Synthesis, Reactions, Spectral (IR and Visible) and Magnetic Studies of Bimetallic Alkoxides Containing Co(μ-OR)₃M (M=Nb or Ta) Bridging Units

Raj Kumar Dubey, Anirudh Singh, and Ram Charan Mehrotra*
Department of Chemistry, University of Rajasthan, Jaipur 302004, India
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Interactions of $CoCl_2$ with $K\{M(OPr^i)_6\}$ in 1:2 molar ratio in Pr^iOH and C_6H_6 result in products with the composition $[Co\{M(OPr^i)_6\}_2]^{[42]}$ (M=Nb or Ta) in quantitative yields. Interchange reactions of these isopropoxide derivatives with alcohols of varying steric bulk (e.g., MeOH, EtOH, Pr^nOH, Bu^nOH, and Bu^tOH, or Am^tOH) yield derivatives of composition, $[Co\{M(OR)_6\}_2]$ (R=Me, Et, Pr^n, and Bu^s); $[Co\{M(OPr^i)_3(OBu^s)_3\}_2]$; $[Co\{M(OPr^i)_5-(OBu^t)\}_2]$ and $[Co\{M(OPr^i)_2(OR)_4\}_2]$ (R=Bu^t or Am^t). All these novel compounds have been characterized by elemental analyses and molecular weight determinations as well as by infrared, visible spectral and magnetic studies.

Experimental

In contrast to the well-known chemistry of alkoxy derivatives of earlier transition metals,[1,2] alkoxides of later transition metals have received only scanty attention possibly due to their insolubility and polymeric nature. One of the fascinating developments in the alkoxide chemistry of later '3d' metals (including cobalt) has been the synthesis[3] of soluble, monomeric, volatile, bimetallic alkoxides, $[M\{Al(OR)_4\}_n]$ (where $n=3$, when M=Cr(III), Fe(III) and $n=2$, when M=Co(II), Ni(II), Cu(II)) in our laboratories. The $\{Al(OR)_4\}^-$ has proved to be an excellent ligand and depicts an interesting variation in its ligating behavior; e.g., it acts as a bidentate ligand towards Cr(III),[4] and Fe(III),[5] but it exhibits a tridentate ligating behavior with Co(II)[6] and Cu(II);[7] and with Ni(II),[8] an ambidentate (both bi- and tri-) behavior has been observed. By contrast, bimetallic alkoxide derivatives containing both early and later d-block elements bridged by alkoxy groups have been much less studied. These bimetallic alkoxides could be expected to find useful applications (i) as homogeneous catalysts,[9] (ii) in ceramic industry[10] and (iii) in organic syntheses. In view of the above, we report herein some aspects of bimetallic alkoxide derivatives of cobalt(II) containing Co(μ-OR)₃M (M=Nb or Ta) bridging units.

Experimental

General. Stringent precautions were taken to exclude atmospheric moisture from the glasswares, solvents and the reagents were purified by literature methods prior to use.

Anhydrous $CoCl_2$ was prepared by heating the hydrated $CoCl_2 \cdot 6H_2O$ in a current of dry HCl gas and analyzed. Analysis for $CoCl_2$: Found: Co, 45.41; Cl, 54.59; Calcd: Co, 45.39; Cl, 54.61%.

Niobium and tantalum isopropoxides were prepared[11] by passing dry NH_3 gas in a solution of their pentachlorides (Fluka) in isopropyl alcohol.

Cobalt in bimetallic derivatives was estimated gravimetrically[12] as $[Co(C_5H_5N)_4](NCS)_2$ and niobium (tantalum) was estimated as oxide. From the solution of the bimetallic alkoxides in hydrochloric acid, hydrated niobium (tantalum) oxide is first precipitated with only slight excess of aqueous ammonia and cobalt is then precipitated as $[Co(C_5H_5N)_4](NCS)_2$ by addition of NH_4SCN followed by pyridine to the filtrate. Blank determinations with known solutions showed that niobium (tantalum) tends to be about 2% higher and cobalt about 1—2% lower under these conditions.

