

Chloride and alkoxide alkoxometallates and termetallic isopropoxides of copper(II) *

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Abstract

Synthesis of chloride bimetallic isopropoxides of copper(II), $[\text{ClCu}\{\text{Zr}_2(\text{OCHMe}_2)_9\}]$ and $[\text{ClCu}\{\text{Ta}(\text{OCHMe}_2)_6\}]$, has been achieved and these have proved to be key precursors in the synthesis of novel bi- and ter-metallic alkoxides of copper(II).

Introduction

The chemistry of metal alkoxides is passing through an exciting phase in view of their growing applications for different types of ceramic materials, including superconductor [1]. For the energy efficient sol-gel process, mixtures of metal alkoxides (which can be easily purified by volatilization) offer highly attractive possibilities. The formation of new chemical bonds in the precursor mixtures of alkoxides has been presumed by a number of workers [2,3]. Extensive work in our laboratories [4,5] on the isolation and characterization of a variety of bimetallic alkoxides, therefore, assumes a special significance, as illustrated [6] by a recent preparation of spinel from $[\text{Mg}\{\text{Al}(\text{OCHMe}_2)_4\}_2]$. Additionally, metal alkoxides are often precursors to metal hydrocarbyls or hydrides, e.g. by reaction with a Grignard reagent or H^- .

In view of the above, the possibility of the formation of ter-metallic alkoxides could open new possibilities. Out of beryllium, magnesium, zinc, cadmium and mercury, a volatile ter-metallic alkoxide of only beryllium, e.g., $[\{\text{Al}(\text{OCHMe}_2)_4\}\text{Be}\{\text{Ta}(\text{OCHMe}_2)\}]$ could be synthesized [7], and its stability was ascribed to the smallness of the central beryllium atom.

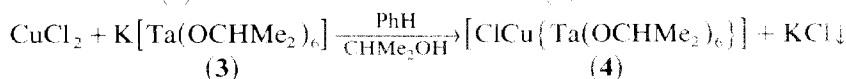
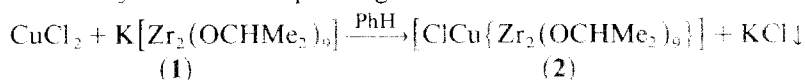
In this paper, we describe the preparation of two chloride isopropoxometallates of copper(II) $[\text{ClCu}\{\text{Zr}_2(\text{OCHMe}_2)_9\}]$ and $[\text{ClCu}\{\text{Ta}(\text{OCHMe}_2)_6\}]$, which have

* Dedicated to Prof. Colin Eaborn on his 65th birthday, as a tribute to his outstanding contributions to organometallic chemistry and his inspiring guidance and support to the younger workers in the field.

been shown to react with alkali metal alkoxides, like $K[OR]$, $K[Al(OCHMe_2)_4]$ and $K[Zr_2(OCHMe_2)_9]$, yielding novel bi- and ter-metallic derivatives of the types $[(RO)Cu\{Zr_2(OCHMe_2)_9\}]$, $[(RO)Cu\{Ta(OCHMe_2)_6\}]$ and $\{[Al(OCHMe_2)_4]Cu\{Zr_2(OCHMe_2)_9\}\}$, $\{[Ta(OCHMe_2)_6]Cu\{Zr_2(OCHMe_2)_9\}\}$ and $\{[Ga(OCHMe_2)_4]Cu\{Zr_2(OCHMe_2)_9\}\}$.

Results and discussion

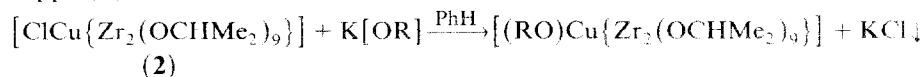
A number of bimetallic isopropoxometallates of copper(II), e.g. $[Cu\{Al(OCHMe_2)_4\}_2]$, $[Cu\{Ta(OCHMe_2)_6\}_2]$, $[Cu\{Zr_2(OCHMe_2)_9\}_2]$ were described recently [8–10]. The reactions of $CuCl_2$ with $K[Zr_2(OCHMe_2)_9]$ (**1**) and $K[Ta(OCHMe_2)_6]$ (**3**) in 1/1 molar ratio in benzene (containing a few drops of $CHMe_2OH$) have been found to yield the corresponding mono-chloride derivatives:



It may be mentioned that the corresponding reaction with $K[Al(OCHMe_2)_4]$ (**5**) tends to give a mixture of $[Cu\{Al(OCHMe_2)_4\}_2]$ and unreacted $CuCl_2$.

