup>)<sub>9</sub>}] with excess Bu<sup>s</sup>OH was refluxed for ~5 h during which no change in colour was observed. Removal of the solvent under reduced pressure afforded a blue coloured compound of the composition, [ClCo{Zr<sub>2</sub>(OPr<sup>t</sup>)<sub>4</sub>(OBu<sup>s</sup>)<sub>5</sub>}].

(iv) Reaction with excess Bu<sup>s</sup>OH (azeotropically): A benzene solution of [ClCo{Zr<sub>2</sub>(OPr<sup>t</sup>)<sub>9</sub>}] with excess Bu<sup>s</sup>OH was refluxed and the liberated isopropanol was azeotroped out with benzene. Drying under reduced pressure afforded a blue solid of the composition, [ClCo{Zr<sub>2</sub>(OBu<sup>s</sup>)<sub>9</sub>}].

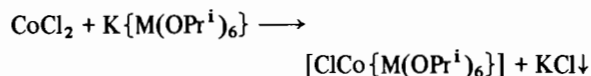
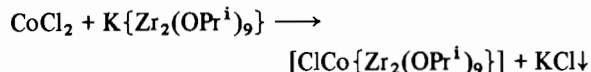
(v) Reaction with Bu<sup>t</sup>OH (azeotropically): A similar procedure was adopted to afford a derivative of the composition, [ClCo{Zr<sub>2</sub>(OPr<sup>t</sup>)<sub>3</sub>(OBu<sup>t</sup>)<sub>6</sub>}].

The physical properties and elemental analyses for all the above products have been collected in Table I.

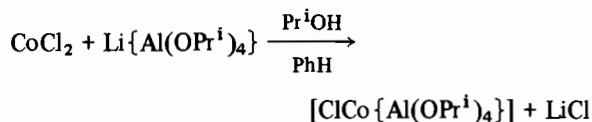
## Results and Discussion

The chloride bimetallic isopropoxides of the types [ClCo{Zr<sub>2</sub>(OPr<sup>t</sup>)<sub>9</sub>}], [ClCo{M(OPr<sup>t</sup>)<sub>6</sub>}] (M = Nb or

Ta) and  $[\text{ClCo}\{\text{Al}(\text{OPr}^i)_4\}]$  have been synthesized by the interactions of  $\text{CoCl}_2$  with  $\text{K}\{\text{Zr}_2(\text{OPr}^i)_9\}$  and  $\text{K}\{\text{M}(\text{OPr}^i)_6\}$  in 1:1 molar ratio in  $\text{C}_6\text{H}_6$  and  $\text{Pr}^i\text{OH}$  (minimum volume):

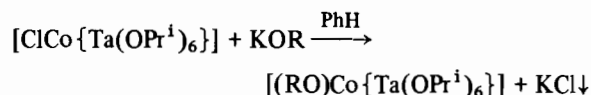
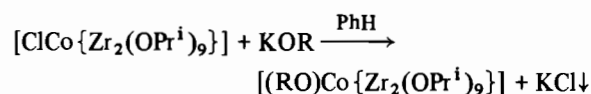


In the reaction of  $\text{CoCl}_2$  with  $\text{K}\{\text{Al}(\text{OPr}^i)_4\}$  under similar conditions, the reaction tended to proceed to the formation of the bis-product and the analyses of the soluble and insoluble fractions showed quite complex formulations. However,  $[\text{ClCo}\{\text{Al}(\text{OPr}^i)_4\}]$  could be obtained by taking a milder reagent  $\text{Li}\{\text{Al}(\text{OPr}^i)_4\}$  in place of  $\text{K}\{\text{Al}(\text{OPr}^i)_4\}$ . The volatiles were removed from the reaction mixture and the product,  $[\text{ClCo}\{\text{Al}(\text{OPr}^i)_4\}]$  was then separated by extraction with benzene in which  $\text{LiCl}$  is insoluble.



