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Precursours for Mixed Metal Oxides Nanoparticles : Synthesis and Characterization of Heterobimetallic Alkoxide of Butyltin(IV) containing Alkoxometallate Ligands

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ABSTRACT : The metathesis reaction of $KM(OR)_4$ or $KM_2(OEt)_9$ with anhydrous $BuSnCl_3$ afford heterobimetallic alkoxide $BuSn\{M(OR)_4\}_nCl_{3-n}$ [where M = Sb, R = Et, n = 1 (**1**); M = Sb, R = Et, n = 2 (**2**); M = Sb, R = Et, n = 3 (**3**); M = Al, R = CH_2Bu^t, n = 1 (**4**);M = Al, R = CH_2Bu^t, n = 2 (**5**); M = Al, R = CH_2Bu^t, n = 3 (**6**)]; and $BuSn\{M_2(OEt)_9\}Cl_2$ [Where M = Ti (**7**); M = Zr (**8**); M = Sn (**9**)]. IR, ^1H, ^{27}Al, and ^{119}Sn NMR studies as well as elemental analysis have been used to describe all of the derivatives.

Keywords: Heterobimetallic Butyltin(IV) derivatives, alkoxide coordination compounds, Butyltin(IV) alkoxometallates.

1. Introduction

Since the early 1950s, the advantages of utilizing monometal alkoxides alone or in mixtures have been well acknowledged. In 1971, complexation processes in the latter systems were predicted [1]. Ceramists, however, found that a large number of these heterometallic complex alkoxides had been previously described in 1987 [2a-c]. The benefits of using heterometal alkoxides as precursors were demonstrated by Mehrotra [3a-d] in 1988. He also proposed a few such systems that would be useful, even for aerogels.

Numerous heterometal alkoxides with the general formula of type $M\{Al(OPr^i)4\}_x$ $\{Ta(OPr^i)_6\}_y$ $\{Zr_2(OPr^i)_9\}_z$ have been successfully synthesized [4–11]. It was feasible to produce a molecular precursor corresponding to the desired material by using the formula Xn−x−y−z, where n and X are simple ligands such as alkoxide/β diketonate/carboxylate moieties and M is a core element of valency. A growing body of research has shown that the final materials produced by using these presynthesized heterometallic derivatives are more homogeneous than those produced by using combinations of component metal alkoxides [12-13].

Ulrich [14] noted that ceramists have benefited much from chemists and ceramists working together more closely. Furthermore, as seen by the publishing of a growing number of articles as well as review articles, the broad applicability of metal alkoxides in general and heterometal alkoxides in particular has led to an unparalleled surge in research activity in these disciplines [15-23]. Indeed, until about ten years ago, the identity of heterometallic alkoxides was viewed with some skepticism because it was primarily determined by elemental analyses, molecular weights in solution, and spectroscopic (primarily NMR) data in addition to their volatillizability, which may be explained by the "ion-pair" effect. Fortunately, actual X-ray crystallographic studies are now gradually verifying practically all of the structures envisioned on this basis [20, 24].
This research reports on results on butyltin (IV) heterometallic isopropoxide species. Our groundbreaking work on heterometallic alkoxide system is now extended to organometallic moieties.Because the heterometallic alkoxides of butyltin (IV) that were produced are volatile and soluble, the current study is especially important because they could serve as good starting points for the synthesis of mixed metal oxide systems using both sol-gel and MOCVD techniques.

2. Experimental Methodology

Every experiment was conducted in a completely anhydrous environment. After being oven dried at 130 to 140 degrees Celsius, the glassware was either cooled in a desiccator that held fused calcium chloride or it was sufficiently shielded from air moisture using guards and side tubes that contained self-indicating silica gel. By using standard procedures, every solvent was dried and purified [25].

