A novel trinuclear copper(II) complex containing a symmetric tetradentate N₂O₂ Schiff base ligand: Synthesis, characterization, crystal structure and its usage as a new precursor for the preparation of CuO particles

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Abstract

A novel linear centrosymmetric trinuclear copper(II) Schiff base complex with the chemical formula $[\{Cu(\mu-L)(H_2O)(\mu-NO_3)\}_2Cu] \cdot H_2O$, where $L = N,N'$ -bis(2-hydroxy-4-methoxybenzophenone)-2,2-dimethyl-1,3-propanediamine, was synthesized and characterized by elemental analyses, FT-IR spectroscopy, TG-TA and X-ray crystallography. Single X-ray diffraction analysis revealed four μ -phenoxido- and two μ -NO₃⁻ bridges in the complex. The equatorial plane of the three linearly arranged copper(II) atoms is formed by oxygen and nitrogen atoms of two anionic tetradentate Schiff base ligands, each of them coordinated to one of the terminal copper(II) ions. The central copper(II) ion is located in an inversion centre and bonded to four μ -oxygen atoms of the same ligand. Thermogravimetric analysis of the complex revealed its thermal stability and decomposition pattern. Finally, the complex was used for the preparation of CuO particles by solid state thermal decomposition.

Keywords: Trinuclear complex, Copper(II) complex, Schiff base, Crystal structure, Thermal decomposition

1. Introduction

Multinuclear copper(II) complexes containing Schiff base ligands have received attention for their structural diversity [1-6] and for various applications and properties, such as electrochemical [7,8] and magnetic properties [9,10] and antiradical effects [11]. Considerable effort has been devoted to the preparation and characterization of multinuclear copper(II) complexes with various Schiff base ligands and bridging dicyanamido [12], azido [13-15] and acetate [16] ligands. Trinuclear linear copper(II) complexes have attracted considerable interest [17-20], but only two of them have been structurally characterized [17,18]. They belong to a series of copper(II) complexes with tetradentate N_2O_2 Schiff base ligands synthesized by Mitra and his group [5,12,13,17,18]. The trinuclear copper(II) complex $[Cu_3(L^1)_2(H_2O)_2](ClO_4)_2$ $\{L^1 = N,N'$ -bis(3-methoxysalicylideneimino)-1,3-diaminopropane $\}$ [18] contains two bridging phenoxido oxygen atoms of the deprotonated Schiff base ligand that connect each terminal copper atom to the central copper atom [18], similarly to this work. However, all the copper(II) ions in $[Cu_3(L^1)_2(H_2O)_2](ClO_4)_2$ are five coordinated and have a distorted square pyramidal geometry, whilst in this work all the copper(II) ions are six coordinated and have a distorted octahedral geometry. Although more than 50 trinuclear copper(II) clusters with N_2O_2 Schiff base ligands are known, only two papers report structures with nitrate bridges connecting the central and terminal copper(II) ions [21,22].

In recent years, our research group has reported tetranuclear copper(II) complexes of tetradentate N_2O_2 Schiff base ligands [6,13,14]. In this present work, we have obtained a novel linear trinuclear copper(II) complex, $[Cu(\mu-L)(H_2O)(\mu-NO_3)_2]Cu \cdot H_2O$, containing a new symmetric tetradentate N_2O_2 Schiff base ligand (Scheme 1).

<Scheme 1>

2. Experimental

2.1. Materials and method

All the reagents and solvents for the synthesis and analysis were commercially available and used as received without further purification. Elemental analyses were carried out using a Heraeus CHN-O-Rapid analyzer, and the results agree with the calculated values. Fourier transform infrared (FT-IR) spectra were recorded as a KBr disk on a FT-IR Perkin–Elmer spectrophotometer. The TG/DTA were performed on a Perkin Elmer TG/DTA lab

system 1 (Technology by SII) under a nitrogen atmosphere with a heating rate of 20 °C/min in the temperature span 50–800 °C. The X-ray powder diffraction (XRD) pattern of the complex was recorded on a Bruker AXS diffractometer D8 ADVANCE with Cu-K α radiation and a nickel beta filter in the range $2\theta = 10^\circ$ – 80° . The scanning electron microscopy (SEM) images were obtained from a Philips XL-30ESEM.