The chloride derivatives **2** and **4** are green solids, the identity of which is corroborated by their solubility in common organic solvents (e.g. C_6H_6 , CCl_4 , $CHCl_3$, etc.). Attempts are being continued to elucidate the structural features of these chloride bimetallic isopropoxides by their alcoholysis reactions and more detailed physico-chemical investigations [9,10].

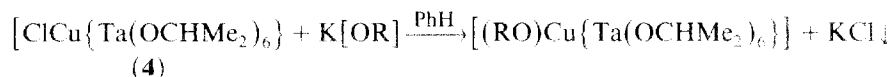
The chlorine in the derivatives **2** and **4** is easily replaceable by alkoxy groups, to afford the corresponding green hydrocarbon-soluble alkoxy-isopropoxometallates of copper(II):



(**2a**, R = Me; **2b**, R = $CHMe_2$;

2c, R = Bu; **2d**, R = $CHMeEt$;

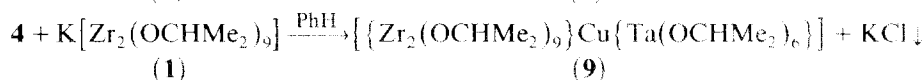
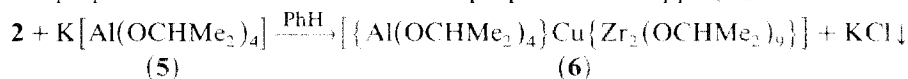
2e, R = CMe_3)



(**4a**, R = Me; **4b**, R = $CHMe_2$;

4c, R = Bu; **4d**, R = $CHMeEt$)

The isolation of **2** and **4** as stable solids has also provided a convenient route for the preparation of novel ter-metallic isopropoxides of copper(II):



All these bi- and ter-metallic alkoxides (Table 1) are highly moisture-sensitive coloured solids or viscous liquids, which, except for the methoxy derivatives, are soluble in hydrocarbon solvents. The ter-metallic isopropoxides can be volatilized unchanged with the exception of the derivative containing the $[\text{Ta}(\text{OCHMe}_2)_6]^-$ moiety, which show a tendency to disproportionation when heated under reduced pressure. Characterization data and physical characteristics of these new complexes are listed in Table 1.

Infrared spectra of these new bi- and ter-metallic isopropoxides of copper(II) exhibit bands characteristic for $\nu(\text{C-O})$, $\nu(\text{Zr-O})$, $\nu(\text{Ta-O})$, $\nu(\text{Al-O}/\text{Ga-O})$, and $\nu(\text{Cu-O})$ in the ranges 1180–940, 620–510, 620–540, 720–690, and 490–410 cm^{-1} [4,11], respectively. In **2** and **4**, the characteristic IR frequencies for $\nu(\text{Cu-Cl})$ appear in the range 360–205 cm^{-1} , which is suggestive of the existence of chloride-bridged [12] five-coordinate species, in addition to the monomeric four-coordinate molecules.

The visible spectra of these chloride- and alkoxide-bimetallic isopropoxides in different organic solvents (C_6H_6 , CHMe_2OH and tetrahydrofuran, thf) show their electronic transitions in the range, 13400–17800 cm^{-1} . The visible spectrum of $[(\text{CHMe}_2\text{O})\text{Cu}\{\text{Zr}_2(\text{CHMe}_2)_9\}]$ displays two incompletely resolved bands at 15400 and 17800 cm^{-1} , similar to those observed [13] for bis(*N*-methylsalicylaldiminato)-copper(II), for which a trigonal bipyramidal structure was proposed. In the case of $[\text{ClCu}\{\text{Zr}_2(\text{OCHMe}_2)_9\}]$, the main band is observed at ca. 13400 cm^{-1} , similar to that at 13200 cm^{-1} reported for $[\text{Cu}(1,2\text{-dimethylimidazole})_3\text{Cl}_2]$, which has been shown to have a distorted trigonal bipyramidal structure [4]. The visible spectra of the termetallic isopropoxides of copper(II) in benzene showed unsymmetrical broad absorption bands, at $(15300 \pm 100) \text{cm}^{-1}$, characteristic of a ${}^2E_g \rightarrow {}^2T_{2g}$ transition in a distorted octahedral geometry around copper(II) [14].

The observed room temperature magnetic moment values for copper(II) termetallic derivatives are observed in the range 1.68–1.78 μ_B , consistent with the theoretical spin-only value (1.73 μ_B) for d^9 systems. However, magnetic moments for the chloride- and alkoxide-bimetallic isopropoxides of copper(II) are slightly lower, 1.58–1.68 μ_B which may possibly be due to antiferromagnetic superexchange in these systems.