$BuSnCl_3$(Sigma aldrich) was distilled (b.p. 93°C/10 mm) before use. $Sb(OEt)_3$ [26], $Al(OCH_2Bu^t)_3$[27], $Zr(OEt)_4$ [28], $Ti(OEt)_4$ [29] and $Sn(OEt)_4$ [30] were prepared by the literature procedures. Antimony determined volumetrically [31] and aluminium was

determined by the oxime method [31]. Titanium, tin, zirconium were determined gravimetrically [31] as their oxides. Chloride was estimated by Volhard's method [31]. Potasiumalkoxometallate : $KSb(Et)_4$ [32], $KAl(OCH_2Bu^t)_4$ [27], $KTi_2(OEt)_9$ [33], $KZr_2(OEt)_9$ [34] and $KSn_2(OEt)_9$ [35] were prepared according to the procedure described in the literature.
NMR (^1H, ^{27}Al and ^{119}Sn) spectra were recorded on JEOL AL 300 FT NMR spectrometer in $CDCl_3$ solution. IR spectra (4000-200 cm^{-1}) were recorded as Nujol mulls using CsI optics on a Nicolet Magna 550 spectrophotometre.

2.1 Preparation of heterobimetallic derivatives of butyltin(IV)

Due to the near similarity of the synthetic processes for the heterobimetallic derivatives discussed here, only one derivative's production is discussed here; the analytical and preparative data for all other derivatives are compiled in Table 1.

2.1.1 $BuSn\{Sb(OEt)_4\}Cl_2$

A freshly created $KSb(OEt)_4$ benzene (~25 ml) solution [prepared by reacting K (0.17 g, 4.56 mmol) with $Sb(OEt)_3$ (1.17 g, 4.56 mmol) in ethyl alcohol (~10 ml) and benzene (~15 ml)] was added gradually to a pre-made benzene (~25 ml) solution of $BuSnCl_3$ (1.28 g, 4.56 mmol). After that, the reaction mixture was heated under reflux for around six hours. By filtering, the precipitated KCl (0.34g, 4.56 mmol) was eliminated. When volatiles were eliminated from the filtrate while the pressure was lowered, the title derivative a colorless semisolid (2.05g, 82% was obtained. As shown in Table 1, derivatives (2) through (9) were likewise made by a comparable reaction employing the proper reaction in the required molar ratio.

3. Result and Discussion

Through salt elimination processes in benzene, various heterometallic alkoxide coordination systems of organotin have been synthesized, utilizing the proper alkoxometallic ligand in the necessary molar ratios as shown by the following equation.

$$BuSnCl_3 + K\{M_x(OR)_y\}_z \longrightarrow BuSn\{M_x(OR)_y\}Cl_{3-z}\} + zKCl$$

M=Sb, x=1, R = Et, y=4, z=1 (**1**),
M=Sb, x=1, R = Et, y=4, z=2 (**2**),
M=Sb, x=1, R = Et, y=4, z=3 (**3**),
M=Al, x=1, R = CH_2Bu^t, y=4, z=1 (**4**),
M=Al, x=1, R = CH_2Bu^t, y=4, z=2 (**5**),
M=Al, x=1, R = CH_2Bu^t, y=4, z=3 (**6**),
M=Ti, x=2, R = Et, y=9, z=1 (**7**),
M=Zr, x=2, R = Et, y=9, z=1 (**8**),
M=Sn, x=2, R = Et, y=9, z=1 (**9**)

All of the derivatives, from (1) to (9), are colorless, soluble in organic solvents and, sensitive to moisture. All derivatives were identified as monomeric using molecular weight measurements. The primary reason for the failure of efforts to create a crystal that is suitable for crysatallography was the nature of the derivatives.

