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# Synthesis and molecular structure of tetranuclear $Cu_4P_4$ complexes with $R_2P–O–PR_2$ ligands

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## ABSTRACT

The reaction of secondary phosphine oxides $R_2P(O)H$ **1** with $Cu(OAc)_2$ under nitrogen atmosphere produced complexes $[(R_2P)_2O(CuOAc)_2]_2$ **2**. A rapid ligand exchange took place when treating complexes **2** with $NH_4Cl$ to generate $[(R_2P)_2O(CuCl)_2]_2$ **3** in good yields. The structures of **3** were determined by X-ray crystallography, showing that the geometries of these tetranuclear copper complexes vary with the R group of the phosphorus units. Compared to complexes **2** which are air sensitive, complexes **3** are stable under air.

## 1. Introduction

Secondary phosphine oxides $R_2P(O)H$ **1** have increasingly attracted attentions as robust preligands for transition metal catalysis [1]. These compounds show unique tautomerism between the pentavalent $R_2P(O)H$ and the trivalent $R_2P(OH)$ tautomers which, likes other trivalent organophosphorus compounds, can ligate to transition metals. During a study on the possible coordination of $R_2P(O)H$ with copper salts, we found that a reaction of $Cu(OAc)_2$ with $R_2P(O)H$ **1b** ($R = Ph(CH_2)_4$) could produce a unique tetranuclear $[(R_2P)_2O(CuOAc)_2]_2$ complex **2b** [2] in which $R_2P–O–PR_2$ formally derived in situ from the dehydration of two secondary phosphine oxides. However, this complex is difficult to handle because it is extremely air sensitive and decomposes readily in air.

Herein, we report the synthesis and structural characterization of similar tetranuclear copper complexes $[(R_2P)_2O(CuCl)_2]_2$ **3**, by simply mixing $R_2P(O)H$ with $Cu(OAc)_2$ and treating the resulted mixture with an aqueous $NH_4Cl$ solution (Eq. (1)). Contrary to $[(R_2P)_2O(CuOAc)_2]_2$, these $[(R_2P)_2O(CuCl)_2]_2$ complexes can be handled under air. It was noted that such $R_2P–O–PR_2$ ligated-complexes are rarely reported in coordination chemistry [3], although similar complexes with $R_2P–(CH_2)_n–PR_2$ [4–7] and $R_2P–NR'–PR_2$ [8] are well known.

$$Cu(OA)_2 \xrightarrow{R_2P(O)H} [(R_2P)_2O(CuOAc)_2]_2 \xrightarrow{NH_4Cl} [(R_2P)_2O(CuCl)_2]_2 \qquad (1)$$

## 2. Experimental

$^1H$, $^{13}C$ and $^{31}P$ NMR spectra were recorded on a JEOL LA-400 instrument (400 MHz for $^1H$, 100 MHz for $^{13}C$, and 162 MHz for $^{31}P$ NMR spectroscopy). $CDCl_3$ was used as the solvent. Chemical shift values for $^1H$ and $^{13}C$ were referred to internal $Me_4Si$ (0 ppm), and that for $^{31}P$ was referred to $H_3PO_4$ (85% solution in $D_2O$, 0 ppm). Melting point was recorded on an OptiMelt instrument (90-264 VAC). Saturated $NH_4Cl$ aqueous solution was not degassed.

### 2.1. Synthesis of $[(n\text{-}Bu_2P)_2O(CuCl)_2]_2$ **3a**

To a flask were added dibutyl secondary phosphine oxide ($n$-$Bu_2P(O)H$, 3 mmol), anhydrous $Cu(OAc)_2$ (2 mmol) and THF (5 mL) under nitrogen atmosphere. The mixture was stirred at room temperature for 2 h, and then 15 mL chilled saturated $NH_4Cl$ aqueous solution was added. The crude product was extracted with $CHCl_3$ and dried over $MgSO_4$. The volatiles were removed under vacuum and the product **3a** was isolated using a preparative GPC using $CHCl_3$ as eluent. Yield: 393 mg, 52%.