Alcohols were determined by an oxidimetric method.[13]

The infrared spectra were recorded in the range 4000—400 cm^{-1} on a Perkin-Elmer 557 spectrometer using Nujol mull. The visible spectra have been recorded on a Pye-Unicam SP8-100 spectrophotometer. The magnetic susceptibilities were measured on a Gouy balance using $Hg[Co(NCS)_4]$ as standard. The magnetic moments, μ_{eff}, were calculated by the expression: $\mu_{eff}=2.84\sqrt{\chi_M^{Corr} \cdot T}$ (where χ_M^{Corr} is the molar susceptibility corrected for the diamagnetism of the constituent atoms by the use of Pascal's constants). Helium gas compressor was used for low temperature susceptibility measurements. Molecular weights were determined cryoscopically.

Syntheses and Reactions. Methods of synthesis of $[Co\{M(OPr^i)_6\}_2]$ derivatives and some of their typical reactions are described briefly below. The amount of chemicals used in each reaction, the yield of the product, the elemental analyses and other details are given in Table 1.

A. Preparation of $[Co\{M(OPr^i)_6\}_2]$ (M=Nb or Ta). A weighed amount of $K\{M(OPr^i)_6\}$ in benzene (40 cm^3) was added to a suspension of $CoCl_2$ in Pr^iOH (30 cm^3). The reaction mixture was refluxed for≈5 h and precipitated KCl was removed by filtration. The excess of solvent was distilled out and the concentrate kept at room temperature; purple-red crystalline solid $[Co\{M(OPr^i)_6\}_2]$ crystallized out. The product was further recrystallized unchanged either from Pr^iOH–PhH or hexane.

B. Reactions of $[Co\{M(OPr^i)_6\}_2]$. (i) **With Excess of MeOH (at Room Temperature).** To a benzene solution of $[Co\{M(OPr^i)_6\}_2]$, an excess of MeOH was added. The reaction mixture was stirred for≈6 h, during which the color changed from purple-red to violet. After removal of the volatiles under reduced pressure a violet colored solid product of composition, $[Co\{M(OMe)_6\}_2]$ was isolated, which could be recrystallized unchanged from hexane.

(ii) **With Excess of EtOH (at Room Temperature).** EtOH was added to a benzene solution of $[Co\{Ta(OPr^i)_6\}_2]$ and stirred for≈6 h at room temperature. The solvent was removed under reduced pressure to yield a violet red solid

Table 1. Synthesis and Alcohol Interchange Reactions of [Co{M(OPr^i)$_6$}$_2$] (M=Nb or Ta)

