Synthesis, Reactions, Spectral and Magnetic Studies of Bimetallic Alkoxides of Cobalt(II) with Zirconium(IV)

R. K. DUBEY, A. SINGH and R. C. MEHROTRA*

Department of Chemistry, University of Rajasthan, Jaipur 302004, India

(Received February 20, 1986)

Abstract

A bimetallic isopropoxide of cobalt(II) with the formula $Co[Zr_2(OPr^i)_9]_2$, prepared by the reaction of $CoCl_2$ with $K[Zr_2(OPr^i)_9]$ in 1:2 molar ratio, has been shown to undergo alcoholysis reactions with graded alcohols (primary, secondary and tertiary) to afford products of the types, $Co[Zr_2(OR)_9]_2$ (where R = Me, Et, Pr^n, Bu^n, Bu^i and Bu^s) $Co[Zr_2(OPr^i)_3(OEt)_6]_2$, $Co[Zr_2(OPr^i)_6(OBu^s)_3]_2$, $Co[Zr_2(OPr^i)_3(OBu^s)_6]_2$, $Co[Zr_2(OPr^i)_6(OBu^t)_3]_2$ and $Co[Zr_2(OPr^i)_3(OR)_6]_2$ (where R = Am^t or Bu^t). These derivatives have been characterized by elemental analyses and molecular weight determinations. Infrared, electronic (visible) spectral and magnetic susceptibility measurements suggest a distorted octahedral geometry for these derivatives.

Introduction

Despite extensive work on transition metal alkoxides by different groups of workers, examples of hydrocarbon-soluble, later transition metal alkoxides are rare. For example, simple alkoxides of cobalt(II) are polymeric [1], nonvolatile and insoluble; thus, their detailed physico-chemical investigations have not been feasible. Hydrocarbon-soluble, volatile and monomeric cobalt(II) alkoxide derivatives have proved exceedingly elusive, with the exception of bimetallic compounds of the composition $Co[Al(OR)_4]_2$ [2], which have been shown to be octahedral in nature. Various types of bimetallic complexes of transition metals with the ligands $[Al(OR)_4]^-$ have aroused considerable interest during the last few years [2–7].

In addition to their importance for structural and bonding studies, bimetallic alkoxide derivatives are finding extensive applications in the ceramic industry [8] as well as in synthetic organic chemistry. Further, in view of the fact that metal cluster compounds have shown greater potential in catalytic systems, it might be expected that some of these bimetallic alkoxide complexes may also be useful in catalytic processes. Interestingly, the chemistry of bimetallic derivatives of later transition metal anions, such as $[Zr_2(OR)_9]^-$, $[Nb(OR)_6]^-$ and $Ta(OR)_6]^-$, has not yet been studied.

In view of the above, it was considered worthwhile to investigate the reactions of $K[Zr_2(OPr^i)_9]$ with cobalt(II) chloride and also to explore the chemistry and bonding characteristics of such derivatives. In this paper we, therefore, report on the synthesis, reactivity and structural aspects (with the help of IR, electronic and magnetic studies) of $Co[Zr_2(OR)_9]_2$.

Experimental

Stringent precautions were taken to exclude atmospheric moisture from the glassware, solvents and the reagents used throughout the experimental work.

Anhydrous $CoCl_2$ was prepared by heating the hydrated $CoCl_2 \cdot 6H_2O$ (B.D.H.) in a current of dry HCl gas and analysed. *Anal.* for $CoCl_2$. Found: Co, 45.41; Cl, 54.59. Calc.: Co, 45.39; Cl, 54.61%.

The $Zr(OPr^i)_4 \cdot Pr^iOH$ [9] was prepared by passing dry NH_3 gas through the solution of zirconium tetrachloride (Fluka) in isopropanol and purified by recrystallisation from isopropanol. *Anal.* for $Zr(OPr^i)_4 \cdot Pr^iOH$. Found: Zr, 23.87; OPr^i, 76.40. Calc.: Zr, 23.55; OPr^i, 76.44%.

Zirconium was estimated as an oxide after precipitation as mandelate [10]; cobalt was estimated as a mixed oxide ($CoO + ZrO_2$). Alcohols [11] were estimated by an oxidimetric method. Infrared spectra were recorded in the range 4000–400 cm^{-1} in Nujol mulls on a Perkin-Elmer 557 spectrometer. Electronic spectra were recorded on a Pye-Unicam SP8-100 spectrophotometer. Magnetic susceptibility measurements were made on Gouy balance. Molecular weights were determined cryoscopically in benzene.

