40 **RESEARCH PAPER** JANUARY, 40–43 JOURNAL OF CHEMICAL RESEARCH 2007

Synthesis, spectroscopic, magnetic and volatility studies of the first copper(II) nonaalkoxodistannates

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Derivatives of the types [CCuI{$Sn_2(OR)_9$}] (R = Et, **1**; R = Pr^i, **2**) and [Cu{$Sn_2(OR)_9$}$_2$] (R = Et, **3**; R = Pr^i, **4**) have been synthesised by the reactions of anhydrous $CuCl_2$ with $NaSn_2(OR)_9$ (R = Et, Pr^i) in 1: 1 and 1: 2 molar ratios in benzene, respectively. The chloro(nonaalkoxodistannato)-copper(II) complexes **1–2** yield, *via* chloride replacement reactions with a variety of monodentate (*e.g.*, EtO^-, Pr^iO^-) or chelating [*e.g.*, $Al(OEt)_4^-$, $Al(OPr^i)_4^-$, $Zr_2(OPr^i)_9^-$, and $Nb(OPr^i)_6^-$] ligands, novel heterometallic alkoxides of copper(II). All of the complexes **1–19** are highly moisture-sensitive, coloured solids, that are soluble in typical organic solvents. They are monomeric in benzene solution and are thermally unstable under reduced pressure.

Keywords: copper(II) nonaalkoxodistannates, copper(II) alkoxides, heterometallic alkoxides

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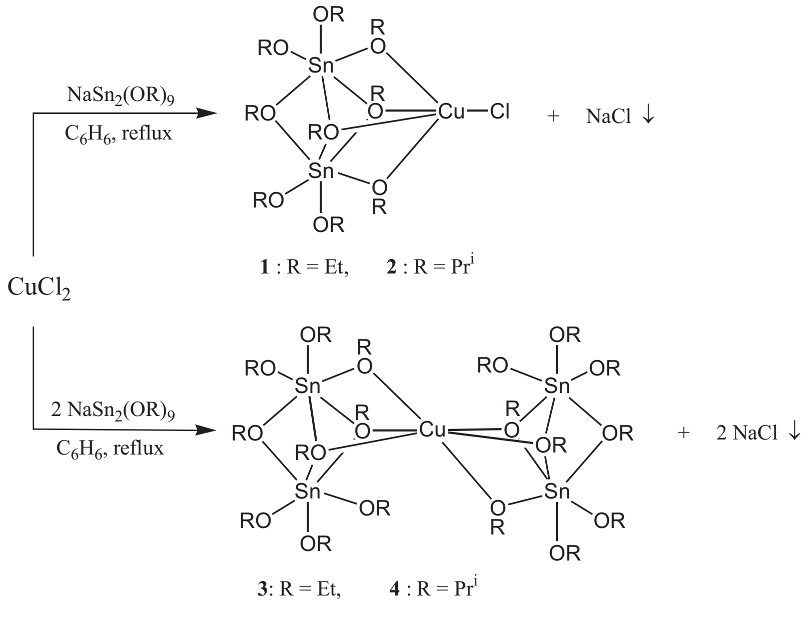
The ligand, $Al(OPr^i)_4^-$, was used for the first time in copper(II) alkoxide chemistry 1984.[1] Later, the hexaisopropoxoniobiate/tantalate,[2a] $M(OPr^i)_6^-$ (M = Nb, Ta), and nonaiso-propoxodizirconate,[2b] $Zr_2(OPr^i)_9^-$, ligands were used to obtain hydrocarbon soluble, volatile and structurally interesting hetero(bi- and tri-) metallic alkoxides of copper(II).[2] Surprisingly, derivatives of copper(II) derived from nonaalkoxodistannate, $Sn_2(OR)_9^-$, ligands are not known, despite the facts that Zr(IV) and Sn(IV) in the six-coordinate state are comparable in size, [Zr(IV) = 0.72Å, Sn(IV) = 0.69Å] and that both $Zr(OPr^i)_4$. Pr^iOH[3] and $Sn(OPr^i)_4$. Pr^iOH[4] are dimeric and isostructural, their alkali metal derivatives $K[Zr_2(OPr^i)_9]$[5] and $K[Sn_2(OPr^i)_9]$[6] exhibit very different behaviour when heated under reduced pressure. For example, the former is volatile[5] and unchanged in analysis, whereas the latter[6] disproportionates into $KOPr^i$ (1 mol) and $Sn(OPr^i)_4$ (2 mol). This contrasting behaviour appears to be due to a stronger chelating capability of $Zr_2(OPr^i)_9^-$ and less electrostatic repulsion amongst its isopropoxo-groups compared to $Sn_2(OPr^i)_9^-$. Such contrasting behaviour between two structurally and compositionally similar nonaalkoxo-dimetallate ligands, prompted us to investigate heteronuclear complexes of copper(II) derived from nonaalkoxodistannate ligands. Additional impetus for the studies of such copper(II) complexes was provided by (i) the potential utility of heterometallic alkoxides as molecular precursors for the sol-gel production of high purity cuprate superconductors and other speciality materials[7] and (ii) tin as modifier for transition metal catalysts to improve their product selectivities.[9] In our continuing research on heterometallic alkoxides,[7c-d,8] we report in this paper for the first time the synthetic, spectroscopic, and magnetic aspects of copper(II) nonaalkoxodistannates.