X-ray structure determination

A single crystal of dimensions $0.74 \times 0.11 \times 0.10$ mm was chosen for the X-ray diffraction study. Crystallographic measurements were done at 120 K with a four circle CCD Gemini diffractometer of Oxford diffraction Ltd., with mirrors-collimated Cu-K α radiation. The crystal structure was easily solved by charge flipping with the program SUPERFLIP [23] and refined with the Jana2006 program package [24] by the full-matrix least-squares technique on F^2 . The molecular structure plots were prepared by Diamond 4.0 [25]. All hydrogen atoms were discernible from difference Fourier maps and could be refined to a reasonable geometry. According to common practice, H atoms bonded to C atoms were kept in ideal positions with C–H = 0.96 Å, $U_{\text{iso}}(\text{H})$ was set to $1.2U_{\text{eq}}(\text{C})$. All non-hydrogen atoms were refined using harmonic refinement. For disordered lattice water molecules, the hydrogen atoms could not be determined. Crystallographic data, details of the data collection, structure solution and refinements are listed in Table 1.

<Table 1>

Preparation of the complex

A solution of 2,2-dimethyl-1,3-diaminopropane (0.10 g, 0.05 mol) in 15 mL methanol was added dropwise to a methanolic solution of 2-hydroxy-4-methoxybenzophenone (1.15 g, 0.02 mol) under stirring conditions. The reaction mixture was then refluxed for 12 h, whereupon the solution color turned yellow. Then, a 10 mL methanolic solution of 0.05 mmol $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was added dropwise under stirring. Stirring was continued for 2.5 h at 60 °C, and the solution was allowed to cool to room temperature. Suitable crystals of the complex were obtained by slow evaporation of the solvent over several days. (Yield: 66%). Anal. Calcd. for $\text{C}_{66}\text{H}_{64}\text{Cu}_3\text{N}_6\text{O}_{17}$: C, 56.55; H, 4.57; N, 6.85%. Found; C, 56.49; H, 4.56; N, 6.79%.

FT-IR (KBr, cm^{-1}): 2921-3050 (C-H aromatic and aliphatic), 2823 (-CH=N), 1580 (-C=N-), 1454-1530 (C=C).

Preparation of CuO particles

The complex (≈ 0.5 g) was loaded into a platinum crucible, placed in an oven and heated at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$ in air. Particles of CuO were obtained at $500\text{ }^{\circ}\text{C}$, after 3 h. The final products were washed with ethanol to remove impurities, if any, and dried at room temperature over several days. The synthesized CuO particles were characterized by FT-IR, XRD and SEM. FT-IR (KBr, cm^{-1}): 541, 495 (Cu-O).

3. Results and discussion

3.1. Thermal studies

The thermal stability of the linear trinuclear copper(II) complex $[\{\text{Cu}(\mu\text{-L})(\text{H}_2\text{O})(\mu\text{-NO}_3)\}_2\text{Cu}]\cdot\text{H}_2\text{O}$ was examined under an Ar atmosphere. The TG curve is presented in Fig. 1. As shown in Fig. 1, there is no detectable change in the TG curve up to $300\text{ }^{\circ}\text{C}$, and then during further heating the complex undergoes decomposition in two stages ($200\text{-}400$ and $400\text{-}800\text{ }^{\circ}\text{C}$). In the first stage, the complex shows a mass loss of $\approx 68\%$ due to major decomposition, while in the second stage the complex shows a mass loss of $\approx 17\%$ due to partial decomposition. It is suggested that the final residue content is 3 Cu ($\approx 12.5\%$) at $750\text{ }^{\circ}\text{C}$ [27].