Reaction Number	Reactant/g	Product/g$^{e)}$	Physical state	Analysis Found (Calcd)			Pr^{i}OH/g Liberated Found (Calcd)
				Co	M	OR	
1	CoCl$_2$+K{Nb(OPr^i)$_6$} 0.86 6.47	[Co{Nb(OPr^i)$_6$}$_2$]$^{a)}$ 5.68 (6.31)	Purple red crystalline solid	5.87 (6.18)	19.55 (19.48)	73.60 (74.34)	
2	[Co{Nb(OPr^i)$_6$}$_2$]+MeOH 1.15 ≈35 cm^3	[Co{Nb(OMe)$_6$}$_2$]$^{b)}$ 0.65 (0.74)	Violet solid	9.54 (9.55)	30.73 (30.11)	—	
3	[Co{Nb(OPr^i)$_6$}$_2$]+EtOH 1.68 ≈40 cm^3	[Co{Nb(OEt)$_6$}$_2$]$^{c)}$ 1.30 (1.38)	Violet solid	7.38 (7.50)	23.60 (23.65)	68.90 (68.84)	
4	[Co{Nb(OPr^i)$_6$}$_2$]+Pr^{n}OH 1.54 ≈40 cm^3	[Co{Nb(OPr^n)$_6$}$_2$]$^{c)}$ 1.50 (1.54)	Violet crystalline solid	5.91 (6.18)	19.65 (19.48)		
5	[Co{Nb(OPr^i)$_6$}$_2$]+Bu^{n}OH 1.02 ≈45 cm^3	[Co{Nb(OBu^n)$_6$}$_2$]$^{c)}$ 1.10 (1.17)	Violet crystalline solid	5.26 (5.25)	16.62 (16.56)	—	
6	[Co{Nb(OPr^i)$_6$}$_2$]+Bu^{s}OH 1.60 ≈40 cm^3	[Co{Nb(OBu^s)$_6$}$_2$]$^{d)}$ 1.85 (1.87)	Violet red solid	5.19 (5.25)	17.50 (16.56)	—	0.81 (0.80)
7	[Co{Nb(OPr^i)$_6$}$_2$]+Bu^{t}OH 1.54 ≈25 cm^3	[Co{Nb(OPr^i)$_5$(OBu^t)}$_2$]$^{c)}$ 1.57 (1.58)	Violet red solid	5.96 (6.00)	18.98 (18.92)	60.16 (60.18)	—
8	[Co{Nb(OPr^i)$_6$}$_2$]+Bu^{t}OH 1.61 ≈45 cm^3	[Co{Nb(OPr^i)$_2$(OBu^t)$_4$}$_2$]$^{d)}$ 1.71 (1.79)	Violet red solid	5.50 (5.53)	17.60 (17.43)	22.10 (22.17)	0.81 (0.81)
9	CoCl$_2$+K{Ta(OPr^i)$_6$} 0.49 4.37	[Co{Ta(OPr^i)$_6$}$_2$]$^{a)}$ 3.85 (4.26)	Purple red crystalline solid	5.16 (5.22)	32.30 (32.03)	62.54 (62.75)	
10	[Co{Ta(OPr^i)$_6$}$_2$]+MeOH 1.41 ≈45 cm^3	[Co{Ta(OMe)$_6$}$_2$]$^{b)}$ 0.95 (0.98)	Violet solid	7.32 (7.43)	46.39 (46.62)	—	
11	[Co{Ta(OPr^i)$_6$}$_2$]+EtOH 1.18 ≈40 cm^3	[Co{Ta(OEt)$_6$}$_2$]$^{c)}$ 1.50 (1.53)	Violet solid	6.17 (6.13)	37.55 (37.64)	56.04 (56.24)	
12	[Co{Ta(OPr^i)$_6$}$_2$]+EtOH 1.24 ≈25 cm^3	[Co{Ta(OPr^i)$_2$(OEt)$_4$}$_2$]$^{b)}$ 1.05 (1.11)	Violet red solid	5.48 (5.79)	36.24 (35.56)	—	
13	[Co{Ta(OPr^i)$_6$}$_2$]+Pr^{n}OH 1.20 ≈35 cm^3	[Co{Ta(OPr^n)$_6$}$_2$]$^{c)}$ 1.18 (1.20)	Violet crystalline solid	5.22 (5.22)	32.12 (32.03)	—	—
14	[Co{Ta(OPr^i)$_6$}$_2$]+Bu^{n}OH 1.45 ≈40 cm^3	[Co{Ta(OBu^n)$_6$}$_2$]$^{c)}$ 1.54 (1.66)	Violet crystalline solid	4.49 (4.54)	27.79 (27.87)	—	—
15	[Co{Ta(OPr^i)$_6$}$_2$]+Bu^{s}OH 1.10 ≈25 cm^3	[Co{Ta(OPr^i)$_3$(OBu^s)$_3$}$_2$]$^{b)}$ 1.17 (1.18)	Violet red solid	4.83 (4.85)	30.67 (29.81)	29.17 (29.20)	—
16	[Co{Ta(OPr^i)$_6$}$_2$]+Bu^{s}OH 1.41 ≈25 cm^3	[Co{Ta(OPr^i)$_2$(OBu^s)$_4$}$_2$]$^{c)}$ 1.49 (1.54)	Violet red solid	4.80 (4.74)	30.05 (29.13)	18.82 (19.03)	—
17	[Co{Ta(OPr^i)$_6$}$_2$]+Am^{t}OH 1.58 ≈50 cm^3	[Co{Ta(OPr^i)$_2$(OAm^t)$_4$}$_2$]$^{d)}$ 1.85 (1.90)	Violet red solid	4.38 (4.35)	26.78 (26.72)	17.40 (17.45)	0.65 (0.66)

a) Yield of the crystallized product and molecular weight of [Co{Nb(OPr^i)$_6$}$_2$], Found: 901; Calcd (954) and for [Co{Ta(OPr^i)$_6$}$_2$] Found: 1015; Calcd (1130). b) Reaction was carried out at room temperature. c) Reaction was carried out in refluxing C$_6$H$_6$ (without azeotropic removal of Pr^{i}OH). d) Reaction was carried out in refluxing C$_6$H$_6$ with azeotropic removal of Pr^{i}OH. e) Stoichiometric yield in parenthesis.