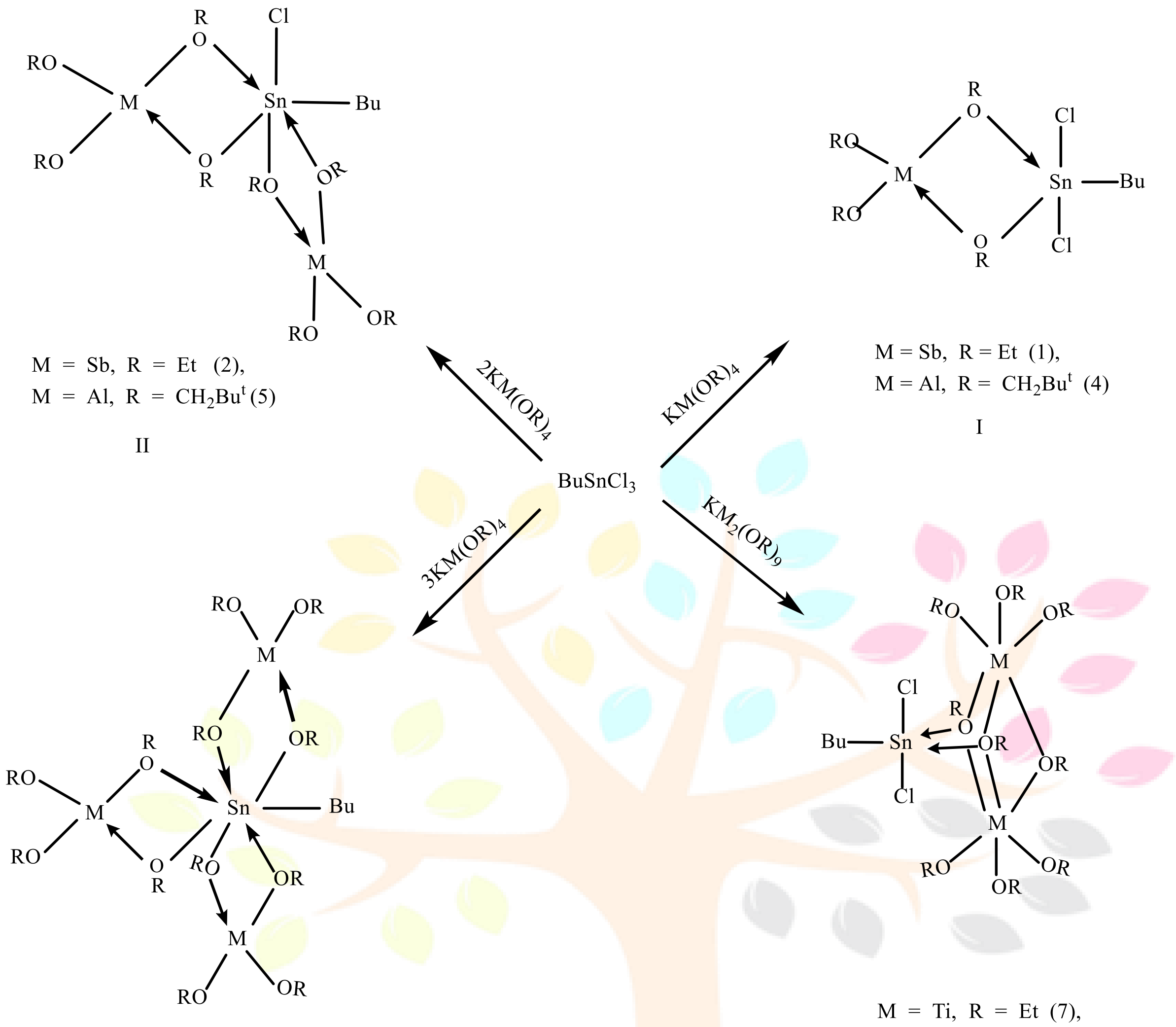
4. Spectral studies

Derivatives (**1**) to (**9**) exhibit infrared absorptions characteristic of metal attached alkoxy group in the regions 1135 - 1020 (terminal alkoxy), 1015-965 (bridging alkoxy), The metal-oxygen stretching mode appeared in the region 680-540 cm^{-1} [6-11, 36-38]
^1H NMR spectra of (**1**)-(**3**) and (**7**)-(**9**) exhibit broad peaks in the regions (δ,ppm) 1.18-1.38 ppm and 1.41-1.53 ppm for terminal and bridging ethoxy group, respectively. Signals due to methylene proton appear as two multiplate in the regions 3.97-4.72 ppm and 4.42-4.89 ppm, which is consistent with the presence of ethoxy fragments in terminal and bridging environments.
Methyl proton signals for CH_2Bu^t in (**4**)-(**6**) appear to be partially buried within the signals due to BuSn moiety and methylene proton signals appear at 3.28-3.35 ppm region. Derivatives (**1**) to (**9**) exhibit multiplate in the regions 0.91-0.95 ppm region due to methyl proton of butyltin moiety.The methylene proton of butyltin appear as a broad signal at 1.18-1.36 ppm which is hidden in derivatives (**1**)-(**3**) & (**7**)-(**9**) within the signals due to ethoxy methyl protons.