Results and discussion

Heterobimetallic alkoxides of copper(II) have been synthesised (Scheme 1) by the 1: 1 and 1: 2 interactions of anhydrous $CuCl_2$ with $Na[Sn_2(OR)_9]$ (R = Et, Pr^i) in benzene.

Complexes **1** and **2** have shown their versatility as starting materials for the synthesis of new varieties of hetero(bi- and tri-)metallic alkoxide complexes of copper(II) according to the (Scheme 2). All of these new derivatives are highly moisture-sensitive, coloured solids, soluble in common organic solvents (*e.g.*, C_6H_6, CH_2Cl_2, $CHCl_3$, THF, *etc.*) and monomeric (cryoscopy/ebullioscopy) in benzene solution. Although all of these complexes show no tendency to disproportionate into the component parent alkoxides on being heated under



Scheme 1

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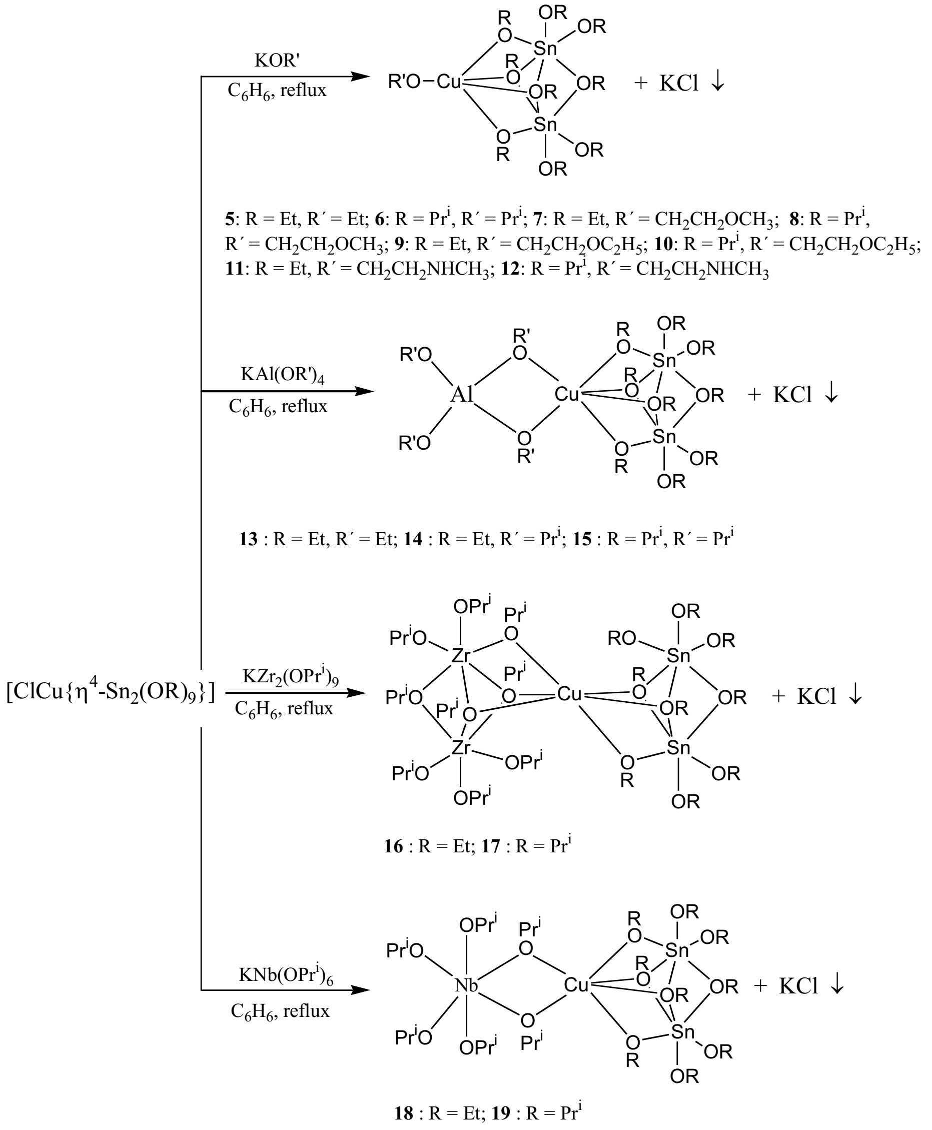