product of composition [Co{Ta(OPr^i)$_2$(OEt)$_4$}$_2$].

(iii) **With EtOH, Pr^{n}OH, and Bu^{n}OH in Refluxing Benzene.** Interaction of a benzene solution of [Co{M(OPr^i)$_6$}$_2$] with excess of EtOH followed by refluxing for≈6 h, resulted the change in color from purple red to violet. Removal of the solvent under reduced pressure afforded a solid of composition [Co{M(OEt)$_6$}$_2$] which could be purified unchanged by recrystallization from hexane.

Derivatives of n-propyl and butyl alcohols were prepared similarly.

(iv) **With Excess of Bu^{s}OH at Room Temperature.** An excess of s-butyl alcohol was added to a benzene solution of [Co{Ta(OPr^i)$_6$}$_2$] and the resulting reaction mixture was stirred for≈6 h. The removal of the solvent produced a violet solid of composition [Co{Ta(OPr^i)$_3$(OBu^s)$_3$}$_2$].

(v) **Reaction with Bu^{s}OH in Refluxing Benzene.** To a benzene solution of [Co{Ta(OPr^i)$_6$}$_2$] s-butyl alcohol was added and the reaction mixture was refluxed for ≈6 h. The removal of the solvent under reduced pressure afforded a violet red solid product of composition, [Co{Ta(OPr^i)$_2$(OBu^s)$_4$}$_2$].

(vi) **With Excess of Bu^{s}OH (Azeotropically).** To a solution of [Co{Nb(OPr^i)$_6$}$_2$] in benzene an excess of s-butyl alcohol was added and reaction mixture was refluxed for ≈6 h during which the liberated isopropyl alcohol was collected and estimated. After complete removal of the isopropyl alcohol, the solvent was stripped off under reduced pressure to afford a violet red solid [Co{Nb(OBu^s)$_6$}$_2$].

(vii) **With Excess of Bu^{t}OH (in Refluxing Benzene).** To a benzene solution of [Co{Nb(OPr^i)$_6$}$_2$] t-butyl alcohol
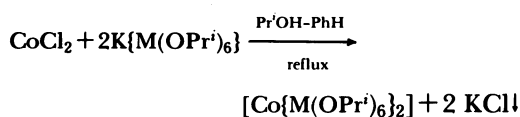
was added and refluxed for $\approx$6 h. After removal of the solvent under reduced pressure and drying a violet red solid product of composition, $[Co\{Nb(OPr^i)_5(OBu^t)\}_2]$ was obtained.

(viii) With Excess of Bu^{t}OH/Am^{t}OH (Azeotropically). $[Co\{Nb(OPr^i)_6\}_2]$ was dissolved in benzene and excess of t-butyl alcohol was then added. The reaction mixture was continued to reflux for $\approx$25 h, with continuous removal of the liberated isopropyl alcohol. When the liberation of isopropyl alcohol ceased off, the volatiles were removed and the product was dried under reduced pressure to afford violet red solid of composition, $[Co\{Nb(OPr^i)_2(OBu^t)_4\}_2]$.