^{27}Al NMR spectra of (**4**),(**5**) and (**6**) show signals at δ 63, 68 and 57 ppm respectively, which are consistent with tetra coordinate [11,39,40] aluminium.
The derivatives (**1**),(**4**),(**7**),(**8**) and (**9**) exhibit sharp ^{119}Sn NMR signal at δ -310, -318, -321, -324 and -326 ppm respectively consistent with penta-coordinated tin (IV) [41] as shown in scheme-I.Six coordinated nature (scheme-I) of tin [42-43] in derivatives (**2**) and (**5**) is supported by the appearance of signals at δ -422 and -418 ppm respectively.The derivatives (**3**) and (**6**) exhibit signals at δ -590 and -517 ppm respectively consistent with structure (scheme-I) involving seven coordinated tin [44]. All spectral data of the derivatives (**1**)-(**9**) are detail in Table 2.

5. Suggested structures

Even though it would be premature to determine the precise connectivity of different alkoxometallate ligands in the systems under study in the absence of X-ray crystallographic data for these derivatives, the observed data for the derivatives (1)–(9) and the available X-ray structural data on a number of heterometallic alkoxides [45–52] tend to favor the structure (I)–(IV) shown in Scheme 1.



M = Sb, R = Et (1),
M = Al, R = CH_2Bu^t (4)

I

M = Sb, R = Et (2),
M = Al, R = CH_2Bu^t (5)

II

M = Sb, R = Et (3),
M = Al, R = CH_2Bu^t (6)

III

M = Ti, R = Et (7),
M = Zr, R = Et (8),
M = Sn, R = Et (9)

IV

Scheme-I

Table 1 : Some analytical and physical data for derivatives (1) - (9)

Reactants (g;mmol)			**Product (Mol. formula) (g, mmol) (%, state)**	**Liberated KCl (g,mmol)**	**% Analysis Found (Calc.)**						**M.wt. Found (Calc.)**
					Sn	**Sb/Al/Ti/Zr**	**C**	**H**	**O**	Cl	
$BuSnCl_3$ (1.28, 4.56)	K (0.17, 4.56)	$Sb(OCH_2CH_3)_3$ (1.17, 4.56)	$\{C_{12}H_{29}O_4Sn.Sb\}Cl_2$ (**1**) (2.05, 4.56) (82, semisolid)	(0.34, 4.56)	21.01 (21.63)	21.98 (22.19)	25.95 (26.26)	5.11 (5.33)	11.32 (11.65)	12.10 (12.94)	558 (548)
$BuSnCl_3$ (1.28, 4.56)	K (0.71, 9.12)	$Sb(OCH_2CH_3)_3$ (4.68, 9.12)	$\{C_{20}H_{49}O_8Sn.Sb_2\}$ Cl (**2**) (2.96, 4.56)(80, semisolid)	(1.36, 9.12)	14.10 (14.56)	29.58 (29.87)	29.01 (29.46)	5.92 (6.06)	15.22 (15.70)	4.01 (4.35)	842 (815)
$BuSnCl_3$ (1.28, 4.56)	K (1.60, 13.68)	$Sb(OCH_2CH_3)_3$ (10.54, 13.68)	$\{C_{28}H_{69}O_{12}Sn.Sb_3\}$(**3**) (3.84, 4.56) (78, semisolid)	(0.23, 13.68)	10.24 (10.97)	33.14 (33.77)	30.91 (31.08)	6.21 (6.43)	17.24 (17.77)	--	1097 (1081)
$BuSnCl_3$ (1.28, 4.56)	K (0.17, 4.56)	$Al(OCH_2Bu^t)_3$ (1.31, 4.56)	$\{C_{24}H_{53}O_4Sn.Al\}Cl_2$ (**4**) (2.32, 4.56) (82, semisolid)	(0.34, 4.56)	18.92 (19.07)	4.18 (4.34)	46.18 (46.31)	8.27 (8.58)	10.01 (10.28)	11.14 (11.42)	654 (622)
$BuSnCl_3$ (1.28, 4.56)	K (0.71, 9.12)	$Al(OCH_2Bu^t)_3$ (5.26, 9.12)	$\{C_{44}H_{97}O_8Sn.Al_2\}$Cl (**5**) (3.32, 4.56) (76, semisolid)	(1.36, 9.12)	12.04 (12.33)	5.28 (5.63)	54.74 (54.91)	10.05 (10.16)	13.14 (13.30)	3.21 (3.69)	984 (962)
$BuSnCl_3$ (1.28, 4.56)	K (1.60, 13.68)	$Al(OCH_2Bu^t)_3$ (11.83, 13.68)	$\{C_{64}H_{141}O_{12}Sn.Al_3\}$ (**6**) (4.38, 4.56) (74, semisolid)	(0.26, 4.48)	8.94 (9.11)	6.04 (6.22)	58.74 (59.02)	10.62 (10.91)	14.58 (14.74)	-	1362 (1302)
$BuSnCl_3$ (1.28, 4.56)	K (0.17, 4.56)	$Ti(OCH_2CH_3)_4$ (4.16, 9.12)	$\{C_{22}H_{54}O_9Sn.Ti_2\}Cl_2$ (**7**) (2.69, 4.56) (79, viscous liquid)	(0.34, 4.56)	15.56 (15.87)	12.58 (12.79)	35.18 (35.32)	7.09 (7.28)	19.10 (19.25)	9.16 (9.49)	754 (748)
$BuSnCl_3$ (1.28, 4.56)	K (0.17, 4.56)	$Zr(OCH_2CH_3)_4$ (4.95, 9.12)	$\{C_{22}H_{54}O_9Sn.Zr_2\}Cl_2$ (**8**) (3.04, 4.56) (80, semisolid)	(0.34, 4.56)	14.10 (14.22)	21.45 (21.85)	31.42 (31.65)	6.42 (6.51)	17.12 (17.25)	8.18 (8.50)	845 (834)
$BuSnCl_3$ (1.28, 4.56)	K (0.17, 4.56)	$Sn(OCH_2CH_3)_4$ (5.45, 9.12)	$\{C_{22}H_{54}O_9Sn_3\}Cl_2$ (**9**) (3.11, 4.56) (77, semisolid)	(0.34, 4.56)	39.95 (40.02)	-	29.55 (29.70)	5.92 (6.12)	16.05 (16.18)	7.46 (7.98)	895 (889)

