



# First copper(II)-cyclophosphato complex with macrocyclic N-donor ligand: Single crystal structure elucidation with Hirshfeld surface analysis, optical, electrochemical and antioxidant properties



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## ABSTRACT

From the system metal-cyclam-condensed phosphate is isolated the first complex of  $\{(H_3O^+)_2[Cu(II)(\mu-P_4O_{12})(cyclam)]\}_n$  (**1**). This complex was characterized by X-ray diffraction (XRD), spectroscopy (diffuse reflectance, UV–Vis and FT-IR) and thermal analysis (DTA/TGA). The solved molecular structure of **1** revealed one rare 1D-anionic polymeric copper(II)-complex,  $\{[Cu(II)(\mu-P_4O_{12})(cyclam)]\}_n$ , involving two distinct ring ligands (cyclam / cyclotetraphosphate), in which a new coordination mode of the  $P_4O_{12}^{4-}$  was observed. The counterions ( $H_3O^+$ ) ensure the connection between 1D-polymers by acting as donor in a strong "charge-assisted" hydrogen bonds with  $P_4O_{12}$  rings leading to 2D-supramolecular frameworks arranged in -A-B-A- fashion. The 2D-supramolecular network is stabilized by O/N-H...O interactions whereas the van der Waals contacts play a key role in the consolidation of the 3D packing as verified by Hirshfeld surface analysis in combination with 2D fingerprint plots. The biochemical properties of **1** was also evaluated via DDPH, ABTS, hydroxyl radical scavengers and ferric reducing power (FRP) showing promising antioxidant activities which has been clarified by means of the cyclic voltammetric study.

## 1. Introduction

Organotransition-metal complexes (OTMC) based on O-donor polyoxoanions ligands have attracted great attention not only for their potential applications in various fields such as biology, catalysts, conductivity, magnetism [1] but also for their intriguing network topologies with a large variety of multi-dimensional structures [2]. Furthermore, a considerable number of metal complexes containing polyoxometalate, monophosphates, monophosphonates and monophosphinates have been successfully synthesized and several frameworks have constructed with (1D, 2D or 3D)-dimensional networks [3]. Nevertheless, the structural diversity of (OTMC) based on O-donor cyclophosphato ( $P_nO_{3n}$ )<sup>n-</sup> ligands is still limited. Recently, cyclotetraphosphates, as an important class of cyclophosphates, have attracted several groups. Thus, an increasing interest has been shown in the coordination chemistry incorporating the tetra-anionic  $P_4O_{12}^{4-}$  as O-donor ligand since the synthesis of the first series of organometallic-cyclophosphato complexes:  $(PPN)_2\{[M(cod)]_2(P_4O_{12})\}$  ( $M = Rh, Ir$ ;  $cod = 1,5$ -cyclooctadiene;  $(PPN)^+ = bis(triphenylphosphine)iminium$ );  $\{[Ru(MeCN)_2(PPh_3)_2]_2(P_4O_{12})\}$ ;  $(PPN)_2\{[Pd(C_3H_5)]_2(P_4O_{12})\}$  and  $\{[Rh(cod)]_4(P_4O_{12})\}$ , reported by Kamimura *et al.* [4]. They have also

described the synthesis of di- and trinuclear  $\mu$ -oxo titanium(IV) cyclotetraphosphato-complexes:  $(PPN)_2-[(Cp^*Ti)(P_4O_{12})_2]$  and  $(PPN)[(Cp^*Ti)_3(\mu-O)_3(P_4O_{12})]$  ( $Cp^* = \eta^5-C_5Me_5$ ) [5]. Later, a successful isolation of one Co(III)-cyclophosphato complex,  $Na[Co(P_4O_{12})]$  (TACN) (TACN = 1,4,7-triazacyclononane), has been reported by Montag *et al.* [6], in which  $P_4O_{12}$  binds to a transition metal in a  $\kappa_3$ -fashion. Currently, Manna *et al.* described the preparation of four mononuclear-cyclotetraphosphato complexes using simple techniques and mild conditions:  $(TBA)_4[(P_4O_{12})Mo(CO)_3] \cdot 2H_2O$ ,  $(TBA)_3[(P_4O_{12})Mo(CO)_2(\eta^3-C_3H_5)]$ ,  $(TBA)_3[(P_4O_{12})MoO_2Cl]$  and  $(TBA)_3[(P_4O_{12})VOF_2] \cdot Et_2O$  (TBA = tetra-*n*-butylammonium) [7]. Then, Yanfeng Jiang *et al.* proposed a novel and powerful strategy for the preparation of unusual cyclotetraphosphate metal complexes:  $(PPN)_2[\kappa_4-Sn(P_4O_{12})]$  and  $(PPN)_4[\mu_2, \kappa_2, \kappa_2-Cr_2(P_4O_{12})_2]$  using protonolysis procedure [8]. Thus, the  $P_4O_{12}^{4-}$  is of special interest due to: (i) its flexible eight membered ring structure that can exhibit versatile coordination modes (ii) its ability to form an extensive hydrogen bond network (iii) its promising photophysical properties of its transition metal(II) complexes, but to the best of our knowledge copper-cyclotetraphosphato complexes have received scant attention.