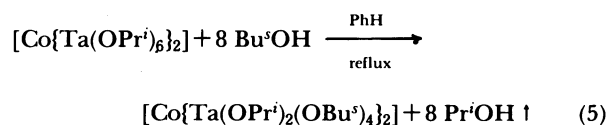A similar procedure was employed for the preparation of $[Co\{Ta(OPr^i)_2(OAm^t)_4\}_2]$.
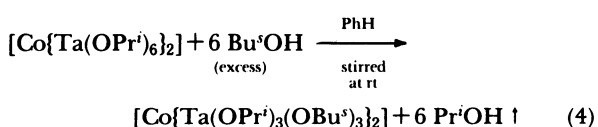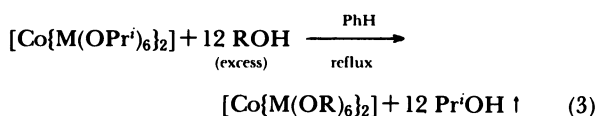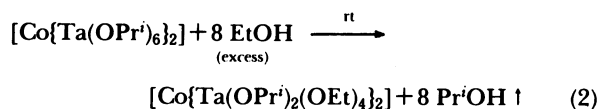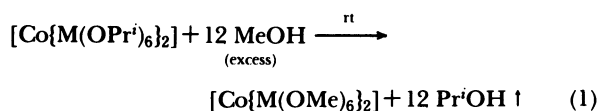
Results and Discussion

Bis(hexaisopropoxy) derivatives $[Co\{M(OPr^i)_6\}_2]$ (M=Nb or Ta) have been synthesized by the reactions of anhydrous cobalt(II) chloride with $K\{M(OPr^i)_6\}$ in 1:2 molar ratio in Pr^{i}OH and C_6H_6:

$$CoCl_2 + 2K\{M(OPr^i)_6\} \xrightarrow[\text{reflux}]{\text{Pr}^i\text{OH-PhH}}$$

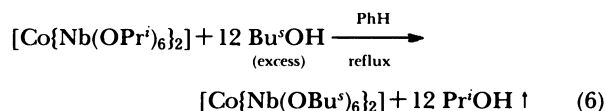$$[Co\{M(OPr^i)_6\}_2] + 2\ KCl\downarrow$$

Products from the above reactions have been isolated in quantitative yields and purified by recrystallization either from Pr^{i}OH-PhH or hexane. These bimetallic isopropoxides are purple red crystalline solids and depict monomeric behavior (cryoscopically) in benzene. On heating even under reduced pressure, these appear to disproportionate into the corresponding volatile isopropoxide, $M(OPr^i)_5$ and non-volatile, $\{Co(OPr^i)_2\}_n$.
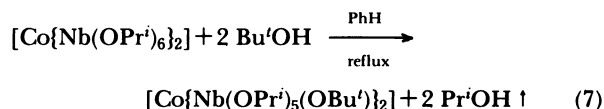
Alcoholysis reactions of these bimetallic isopropoxides $[Co\{M(OPr^i)_6\}_2]$ with different alcohols have shown interesting results. The extent of substitution reactions vary with experimental conditions and the bulk of the reacting alcohol; these are indicated by the following equations:
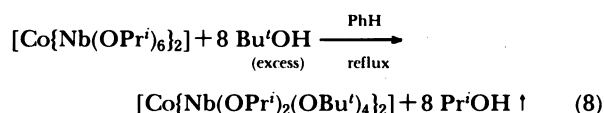
$$[Co\{M(OPr^i)_6\}_2] + 12 \underset{\text{(excess)}}{\text{MeOH}} \xrightarrow{\text{rt}}$$

$$[Co\{M(OMe)_6\}_2] + 12\ Pr^iOH\uparrow \qquad (1)$$

$$[Co\{Ta(OPr^i)_6\}_2] + 8 \underset{\text{(excess)}}{\text{EtOH}} \xrightarrow{\text{rt}}$$

$$[Co\{Ta(OPr^i)_2(OEt)_4\}_2] + 8\ Pr^iOH\uparrow \qquad (2)$$

$$[Co\{M(OPr^i)_6\}_2] + 12 \underset{\text{(excess)}}{\text{ROH}} \xrightarrow[\text{reflux}]{\text{PhH}}$$

$$[Co\{M(OR)_6\}_2] + 12\ Pr^iOH\uparrow \qquad (3)$$

$$[Co\{Ta(OPr^i)_6\}_2] + 6 \underset{\text{(excess)}}{\text{Bu}^s\text{OH}} \xrightarrow[\substack{\text{stirred} \\ \text{at rt}}]{\text{PhH}}$$

