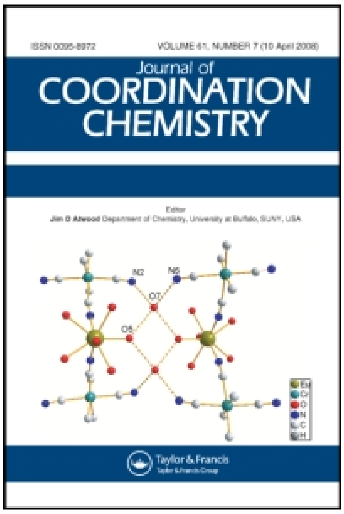

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SYNTHESIS AND MOLECULAR STRUCTURE OF [Cu(μ-OC$_6$H$_3$-2,6-Me$_2$)(thd)]$_2$: A LIGAND-MEDIATED REDUCTION TO METALLIC COPPER

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SYNTHESIS AND MOLECULAR STRUCTURE OF $[Cu(\mu\text{-}OC_6H_3\text{-}2,6\text{-}Me_2)(thd)]_2$: A LIGAND-MEDIATED REDUCTION TO METALLIC COPPER

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The reaction between barium 2,6-dimethylphenoxide (**1**) and copper 2,2,6,6-tetramethylheptane-3,5-dionate gave the volatile β-diketonatoaryloxide $[Cu(\mu\text{-}OC_6H_3\text{-}2,6\text{-}Me_2)(thd)]_2$ (**2**). The complex was characterized by elemental analysis, IR and ESR spectroscopy as well as single-crystal X-ray diffraction. It crystallises in the space group $P2_1/c$ with $a = 6.602(2)$, $b = 24.454(5)$, $c = 12.391(4)$ Å, $\beta = 95.49(2)°$. TGA experiments at 1 atmosphere show that **2** is volatile and decomposes at 292°C to metallic copper by a ligand-mediated reduction.

Keywords: Aryloxide; Copper; MOCVD; β-diketonate; X-ray structure

INTRODUCTION

Given the importance of cuprates for high Tc superconductors [1] and the potential of copper in microelectronics application [2], a large number of copper derivatives has been developed especially for Metal-Organic Chemical Vapor Deposition (MOCVD) applications [3]. We have reported the synthesis and structural characterization of volatile copper(II) β-diketonatoalkoxides such as $[Cu_3(O^tBu)_3(thd)_3]$ [4] or $[Cu_4(acac)_4(OC_2H_4OPr^i)_4]$ [5] and a Ba–Cu species $[BaCu_2(ORf)_4(thd)_2]$ with $ORf = OCH(CF_3)_2$ [6].

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Sterically hindered aryloxides have been used as another means to limit nuclearity and thus to provide volatility, solubility and/or to stabilize special oxidation states [7]. Control of oligomerization might be achieved *via* the bulky and/or functional substituents of the ring especially those in 2 and 6 positions. For instance whereas yttrium aryloxide is obtained as a monomeric species for 2,6-diterbutylphenoxide, the 2,6-dimethylphenoxide ligand afforded solvent-free dinuclear species or monomeric adducts with accessible coordination sites [8]. Copper(II) aryloxide complexes are also of interest due to their potential relevance to tyrosinase catalysis [9] as well as catalytic oxidation [10]. Cu aryloxides in oxidation state 2 or 1 generally require neutral ligands for stabilization [11] as illustrated by the isolation of $[Cu_2(OPh)_4(en)]_2 \cdot PhOH$ [12] (en = ethylenediamine) or $[Cu(\mu\text{-}OC_6H_3\text{-}2,6\text{-}Me_2)Lx]_2$, [$L = PPh_3$, $x = 2$; $L = PhCH{=}NC_2H_4N{=}CHPh$, $x = 1$] [13]. Monomeric species $[Cu(OAr)\{CHB(3,5\text{-}Pr^i_2pz)\}_3]$ (Ar = C_6H_4-4-F; C_6H_3-2,6-Me_2; C_6H_3-2,6-Bu^t_2) were reported recently. They are stable only below −50°C in the absence of electronegative substituents on the aryloxide ring [14]. We report here the synthesis and structural characterization of the dimeric β-diketonatoaryloxide $[Cu(OC_6H_3\text{-}2,6\text{-}Me_2)(thd)]_2$. Thermogravimetric data are discussed.