5: R = Et, R′ = Et; **6**: R = Pr^i, R′ = Pr^i; **7**: R = Et, R′ = $CH_2CH_2OCH_3$; **8**: R = Pr^i, R′ = $CH_2CH_2OCH_3$; **9**: R = Et, R′ = $CH_2CH_2OC_2H_5$; **10**: R = Pr^i, R′ = $CH_2CH_2OC_2H_5$; **11**: R = Et, R′ = $CH_2CH_2NHCH_3$; **12**: R = Pr^i, R′ = $CH_2CH_2NHCH_3$

13 : R = Et, R′ = Et; **14** : R = Et, R′ = Pr^i; **15** : R = Pr^i, R′ = Pr^i

16 : R = Et; **17** : R = Pr^i

18 : R = Et; **19** : R = Pr^i

Scheme 2

reduced pressure, nevertheless, they could not be volatilised up to a bath temperature of 360°C under reduced pressure (0.2 mm Hg). Instead a black non-volatile product was left. Under similar experimental conditions the amount of the residual non-volatile materials obtained after heating the complexes **2**, **10**, and **15** up to 360°C at 0.2 mm Hg and their elemental analyses corresponded to the formulations $CuSn_2ClO_3(OPr^i)_3$, $CuSn_2O_5$, and $CuSn_2AlO_5(OPr^i)_3$, respectively. Further analytical details are given in the Experimental section. The formation of these non-volatile species may be explained on the basis of reactions as illustrated in equations (1), (2) and (3), respectively.

Spectral studies

The IR absorptions[10] due to ν(OEt), ν(OPr^i), ν(C–O), ν(Al–O), ν(Sn–O), ν(Zr–O), ν(Nb–O), ν(Cu–O) for hetero(bi- and tri-) metallic complexes **1**–**19** are summarised in Table 2, along with ν(N-H) and ν(C–N)[10] absorptions, respectively, for complexes **11** and **12**.

The electronic spectra of complexes **1**, **2**, **5**–**12** (Table-3) show a single broad band maxima in the region 12579–13717 cm^{-1}, consistent with five-coordinate Cu(II) adopting a distorted trigonal bipyramidal[11,12] geometry involving tetradentate ligation of $Sn_2(OR)_9^-$ and monodentate ligation of Cl^- (Scheme 1) or $^-OR'$ (Scheme 2). By contrast, complexes

$$ClCuSn_2(OPr^i)_9 \xrightarrow[1\ h]{360°C,\ 0.2\ mm\ Hg} CuSn_2ClO_3(OPr^i)_3 + 3\ Pr^i_2O \quad (1)$$

$$[(C_2H_5OCH_2CH_2O)Cu\{Sn_2(OPr^i)_9\}] \xrightarrow[1\ h]{360°C,\ 0.2\ mm\ Hg}$$