$$[Co\{Ta(OPr^i)_3(OBu^s)_3\}_2] + 6\ Pr^iOH\uparrow \qquad (4)$$

$$[Co\{Ta(OPr^i)_6\}_2] + 8\ Bu^sOH \xrightarrow[\text{reflux}]{\text{PhH}}$$

$$[Co\{Ta(OPr^i)_2(OBu^s)_4\}_2] + 8\ Pr^iOH\uparrow \qquad (5)$$

However, Reaction 5 also could be pushed to completion if the liberated isopropyl alcohol is removed azeotropically with benzene:

$$[Co\{Nb(OPr^i)_6\}_2] + 12 \underset{\text{(excess)}}{\text{Bu}^s\text{OH}} \xrightarrow[\text{reflux}]{\text{PhH}}$$

$$[Co\{Nb(OBu^s)_6\}_2] + 12\ Pr^iOH\uparrow \qquad (6)$$

Reactions of $[Co\{Ta(OPr^i)_6\}_2]$ with an excess of t-butyl alcohol in benzene at room temperature showed no evidence of reaction. However, when the reactions were carried out in refluxing benzene without azeotropic removal of isopropyl alcohol, two moles of isopropyl alcohol could be replaced and the analyses of the product corresponded to the formulae $[Co\{Nb(OPr^i)_5(OBu^t)\}_2]$:

$$[Co\{Nb(OPr^i)_6\}_2] + 2\ Bu^tOH \xrightarrow[\text{reflux}]{\text{PhH}}$$

$$[Co\{Nb(OPr^i)_5(OBu^t)\}_2] + 2\ Pr^iOH\uparrow \qquad (7)$$

Further, the reactions of $[Co\{Nb(OPr^i)_6\}_2]$ with an excess of t-butyl alcohol in benzene under azeotropic conditions gave only mixed derivative of composition $[Co\{Nb(OPr^i)_2(OBu^t)_4\}_2]$ even after $\approx$25 h of fractionation:

$$[Co\{Nb(OPr^i)_6\}_2] + 8 \underset{\text{(excess)}}{\text{Bu}^t\text{OH}} \xrightarrow[\text{reflux}]{\text{PhH}}$$

$$[Co\{Nb(OPr^i)_2(OBu^t)_4\}_2] + 8\ Pr^iOH\uparrow \qquad (8)$$

The reactions with Am^{t}OH were slower in comparison to Bu^{t}OH and required $\approx$30 h of fractionation to yield product of the composition $[Co\{Ta(OPr^i)_2(OAm^t)_4\}_2]$.

The above alcoholysis experiments indicate that the ease of replacement of isopropoxy groups in $[Co\{M(OPr^i)_6\}_2]$ decreases with the size and ramification of the alkyl group. The extent of replacement increases under refluxing conditions. However, even when attempt is made to shift the equilibrium by continuous removal of Pr^{i}OH, the reactions can not be pushed to completion with tertiary alcohols.

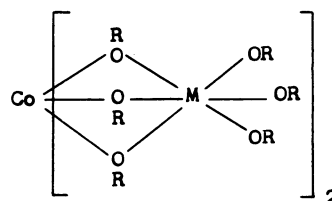These alcoholysis results as well as physico-chem-

Fig. 1. Proposed structure for $[Co\{M(OR)_6\}_2]$ (M=Nb or Ta).

Table 2.   Room Temperature Magnetic Moments and Some Characteristic IR
Absorption Frequencies (cm^{-1}) for [Co{M(OR)$_6$}$_2$] (M=Nb or Ta)