EXPERIMENTAL

All manipulations were performed under dry nitrogen using Schlenk tubes and vacuum line techniques. Solvents were purified by standard methods. $Cu(thd)_2$ was prepared according to the literature [5]. ^1H NMR spectra were recorded on a Bruker AC-200 instrument. IR spectra were recorded as Nujol mulls on a IR-FTS 45 spectrophotometer. Cyclic voltammetry was performed on a Parr system. TGA experiments were carried out under nitrogen (1 atm) with a Shimadzu system using a heating rate of 5°C/min. Microanalyses were performed at the Centre de Microanalyses du CNRS.

Synthesis of $Ba(OC_6H_3\text{-}2,6\text{-}Me_2)_2(THF)_2$ (1)

Barium granules (2 g, 14.5 mmol), 2,6-dimethylphenol (3.55 g, 29 mmol) and THF (50 cm^3) were refluxed for 10 h until all metal was consumed. After filtration, the filtrate was stripped to dryness. Recrystallization of the crude product in THF gave colourless crystals of $Ba(OC_6H_3\text{-}2,6\text{-}Me_2)_2(THF)_2$ (66%). *Anal.* Found (%): C, 54.45; H, 6.12; calc. for $C_{24}H_{34}O_4Ba$: C, 55.03;

H, 6.54. ^1H NMR (C_6D_6): 6.86 (*m*, 6H, CH), 3.56 (*t*, 4H, THF), 2.32 (*s*, 6H, Me), 1.74 (*s*, 6H, Me), 1.66 (*t*, 4H, THF). IR (cm^{-1}): 1585 ν(C=C); 1279, 1232 ν(C—O); 1086, 1040, 883, 843, 744 ν(C—C); 679, 505 ν(Ba—O).

Synthesis of [Cu(OC$_6$H$_3$-2,6-Me$_2$)(thd)]$_2$ (2)

Cu(thd)$_2$ (3.24 g, 7.54 mmoles) in 60 mL of hexane was added to a suspension of **1** (1.97 g, 3.77 mmoles) in 30 cm^3 of hexane. Solubilisation was observed while the colour changed from blue to dark brown. After stirring for 2 h, filtration was achieved. Brown crystals of **2** were formed at −20°C (57%). Mp: dec. 292°C. subl. 160°C/10^{-3} torr. *Anal.* Found (%): C, 62.35, H, 7.55. Calc. for $C_{19}H_{28}O_3Cu$: C 62.02, H 7.67. IR (cm^{-1}): 1595 m, 1566 s, 1555 vs, 1537 m, 1502 vs ν(C=C), ν(C=O); 1265 m, 1250 w, 1217 vs, 1199 m, 1180 m, 1149 m, 1090 m, 1028 w, 937 w, 920 w, 874 m, 850 m, 790 m, 765 vs, 744 w, 693 vs; 644, 622 m; 528 w, 514 m, 503 sh, 485 w, 474 w, 399 m ν(Cu—O). ESR (hexane, RT): $\langle g \rangle = 2.102$, $\langle A \rangle = 81.6$ G; $\mu = 0.77\ \mu B$.

Cu(thd)$_2$ (2.66 g, 1.3 mmol) in 80 cm^3 of hexane was added to a suspension of sodium 2,6-dimethylphenoxide (0.9 g, 1.3 mmol) in 15 cm^3 of hexane. The solution was filtered after 18 h. Compound **2** crystallized in 70% yield. Further crops of crystals were contaminated by Nathd and required purification by sublimation. Compound **2** is slightly soluble in hydrocarbons, and more soluble in diethylether, THF, DME.

Crystallography of [Cu(OAr)(thd)]$_2$

Suitable crystals of **2** were obtained from the reaction medium. Accurate cell dimensions and orientation matrices were obtained by least-squares refinement of 25 accurately centred reflections. No significant variations were observed in the intensities of two check reflections during data collection. Complete crystallographic data and collection parameters are listed in Table I. The data were corrected for Lorentz and polarization effects. Computations were performed by using the PC version of CRYSTALS [15]. Scattering factors and corrections for anomalous absorption were taken from Ref. [16]. The structure was solved by Patterson techniques and Fourier analyses and refined by full-matrix least-squares methods with anisotropic displacement parameters for all non hydrogen atoms. Hydrogen atoms were located in a difference Fourier map; their coordinates and an overall isotropic displacement parameter were refined.