$$CuSn_2O_5 + 4.5\ Pr^i_2O + 0.5\ C_2H_5OCH_2CH_2OCH_2CH_2OC_2H_5 \quad (2)$$

$$\downarrow$$

$$CH_2{=}CHOC_2H_5 + 0.5\ H_2O$$

$$\xrightarrow[1\ h]{360°C,\ 0.2\ mm\ Hg} [\{Al(OPr^i)_4\}Cu\{Sn_2(OPr^i)_9\}]$$

$$CuSn_2AlO_5(OPr^i)_3 + 5\ Pr^i_2O \quad (3)$$

3, **4**, **13**–**19** show broad unsymmetrical absorption bands in the region 14005–14706 cm^{-1}, which is characteristic of a $^2E_g \rightarrow {}^2T_{2g}$ transition in a distorted octahedral[13] geometry around the copper(II) ion. These electronic absorption data can be explained in terms of η^3-bonding of $Sn_2(OR)_9^-$ groups (Scheme 1) in **3** and **4**, whereas in complexes **13**–**15**, **18**, **19** $Sn_2(OR)_9^-(\eta^4)$ (Scheme 2) and $Al(OR)_4^-/Nb(OPr^i)_6^-$ (η^2)

(Scheme 2) are bonded in tetradentate and bidentate fashion, respectively. $Sn_2(OR)_9^-$ and $Zr_2(OPr^i)_9^-$ in complexes **16** and **17** are more likely to be tridentedly bonded (Scheme 2). When the electronic spectra of complexes **1**–**19** were recorded in different (coordinating and non-coordinating) solvents (*e.g.*, benzene, tetrahydrofuran, pyridine), only a small blue shift (shorter in wavelength or increase in energy) was observed in the positions of absorption band maxima in the following order: benzene < tetrahydrofuran < pyridine.

The observed magnetic moment (μ_{eff}) data (Table 2) for complexes **1**–**19** are in the 1.84–2.35 BM range, which is higher than the spin only value (1.73 BM) of d^9 copper(II) derivatives, and may be ascribed to mixing of some orbital angular momentum from the excited states *via* spin orbit coupling.[14a,d]

Although we have not been successful in X-ray crystallographic characterisation of at least one of these hetero(bi- and tri-) metallic alkoxides due to the difficulty in obtaining crystallographically suitable crystals, nevertheless the observed physicochemical data are supportive of five-coordinate geometry of Cu(II) in **1, 2,** and **5**–**12**, and an octahedral coordination environment around Cu(II) in **3**,**4**, and **13**–**19**.

Experimental

All manipulations were carried under stringently anhydrous conditions, using quick-fit glass apparatus with interchangeable joints and protected with guard-tubes and side-tubes filled with fused $CaCl_2$. Benzene, *n*-hexane and tetrahydrofuran (Merck, India) were distilled from sodium benzophenone ketyl. Isopropyl alcohol (S.D. Fine Chem. Ltd, India) were refluxed over $Al(OPr^i)_3$ and fractionally distilled. Ethyl alcohol (Jai-Chemicals, India) was first refluxed over ignited CaO and distilled, the distillate was finally refluxed over $Mg(OEt)_2$ and distilled before use. Pyridine (Merck, India) was refluxed over KOH pellets and distilled. $Al(OEt)_3$, $Al(OPr^i)_3$, $Zr(OPr^i)_4.Pr^iOH$, and $Nb(OPr^i)_5$ were prepared by the literature methods.[7d] Sodium nonaalkoxodistannate[15] was prepared by the method described previously. Anhydrous $CuCl_2$ was made by heating $CuCl_2.2H_2O$ under reduced pressure for ~10 h and then analysed for metal and chloride contents [Found: Cu, 47.0; Cl, 52.65%; Calcd.: Cu, 47.3; Cl, 52.7%]. Tin and niobium were determined as their oxides SnO_2, Nb_2O_5, respectively or as mixed metal oxides. Zirconium was precipitated as the mandelate and determined as oxide after ignition. Aluminium was estimated as oxinate,[16] Copper was determined iodometrically, chloride by Volhard's method,[16] and nitrogen by Kjeldhal's method.[16] Ethoxy or isopropoxy contents were determined by an oxidimetric method.[17] IR spectra (4000–400 cm^{-1}) were recorded as Nujol mulls/KBr pellets using CsI optics on a FT-IR spectrophotometer. Electronic spectra were recorded in different solvents using quartz optics on a Cary 50 Bio UV-visible spectrophotometer. Magnetic susceptibility measurements were on a Polytronic Gouy balance (EMP-75) using $Hg[Co(CNS)_4]$ as standard. Molecular weights were determined cryoscopically/ebullioscopically in benzene solution.