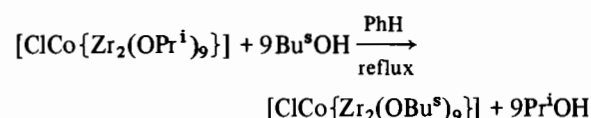
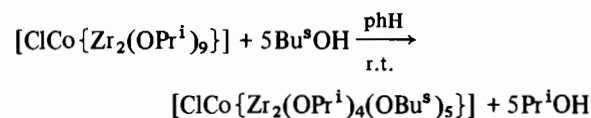
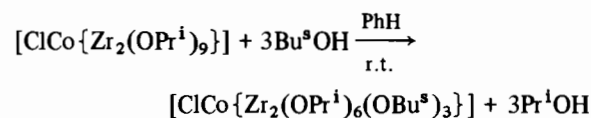
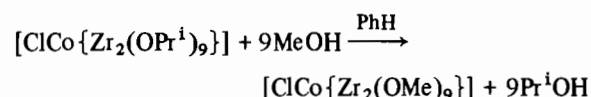
From the above reactions, chloride isopropoxy-metallates of cobalt have been isolated in almost quantitative yields; these could be purified by crystallization from  $\text{C}_6\text{H}_6/\text{Pr}^i\text{OH}$ . On heating, even under reduced pressure, these compounds tend to undergo decomposition. For example,  $[\text{ClCo}\{\text{Al}(\text{OPr}^i)_4\}]$  on being heated to  $\sim 135/0.5$  mm pressure gave a volatile viscous mass (purple) which corresponded in analysis to  $[\text{Co}\{\text{Al}(\text{OPr}^i)_4\}_2]$ . All the derivatives of cobalt(II) are royal blue coloured solids and soluble, when freshly prepared, in common organic solvents (such as benzene, carbon tetrachloride and n-hexane).

Replacement of chloride from derivatives such as  $[\text{ClCo}\{\text{Zr}_2(\text{OPr}^i)_9\}]$  and  $[\text{ClCo}\{\text{Ta}(\text{OPr}^i)_6\}]$  by alkoxy groups produced alkoxide isopropoxymetallates of the types  $[(\text{OR})\text{Co}\{\text{Zr}_2(\text{OPr}^i)_9\}]$  and  $[(\text{OR})\text{Co}\{\text{Ta}(\text{OPr}^i)_6\}]$  ( $\text{R} = \text{Me}, \text{Pr}^n, \text{Pr}^i, \text{Bu}^n, \text{Bu}^s$  or  $\text{Bu}^t$ ) according to the following reactions:

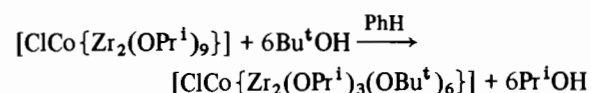


Most of these alkoxide isopropoxymetallates are violet crystalline solids, soluble in organic solvents and some of them such as  $[(\text{RO})\text{Co}\{\text{Zr}_2(\text{OPr}^i)_9\}]$  ( $\text{R} = \text{Pr}^i$  and  $\text{Bu}^n$ ) can be volatilized under reduced pressure.

Alcohol interchange reactions of  $[\text{ClCo}\{\text{Zr}_2(\text{OPr}^i)_9\}]$  have been carried out indicating a gradation in the replaceability of isopropoxy groups present, as indicated by the following equations:



With an excess of t-butanol, even under the condition of azeotropic removal of liberated isopropanol, a solid product corresponding in analysis to  $[\text{ClCo}\{\text{Zr}_2(\text{OPr}^i)_3(\text{OBu}^t)_6\}]$  could be finally obtained:



#### Infrared Spectral Studies

The characteristic infrared frequencies [13, 14] of the metal alkoxy groups have been observed in the range,  $1170\text{--}930$   $\text{cm}^{-1}$  for  $\nu(\geq\text{C}-\text{O})\text{M}$ ;  $620\text{--}550$   $\text{cm}^{-1}$  for  $\nu(\text{M}'-\text{O})$  ( $\text{M}' = \text{Zr}, \text{Ta}/\text{Nb}$ ) and  $480\text{--}400$   $\text{cm}^{-1}$  for  $\nu(\text{Co}-\text{O})$ . Chloride bimetallic isopropoxides exhibited additional bands [15–17] of medium to strong intensity in the range  $360\text{--}210$   $\text{cm}^{-1}$  possibly due to  $\nu(\text{Co}-\text{Cl})$  (Table II).