The EPR spectra of chloride- and alkoxide-bimetallic isopropoxides recorded at room temperature, as well as at 77 K, show a single sharp resonance at $g_{\parallel} = 2.351$, indicating that these are predominantly monomeric in nature.

Experimental

Apparatus, experimental and analytical procedures, preparation of starting materials, drying of the chemicals, and physical measurements (IR, UV-VIS, and EPR spectral and magnetic) have been described elsewhere [9,10].

Preparation of bi- and ter-metallic isopropoxides of copper(II)

Three types of compounds, chloride-, and alkoxide-bimetallic isopropoxides and ter-metallic isopropoxides of copper(II), have been described in this paper. As the synthetic procedures within each class of compounds are similar, only one typical example of each is given in detail. Results of all the preparations are summarized in Table 1.

Table 1. Analytical and physical characteristics for the novel alkoxide complexes

Reactants (in 1/1 molar ratio)	Product ^a	Yield (%)	Volatility ^b (°C/Torr)	Analysis (%) ^c					μ_{eff} (μ_{B}) (298 K)	
				Cu	Zr	Ta	Al	Ga		
$\text{CuCl}_2 + \text{K}[\text{Zr}_2(\text{OCHMe}_2)_6]$ (1)	$[\text{ClCu}(\text{Zr}_2(\text{OCHMe}_2)_6)]$ (2)	98	Decomposed at -180/0.2	7.68 (7.81)	22.54 (22.43)				4.20 (4.36)	1.68
$2 + \text{K}[\text{OMe}]$	$[(\text{MeO})\text{Cu}(\text{Zr}_2(\text{OCHMe}_2)_6)]$ (2a)	92	180/0.4	7.68 (7.86)	22.80 (22.56)					1.62
$2 + \text{K}[\text{OCHMe}_2]$	$[(\text{CHMe}_2\text{O})\text{Cu}(\text{Zr}_2(\text{OCHMe}_2)_6)]$ (2b)	96	175/0.2	7.15 (7.59)	22.28 (21.80)					1.59
$2 + \text{K}[\text{O}i\text{Bu}]$	$[(i\text{BuO})\text{Cu}(\text{Zr}_2(\text{OCHMe}_2)_6)]$ (2c)	99	185/0.4	7.38 (7.49)	22.02 (21.44)					1.58
$2 + \text{K}[\text{OCHMeEt}]$	$[(\text{CHMe}_2\text{O})\text{Cu}(\text{Zr}_2(\text{OCHMe}_2)_6)]$ (2d)	98	180/0.3	7.41 (7.47)	21.87 (21.44)					1.60
$2 + \text{K}[\text{OCMe}_3]$	$[(\text{CMe}_3\text{O})\text{Cu}(\text{Zr}_2(\text{OCHMe}_2)_6)]$ (2e)	97	190/0.3	7.28 (7.47)	22.02 (21.44)					1.62
$\text{CuCl}_2 + \text{K}[\text{Ta}(\text{OCHMe}_2)_6]$ (3)	$[\text{ClCu}(\text{Ta}(\text{OCHMe}_2)_6)]$ (4)	90	<i>f</i>	9.90 (10.02)	29.01 (28.52)				5.60 (5.59)	1.60
$4 + \text{K}[\text{OMe}]$	$[(\text{MeO})\text{Cu}(\text{Ta}(\text{OCHMe}_2)_6)]$ (4a)	97	<i>f</i>	9.98 (10.08)	29.11 (28.71)					1.58
$4 + \text{K}[\text{OCHMe}_2]$	$[(\text{CHMe}_2\text{O})\text{Cu}(\text{Ta}(\text{OCHMe}_2)_6)]$ (4b)	98	<i>f</i>	9.58 (9.65)	28.25 (27.91)					1.59
$4 + \text{K}[\text{O}i\text{Bu}]$	$[(i\text{BuO})\text{Cu}(\text{Ta}(\text{OCHMe}_2)_6)]$ (4c)	98	<i>f</i>	9.29 (9.45)	27.44 (26.92)					1.58
$4 + \text{K}[\text{OCHMeEt}]$	$[(\text{CHMe}_2\text{O})\text{Cu}(\text{Ta}(\text{OCHMe}_2)_6)]$ (4d)	98	<i>f</i>	9.32 (9.45)	27.32 (26.92)					1.60
$2 + \text{K}[\text{Al}(\text{OCHMe}_2)_4]$ (5)	$[(\text{Al}(\text{OCHMe}_2)_4)\text{Cu}(\text{Zr}_2(\text{OCHMe}_2)_6)]$ (6)	76	185/0.3	6.18 (6.10)	18.03 (17.52)		2.38 (2.59)			1.78
$2 + \text{K}[\text{Ga}(\text{OCHMe}_2)_4]$ (7)	$[(\text{Ga}(\text{OCHMe}_2)_4)\text{Cu}(\text{Zr}_2(\text{OCHMe}_2)_6)]$ (8)	91	179/0.2	5.25 (5.86)	17.22 (16.84)		6.38 (6.43)			1.78
$4 + \text{K}[\text{Zr}_2(\text{OCHMe}_2)_6]$ (1)	$[(\text{Zr}_2(\text{OCHMe}_2)_6)\text{Cu}(\text{Ta}(\text{OCHMe}_2)_6)]$ (9)	94	<i>f</i>	4.66 (4.84)	14.30 (13.89)		14.22 (13.78)			1.68