Synthesis of hetero(bi- and tri-)metallic alkoxides of copper(II)

Due to similarities in the method of preparation and also for the sake of brevity, preparative details of only three typical derivatives are described. The analytical data and some physical properties of the new compounds are summarised in Table 1.

[ClCu{Sn₂(OEt)₉}] (**1**)**:** The reaction mixture containing anhydrous $CuCl_2$ (0.67 g, 4.98 mmol) and $Na[Sn_2(OEt)_9]$ (3.32 g, 4.98 mmol) in benzene (~60 ml) was stirred at room temperature for ~8 h, during which time the colour of the reaction mixture changed from brown to sea-green. To ensure completion of the reaction, the reaction mixture was finally heated at 40°C for ~2 h. The precipitated NaCl (0.29 g, 4.98 mmol) was removed by filtration. Excess solvent was removed from the filtrate under reduced pressure to obtain a sea-green crystalline solid (3.58 g, 97%). The title compound was purified by recrystallisation from *n*-hexane at –20°C in 2.90 g (78%) yield.

By adopting a procedure similar to that described for **1**, the derivatives **2**, **3** and **4** were prepared by using appropriate quantities of the reactants as shown below for each compound.

2: $CuCl_2$ (0.58 g, 4.30 mmol) and $Na[Sn_2(OPr^i)_9]$ (3.41 g, 4.30 mmol).
3: $CuCl_2$ (0.41 g, 3.04 mmol) and $Na[Sn_2(OEt)_9]$ (4.06 g, 6.10 mmol).
4: $CuCl_2$ (0.40 g, 2.98 mmol) and $Na[Sn_2(OPr^i)_9]$ (4.71 g, 5.96 mmol).

[(CH₃OCH₂CH₂O)Cu{Sn₂(OEt)₉}] (**7**)**:** A solution of $[ClCu\{Sn_2(OEt)_9\}]$ **1** (2.01 g, 2.71 mmol) in benzene (~ 50 ml) was treated with freshly prepared $KOCH_2CH_2OCH_3$ {prepared by reacting potassium metal (0.105 g, 2.81 mgatom) and $CH_3OCH_2CH_2OH$ (0.21 g, 2.76 mmol) in THF (~25 ml), followed by removal of excess of solvent under reduced pressure}. The mixture was stirred ~18 h, during which time the colour of the reaction mixture changed from sea-green to bluish green. Finally the reaction mixture was refluxed for ~3 h to ensure completion of the reaction. KCl (0.21 g, 2.82 mmol) was removed by filtration. Volatile components were removed from the filtrate under reduced pressure to obtain $[(CH_3OCH_2CH_2O)Cu\{Sn_2(OEt)_9\}]$ **7** as an intense green solid in 1.95 g (92%) yield. The compound was purified by recrystallisation from *n*-hexane at –20°C in 1.50 g (71%) yield. By using a similar procedure, the derivatives **5**,**6**, and **8**–**12** were prepared from the required quantities of the appropriate reactants as shown below for each compound:

5: $[ClCu\{Sn_2(OEt)_9\}]$ (2.00 g, 2.69 mmol) and KOEt (0.23 g, 2.73 mmol).
6: $[ClCu\{Sn_2(OPr^i)_9\}]$ (4.22 g, 4.86 mmol) and $KOPr^i$ (0.48 g, 4.88 mmol).
8: $[ClCu\{Sn_2(OPr^i)_9\}]$ (2.01 g, 2.31 mmol) and $KOCH_2CH_2OCH_3$ (0.27 g, 2.36 mmol).
9: $[ClCu\{Sn_2(OEt)_9\}]$ (2.25 g, 3.03 mmol) and $KOCH_2CH_2OC_2H_5$ (0.39 g, 3.04 mmol).
10: $[ClCu\{Sn_2(OPr^i)_9\}]$ (2.30 g, 2.65 mmol) and $KOCH_2CH_2OC_2H_5$ (0.34 g, 2.65 mmol).
11: $[ClCu\{Sn_2(OEt)_9\}]$ (3.98 g, 5.37 mmol) and $KOCH_2CH_2NHCH_3$ (0.61 g, 5.30 mmol).
12: $[ClCu\{Sn_2(OPr^i)_9\}]$ (5.15 g, 5.93 mmol) and $KOCH_2CH_2NHCH_3$ (0.67 g, 5.92 mmol).