---

*Author to whom correspondence should be addressed.

0020-1693/86/$3.50

Preparation of $Co[Zr_2(OPr^i)_9]_2$

To a suspension of $CoCl_2$ (0.12 g, 0.93 mmol) in ~10 ml benzene was added a benzene (~20 ml) solution of $K[Zr_2(OPr^i)_9]$ (1.40 g, 1.86 mmol) containing few drops of pyridine to increase the solubility of $CoCl_2$ and refluxed for ~6 h. During this period the colour of the reaction mixture changed from violet to purple–red. The precipitated KCl was removed by filtration, and the purple filtrate was concentrated (~10 ml) and left for a few hours at room temperature to afford a purple-coloured crystalline product (1.33 g, 98%). Analysis and physical characteristics of $Co[Zr_2(OPr^i)_9]_2$ are given in Table I.

Reactions of $Co[Zr_2(OPr^i)_9]_2$

(a) With excess of MeOH

When an excess of methanol (~30 ml) was added to a benzene (~25 ml) solution of $Co[Zr_2(OPr^i)_9]_2$ (2.51 g) an exothermic reaction took place. The reaction mixture was stirred for ~6 h during which the insoluble violet–red compound settled out. It was filtered, washed and dried under reduced pressure to yield a violet–red powdery solid product (1.62 g, 98%).

(b) With excess of EtOH at room temperature

Ethanol (~20 ml) was added to a benzene solution (~10 ml) of $Co[Zr_2(OPr^i)_9]_2$ (1.21 g) and stirred for ~6 h at room temperature. The solvent was removed under reduced pressure and the violet–red coloured solid (1.01 g, 94%) compound of composition $Co[Zr_2(OPr^i)_3(OEt)_6]_2$ was isolated.

(c) With excess of EtOH (under refluxing condition)

After dissolving $Co[Zr_2(OPr^i)_9]_2$ (1.69 g) in benzene (~20 ml) an excess of ethanol (~35 ml) was added and then refluxed for ~7 h during which the colour changed from purple–red to violet–red. After removal of the solvent under reduced pressure, a violet–red solid (1.35 g, 96%) product of the composition $Co[Zr_2(OEt)_9]_2$ was obtained.

Derivatives of n-propanol, n-butanol and i-butanol were prepared in a similar manner.

(d) With excess of Bu^sOH (at room temperature)

An excess of s-butanol (~25 ml) was added to a benzene (~20 ml) solution of $Co[Zr_2(OPr^i)_9]_2$ (1.48 g) and stirred for ~8 h. The solvent was stripped off under reduced pressure, and a purple-coloured solid product (1.54 g, 98%) of the composition $Co[Zr_2(OPr^i)_6(OBu^s)_3]_2$ was obtained.

(e) With excess Bu^sOH in refluxing benzene (without azeotropic removal of Pr^iOH)

To a benzene (~20 ml) solution of $Co[Zr_2(OPr^i)_9]_2$ (1.45 g) was added s-butanol (~25 ml), and the mixture was refluxed for ~6 h. The solvent was removed under reduced pressure. The purple–blue solid product (1.58 g, 98%) of composition $Co[Zr_2(OPr^i)_3(OBu^s)_6]_2$ was obtained.

(f) With excess of Bu^sOH (azeotropically)

The s-butanol (~40 ml) was added to a benzene (~15 ml) solution of $Co[Zr_2(OPr^i)_9]_2$ (2.1 g) and the reaction mixture was refluxed for ~7 h. The isopropanol liberated during the reaction was continuously fractionated out azeotropically. After complete removal of isopropanol the solvent was removed under reduced pressure. The purple-coloured solid (2.37, 94%) product of the composition $Co[Zr_2(OBu^s)_9]_2$ was obtained.

(g) With excess of Bu^tOH in refluxing benzene

To a benzene solution (~20 ml) of $Co[Zr_2(OPr^i)_9]_2$ (1.40 g) was added Bu^tOH (~25 ml) and the mixture was refluxed for ~6 h. The solvent was removed under reduced pressure, and the violet–red coloured solid (1.42, 97%) product of composition $Co[Zr_2(OPr^i)_6(OBu^t)_3]_2$ was isolated.