^a Green solid, unless otherwise stated. ^b % yield of the sublimed/distilled products are indicated in parentheses. ^c Calculated values are given in parentheses. ^d These values include corrections due to copper(II). ^e Isopropoxy content determined by alcoholysis reactions of the parent compound with higher boiling alcohols. ^f Decomposed with disproportionation at 160 °C/0.1–0.2 Torr. ^g Blue-green viscous liquid. ^h Green viscous liquid. ⁱ Blue-green solid.

Preparation of $[\text{ClCu}\{\text{Zr}_2(\text{OCHMe}_2)_9\}]$ (2). To a suspension of CuCl_2 (0.52 g, 3.86 mmol) in benzene (ca. 30 ml) containing few drops of CHMe_2OH was added a solution of $\text{K}[\text{Zr}_2(\text{OCHMe}_2)_9]$ (2.89 g, 3.84 mmol) in benzene (ca. 20 ml). The reaction mixture was heated under reflux for 3 h, whence its colour changed from yellowish to dark green. The precipitated KCl (0.29 g, 3.89 mmol) was removed by filtration. The filtrate was concentrated to ca. 25 ml and left at room temperature overnight to afford a green crystalline solid (3.10 g, 98%).

A similar procedure was adopted for the preparation of **4** (Table 1).

Preparation of $[(\text{CHMe}_2\text{O})\text{Cu}\{\text{Zr}_2(\text{OCHMe}_2)_9\}]$ (2b). A solution of $[\text{ClCu}\{\text{Zr}_2(\text{OCHMe}_2)_9\}]$ (1.45 g, 1.78 mmol) in benzene (ca. 20 ml) was added to a suspension of $\text{K}[\text{OCHMe}_2]$ (0.17 g, 1.7 mmol) in benzene (ca. 20 ml) and heated under reflux for 1 h. The precipitated KCl (0.17 g, 1.73 mmol) was removed by filtration. The filtrate was evaporated to dryness under reduced pressure, to yield a green crystalline solid (1.44 g, 93%), which can be further purified by volatilization in > 50% yield.

Other alkoxide bimetallic isopropoxides were prepared similarly, and are detailed in Table 1.

Preparation of $[\{\text{Al}(\text{OCHMe}_2)_4\}\text{Cu}\{\text{Zr}_2(\text{OCHMe}_2)_9\}]$ (6). To a solution of freshly prepared $[\text{ClCu}\{\text{Zr}_2(\text{OCHMe}_2)_9\}]$ (2.50 g, 3.07 mmol) in benzene (ca. 30 ml) was added $\text{K}[\text{Al}(\text{OCHMe}_2)_4]$ (0.93 g, 3.07 mmol) {prepared by dissolving potassium (0.122 g, 3.07 mmol) in CHMe_2OH (ca. 10 ml) in the presence of $\text{Al}(\text{OCHMe}_2)_3$ (0.63 g, 3.08 mmol) in benzene (ca. 30 ml) and dried under reduced pressure}. The reaction mixture was heated under reflux for 2 h. The precipitated KCl (0.23 g, 3.08 mmol) was removed by filtration. The volatiles were removed from the filtrate under reduced pressure to afford a blue-green viscous liquid (2.45 g, 77%), which could be volatilized (185 °C/0.3 Torr) unchanged.

Similar procedures were used for the synthesis of **8** and **9**; synthetic and analytical data are summarised in Table 1.