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The complex **3a** was dissolved in a mixed solvent of THF (2 mL) and $Et_2O$ (2 mL), and then hexane (10 mL) was added. The solution was slowly cooled down to −30 °C to give colorless crystals suitable for X-ray analysis.

$^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 1.87–1.76 (m, 16H, $CH_2$), 1.62–1.52 (m, 16H, $CH_2$), 1.48–1.39 (m, 16H, $CH_2$), 0.93 (t, 24 H, $J = 7.0$, $CH_3$). $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ 31.5 (d, $J_{CP} = 11.1$ Hz, $CH_2$), 24.9 (s, br, $CH_2$), 24.1 (d, $J_{CP} = 6.5$ Hz, $CH_2$), 13.6(s, $CH_2$), $^{31}P$ NMR ($CDCl_3$, 162 MHz): $\delta$ 123.1. M.P.: 76.1–77.3 °C; decomposed at 210.0 °C. *Anal.* Calc. for $C_{32}H_{72}Cl_4Cu_4O_2P_4$: C, 38.10; H, 7.19; Cl, 14.06. Found: C, 38.35; H, 7.16; Cl, 13.84% (see Scheme 1).

If the reaction mixture was exposed to air (<10 min) before the addition of $NH_4Cl$ aqueous solution, $[(n\text{-}Bu_2P)_2O(CuCl)_2]_2$ **3a** could not be obtained at all but $n$-$Bu_2P(O)OH$ was obtained in 92% yield as a white solid: $^1H$ NMR (CDCl3, 400 MHz): $\delta$ 9.00 (s, 1H, O*H*), 1.71–1.62 (m, 4H, $CH_2$), 1.61–1.53 (m, 4H, $CH_2$), 1.45–1.36 (m, 4H, $CH_2$), 0.92 (t, 6H, $J = 6.86$ Hz, $CH_3$). $^{13}C$ NMR (CDCl3, 100 MHz): $\delta$ 28.7 (d, $J_{CP} = 92.0$ Hz, $CH_2$), 23.9 (d, $J_{CP} = 15.5$ Hz, $CH_2$), 23.6 (d, $J_{CP} = 4.0$ Hz, $CH_2$), 13.6. $^{31}P$ NMR (CDCl3, 201.95 MHz): $\delta$ 59.6.

### 2.2. Synthesis of $[((Ph(CH_2)_4)_2P)_2O(CuCl)_2]_2$ **3b**

$[((Ph(CH_2)_4)_2P)_2O(CuOAc)_2]_2$ **2b** [2] (343 mg, 0.2 mmol) in 5 mL $CHCl_3$ was added to 20 mL chilled saturated $NH_4Cl$ aqueous solution and stirred vigorously for 10 min. The product was then extracted with $CHCl_3$ and dried over $MgSO_4$. The product was isolated using a preparative GPC using $CHCl_3$ as eluent. Yield: 278 mg, 86%. The product was dissolved in THF (2 mL) and $Et_2O$ (2 mL). Hexane (8 mL) was then added. The solution was slowly cooled to −30 °C to give colorless crystals suitable for X-ray analysis. White solid: $^1H$ NMR (CDCl3, 400 MHz): $\delta$ 7.20–7.16 (m, 16H), 7.10–7.05 (m, 24H), 2.54 (t, $J = 7.4$ Hz, 16H, $CH_2$), 1.71–1.52 (m, 48H, $CH_2$). $^{13}C$ NMR (CDCl3, 100 MHz): $\delta$ 142.0, 128.4, 128.3, 125.7, 35.4, 32.6 (t, $J_{CP} = 6.6$ Hz, $CH_2$), 31.7 (d, $J_{CP} = 10.7$ Hz, $CH_2$), 22.6. $^{31}P$ NMR (CDCl3, 161.84 MHz): $\delta$ 123.0. *Anal.* Calc. for $C_{80}H_{104}Cl_4Cu_4O_2P_4$: C, 59.40; H, 6.48. Found: C, 60.11; H, 6.41%. M.P.: 84.6–85.5 °C; decomposed at 270 °C (see Scheme 2).