(h) With excess of Bu^tOH/Am^tOH (azeotropically)

An excess of t-butanol (~45 ml) was added to a benzene (~20 ml) solution of $Co[Zr_2(OPr^i)_9]_2$ (1.98 g) and refluxed for ~22 h; the liberated isopropanol was removed continuously and estimated. When liberation of isopropanol was found to be negligible, the solvent was removed to yield a violet–red solid (2.10, 95%) product of composition $Co[Zr_2(OPr^i)_3(OBu^t)_6]_2$.

In a similar manner the reaction was carried out with Am^tOH.

Analyses as well as physical characteristics for all the products isolated from the above reactions are given in Table I.

Results and Discussion

Bimetallic isopropoxide of cobalt(II) $Co[Zr_2(OPr^i)_9]_2$ has been prepared in quantitative yield by the interaction of $CoCl_2$ with $K[Zr_2(OPr^i)_9]$ in 1:2 molar ratio in benzene containing a few drops of pyridine (which facilitates the dissolution of $CoCl_2$ in the solvent):

$$CoCl_2 + 2K[Zr_2(OPr^i)_9] \xrightarrow[\text{reflux}]{\text{PhH}} Co[Zr_2(OPr^i)_9]_2 + 2KCl\downarrow$$

The purple-red coloured, monomeric, volatile and hydrocarbon-soluble product $Co[Zr_2(OPr^i)_9]_2$ could be purified unchanged by distillation (165 °C/ 0.2 mm) or recrystallisation (from benzene/n-hexane).

TABLE I. Synthesis and Alcoholysis Reactions of $Co[Zr_2(OPr^i)_9]_2$

Reactants (g)	Product (g) Reaction conditions^{a,b,c}	Nature of product	Analysis/Found (calc.) (%)			Pr^iOH liberated (g)
			Co	Zr	OR	
$CoCl_2 + 2K[Zr_2(OPr^i)_9]$ (0.12) (1.40)	$Co[Zr_2(OPr^i)_9]_2$ 1.33(1.34)	Purple–red crystalline solid	3.82 (3.92)	24.75 (24.54)	71.02 (71.54)	
$Co[Zr_2(OPr^i)_9]_2 + MeOH$ (2.51) (~40 ml)	$Co[Zr_2(OMe)_9]_2{}^a$ 1.62(1.65)	Violet–red powdery solid	5.91 (6.00)	37.97 (37.16)		
$Co[Zr_2(OPr^i)_9]_2 + EtOH$ (1.21) (~20 ml)	$Co[Zr_2(OPr^i)_3(OEt)_6]_2{}^a$ 1.01(1.07)	Violet–red solid	4.50 (4.46)	28.25 (27.67)		
$Co[Zr_2(OPr^i)_9]_2 + EtOH$ (1.69) (~35 ml)	$Co[Zr_2(OEt)_9]_2{}^b$ 1.35(1.40)	Violet crystalline solid	4.47 (4.77)	30.15 (29.57)	64.47 (65.65)	
$Co[Zr_2(OPr^i)_9]_2 + Pr^nOH$ (2.62) (~50 ml)	$Co[Zr_2(OPr^n)_9]_2{}^b$ 2.58(2.62)	Light blue crystalline solid	4.07 (3.86)	24.87 (24.53)		
$Co[Zr_2(OPr^i)_9]_2 + Bu^nOH$ (2.20) (~50 ml)	$Co[Zr_2(OBu^n)_9]_2{}^b$ 2.35(2.56)	Sticky solid purple–blue	3.77 (3.39)	21.36 (20.99)		
$Co[Zr_2(OPr^i)_9]_2 + Bu^iOH$ (1.86) (~50 ml)	$Co[Zr_2(OBu^i)_9]_2{}^b$ 2.10(2.11)	Purple–blue solid	3.40 (3.39)	22.05 (21.00)		
$Co[Zr_2(OPr^i)_9]_2 + Bu^sOH$ (1.48) (~30 ml)	$Co[Zr_2(OPr^i)_6(OBu^s)_3]_2{}^a$ 1.54(1.56)	Purple–red solid	3.82 (3.75)	23.68 (23.22)	45.40 (45.13)	
$Co[Zr_2(OPr^i)_9]_2 + Bu^sOH$ (1.45) (~25 ml)	$Co[Zr_2(OPr^i)_3(OBu^s)_6]_2{}^b$ 1.58(1.61)	Violet–red solid	3.58 (3.56)	22.65 (22.05)	21.50 (21.43)	
$Co[Zr_2(OPr^i)_9]_2 + Bu^sOH$ (2.10) (~45 ml)	$Co[Zr_2(OBu^s)_9]_2{}^c$ 2.31(2.45)	Purple solid	3.45 (3.39)	21.85 (20.99)		1.50 (1.52)
$Co[Zr_2(OPr^i)_9]_2 + Bu^tOH$ (1.40) (~25 ml)	$Co[Zr_2(OPr^i)_6(OBu^t)_3]_2{}^b$ 1.42(1.47)	Violet–red solid	3.83 (3.75)	24.15 (23.22)	45.35 (45.13)	
$Co[Zr_2(OPr^i)_9]_2 + Bu^tOH$ (1.98) (~45 ml)	$Co[Zr_2(OPr^i)_3(OBu^t)_6]_2{}^c$ 2.10(2.20)	Violet–red solid	3.50 (3.56)	22.88 (22.05)	20.85 (21.43)	0.91 (0.94)
$Co[Zr_2(OPr^i)_9]_2 + Am^tOH$ (2.15) (~50 ml)	$Co[Zr_2(OPr^i)_3(OAm^t)_6]_2{}^c$ 2.51(2.63)	Violet–red solid	3.21 (3.23)	21.20 (20.02)	19.06 (19.45)	1.02 (1.03)