[{Al(OEt)₄}Cu{Sn₂(OEt)₉}] (**13**)**:** In a typical experiment, to a benzene (~50 ml) solution of $[ClCu\{Sn_2(OEt)_9\}]$ **1** (2.62 g, 3.53 mmol) was added $KAl(OEt)_4$ {freshly prepared by the interaction of potassium metal (0.14 g, 3.58 mgatom) in ~ 15 ml ethyl alcohol and aluminium ethoxide (0.57 g, 3.53 mmol) in ~ 20 ml benzene and refluxing of the reaction mixture ~2 h, followed by removal of the excess solvent under reduced pressure}. The mixture was stirred at room temperature for ~8 h. During this period, the colour of the solution changed from green to sky blue. To ensure completion of the reaction, the mixture was refluxed ~4 h. Precipitated KCl (0.27 g, 3.62 mmol) was removed by filtration. Volatiles from the filtrate were removed under reduced pressure to afford a sky blue solid (3.10 g, 96%). The compound **13** was purified by recrystallisation from *n*-hexane at –20°C in 2.30 g (71%) yield.

By adopting a procedure similar to that described for **13**, the derivatives **14**–**19** were prepared by using appropriate quantities of the reactants as shown below for each compound.

14: $[ClCu\{Sn_2(OEt)_9\}]$ (2.93 g, 3.95 mmol) and $KAl(OPr^i)_4$ (1.19 g, 3.95 mmol).
15: $[ClCu\{Sn_2(OPr^i)_9\}]$ (1.87 g, 2.15 mmol) and $KAl(OPr^i)_4$ (0.65 g, 2.15 mmol).
16: $[ClCu\{Sn_2(OEt)_9\}]$ (2.10 g, 2.83 mmol) and $KZr_2(OPr^i)_9$ (2.13 g, 2.83 mmol).
17: $[ClCu\{Sn_2(OPr^i)_9\}]$ (1.89 g, 2.18 mmol) and $KZr_2(OPr^i)_9$ (1.64 g, 2.18 mmol).
18: $[ClCu\{Sn_2(OEt)_9\}]$ (2.40 g, 3.23 mmol) and $KNb(OPr^i)_6$ (1.57 g, 3.23 mmol).
19: $[ClCu\{Sn_2(OPr^i)_9\}]$ (3.19 g, 3.67 mmol) and $KNb(OPr^i)_6$ (1.79 g, 3.67 mmol).

Attempted volatilisation under reduced pressure

In typical experiments of volatilisation of complexes **2**, **10**, and **15** under reduced pressure (0.2 mm Hg) up to a bath temperature of 360°C, black non-volatile residues were left, which were analysed in each case as below. **2**; Found: Cu, 12.0; Sn, 44.8; Cl, 7.1; (OPr^i), 31.1%. Calcd.: Cu, 11.3; Sn, 42.3; Cl, 6.3; (OPr^i), 31.6%. **10**; Found: Cu, 16.8; Sn, 63.2.Calcd.: Cu, 16.7; Sn, 62.3%. **15**; Found: Cu, 11.4; Sn, 43.05; Al, 4.85; (OPr^i), 26.05%. Calcd.: Cu, 10.9; Sn, 40.6; Al, 4.6; (OPr^i), 30.29%.

The authors thank Dr P.K. Santra, Chemistry Department, Vanasthali Vidhyapith, Vanasthali (Rajasthan), for help in obtaining magnetic susceptibility data and Mr D.K. Gupta for recording the IR and electronic spectra. N.A. is grateful to the Department of Chemistry, University of Rajasthan, Jaipur and the State Government of Rajasthan for a fellowship under the Special Assistance Programme of the Department.

Received 19 October 2006; accepted 17 January 2007
Paper 06/4237

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