## 3. Results and discussion

### 3.1. Synthesis of $[(R_2P)_2O(CuCl)_2]_2$ **3** complexes

As indicated by $^{31}P$ NMR spectroscopy, the reaction of $n$-$Bu_2P(O)H$ with $Cu(OAc)_2$ in THF-$d_8$ at room temperature under nitrogen gave two new signals at 55.7 ppm and 122.6 ppm [2], which were assigned to $n$-$Bu_2P(O)OH$ and $[(n\text{-}Bu_2P)_2O(CuOAc)_2]_2$ **2a**, respectively. Complex **2a** was air sensitive that collapsed rapidly to $n$-$Bu_2P(O)OH$ when exposed to air. Surprisingly, however, by pouring the above reaction mixture into a chilled saturated aqueous $NH_4Cl$ solution, a complex $[(n\text{-}Bu_2P)_2O(CuCl)_2]_2$ **3a** was obtained via ligand exchange of the acetate group in **2a** with the chloro anion of $NH_4Cl$. Contrary to complex **2a**, complex **3a** could be handled in air without decomposition.

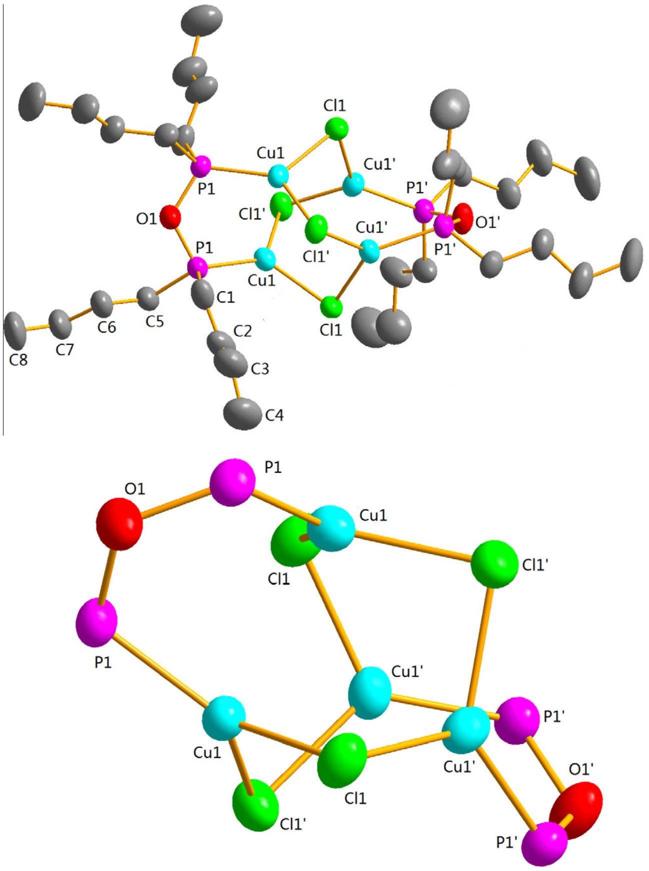
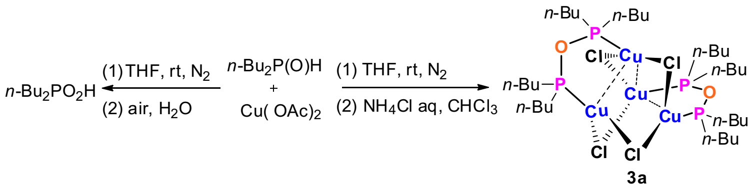
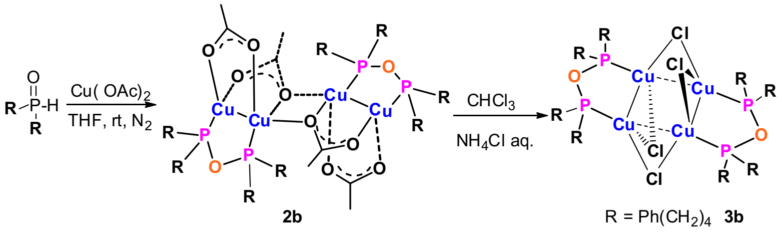


**Fig. 1.** Molecular structure of **3a**. Hydrogen atoms are omitted for clarity. Bottom: Core structure of **3a** (only Cu, P, O and Cl are shown).