[a]Reaction carried out at room temperature. [b]Under refluxing conditions. [c]In refluxing benzene (azeotropic condition).

The reactivity of the product $Co[Zr_2(OPr^i)_9]_2$ towards alcohols of different steric bulk (primary, secondary and tertiary) has shown interesting variations.

The reaction with methanol is exothermic and facile even at room temperature:

$$Co[Zr_2(OPr^i)_9]_2 + \underset{\text{excess}}{18MeOH} \longrightarrow Co[Zr_2(OMe)_9]_2 + 18Pr^iOH\uparrow$$

However, with EtOH, Pr^nOH, Bu^nOH, Bu^iOH and Bu^sOH at room temperature, only twelve isopropoxy groups out of eighteen could be replaced:

$$Co[Zr_2(OPr^i)_9]_2 + \underset{\text{excess}}{12ROH} \longrightarrow Co[Zr_2(OPr^i)_3(OR)_6]_2 + 12Pr^iOH\uparrow$$

Complete replacement of the isopropoxy groups with these alcohols could also be accomplished by refluxing $Co[Zr_2(OPr^i)_9]_2$ with excess of alcohols followed by removal of all volatile components and refluxing the resulting product again with excess of alcohol:

$$Co[Zr_2(OPr^i)_9]_2 + \underset{\text{excess}}{18ROH} \xrightarrow[\text{reflux}]{\text{PhH}} Co[Zr_2(OR)_9]_2 + 18Pr^iOH\uparrow$$

R = Et, Pr^n, Bu^n and Bu^i

By contrast, reaction with s-butanol in refluxing benzene resulted in the product of the composition $Co[Zr_2(OPr^i)_3(OBu^s)_6]_2$:

$$Co[Zr_2(OPr^i)_9]_2 + \underset{\text{excess}}{12Bu^sOH} \xrightarrow[\text{reflux}]{\text{PhH}} Co[Zr_2(OPr^i)_3(OBu^s)_6]_2 + 12Pr^iOH\uparrow$$

The complete replacement of isopropoxy groups with s-butanol was possible under the condition of azeotropic removal of isopropanol:

$$\mathrm{Co[Zr_2(OPr^i)_9]_2 + \underset{excess}{18Bu^sOH} \longrightarrow Co[Zr_2(OBu^s)_9]_2 + 18Pr^iOH\uparrow}$$

With $\mathrm{Bu^tOH}$ at room temperature, no reaction appeared to take place, but in refluxing benzene six isopropoxy groups could be replaced:

$$\mathrm{Co[Zr_2(OPr^i)_9]_2 + \underset{excess}{6Bu^tOH} \longrightarrow Co[Zr_2(OPr^i)_6(OBu^t)_3]_2 + 6Pr^iOH\uparrow}$$

The above reaction was repeated with a large excess of t-butanol, removing the liberated isopropanol continuously in the form of an azeotrope with the solvent benzene. The reaction appeared to become very slow towards the end and was continued until isopropanol could not be detected in the distillate. The final reaction can be represented by the following equation:

$$\mathrm{Co[Zr_2(OPr^i)_9]_2 + \underset{excess}{12Bu^tOH} \longrightarrow Co[Zr_2(OPr^i)_3(OBu^t)_6]_2 + 12Pr^iOH\uparrow}$$

A product of similar composition could be prepared with $\mathrm{Am^tOH}$, but it took comparatively more hours of refluxing.