Meanwhile, macrocyclic  $N_4$ -donor ligands, such as cyclam, at-

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tracted considerable attention because of their ability to form kinetically and thermodynamically stable transition metal complexes [9]. There is also much interest in the transition-metal complexes of macrocycles due to their potential uses in cancer therapy [10].

Inspired by the aforementioned points, we tried to synthesize a new copper complex using respectively the tetra-anionic cyclophosphate  $P_4O_{12}^{4-}$  and cyclam as O- and N-donor ligands as a part of our research interest on copper(II)-cyclotetraphosphate complexes with N,O-donor ligands [11]. This paper reports the synthesis, crystal structure and characterization of one rare 1D-anionic polymeric complex of copper(II) involving simultaneously 8- and 14-membered ring ligands,  $\{(H_3O^+)_2[Cu(II)(\mu-P_4O_{12})(cyclam)]\}_n$ . To the best of our knowledge, this is the first case of copper(II)-cyclophosphato complex with chelating N-donor ligand as well as the first transition metal-complex based on cyclam and condensed phosphate.

## 2. Materials and methods

### 2.1. Synthesis of $\{(H_3O^+)_2[Cu(II)(\mu-P_4O_{12})(cyclam)]\}_n$ (1)

An aqueous solution of  $H_4P_4O_{12}$  (1 mL;  $C = 10^{-2}$  M) was added dropwise to a mixture of cyclam (0.1 g; 0.5 mmol) and  $CuCl_2 \cdot 2H_2O$  (0.085 g; 0.5 mmol) in distilled water (25 mL) (Scheme 1). The cyclotetraphosphoric acid  $H_4P_4O_{12}$  was produced from  $Na_4P_4O_{12} \cdot 4H_2O$ , prepared according to ONDIK process [12] through anion-exchange resin H-sate (Amberlite IR 120). The resulting purple solution was stirred at room temperature for 1 h and allowed to stand over a week to give dark-purple prismatic crystals. Yield: 76%. Anal. Calcd (%) for  $C_{10}H_{30}CuN_4O_{14}P_4$  (617.81): C, 19.42; H, 4.85; N, 9.06. Found (%): C, 19.48; H, 4.77; N, 9.09. IR (4000–400  $cm^{-1}$ , ATR): 3452 m, 3261 s, 3183 w, 3259 s, 3025 m, 3035 m, 2842 m, 1669 m, 1478 m, 1430 m, 1264 s, 1199 m, 1110 s, 1083 m, 998 vs, 966 vs, 745 s, 702 s, 547 s, 574 vs, 494 vs. UV–vis: in aqueous solution 520 nm, in solid state: 502 nm. The obtained compound **1** is stable in air at room temperature for more than several months. The crystalline phase purity of **1** is evidenced by the similarity of simulated and experimental (PXRD) pattern as depicted in Fig. 1.

