Synthesis and characterisation of some hetero- and homo-metal aryloxides of copper(II)

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Hetero- and homo-metallic aryloxides of copper(II) of the type, Cu[Ta(OAr')₆]₂ (1-4) [where OAr' = 3,5-dimethylphenoxo (1), 3,4-dimethylphenoxo (2), 2,4,6-trimethylphenoxo (3) and 4-chlorophenoxo (4)] and CuCl₂(OAr')ₓ(2,2'-bipy) (5-7) [OAr' = 3,4-dimethylphenoxo, x = 1 (8), x = 2 (5); 3,5-dimethylphenoxo, x = 2 (6); 2,4,6-trimethylphenoxo, x = 2 (7) have been synthesised and characterised by elemental analyses, spectroscopic (IR, electronic, UV-visible) studies, magnetic moments and molecular weights.

Although during the last 5-6 years hetero bi- and tri-metallic alkoxides of copper(II) have attracted considerable attention, no work appears to have been carried out on analogous arylox derivatives of copper(II). Further, even homoleptic aryloxo complexes of copper(II) are limited in number, e.g., Cu(OC₆H₅Cl)₂ (2,2'-bipy) (ref. 7), Cu(OC₆H₅)₂ (2,2'-bipy) (ref. 8), Cu(OC₆H₅)₂(en).PhOH (ref. 9), CuL₂L' (ref. 10) (where L = appropriate phenoxy ligand and L' = bidentate neutral ligand). This prompted us to synthesise and characterise heterobimetallic aryloxides of copper(II) with tantalum(V) for the first time, and molecular adducts of alkyl substituted phenoxides of copper(II).

Materials and Methods

The reactions were carried under hermetically sealed set-up. Benzene (b.p. 80.1°), tetrahydrofuran (THF) (b.p. 65°) and n-hexane (b.p. 68°) were dried over sodium benzophenone ketyl.11 Nitrobenzene was dried over anhydrous CaCl₂ for 48 hr and then distilled, b.p. 211°. Pyridine was dried over solid KOH for 48 hr and then distilled, b.p. 118°.

All the substituted phenols (Fluka) were purified by recrystallisation from n-hexane, followed by sublimation (2-times).12 2,2'-Bipyridine was crystallised from warmed n-hexane as white crystalline solid m.p. 71°. Anhydrous copper(II) chloride was prepared13 from CuCl₂.H₂O (BDH) by heating at 150-200° in an atmosphere of anhydrous hydrogen chloride gas and analysed [Found: Cu = 47.09; Cl = 52.71. Calc for CuCl₂: Cu = 47.26; Cl = 52.73%]. CuCl₂(2,2'-bipy) and Cu(OC₆H₅)₂ (2,2'-bipy) were prepared by the literature method.14 Copper(II) and tantalum(V) in the heterobimetallic aryloxides were determined as follows: the complexes were digested with 50% HNO₃ and then the reaction mixture diluted with water (100 ml). The insoluble hydrated oxide of tantalum(V), Ta₂O₅.xH₂O was separated and determined gravimetrically as Ta₂O₅. The filtrate containing copper(II) was evaporated to a small volume and to the residual mass was added a mixture of conc. HNO₃ (~ 10 ml) and conc. H₂SO₄ (~ 10 ml) and evaporated till the evolution of white fumes of SO₂ ceased. The residue was dissolved in dil. HCl, and filtered and Cu(II) in the filtrate estimated iodometrically.14 Chlorine in the chloroderivative was determined gravimetrically as AgCl.

Infrared spectra were recorded in nujol mull using CsI plates in the range 4000-200 cm⁻¹ on a Perkin-Elmer 557 spectrophotometer. Electronic spectra were recorded in benzene, nitrobenzene or pyridine on a Pye-Union SP-100 and Hitachi U-2000 spectrophotometers. Magnetic susceptibilities were determined by Faraday's method, using a Princeton Applied Research model 155, vibrating sample magnetometer (VSM) calibrated with nickel.15 The observed magnetic moments were corrected for diamagnetic corrections employing Pascal constants.16 Molecular weights were determined ebullioscopically in refluxing benzene/tetrahydrofuran.