All these new bimetallic alkoxides are highly soluble in common organic solvents (such as benzene, carbon tetrachloride and n-hexane), but have lower solubility in parent alcohols. However, the methoxy derivative is completely insoluble in methanol as well as in other organic solvents.

The analytical data and physical characteristics of these derivatives are given in Table I.

Infrared Spectral Studies

The infrared spectra of the bimetallic alkoxides $\mathrm{Co[Zr_2(OR)_9]_2}$ have been measured in Nujol mull in the range 4000–400 $\mathrm{cm^{-1}}$ (Table II). The characteristic [12, 13] features of their infrared spectra are appearance of bands, for ν(C–O)M in the range 1010–1170 $\mathrm{cm^{-1}}$; for ν(Zr–O) in the range 530–610 $\mathrm{cm^{-1}}$; and for ν(Co–O) in the range 405–480 $\mathrm{cm^{-1}}$.

Visible Spectral Studies

Cobalt(II) forms complexes in three common geometrical forms: (i) tetrahedral, (ii) trigonal bipyramidal and (iii) octahedral, which can be distinguished by electronic spectral studies [14]. For example, tetrahedral cobalt(II) exhibits three bands in the ranges: ~3000–5000 $\mathrm{cm^{-1}}$ ($\mathrm{^4A_2(F) \xrightarrow{\nu_1} {}^4T_2(F)}$), 5500 $\mathrm{cm^{-1}}$ ($\mathrm{^4A_2(F) \xrightarrow{\nu_2} {}^4T_1(F)}$), and ~15 000 $\mathrm{cm^{-1}}$ ($\mathrm{^4A_2(F) \xrightarrow{\nu_3} {}^4T_1(P)}$). In the contrast, the trigonal bipyramidal compound $\mathrm{Co(Me_6tren)Cl^+}$ (D_{3h} symmetry) shows four bands at ~5500 $\mathrm{cm^{-1}}$ ($\mathrm{^4E''(F) \leftarrow {}^4A_2'(F)}$), 15 600–16 100 $\mathrm{cm^{-1}}$ ($\mathrm{^4A_2'(P) \leftarrow {}^4A_2'(F)}$), 12 500 $\mathrm{cm^{-1}}$ ($\mathrm{^4E'(F) \leftarrow {}^4A_2'(F)}$), and 2000 $\mathrm{cm^{-1}}$ ($\mathrm{^4E''(P) \leftarrow {}^4A_2'(F)}$). The transition for octahedral cobalt(II) shows three bands in the ranges: ~8000 $\mathrm{cm^{-1}}$ ($\mathrm{^4T_{1g}(F) \xrightarrow{\nu_1} {}^4T_{2g}}$), ~17 000 $\mathrm{cm^{-1}}$ ($\mathrm{^4T_{1g}(F) \xrightarrow{\nu_2} {}^4A_{2g}}$), and ~19 500 $\mathrm{cm^{-1}}$ ($\mathrm{^4T_{1g}(F) \xrightarrow{\nu_3} {}^4T_{1g}(P)}$).

The compounds synthesised during the present investigation show visible bands at ~17 500 $\mathrm{cm^{-1}}$ (ν_2) and at ~19 600 $\mathrm{cm^{-1}}$ (ν_3), which indicate a distorted octahedral (D_{4h}) symmetry. The first band (ν_1) is in the near IR region (out of range of the equipment used) and could not be recorded. The various ligand field parameters have been calculated using the Underhill and Billing equation [15] and are given in Table III. A comparison of the observed ligand field of $\mathrm{[Zr_2(OPr^i)_9]^-}$ with the other ligands shows the following trend:

$$\begin{array}{ccccccccc} \mathrm{Br^-} & < & \mathrm{Cl^-} & < & \mathrm{H_2O} & < & \mathrm{Zr_2OPr^i)_9^-} & \leq & \mathrm{NH_3} \\ (649) & & (764) & & (920) & & (949) & & (1020) \end{array}$$

The covalency factor (β) for $\mathrm{Co[Zr_2(OPr^i)_9]_2}$ is less than that ($\beta = 0.85$) for the hexaaquo complex of cobalt(II), indicating a more covalent nature of the compound.