#### Visible Spectral Studies

These new bimetallic derivatives exhibit bands at  $\sim 16.0 \times 10^3$  and  $\sim 19.0 \times 10^3$   $\text{cm}^{-1}$  in the visible region (Table III). The tetrahedral cobalt(II) complexes [18] exhibit three bands in the ranges:  $3.0\text{--}5.0 \times 10^3$   $\text{cm}^{-1}$  ( ${}^4\text{A}_2(\text{F}) \xrightarrow{\nu_1} {}^4\text{T}_2(\text{F})$ ),  $5.5 \times 10^3$   $\text{cm}^{-1}$  ( ${}^4\text{A}_2(\text{F}) \xrightarrow{\nu_2} {}^4\text{T}_1(\text{F})$ ), and at  $\sim 15.0 \times 10^3$   $\text{cm}^{-1}$  ( ${}^4\text{A}_2(\text{F}) \xrightarrow{\nu_3} {}^4\text{T}_1(\text{P})$ ), whereas the five coordinated trigonal bipyramidal compound [18],  $\text{Co}(\text{Me}_6\text{tren})\text{Cl}^+$  ( $D_{3h}$  symmetry) has been reported to show four bands at  $\sim 5.5 \times 10^3$   $\text{cm}^{-1}$  ( ${}^4\text{E}' \leftarrow {}^4\text{A}_2(\text{F})$ ),  $12.5 \times 10^3$   $\text{cm}^{-1}$  ( ${}^4\text{E}' \rightarrow {}^4\text{A}'_2(\text{F})$ ) (in the near IR region),  $15.6\text{--}16.1 \times 10^3$   $\text{cm}^{-1}$  ( ${}^4\text{A}'_2(\text{P}) \leftarrow {}^4\text{A}_2(\text{F})$ ) and  $20.0 \times 10^3$   $\text{cm}^{-1}$  ( $\text{E}''(\text{P}) \leftarrow {}^4\text{A}'_2(\text{F})$ ) (in the visible region). In these new chloride and alkoxide isopropoxymetallates, two bands are observed in the visible region at  $\sim 16.0 \times 10^3$  and  $\sim 19.0 \times 10^3$   $\text{cm}^{-1}$ , and the bands in

TABLE II. Some Characteristic IR Frequencies ( $\text{cm}^{-1}$ ) and Room Temperature Magnetic Moments for Chloride and Alkoxide Isopropoxymetallates of Cobalt(II)

Compound	$\mu_{\text{eff}}$	$\nu(\geq \text{C}-\text{O})\text{M}$	$\nu(\text{M}'-\text{O})$	$\nu(\text{Co}-\text{O})$	$\nu(\text{Co}-\text{Cl})$
$[\text{ClCo}\{\text{Zr}_2(\text{OPr}^i)_9\}]$	4.78	1160w, 1130w 1015m, 950m	565m	470m	356m, 280m, 225s
$[(\text{OMe})\text{Co}\{\text{Zr}_2(\text{OPr}^i)_9\}]$	4.60	1160s, 1130m 1010m, 960m	570m	450m br	
$[(\text{OPr}^i)\text{Co}\{\text{Zr}_2(\text{OPr}^i)_9\}]$	4.65	1170w, 1150w, 1010w	550sbr	465br	
$[(\text{OBu}^s)\text{Co}\{\text{Zr}_2(\text{OPr}^i)_9\}]$	4.61	1130s, 1000s, 935m	570br	430sbr	
$[(\text{OBu}^n)\text{Co}\{\text{Zr}_2(\text{OPr}^i)_9\}]$	4.80	1170m, 1130m, 1020m, 960m	580wbr	460wbr	
$[(\text{OBu}^t)\text{Co}\{\text{Zr}_2(\text{OPr}^i)_9\}]$	5.23	1160m, 1010m	560mbr	450mbr	
$[\text{ClCo}\{\text{Ta}(\text{OPr}^i)_6\}]$	4.71	1155s, 1110s	595s	480m, 435m	
$[(\text{OMe})\text{Co}\{\text{Ta}(\text{OPr}^i)_6\}]$	4.62	1160s, 1130s, 960m, 980m	590m, 620m	480wbr	
$[(\text{OPr}^i)\text{Co}\{\text{Ta}(\text{OPr}^i)_6\}]$	4.69	1150m, 980m	595wbr	450wbr	
$[(\text{OBu}^n)\text{Co}\{\text{Ta}(\text{OPr}^i)_6\}]$	4.65	1130s, 1000m, 980m, 940m	570s, 540mbr	420m	
$[\text{ClCo}\{\text{Al}(\text{OPr}^i)_4\}]$	5.19	1170s, 1130s, 980s, 950s	615m, 580m, 550m	490m, 450m	356m, 271m, 227s, 211s

TABLE III. Visible Spectra of Chloride and Alkoxide Isopropoxymetallates of Cobalt(II)