TABLE I Crystal data for $[Cu(\mu\text{-}OC_6H_3\text{-}2,6\text{-}Me_2)(thd)]_2$

Chemical formula	$C_{38}H_{56}O_6Cu_2$
Fw	735.94
a (Å)	6.602(2)
b (Å)	24.454(5)
c (Å)	12.391(2)
β (°)	95.49(2)
V (Å^3)	1991(4)
Z	2
Crystal system	Monoclinic
Space group	$P\,2_1/c$
Linear absorption coefficient μ (cm^{-1})	11.08
Density (g cm^{-3})	1.23
Diffractometer	CAD4 Enraf-Nonius
Radiation	MoKα ($\lambda = 0.71069$ Å)
Scan type	$\omega\ 2/\theta$
Scan range (°)	$0.8 + 0.345\,\mathrm{tg}\theta$
θ Limits (°)	1 – 23
Temperature of measurement	room temperature
Octants collected	−7,7; 0,26; 0,13
No. of data collected	2903
No. of unique data collected	2760 ($R_{\mathrm{int}} = 0.046$)
No. of unique data used for refinement	1697 $(Fo)^2 > 3\sigma(Fo)^2$
$R = \Sigma\|\|Fo\| - \|Fc\|\|/\Sigma\|Fo\|$	0.049
$R_w = [\Sigma w(\|Fo\| - \|Fc\|)^2/\Sigma wFo^2]^{1/2}$	0.051

TABLE II Fractional positional and equivalent thermal parameters (Å^2) for $[Cu_2(OAr)_2(thd)_2]$

Atom	x/a	y/b	z/c	$U(eq)$
Cu(1)	0.0700(1)	0.04915(4)	0.06610(7)	0.0422
O(1)	0.0966(8)	−0.0290(2)	0.0640(4)	0.0488
O(2)	0.2356(8)	0.0588(2)	0.1970(4)	0.0535
O(3)	0.0239(8)	0.1243(2)	0.0436(4)	0.0526
C(1)	0.190(1)	−0.0631(3)	0.1385(6)	0.0386
C(2)	0.110(1)	−0.0722(3)	0.2370(6)	0.0516
C(3)	0.204(2)	−0.1079(5)	0.3106(8)	0.0750
C(4)	0.373(2)	−0.1355(5)	0.289(1)	0.0870
C(5)	0.456(1)	−0.1269(4)	0.195(1)	0.0683
C(6)	0.367(1)	−0.0910(3)	0.1165(7)	0.0536
C(7)	0.458(2)	−0.0828(5)	0.013(1)	0.0801
C(8)	−0.077(2)	−0.0417(6)	0.262(1)	0.0815
C(9)	0.289(1)	0.1042(3)	0.2402(6)	0.0451
C(10)	0.228(1)	0.1547(3)	0.1975(7)	0.0565
C(11)	0.097(1)	0.1628(3)	0.1041(6)	0.0413
C(12)	0.037(1)	0.2199(3)	0.0637(7)	0.0558
C(13)	0.151(2)	0.2663(4)	0.121(1)	0.0860
C(14)	−0.193(2)	0.2256(5)	0.078(1)	0.0985
C(15)	0.063(3)	0.2227(5)	−0.057(1)	0.1002
C(16)	0.424(2)	0.0992(4)	0.3457(7)	0.0640
C(17)	0.534(3)	0.1514(8)	0.380(1)	0.1220
C(18)	0.292(3)	0.084(1)	0.432(1)	0.1422
C(19)	0.556(4)	0.053(1)	0.342(2)	0.1407

Atomic coordinates are given in Table II. Tables of thermal parameters, full list of bond lengths and angles, H coordinates, and observed and calculated structure factors are available from the authors upon request.

RESULTS AND DISCUSSION

Synthesis and Characterization

A number of reactions between metal alkoxides or aryloxides and β-diketonates has afforded mixed-metal species by self-assembly [17]. However by contrast with such reactions involving classical or functional barium alkoxides and copper tetramethylheptanedionate [4, 6, 18, 19], reaction between the THF adduct of barium bis 2,6-dimethylphenyloxide, **1**, and $Cu(thd)_2$ afforded only an homometallic species of empiral formula $[Cu(OC_6H_3\text{-}2,6\text{-}Me_2)(thd)]$, **2**, according to analytical data, isolated by crystallization (57% yield). The compound was also obtained in $\approx 70\%$ yield by metathesis between $Cu(thd)_2$ and sodium 2,6-dimethylphenoxide. Purification could be achieved by sublimation at 160°C/10^{-3} torr. The FT-IR spectra of the barium and copper aryloxides display absorption bands for the $\nu C{=}C$ vibrations between 1600 and 1500 cm^{-1} as well as additional bands due to νCO stretches for the β-diketonate derivative, **2**. Compound **2** is paramagnetic as shown by its ESR spectrum ($\langle g\rangle = 2.102$, $\langle A\rangle = 81.6\,G$) and magnetic moment, thus confirming divalent copper. The presence of the aryloxide ligand modifies electronic properties. Whereas Cu(II) tetramethylheptanedionate derivatives based on alkoxide ligands usually have an absorption band around 450 nm, the electronic spectrum of **2**, a dark brown coloured species, displays two broad absorptions at 580 and 760 nm. As observed for other barium aryloxides [20], **1** is not volatile, and thus its properties were not further investigated.