The above observed data favor a distorted octahedral geometry of cobalt(II) and suggest a tridentate nature for the $\mathrm{[Zr_2(OR)_9]^-}$ ligand (Fig. 1); this is

TABLE II. Some Characteristic IR Absorption Frequencies ($\mathrm{cm^{-1}}$) and Room Temperature Magnetic Moments for Bimetallic Alkoxides of Cobalt(II) with Zirconium(IV)

Compound	ν(C–O)M	ν(Zr–O)	ν(Co–O)	μ_{eff} (BM)
$\mathrm{Co[Zr_2(OMe)_9]_2}$	1060s, 1020m	570s, 540w	470wbr, 410wbr	4.89
$\mathrm{Co[Zr_2(OEt)_9]_2}$	1070m, 1050m, 1010w	540wbr, 490wbr	440wbr	5.01
$\mathrm{Co[Zr_2(OPr^n)_9]_2}$	1070m, 1020m	610mbr	450wbr	5.10
$\mathrm{Co[Zr_2(OBu^n)_9]_2}$	1070mw, 1040mbr	580wbr, 530wbr	480br	5.12
$\mathrm{Co[Zr_2(OBu^i)_9]_2}$	1025s	590br, 535wbr	435m, 405w	5.20
$\mathrm{Co[Zr_2(OPr^i)_9]_2}$	1170s, 1040s	580s, 570s, 520m	480wbr, 440wbr	
$\mathrm{Co[Zr_2(OBu^s)_9]_2}$	1120s, 1080s	590wbr, 515s	405wbr	5.08
$\mathrm{Co[Zr_2(OPr^i)_3(OBu^t)_6]_2}$	1030s, 1040w, 1010s	590wbr	470w	5.09
$\mathrm{Co[Zr_2(OPr^i)_3(OAm^t)_6]_2}$	1040mbr, 1110wbr, 1050w	570s	440wbr, 420w	5.11

TABLE III. Electronic Spectral Parameters

Compound	${}^4T_{1g}(F) \xrightarrow{\nu_2} {}^4A_{2g}$ (cm^{-1})	${}^4T_{1g}(F) \xrightarrow{\nu_3} {}^4T_{1g}(P)$ (cm^{-1})	*Dq* (cm^{-1})	*B* (cm^{-1})	β
$Co[Zr_2(OPr^i)_9]_2$	17857	19607	949.53	825	0.73
$Co[Zr_2(OPr^n)_9]_2$	17241	19685	918.34	850	0.75
$Co[Zr_2(OEt)_9]_2$	17605	19531	936.42	828	0.74
$Co[Zr_2(OBu^n)_9]_2$	17482	19685	930.63	842	0.75
$Co[Zr_2(OBu^i)_9]_2$	17482	19841	930.96	853	0.76
$Co[Zr_2(OBu^s)_9]_2$	17342	19705	923.46	848	0.75
$Co[Zr_2(OPr^i)_3(OAm^t)_6]_2$	17241	19685	918.34	850	0.75

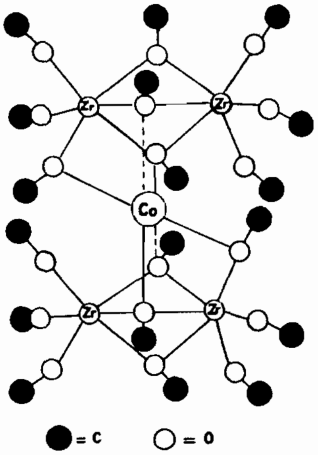

Fig. 1. Structure proposed for $Co[Zr(OPr^i)_9]_2$.