(a) Preparation of Cu[Ta(OC₆H₅₂₀,Me₂-3,5)₆]₂ (1)

Potassium hexa-3, 5-dimethylphenoxytantalate (V) [freshly prepared by the interaction of pota-
Sodium 3,4-dimethylphenoxide (prepared by the reaction of sodium (0.117 g, 5.09 mmol) and tantalum(V) chloride (0.065 g, 0.0484 mmol) in THF (20 ml) was slowly transferred to the pale green suspension of CuCl₂(2,2'-bipy) (0.729 g, 2.51 mmol) in THF (20 ml) during the addition. The colour of the reaction mixture changed instantaneously from pale green to intense brown. The reaction mixture was stirred for ~18 hr at room temperature followed by separation of the precipitated sodium chloride (0.2996 g, 5.12 mmol) and Cu[Ta(OAr')₆](2,2'-bipy) (5). This was crystallized from THF as an intense brown crystalline solid.

A similar procedure was employed for the preparation of Cu[OC₆H₃Me₂-3,5]₂(2,2'-bipy) (6), Cu[OC₆H₃Me₂-2,4,6]₂(2,2'-bipy) (7) and CuCl[OC₆H₃Me₂-3,4]₂(2,2'-bipy) (8).

**Results and Discussion**

Reaction of potassium (or sodium) hexaaryloxide with anhydrous copper(II) chloride in THF, leads to compounds 1-4 in quantitative yields (Table 1) as brown viscous materials (Eq. 1).

\[
\text{CuCl}_2 + 2\text{M}[\text{OA}r']_n \xrightarrow{\text{THF/C}_6\text{H}_6, \text{reflux, } 16 \text{ hr}} \text{Cu}[\text{Ta(OAr')}_6]_2 + 2\text{MCl} \downarrow \quad (1)
\]

1: M = K; OA'r = 3,5-dimethylphenoxo;
2: M = K; OA'r = 3,4-dimethylphenoxo;
3: M = K; OA'r = 2,4,6-trimethylphenoxo;
4: M = Na; OA'r = 4-chlorophenoxo.

Interaction of CuCl₂(2,2'-bipy) with potassium (or sodium) aryloxide in 1:1 stoichiometric molar ratio in THF, leads to quantitative formation of intense brown crystalline solids having the composition CuCl₂(OAr')₂(2,2'-bipy) (5-8) (Eq. 2):

\[
\text{CuCl}_2(2,2'-\text{bipy}) + x\text{MOAr'} \xrightarrow{\text{THF, stir, } 18 \text{ hr}} \text{CuCl}_2(\text{OA}r')_x(2,2'-\text{bipy}) + x\text{MCl} \downarrow \quad (2)
\]

5-8

All these products 1-8 (Table 1) are sensitive to moisture. Compounds 1-4 are yellow coloured viscous materials, soluble in organic solvents (e.g., benzene, toluene, n-hexane or THF) and are monomeric as revealed by its molecular weight in refluxing benzene. Compounds 5-8 are soluble in THF, pyridine etc. as well as in nitrobenzene. The adducts 5-7 are freely soluble in THF, while CuCl[OC₆H₃Me₂-3,4](2,2'-bipy) (8), Cu(OPh)₂(2,2'-bipy) and CuCl₂(2,2'-bipy) showed moderate to sparing solubility.

**Infrared spectra**

Infrared spectra of compounds 1-8 exhibit bands in the regions of 1150-1190; 445±10; 520-600; 1025-1070 cm⁻¹ assignable to νC=O (aryloxy); νCu–O; νTa–O; νC=C; and νC=N (of bipyridyl) groups respectively. The peak appearing at 415±10 cm⁻¹ may tentatively be assigned to νCu–N mode. The νC=N observed at 1555 and 1548 cm⁻¹ in free 2,2'-bipyridine is located at 1550 cm⁻¹ in the adducts 5-8. The compound CuCl[OC₆H₃Me₂-3,4](2,2'-bipy) exhibits a peak in the far IR at 280 cm⁻¹ assignable to bridged νCu–Cl.