S. No.	Compound	μ_{eff}/BM	$\nu_{(C-O)M}$	$\nu_{(M-O)}$	$\nu_{(Co-O)}$
1	[Co{Nb(OMe)$_6$}$_2$]	4.85	1120 mw, 1130 mw, 1050 s	595 wbr, 530 wbr	460 wbr
2	[Co{Ta(OMe)$_6$}$_2$]	4.90	1165 mbr, 1065 s, 1150 mbr	595 wbr, 510 wbr	465 wbr
3	[Co{Nb(OEt)$_6$}$_2$]	4.90	1165 s, 1030 s, 900 w, 1070 m, 1050 m	610 mbr, 580 wbr, 550 wbr	420 wbr
4	[Co{Ta(OEt)$_6$}$_2$]	5.06	1160 s, 1120 s, 1090 wbr, 1050 w	610 wbr, 590 wbr	480 wbr
5	[Co{Nb(OPr^n)$_6$}$_2$]	5.12	1130 m, 1080 mbr, 1000 wbr	610 wbr, 580 mbr	470 wbr, 450 w
6	[Co{Ta(OPr^n)$_6$}$_2$]	5.11	1155 s, 1115 s, 995 m, 935m	585 m, 565 w	455 w, 410 wbr
7	[Co{Nb(OBu^n)$_6$}$_2$]	5.11	1110 wm, 960 m, 1020 wm	570 wbr, 510 wbr	430 w
8	[Co{Ta(OBu^n)$_6$}$_2$]	5.07	1150 m, 1110 s, 1050s, 970 w	610 m, 560 w	480 wbr
9	[Co{Nb(OPr^i)$_6$}$_2$]	5.08	1170 s, 1140 s, 1030 m, 990 s	595 s, 540 w	475 wbr
10	[Co{Ta(OPr^i)$_6$}$_2$]	5.07	1150 m, 1120 s, 1020 w, 900 s, 935 m	580 mbr, 600 w	450 w
11	[Co{Nb(OBu^s)$_6$}$_2$]	5.01	1160 s, 1120 s, 1020 s, 995 s, 940 m	590 s, 560 m	465 m, 410 w
12	[Co{Ta(OPr^i)$_2$(OBu^t)$_4$}$_2$]	4.94	1175 w, 1135 s, 1110 s, 1065 s, 965 s	565 m, 550 mbr	425 wbr

ical (magnetic and spectroscopic) properties described later can be explained on the basis of the plausible structure (Fig. 1) for these bimetallic species.

On making actual models of the above structures, it becomes apparent that out of the three bridging alkoxy groups per niobium (tantalum) atom, one would be in a rather strained state; this is reflected in the alcoholysis results, where four of the six isopropoxy groups per niobium (tantalum) atom tend to behave differently from the remaining two. Further steric crowding around niobium (tantalum) atoms in derivatives like [Co{(OPr^i)$_2$(OBu^t)Nb(OBu^t)$_3$}$_2$] appears to hinder any further alcoholysis with excess tertiary alcohol, but in the corresponding less crowded structures as in [Co{(OPr^i)$_2$(OBu^n)Nb(OBu^n)$_3$}$_2$], further replacement with excess Bu^{n}OH could be expected and is actually observed.

All these new bimetallic cobalt(II) alkoxides are colored (purple-red/violet) solids which are highly soluble in organic solvents such as benzene, carbon tetrachloride and hexane, but these exhibit lower solubility in parent alcohols except the methoxide derivatives which are highly soluble in methanol also. It may be pertinent to note that whereas the methoxides of most of the metals (e.g., Al, Ga, Ti, and Zr) are insoluble in organic solvents, methoxides of niobium and tantalum are quite readily soluble possibly due to their monomeric nature.

Infrared Spectral Studies. The infrared spectra (in the range 4000—400 cm^{-1}) of these new bimetallic alkoxides exhibited structurally significant absorption bands[1,14-16] (Table 2) at 1180—900 cm^{-1} for $\nu_{(C-O)M}$ and

Table 3.   Visible Spectral[a] Data of Bimetallic Alkoxide of Cobalt(II) with Nb(V) or Ta(V)