TABLE IV. Variable Temperature Magnetic Susceptibility Data for $Co[Zr_2(OPr^i)_9]_2$

K	$\chi_g \times 10^6$ (cgs)	$\chi_M \times 10^6$ (cgs)	$\chi_M^{corr} \times 10^6$ (cgs)	μ_{eff} (BM)
80.5	28.179	41919.82	42815.0	5.25
86.5	26.080	38798.32	39693.5	5.24
110.0	20.220	30080.52	30975.7	5.22
120.0	18.485	27499.12	28394.3	5.22
131.0	16.815	25015.32	25910.5	5.21
140.0	15.633	23256.72	24151.9	5.20
150.0	14.551	21646.52	22541.7	5.20
175.0	12.286	18277.92	19173.1	5.18
180.0	11.880	17673.42	18568.6	5.17
190.5	11.192	16650.02	17545.2	5.17
220.5	9.587	14262.92	15158.1	5.17
295.0	6.900	10391.03	11286.2	5.16

similar to the one proposed [1] for $K[Zr_2(OPr^i)_9]$ and to the structure of $K[U_2(OCMe_3)_9]$ determined recently [16]. In the alcoholysis of metal alkoxides [1], it has been observed that the terminal groups are, in general, replaced with greater facility than the bridging alkoxy groups; keeping this in view, the number of bridging and terminal isopropoxy groups in the proposed structure are in general conformity with the results of alcoholysis experiments.

Magnetic Studies

For cobalt(II) (d^7) high spin complexes, the theoretical magnetic moment values (μ_{eff}) are expected to be 3.90 BM, but the actual experimental values generally fall in the range of 4.4–5.2 BM due to orbital contributions [17] and vary with the stereochemistry (4.4–4.8 for tetrahedral, 4.8–5.4 for trigonal bipyramidal and 4.7–5.2 for octahedral) of the complex. For low spin complexes, these values generally lie in the range 1.7–2.9 BM (2.2–2.9 BM for tetrahedral, 1.7–2.0 for trigonal bipyramidal and 1.8–2.8 BM for octahedral geometries).

The magnetic moments of the new cobalt(II) bimetallic alkoxides have been measured at room temperature and lie within the range 5.09 ± 0.11 BM (Table II); these values are in agreement with the reported range for high spin octahedral geometry.

Variable temperature magnetic susceptibility data for $Co[Zr_2(OPr^i)_9]_2$ measured in the range of 80.6–295 K (Table IV) exhibit temperature-dependent magnetic moments. The plot of *T vs.* $1/\chi_M^{corr}$ is a straight line in accordance with Curie–Weiss law with a positive value of θ; this is suggestive of the presence of a weak cooperative phenomenon. The magnetic moment values increase slightly with decrease of temperature, possibly due to ferromagnetic interaction.

Acknowledgements

We wish to thank Prof. S. Mitra, T.I.F.R. Bombay, India for providing facilities in his laboratories to measure the magnetic susceptibilities. One of the authors (R.K.D.) gratefully acknowledges the financial assistance from the D.S.T. New Delhi.

References

1 D. C. Bradley, R. C. Mehrotra and D. P. Gaur, 'Metal Alkoxides', Academic Press, London, 1978.

2 R. C. Mehrotra and J. V. Singh, *J. Coord. Chem., 13,* 273(1984).

3 R. C. Mehrotra, *Coord. Chem.* (IUPAC), *21,* 113 (1981).

4 A. Mehrotra and R. C. Mehrotra, *J. Chem. Soc. A,* 1203 (1972).

5 R. C. Mehrotra and J. V. Singh, *Inorg. Chem., 23,* 1046 (1984).

6 R. C. Mehrotra and J. V. Singh, *Z. Anorg. Chem., 512,* 221 (1984).

7 R. C. Mehrotra and J. V. Singh, *Can. J. Chem., 62,* 1003 (1984).

8 J. D. Mackenzie, *J. Non-Cryst. Solid, 48,* 1 (1982).

9 R. C. Mehrotra and M. M. Agrawal, *J. Chem. Soc. A,* 1026 (1967).

10 A. I. Vogel, 'A Text Book of Quantitative Inorganic Analysis', Longman, London, 1978.

11 R. C. Mehrotra, *J. Ind. Chem. Soc., 30,* 585 (1953).

12 L. J. Bellamy. 'The Infrared Spectra of Complex Molecules', Chapman and Hall, London, 1975.

13 K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds', Wiley-Interscience, London, 1970.

14 A. B. P. Lever, 'Inorganic Electronic Spectroscopy', 2nd edn., Elsevier, London, 1984.

15 A. E. Underhill and D. E. Billing, *Nature (London), 210,* 834 (1966).

16 F. A. Cotton, D. O. Marler and W. Schwotzer, *Inorg. Chem., 23,* 4211 (1984).

17 B. N. Figgis and J. Lewis, *Prog. Inorg. Chem., 6,* 37 (1964).