Structurally significant IR and UV-VIS absorptions ($\tilde{\nu}_{\text{max}}$ (cm^{-1})) of these novel bi- and ter-metallic alkoxide complexes are given below:

- 2** : IR: 1170s, 1140m $\nu(\text{OCHMe}_2)$; 1050s, 1030s, 960s $\nu(\text{C-O})$; 580s $\nu(\text{Zr-O})$; 490m $\nu(\text{Cu-O})$; 355s, 325s, 207s $\nu(\text{Cu-Cl})$. UV-VIS: 13400 (in C_6H_6), 15600 (in CHMe_2OH).
- 2a**: IR: 1180s, 1145m $\nu(\text{OCHMe}_2)$; 1030m, 990s $\nu(\text{C-O})$; 570m $\nu(\text{Zr-O})$; 480w,br $\nu(\text{Cu-O})$.
- 2b**: IR: 1160s, 1130m $\nu(\text{OCHMe}_2)$; 1020m, 950m $\nu(\text{C-O})$; 560m $\nu(\text{Zr-O})$; 460s $\nu(\text{Cu-O})$. UV-VIS: 15400, 17800sh (in C_6H_6); 14900 (in thf).
- 2c**: IR: 1160m, 1130m $\nu(\text{OCHMe}_2)$; 1020m, 950m $\nu(\text{C-O})$; 580m,br $\nu(\text{Zr-O})$; 490m,br $\nu(\text{Cu-O})$. UV-VIS: 15100 (in C_6H_6).
- 2d**: IR: 1170m, 1135m $\nu(\text{OCHMe}_2)$; 1090m, 1015s, 960s $\nu(\text{C-O})$; 600m, 570m $\nu(\text{Zr-O})$; 480m $\nu(\text{Cu-O})$.
- 2e**: IR: 1170m, 1140m $\nu(\text{OCHMe}_2)$; 1050m, 1000m $\nu(\text{C-O})$; 580m,br $\nu(\text{Zr-O})$; 460m $\nu(\text{Cu-O})$.
- 4** : IR: 1150s, 1120s $\nu(\text{OCHMe}_2)$; 1045m, 960s $\nu(\text{C-O})$; 600m, 560m $\nu(\text{Ta-O})$; 460m,br $\nu(\text{Cu-O})$; 355s, 326m, 230s, 224s, 210s $\nu(\text{Cu-Cl})$. UV-VIS: 14000 (in C_6H_6).
- 4a**: IR: 1165s, 1135s $\nu(\text{OCHMe}_2)$; 1080s, 1040s, 920s $\nu(\text{C-O})$; 610s, 580m $\nu(\text{Ta-O})$; 480m $\nu(\text{Cu-O})$.

- 4b:** IR: 1162s, 1130s $\nu(\text{OCHMe}_2)$; 1080s, 950s, 900s $\nu(\text{C}-\text{O})$; 540m $\nu(\text{Ta}-\text{O})$; 420m,br $\nu(\text{Cu}-\text{O})$. UV-VIS: 13700 (in C_6H_6).
- 4c:** IR: 1160s, 1132m $\nu(\text{OCHMe}_2)$; 1000s, 950s $\nu(\text{C}-\text{O})$; 590s $\nu(\text{Ta}-\text{O})$; 465m $\nu(\text{Cu}-\text{O})$.
- 4d:** IR: 1170s, 1140m $\nu(\text{OCHMe}_2)$; 1020s, 940s, 900s $\nu(\text{C}-\text{O})$; 620s, 600s $\nu(\text{Ta}-\text{O})$; 425m,br $\nu(\text{Cu}-\text{O})$.
- 6:** IR: 1165s, 1135s $\nu(\text{OCHMe}_2)$; 990s, 950s $\nu(\text{C}-\text{O})$; 720s, 690s $\nu(\text{Al}-\text{O})$; 620s, 590s $\nu(\text{Zr}-\text{O})$; 460m, 440m $\nu(\text{Cu}-\text{O})$. UV-VIS: 15400 (in C_6H_6).
- 8:** IR: 1160s, 1130s $\nu(\text{OCHMe}_2)$; 1000s, 985s, 945m $\nu(\text{C}-\text{O})$; 720s $\nu(\text{Ga}-\text{O})$; 590m,br $\nu(\text{Zr}-\text{O})$; 465m, 440m $\nu(\text{Cu}-\text{O})$.
- 9:** IR: 1170s, 1130s $\nu(\text{OCHMe}_2)$; 1015m, 960m $\nu(\text{C}-\text{O})$; 600m,br $\nu(\text{Zr}-\text{O})$; 580m $\nu(\text{Ta}-\text{O})$; 470m, 440m $\nu(\text{Cu}-\text{O})$. UV-VIS: 15400 (in C_6H_6).

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