### 2.2. X-ray structure analysis

The crystal structure was determined from the single crystal X-ray diffraction data obtained with an Enraf-Nonius CAD-4 diffractometer (AgK  $\alpha$  monochromatic radiation;  $\lambda = 0.56085$  Å). The structure was solved by direct methods and refined on  $F^2$  by full matrix least squares method, using SHELX-97 [13] in the WINGX software [14]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms of the organic ligand were positioned geometrically and treated as riding on their parent atoms (N, C), with N–H = 0.86, C–H = 0.93 Å and with  $U_{iso}(H) = 1.2 U_{eq}(C, N)$ . Whereas, those of water molecules were located from difference Fourier maps and refined with distance restraints of O–H = 0.85 Å and H...H = 1.38 Å. The details of structural refinement and crystallographic data of title compound **1** are gathered in Table 1. Crystallographic data for the structure reported in this paper have been deposited in the Cambridge Crystallographic Data

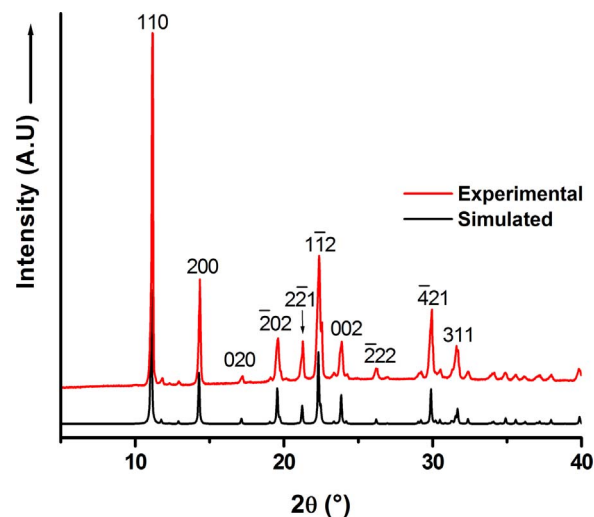


Fig. 1. Simulated and experimental powder X-ray diffraction pattern of **1**.

Table 1

Crystal data, intensity collection parameters and refinement results for **1**.

Empirical formula	$C_{10}H_{24}CuN_4O_{12}P_4 \cdot 0.2(H_3O)$
Formula weight ( $g\ mol^{-1}$ )	617.81
Crystal system / space group	Monoclinic / C2/m
$a$ (Å)	14.840 (4)
$b$ (Å)	10.214 (2)
$c$ (Å)	8.986 (4)
$\beta$ (°)	124.65 (3)
Volume ( $\text{\AA}^3$ )	1120.5 (6)
$Z$	2
Density (calc.) ( $g\ cm^{-3}$ )	1.831
$F(000)$	638
$\theta$ -range for data collection (°)	2.1 – 27.0
Index ranges	$-24 \leq h \leq 23, -3 \leq k \leq 16, -5 \leq l \leq 14$
Reflections collected	4738
Independent reflections	2515 [ $R_{int} = 0.029$ ]
Observed reflections [ $I > 2\sigma(I)$ ]	1898
Data / restraints / parameters	2515 / 6 / 90
Goodness-of-fit on $F^2$	1.02
R final indices [ $I > 2\sigma(I)$ ]	$^a R_1 = 0.038; ^b wR_2 = 0.089$
Largest diff. peak and hole ( $e. \text{\AA}^{-3}$ )	1.12 and $-0.84$

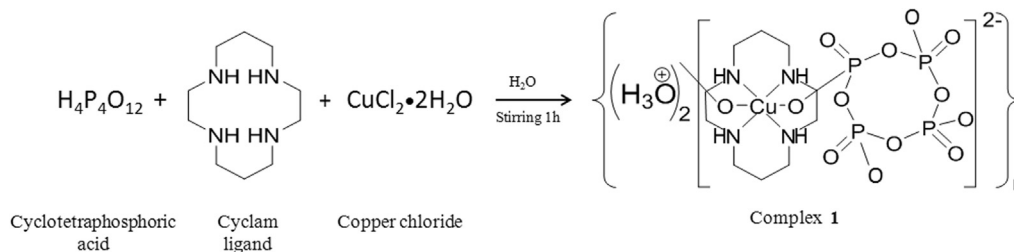
$$^a R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

$$^b R_w = \frac{[\sum_w (F_o^2 - F_c^2)^2 / \sum_w (F_o^2)^2]^{1/2}}$$

Centre as supplementary publication number 1469259. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (44) 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

### 2.3. Spectral measurements

UV–vis diffuse reflectance was performed on a Perkin Elmer spectrophotometer type instrument Lambda-45 coupled to an integration sphere type RSA-PE-20 in the range of 400–850 nm with a scan speed of 960  $nm\ min^{-1}$  and an aperture of 4 nm. The electronic



Scheme 1. Synthesis of complex **1**.

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