A large number of Ba–Cu species of various stoichiometrics have been obtained usually by Lewis acid–base reactions [17, 19]. The assembling ligands are classical alkoxides, functionalized examples such as 2-methoxyethoxide [16], fluoroalkoxides [21] and aryloxides such as 2,4,6-tris(dimethylaminomethyl)phenoxide [18]. Despite its ability to act as bridging ligand, as observed for yttrium or for **2**, no stable mixed-metal species was formed between copper and barium, in the case of the 2,6-dimethylphenoxide ligand.

The molecular structure of **2** corresponds to a centrosymmetric dimer, $[Cu(\mu\text{-}OAr)(thd)]_2$ as depicted in Figure 1. Selected bond lengths and angles

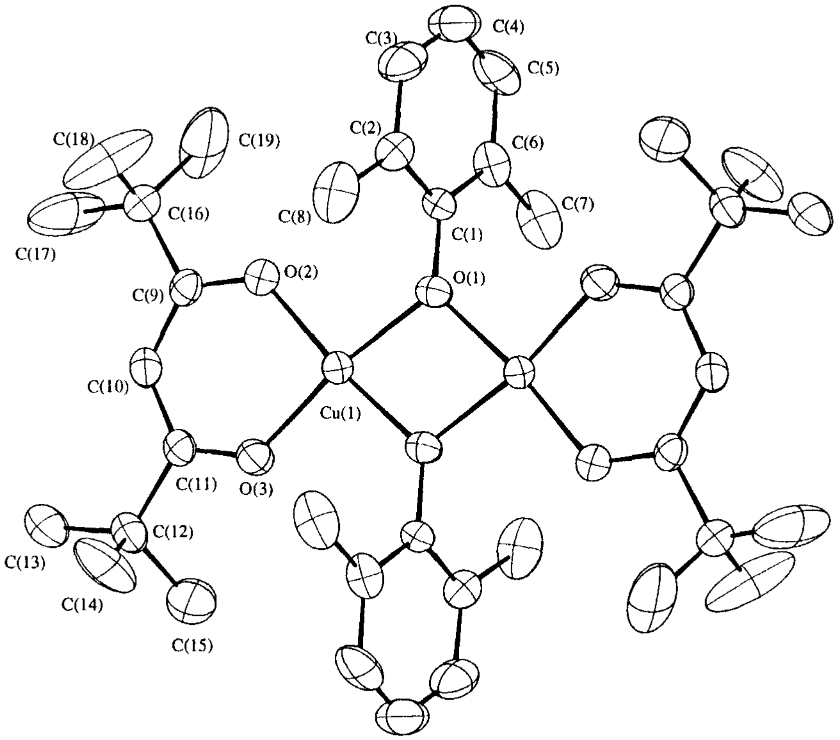

FIGURE 1 Molecular structure of $Cu_2(\mu\text{-}OC_6H_3\text{-}2,6\text{-}Me_2)_2(thd)_2$ showing the atom numbering scheme (thermal ellipsoids are drawn at 20% probability levels).

TABLE III Selected interatomic distances (Å) and bond angles (°) for $[Cu_2(OAr)_2(thd)_2]$

Cu(1)....Cu(1′)	3.004(2)		
Cu(1)—O(1′)	1.926(5)	Cu(1)—O(1)	1.921(5)
Cu(1)—O(2)	1.882(5)	Cu(1)—O(3)	1.879(5)
Angels (°)			
O(1)—Cu(1)—O(1′)	77.3(2)	O(1)—Cu(1)—O(2)	95.2(2)
O(1)—Cu(1)—O(2′)	172.4(2)	O(1)—Cu(1)—O(3)	170.2(2)
O(1)—Cu(1)—O(3′)	93.1(2)	O(2)—Cu(1)—O(3)	94.5(2)
Cu(1)—O(1)—Cu(1′)	102.7(2)	Cu(1)—O(1)—C(1)	129.9(4)
Cu(1)—O(1′)—C(1′)	127.1(4)	Cu(1)—O(2)—C(9)	126.0(5)
Cu(1)—O(3)—C(11)	126.2(5)		

are collected in Table III. The Cu—O distances vary from 1.879(5) to 1.925(5) Å, the CuO(thd) bonds being slightly shorter than those of the bridging Cu-μ-OAr unit. The copper atoms have a distorted square planar geometry with a O(1)—Cu(1)—O′(1) intrabridge angle of 77.3(2)°. The Cu···Cu distance of 3.004(2) Å is, as well as the other metric parameters, in agreement with the literature [22].