**Electronic spectral and magnetic moment data**

Heterobimetallic aryloxides 1-4 in benzene solution exhibit an intense and broad ligand → metal charge transfer [phenoxo → copper(II)] absorption bands in the regions of 17,000-24,000 cm⁻¹ (centered at 21,900±300 cm⁻¹), in which d-d transitions for square planar copper(II) species appear to be obscured. The absorption spectra of 1-4 in pyridine were similar to those in benzene except for greater broadening of the band. The magnetic moments of 1-4 lie in the range 1.98-2.06 B.M. The slight increase in the magnetic moments; (from 1.73 B.M, Table 2) in comparison to square planar Cu(II) complexes is consistent with an orbitally non-degen-
Table 1—Analytical and physical data for some homo- and heterometal aryloxides of copper(II)

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Reactants* (g, mmole)</th>
<th>Product Yield, Found (Calc)</th>
<th>Physical characteristics (m.p., °C)</th>
<th>Found (Calc)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cu[Ta(OAr')₆Cl] ,₆</td>
<td>Yellow viscous mass soluble in THF/PhH/pyridine</td>
<td>3.11 19.03</td>
</tr>
<tr>
<td>1</td>
<td>KOC₆H₃Me₂-3,5 + TaCl₃ + CuCl₂ (0.931, 5.81) (0.350, 0.97) (0.065, 0.484)</td>
<td>Cu[Ta(OOC₆H₃Me₂-3,5)]₂</td>
<td>Pale yellow viscous mass, soluble in THF/PhH or pyridine</td>
<td>(3.38, 19.26)</td>
</tr>
<tr>
<td>2</td>
<td>KOC₆H₃Me₂-3,4 + TaCl₃ + CuCl₂ (1.739, 10.85) (0.647, 1.81) (0.122, 0.91)</td>
<td>Cu[Ta(OOC₆H₃Me₂-3,4)]₂</td>
<td>Yellow brown viscous mass, soluble in THF/PhH/pyridine</td>
<td>2.84 16.04</td>
</tr>
<tr>
<td>3</td>
<td>KOC₆H₃Me₂-2,4,6 + TaCl₃ + CuCl₂ (0.803, 5.98) (0.729, 2.51)</td>
<td>Cu[OC₆H₃Me₂-2,4,6]Cl₂</td>
<td>Rusty brown sticky viscous mass, soluble in THF/PhH</td>
<td>3.15 18.55</td>
</tr>
<tr>
<td>4</td>
<td>NaOCoH₃Me₂-2,4,6 + TaCl₃ + CuCl₂ (1.534, 10.19) (0.61, 1.70) (0.111, 0.83)</td>
<td>Cu[OC₆H₃Me₂-2,4,6]Cl₂</td>
<td>Intense brown solid, soluble in THF/PhNO₃/PhH</td>
<td>13.59 (13.75)</td>
</tr>
<tr>
<td>5</td>
<td>NaOCoH₃Me₂-3,4 + CuCl₂(2,2'-bipy) (0.363, 2.52) (0.737, 2.53)</td>
<td>Cu[OC₆H₃Me₂-3,4]Cl(2,2'-bipy)</td>
<td>Brown crystalline solid, soluble in THF/PhNO₃</td>
<td>13.86 (13.75)</td>
</tr>
<tr>
<td>6</td>
<td>NaOCoH₃Me₂-3,5 + CuCl₂(2,2'-bipy) (0.803, 5.98) (0.729, 2.51)</td>
<td>Cu[OC₆H₃Me₂-3,5]Cl(2,2'-bipy)</td>
<td>Intense dark brown crystalline solid, soluble in THF/PhNO₃</td>
<td>12.71 (12.91)</td>
</tr>
<tr>
<td>7</td>
<td>NaOCoH₃Me₂-2,4,6 + CuCl₂(2,2'-bipy) (0.618, 4.29) (0.621, 2.14)</td>
<td>Cu[OC₆H₃Me₂-2,4,6]Cl(2,2'-bipy)</td>
<td>Brown powdered solid, moderately soluble in THF, soluble in pyridine</td>
<td>20.56 9.51</td>
</tr>
<tr>
<td>8</td>
<td>NaOCoH₃Me₂-3,4 + CuCl₂(2,2'-bipy) (0.363, 2.52) (0.737, 2.53)</td>
<td>Cu[OC₆H₃Me₂-3,4]Cl(2,2'-bipy)</td>
<td>Brown powdered solid, moderately soluble in THF, soluble in pyridine</td>
<td>20.78 (9.53)</td>
</tr>
</tbody>
</table>

*aCalculated values of alkali aryloxides are based on alkali metal or phenols used, THF = tetrahydrofuran, PhH = benzene, PhNO₃ = nitrobenzene.