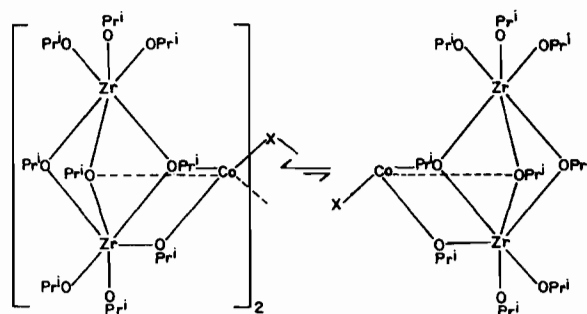
Compound	Medium	$\nu_{\text{max}} \times 10^{-3}$ ( $\text{cm}^{-1}$ )
$[\text{ClCo}\{\text{Zr}_2(\text{OPr}^i)_9\}]$	(i) $\text{C}_6\text{H}_6$	16.3, 18.5
	(ii) THF	16.4, 17.5
	(iii) $\text{Pr}^i\text{OH}$	18.3
$[(\text{OPr}^i)\text{Co}\{\text{Zr}_2(\text{OPr}^i)_9\}]$	$\text{C}_6\text{H}_6$	16.3, 19.5
$[(\text{OMe})\text{Co}\{\text{Zr}_2(\text{OPr}^i)_9\}]$	$\text{C}_6\text{H}_6$	14.7, 19.6
$[(\text{OBu}^t)\text{Co}\{\text{Zr}_2(\text{OPr}^i)_9\}]$	$\text{C}_6\text{H}_6$	17.5, 19.5

the near IR region (out of range of the equipment used) could not be recorded.

On the basis of the above observations, a trigonal bipyramidal environment appears to be more probable around cobalt(II) (Fig. 1) in these derivatives, although the tetrahedral form cannot be ruled out.

### Magnetic Studies

The room temperature magnetic moment values for these new chloride and alkoxide isopropoxymetallates are in the range 4.61–5.23 BM (Table II). The magnetic moment values reported for high spin tetra-

Fig. 1. Proposed structures for  $[(\text{X})\text{Co}\{\text{Zr}_2(\text{OPr}^i)_9\}]$  ( $\text{X} = \text{Cl}, \text{OR}$ ).

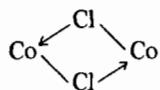
hedral [19] cobalt(II) complexes lie in the range 4.4–4.7 BM, whereas for five coordinated cobalt(II) high spin complexes [20], the values are in the range 4.5–5.5 BM. These values, therefore, are suggestive of a trigonal bipyramidal geometry for these cobalt(II) derivatives. These findings are also supported by the electronic spectral studies on some of these chloride and alkoxide bimetallic isopropoxides.

The low temperature (75–295 K) magnetic susceptibilities (Table IV) for chloride tetraisopropoxyaluminate,  $[\text{ClCo}\{\text{Al}(\text{OPr}^i)_4\}]$ , exhibit lowering in the magnetic moments with decrease of temperature indicating antiferromagnetic exchange between

TABLE IV. Variable Temperature Magnetic Susceptibility Data for  $[\text{Co}\{\text{Al}(\text{OPr}^i)_4\}]$ 

Temperature (K)	$\chi_g \times 10^6$	$\chi_M \times 10^6$	$\chi_M^{\text{corr}} \times 10^6$	$\mu_{\text{eff}}$ (BM)
75.0	109.05	38969	39163	4.85
81.1	103.12	36850	37044	4.90
87.2	96.196	34376	34570	4.91
93.3	91.252	32609	32803	4.95
99.4	86.061	30754	39948	4.96
105.5	81.365	29076	29270	4.97
111.6	77.163	27574	27769	4.98
117.7	73.702	26337	26532	5.00
123.8	70.242	25101	25295	5.00
129.9	67.275	24041	24235	5.02
136.0	64.556	23069	23263	5.03
142.1	61.837	22097	22292	5.03
148.2	59.613	21303	21497	5.05
154.3	57.635	20596	20790	5.06
160.4	55.411	19801	19996	5.06
166.5	53.680	19183	19377	5.08
172.6	51.703	18476	18670	5.08
178.6	50.220	17946	18141	5.09
184.7	48.737	17416	17611	5.10
190.8	47.006	16798	16992	5.09
203.0	44.287	15826	16020	5.10
209.1	43.299	15473	15667	5.12
215.2	42.063	15031	15226	5.12
221.3	41.074	14678	14873	5.13
227.4	40.085	14324	14519	5.14
233.5	39.097	13971	14166	5.14
239.6	38.108	13618	13812	5.14
245.7	37.119	13264	13459	5.14
251.8	36.378	12999	13194	5.15
257.9	35.636	12740	12934	5.16
264.0	34.894	12469	12664	5.17
270.1	34.153	12205	12399	5.17
276.2	33.411	11939	12134	5.18
282.3	32.670	11675	11869	5.18
288.4	31.928	11409	117604	5.17
294.5	31.434	11233	11427	5.19

two cobalt(II) metal centres, which might be through the chlorine bridges in a species of the type:



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