**Scheme 1.** Synthesis of $[(n\text{-}Bu_2P)_2O(CuCl)_2]_2$ **3a**.



**Scheme 2.** Synthesis of $[((Ph(CH_2)_4)_2P)_2O(CuCl)_2]_2$ **3b**.

**Table 1**
Selected bond lengths and bond angles for complex **3a**.

| Bond lengths (Å) | | Bond angles (°) | |
|---|---|---|---|
| Cu1–P1 | 2.1796(7) | P1–Cu1–Cl1 | 128.29(3) |
| Cu1–Cl1 | 2.2742(7) | P1–Cu1–Cl1′ | 124.47(3) |
| Cu1–Cl′ | 2.2907(7) | Cl1–Cu1–Cl1′ | 107.103(17) |
| O1–P1 | 1.6428(15) | P1–Cu1–Cu1 | 83.46(2) |
| Cu1–Cu1 | 2.9570(6) | Cl1–Cu1–Cu1 | 85.62(2) |
| Cu1–Cu1′ | 3.2883(4) | Cl1′–Cu1–Cu1 | 106.58(2) |
| | | P1–O1–P1 | 120.45(17) |
| | | Cu1–Cl1–Cu1′ | 92.16(3) |
| | | Cu1–Cu1–Cu1′ | 63.28(1) |
| | | Cu1–Cu1′–Cu1 | 53.440(9) |

**Table 2**
Selected bond lengths and bond angles for complex **3b**.

| Bond lengths (Å) | | Bond angles (°) | |
|---|---|---|---|
| Cu1–P2 | 2.1727(6) | P1–O1–P2 | 123.58(8) |
| Cu1–Cl1 | 2.2863(6) | P1–Cu2–Cu1 | 91.59(2) |
| Cu1–Cl2 | 2.3047(6) | P2–Cu1–Cu2 | 87.75(2) |
| Cu1–Cu2 | 2.8409(5) | Cu2–Cl2–Cu1′ | 84.321(19) |
| Cu1–Cu2′ | 3.0697(5) | Cu1–Cl1–Cu2 | 76.067(16) |
| Cu2–P1 | 2.1716(6) | Cu1–Cu2–Cl2′ | 130.418(17) |
| Cu2–Cl2 | 2.2684(6) | Cu2–Cu1–Cl2 | 144.260(16) |
| Cu2–Cl1 | 2.3244(6) | Cu1–Cu2–Cu1′ | 82.51(1) |
| O1–P1 | 1.6389(13) | Cu2–Cu1–Cu2′ | 97.490(11) |
| O1–P2 | 1.6518(13) | | |