Table-2: The following is a list of significant spectrum data for the derivatives (1) - (9):

Derivatives	**IR** (Nujol, cm^{-1})	**NMR** (δ,ppm)		
		^{1}**H**	^{119}**Sn**	^{27}**Al**
1	319 υ(Sn-Cl), 515, 540 υ(Sb-O), 580 υ(Sn-O), 581 υ(Sn-C), 970, 1020 υ(C-O)	0.91 (m, 3H, $Sn(CH_2)_3C\mathbf{H_3}$), 1.18 (m, 12H, $(OCH_2C\mathbf{H_3})_t$ + $Sn(C\mathbf{H_2})_3CH_3$), 1.41 (m, 6H, $(OCH_2C\mathbf{H_3})_b$), 3.97 (m, 4H, $(OC\mathbf{H_2}CH_3)_t$), 4.42 (m, 4H, $(OC\mathbf{H_2}CH_3)_b$)	10	
2	375 υ(Sn-Cl), 520, 542 υ(Sb-O), 582 υ(Sn-O), 584 υ(Sn-C), 980, 1035 υ(C-O)	0.92 (m, 3H, $Sn(CH_2)_3C\mathbf{H_3}$), 1.20 (m, 18H, $(OCH_2C\mathbf{H_3})_t$ + $Sn(C\mathbf{H_2})_3CH_3$), 1.44 (m, 12H, $(OCH_2C\mathbf{H_3})_b$), 3.99 (m, 8H, $(OC\mathbf{H_2}CH_3)_t$), 4.44 (m, 8H, $(OC\mathbf{H_2}CH_3)_b$)	422	
3	518, 544 υ(Sb-O), 584 υ(Sn-O), 585 υ(Sn-C), 985, 1080 υ(C-O)	0.94 (m, 3H, $Sn(CH_2)_3C\mathbf{H_3}$), 1.22 (m, 24H, $(OCH_2C\mathbf{H_3})_t$ + $Sn(C\mathbf{H_2})_3CH_3$), 1.46 (m, 18H, $(OCH_2C\mathbf{H_3})_b$), 4.02 (m, 12H, $(OC\mathbf{H_2}CH_3)_t$), 4.48 (m, 12H, $(OC\mathbf{H_2}CH_3)_b$)	590	
4	322 υ(Sn-Cl), 582 υ(Sn-C), 586 υ(Sn-O), 640, 670 υ(Al-O), 1090, 1095 υ(C-O)	0.91 (m, 39H, $OCH_2C(C\mathbf{H_3})_{3(t)}$ + $OCH_2C(C\mathbf{H_3})_{3(b)}$ + $Sn(CH_2)_3C\mathbf{H_3}$), 1.20 (m, 6H, $Sn(C\mathbf{H_2})_3CH_3$), 3.28 (br, 8H, $OC\mathbf{H_2}C(CH_3)_3$)	318	3
5	377 υ(Sn-Cl), 584 υ(Sn-C), 584 υ(Sn-O), 662, 682 υ(Al-O), 992, 1120 υ(C-O)	0.92 (m, 75H, $OCH_2C(C\mathbf{H_3})_{3(t)}$ + $OCH_2C(C\mathbf{H_3})_{3(b)}$ + $Sn(CH_2)_3C\mathbf{H_3}$), 1.22 (m, 6H, $Sn(C\mathbf{H_2})_3CH_3$), 3.30 (br, 16H, $OC\mathbf{H_2}C(CH_3)_3$)	418	8