Thermal Behaviour

Thermogravimetric analyses of **2** have been made at 1 atmosphere under nitrogen. The residues have been analysed by EDX (Energy Dispersive X-ray Analysis). The thermogram of **2** presents a rapid weight loss (78%) in the range 183–292°C and a smaller one (9.2%) in the range 292–430°C. The residue of 12.8% was analysed as metallic copper. This residue, less than the value of 17.2% corresponding to 100% conversion into metallic copper, indicates partial volatilization. A film of copper was formed on the platinum substrate, confirming that **2** has been volatilized and decomposed. This decomposition of **2** into the metal occurs in the absence of an external reactant such as dihydrogen [2]. The reduction has thus been mediated by the aryloxide ligand. Aryloxide derivatives are prone to decomposition by oxidation of the aryloxo ligands *via* aryloxo radicals giving 2,6-dialkyl-1,2-benzoquinone (benzoquinone) or the coupled product 3,3′,5,5′-tetra-alkyl-diphenoquinone (diphenoquinone). The decomposition is enhanced by an oxygen atmosphere.

Figure 2 compares the TGA profiles of various Cu(II) derivatives, namely $Cu(thd)_2$, $[Cu_3(OtBu)_3(thd)_3]$, $[Cu_2(OtBu)_2(thd)_2(THF)_2]$ [4] and $[Cu_2(OAr)_2(thd)_2]$, under nitrogen and at a pressure of 1 atmosphere. The residues obtained for $Cu(thd)_2$ and the β-diketonatobutoxides correspond to copper oxide. At low temperatures (< 250°C), **2** displays behaviour comparable to that of $Cu(thd)_2$ but whereas the latter continues to sublime, **2** decomposes at 292°C into copper. However, this temperature is quite high for practical applications in comparison to those of the liquid Cu(I) precursors developed recently, and which decompose in the 130–240°C temperature range [3].

Cyclic voltammetry studies of $[Cu_2(OC_6H_3\text{-}2,6\text{-}Me_2)_2(thd)_2]$ in THF with $Bu_4N^+PF6^-$ (TBAH 0.2 M) as supporting electrolyte confirm that **2** is an electroactive species. The voltammogramms show reduction waves at −0.78 V and at −1.4 V. The second transformation is irreversible, no significant anodic wave being present. However, the overall behaviour was quite complex with evidence of several chemical–electrochemical reactions and was not further investigated.

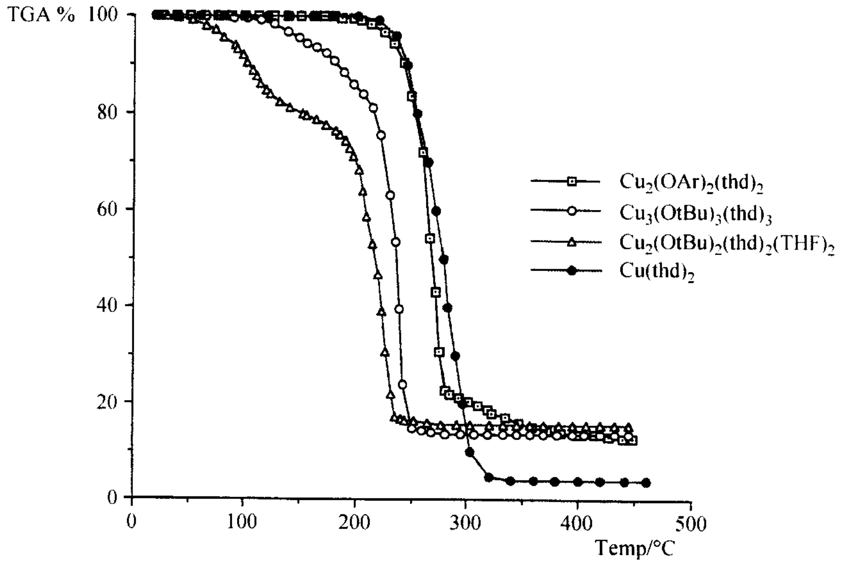

FIGURE 2 Comparison of the TGA profiles of various Cu(II) species (under nitrogen, 1 atmosphere).

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