Table 2—Electronic (visible) absorptions* and magnetic moments of heterobimetallic aryloxides of copper(II) with tantalum(V) and homometallic aryloxo derivatives of copper(II)

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Compound</th>
<th>(v_{\text{max}} \times 10^3 \text{ cm}^{-1})</th>
<th>(\mu_{\text{eff}} \text{ (BM)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cu[Ta(OOC₆H₃Me₂-3,5)]₂</td>
<td>21.98, 27.78 (benzene)</td>
<td>2.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td>22.03, 25.58 (pyridine)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Cu[Ta(OOC₆H₃Me₂-3,4)]₂</td>
<td>21.60, 25.25 (benzene)</td>
<td>1.99</td>
</tr>
<tr>
<td></td>
<td></td>
<td>21.59, 25.25 (pyridine)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Cu[Ta(OOC₆H₃Cl₄)]₂</td>
<td>22.22 (benzene)</td>
<td>1.98</td>
</tr>
<tr>
<td></td>
<td></td>
<td>22.22 (pyridine)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Cu[Ta(OOC₆H₃Me₂-2,4,6)]₂</td>
<td>22.22 (benzene)</td>
<td>2.02</td>
</tr>
<tr>
<td>5</td>
<td>Cu[OC₆H₃Me₂-3,4]Cl₂(2,2'-bipy)</td>
<td>19.72, 20.96, 23.36 (nitrobenzene)</td>
<td>1.76</td>
</tr>
<tr>
<td>6</td>
<td>Cu[OC₆H₃Me₂-3,5]Cl₂(2,2'-bipy)</td>
<td>20.25 (nitrobenzene)</td>
<td>1.73</td>
</tr>
<tr>
<td>7</td>
<td>Cu[OC₆H₃Me₂-2,4,6]Cl₂(2,2'-bipy)</td>
<td>20.25 (nitrobenzene)</td>
<td>1.86</td>
</tr>
<tr>
<td>8</td>
<td>Cu[OC₆H₃Me₂-3,4]Cl(2,2'-bipy)</td>
<td>13.07, 24.21, 27.32 (pyridine)</td>
<td>1.57</td>
</tr>
<tr>
<td>9</td>
<td>Cu[OC₆H₃Cl₂(2,2'-bipy)]</td>
<td>19.72 (nitrobenzene)</td>
<td>1.69</td>
</tr>
<tr>
<td>10</td>
<td>Cu[OC₆H₃Cl₂(2,2'-bipy)]</td>
<td>20.35 (benzene)</td>
<td>—</td>
</tr>
</tbody>
</table>

(a) The solvents used are given in parenthesis.
(b) CuCl₂(2,2'-bipy) maxima absorb at 12.95 \(\times 10^3 \text{ cm}^{-1}\) in pyridine.
(c) Electronic spectrum was not available in ref. 8, while magnetic moment value is reproduced.
(d) Absorption maxima value was taken from ref. 7.

The electronic absorption spectra of aryloxides 5-7 of Cu(II) in nitrobenzene exhibit a very broad unsymmetrical band (Table 2) in the region of 17,700 to 23,400 cm⁻¹ (with maxima centred at 21,100 ± 900 cm⁻¹) due to both \(d-d\) transitions and ligand → metal CT bands. The electronic spectrum of Cu[OC₆H₃Cl₂(2,2'-bipy)] in the region of 16,030 to 23,930 cm⁻¹ with maximum at 19,720 cm⁻¹.

The above observations tend to indicate square planar geometries for the complexes, Cu[Ta(OAr')₆Cl]₂ and Cu(OAr')₂(2,2'-bipy).
cm\(^{-1}\), for a trigonal bipyramidal copper(II) species\(^{30,31}\), whereas ligand → metal CT band is observed at 24,210 and 27,310 cm\(^{-1}\) (refs 22, 32). The structure 1C is also corroborated by the observed magnetic moment\(^{31}\) data (Table 2).

Although more definitive structural evidence can only be obtained by X-ray crystal diffraction studies, our attempt to obtain suitable crystals for crystallographic work was unsuccessful. However, in view of the available electronic and magnetic data, as well as published data on some related derivatives\(^3\), the complexes of the types, Cu[Ta(OAr')\(_6\)] and (2,2'-bipy) Cu(OAr')\(_2\); and [(2,2'-bipy) (Ar'O)Cu(μ-Cl)]\(_2\) Cu(OAr') (2,2'-bipy)] appear to adopt square planar (see structures 1a and 1b) and trigonal bipyramidal geometry (see structure 1c).

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References