| S. No.	Compound	$^4T_{1g}(F) \xrightarrow{\nu_3} {}^4T_{1g}(P)$ $10^{-3}\,\nu_{max}$/cm^{-1}
1	[Co{Nb(OPr^i)$_6$}$_2$][b]	18.0, 19.3 (sh)
2	[Co{Ta(OPr^i)$_6$}$_2$]	(i) 18.0, 19.8 (sh) (ii) 18.5 (Pyridine)
3	[Co{Nb(OBu^s)$_6$}$_2$]	18.1, 19.5 (sh)
4	[Co{Ta(OEt)$_6$}$_2$]	18.1, 19.7 (sh)
5	[Co{Nb(OBu^n)$_6$}$_2$]	18.1, 19.6 (sh)
6	[Co{Nb(OMe)$_6$}$_2$]	17.5, 19.6 (sh)
7	[Co{Ta(OMe)$_6$}$_2$]	17.5, 19.6 (sh)
8	[Co{Ta(OPr^n)$_6$}$_2$]	17.4, 19.7 (sh)
9	[Co{Ta(OPr^i)$_2$(OBu^t)$_4$}$_2$]	17.8, 19.7 (sh)

a) All spectra recorded in benzene unless otherwise indicated.   b) Only in the case of [Co{Nb(OPr^i)$_6$}$_2$] (see the text), an additional band was observed at 14.9×10^3 cm^{-1}, which can be ascribed to $^4T_{1g}(F)$ $\xrightarrow{\nu_2}$ $^4A_{2g}(F)$.

at 610—510 cm^{-1} for $\nu_{(M-O)}$ (M=Nb or Ta) and at 480—410 cm^{-1} for $\nu_{(Co-O)}$.

Visible Spectral Studies. The visible spectra of cobalt(II) bimetallic derivatives studied herein showed a multiple band (asymmetric) (Table 3) in the region 17.8×10^3 cm^{-1} which may assigned[17,18,20] as $^4T_{1g}$-(F) $\xrightarrow{\nu_3}$ $^4T_{1g}$(P) transition and the shoulder on the higher frequency side in the region 19.5×10^3 cm^{-1} being assigned to spin forbidden transitions to doublet states derived from the free ion ^2G and ^2H terms, which are characteristic of octahedral geometry.[17,19] The $^4A_{2g}$(F) $\xleftarrow{\nu_2}$ $^4T_{1g}$(F) transition is not normally

observed in most of the cobalt(II) derivatives, being formally a two electron transition. However, only the spectrum of $[Co\{Nb(OPr^i)_6\}_2]$ in visible region did show a very weak band at 14.9×10^3 cm^{-1} (sh) possibly due to the ν_2 transition.

The value of Dq for $[Co\{Nb(OPr^i)_6\}_2]$ has been calculated to be 795 cm^{-1} by using Underhill and Billing equation[21] and the ligand $\{Nb(OPr^i)_6\}^-$ can be placed in the following spectrochemical order:

$$Br^- < Cl^- < \{Nb(OPr^i)_6\}^- < H_2O < NH_3$$
$$(649) \quad (764) \quad (795) \quad (920) \quad (1020)$$
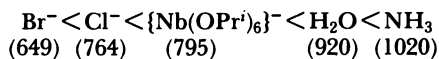
The nephelauxetic ratio (β) is 0.71 for $[Co\{Nb-(OPr^i)_6\}_2]$ which is less than that (0.85) for $\{Co-(H_2O)_6\}^{2+}$ ion, indicating a more covalent nature of the bimetallic derivative.

Magnetic Studies. For high spin octahedral cobalt(II) derivatives, magnetic moment values are expected to lie in the range of 4.7—5.3 BM, depending upon the extent of orbital contribution.[22] The room temperature magnetic moment values for new cobalt(II) bimetallic derivatives are in the range 5.01 ± 0.11 BM (Table 2), which are in agreement with the values reported for cobalt(II) in octahedral geometry.

The variable temperature data for $[Co\{Ta(OPr^i)_6\}_2]$ have been measured in the temperature range 14.4—295 K; the calculated values of χ_M (including correction of 545×10^{-6} CGS) are 200340 (16.4), 180490 (17.8), 152700 (21.0), 132860 (25.2), 113670 (28.8), 75960 (43.6), 36930 (86.6), 23700 (134), 10930 (295), with temperatures in parenthesis. The plot of $1/\chi_M{}^{Corr}$ versus T is a straight line obeying the Curie-Weiss law. The magnetic moment values increase slightly (from 5.07 to 5.28 BM) with decrease of temperature (from 295 to 16.4 K) resulting in a positive value of θ and showing the presence of weak cooperative phenomenon.

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