6	582 υ(Sn-C), 586 υ(Sn-O), 660, 684 υ(**Al**-O), 1010, 1135 υ(C-O)	0.92 (m, 111H, $OCH_2C(C\mathbf{H_3})_{3(t)}$ + $OCH_2C(C\mathbf{H_3})_{3(b)}$ + $Sn(CH_2)_3C\mathbf{H_3}$), 1.24 (m, 6H, $Sn(C\mathbf{H_2})_3CH_3$), 3.32 (m, 24H, $OC\mathbf{H_2}C(CH_3)_3$)	517	7
7	322 υ(Sn-Cl), 548, 575 υ(Ti-O), 582 υ(Sn-O), 583 υ(Sn-C), 970, 1010 υ(C-O)	0.94 (m, 3H, $Sn(CH_2)_3C\mathbf{H_3}$), 1.24 (m, 24H, $(OCH_2C\mathbf{H_3})_t$ + $Sn(C\mathbf{H_2})_3CH_3$), 1.48 (m, 9H, $(OCH_2C\mathbf{H_3})_b$), 4.20 (m, 12H, $(OC\mathbf{H_2}CH_3)_t$), 4.48 (m, 6H, $(OC\mathbf{H_2}CH_3)_b$)	321	
8	320 υ(Sn-Cl), 535, 560 υ(Zr-O), 584 υ(Sn-O), 585 υ(Sn-C), 985, 1030 υ(C-O)	0.95 (m, 3H, $Sn(CH_2)_3C\mathbf{H_3}$), 1.30 (m, 24H, $(OCH_2C\mathbf{H_3})_t$ + $Sn(C\mathbf{H_2})_3CH_3$), 1.50 (m, 9H, $(OCH_2C\mathbf{H_3})_b$), 4.32 (m, 12H, $(OC\mathbf{H_2}CH_3)_t$), 4.52 (m, 6H, $(OC\mathbf{H_2}CH_3)_b$)	324	
9	324 υ(Sn-Cl), 558, 580υ(Sn-O), 582 υ(Sn-C), 995, 1120 υ(C-O)	0.92 (m, 3H, $Sn(CH_2)_3C\mathbf{H_3}$), 1.35 (m, 24H, $(OCH_2C\mathbf{H_3})_t$ + $Sn(C\mathbf{H_2})_3CH_3$), 1.53 (m, 9H, $(OCH_2C\mathbf{H_3})_b$), 4.80 (m, 12H, $(OC\mathbf{H_2}CH_3)_t$), 4.85 (m, 6H, $(OC\mathbf{H_2}CH_3)_b$)	326, -560	

6. Conclusion

Heterobimetallic alkoxide coordination compounds of butyltin(IV) have been prepared and characterized by elemental analysis, spectroscopic studies and molecular weight measurements. Efforts to develop crystallographically suitable crystals were not successful, mainly due to the nature of the compounds, such inherent difficulties in the X-ray crystallographic structural elucidation of heterometallic alkoxide containing large number of alkoxo groups have also been experienced by renowned researchers in this field, such as Bradley [53], Caultor and Ptalzgraf [54].

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