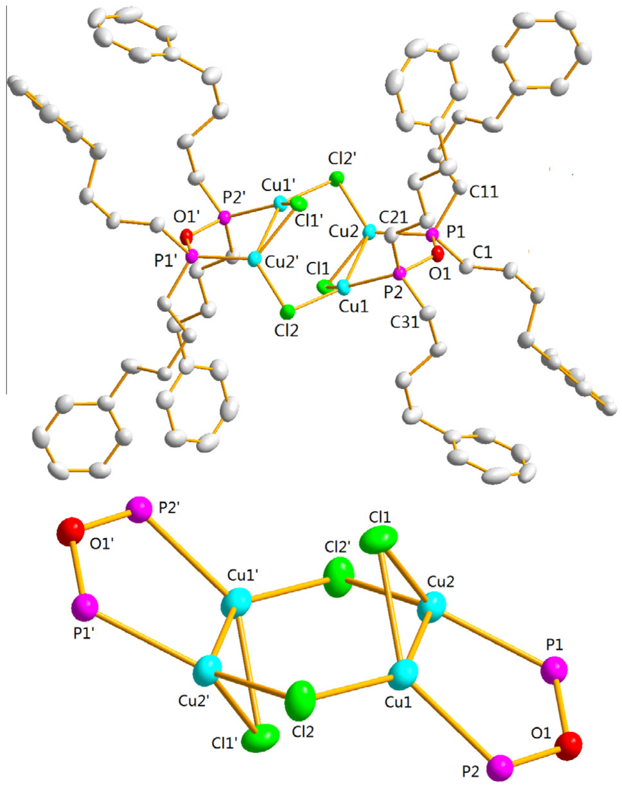


**Fig. 2.** Molecular structure of **3b**. Hydrogen atoms are omitted for clarity. Bottom: Core structure of **3b** (only Cu, P, O and Cl are shown).

Similarly, complex $[((Ph(CH_2)_4)_2P)_2O(CuCl)_2]_2$ **3b** was obtained by treating complex $[((Ph(CH_2)_4)_2P)_2O(CuOAc)_2]_2$ **2b** with an aqueous $NH_4Cl$ solution through ligand-exchange of the acetate group with the chloro atom.

### *3.2. Crystal structure of $[(Bu_2P)_2O(CuCl)_2]_2$ (**3a**)*

X-ray analysis shows that complex **3a** consists of a $Cu_4P_4Cl_4$ unit (Fig. 1, Table 1), where each P–O–P group coordinates to two copper(I) metals and each copper atom is bridged by two $\mu^2$-Cl atoms. Consequently, four 8-membered rings (P–O–P–Cu–Cl–Cu–Cl–Cu) are formed, which form a $Cu_4P_4Cl_4$ cage structure (Fig. 1, bottom). It is noted that this kind of $Cu_4Cl_4P_4O_2$ framework in **3a** is rare [9]. The geometry around the Cu(I) atoms is a distorted tetrahedron (angles: Cu1–Cu1–Cu1′, 63.28(1)°; Cu1–Cu1′–Cu1, 53.440(9)°). The Cu–Cu distances (Cu1–Cu1: 2.9570(6) and Cu1–Cu1′: 3.2883(4) Å) are slightly longer than the sum of their van der Waals radii (2.80 Å) [10]. The chlorine atoms bridge two Cu(I) atoms with classic Cu–Cl–Cu angles (92.16(3)°) and Cu–Cl bond lengths (2.2742(8)–2.2907(7) Å) [11].

### *3.3. Crystal structure of $[((Ph(CH_2)_4)_2P)_2O(CuCl)_2]_2$ (**3b**)*

The complex consists of a six-membered ring of four copper(I) atoms and two chloride atoms, with the four copper atoms in the plane (Fig. 2, Table 2). Pairs of copper atoms on each edge around the plane are both bridged further by a chloride and a $[[Ph(CH_2)_4]_2P]_2O$ ligand, which form two five-membered rings (P–O–P–Cu–Cu) and two three-membered rings (Cu–Cl–Cu), respectively. The Cu–Cu distances of Cu1–Cu2 and Cu1–Cu2′ are of 2.8409(5) and 3.0697(5) Å, respectively, the former is close to the sum of their van der Waals radii (2.80 Å). The Cu–Cu distances of **3b** are slight shorter than those of **3a**, whereas the Cu–Cu distance (2.8409(5) Å) of **3b** is longer than that of the air sensitive complex **2b** (2.6809(6) Å). The Cu–Cl distances vary from 2.27 to 2.32 Å. It is interesting to compare with the structure of complex **3a**. Thus, a slight difference in the alkyl group R of $R_2P(O)H$ can give a different geometry of the resulted complex **3**, i.e. tetrahedron geometry for **3a**, but parallelogram for **3b**.

## 4. Conclusions

We have prepared unique tetranuclear copper complexes $[(R_2P)_2O(CuCl)_2]_2$ through the reaction of secondary phosphine oxide $R_2P(O)H$ with copper acetate followed by ligand exchange with $NH_4Cl$. The core structures of $[(R_2P)_2O(CuCl)_2]_2$ vary with the R group.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2014.07.060.

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