<Fig. 1>

3.2. Crystal structure of $[\{\text{Cu}(\mu\text{-L})(\text{H}_2\text{O})(\mu\text{-NO}_3)\}_2\text{Cu}]\cdot\text{H}_2\text{O}$

Selected bond distances and angles are presented in Table 2. X-ray diffraction for the title complex reveals that the centrosymmetric complex contains three Cu atoms, two NO_3^- anions, three H_2O and two Schiff base ligands. The inversion centre is located at the Cu2 atom. As shown in Fig. 2, the Schiff base ligand acts as a tetradentate chelating ligand around the terminal copper(II) ions, and the phenolic oxygen atoms act as a bridging ligand ($\mu\text{-O}$) between two copper(II) ions. The NO_3 ions also act as bidentate bridging ligands ($\mu\text{-NO}_3$)

between the terminal and central copper(II) ions. The resulting copper(II) complex $[\{\text{Cu}(\mu\text{-L})(\text{H}_2\text{O})(\mu\text{-NO}_3)\}_2\text{Cu}]\cdot\text{H}_2\text{O}$ is trinuclear (Fig. 2), with a distorted octahedral geometry around both symmetry-independent copper(II) atoms. The terminal copper(II) ions are coordinated by one nitrate ion, one oxygen atom from the H_2O molecule, two phenolic oxygen atoms and two iminic nitrogen atoms from the Schiff base ligand, while the central copper(II) ion is coordinated by six oxygen atoms (four phenolic oxygen atoms from two Schiff base ligands and two oxygen atoms from two NO_3^- anions). The Cu1-N1 (1.964(2) Å), Cu1-N2 (1.967(2) Å), Cu1-O1 (1.9820(18) Å) and Cu1-O3 (1.9287(19) Å) distances are comparable to those in the tri-nuclear copper(II) complex $[\text{Cu}_3(\text{L})_2(\text{NO}_3)_2](\text{H}_2\text{O})(\text{CH}_3\text{CH}_2\text{OH})$ [22]. In the complex, there are two bridging nitrate ions with the oxygen atoms O6 in *trans* positions, Cu2-O6 = 2.40(8) Å. These nitrates form bridges to adjacent copper atoms such that Cu1 is bonded to O5 at 2.45(8) Å. The intermolecular separation between Cu1...Cu2 is 2.98(7) Å, which is similar to the Cu...Cu distance in the tri-nuclear copper(II) complex $[\text{Cu}_3(\text{L})_2(\text{NO}_3)_2](\text{H}_2\text{O})(\text{CH}_3\text{CH}_2\text{OH})$ [22].

<Table 2> and <Fig. 2>

The angles around the copper(II) centers deviate from 90° (Table 2), indicating distortion of the octahedral geometry. The highly distorted tetrahedral geometry around the terminal copper(II) ions is also due to the small bite angle of the chelating Schiff base ligand N1-Cu1-N2 (99.40(9)°). The bridging angles Cu1-O1-Cu2 and Cu1-O3-Cu2 are 98.56 and 99.83°, indicating a non-collinear Cu1-O-Cu2 unit.

3.3. XRD and SEM

Fig. 3 shows the X-ray powder diffraction (XRPD) pattern recorded in the 2θ range 10° to 80° in Bragg-Brentano geometry. The powder profile of the synthesized copper(II) oxides can be fully indexed on the basis of monoclinic CuO (JCPDS: 801268) [26]. The XRPD result thus indicates the complete conversion of the complex to CuO. No obvious impurities were detected, indicating the high phase purity of the as-prepared samples. Also, the low broadening of all the peaks in the XRD pattern indicates that the particles are of

micrometric size usual for a well-diffracting power material. SEM images of the as-prepared CuO particles at two different scales are shown in Fig. 4.

<Figs. 3 and 4>

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Supplementary data

Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Center, CCDC No. 1486598. Copies of the data can be obtained free of charge on deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>.

References

- [1] S. Biswas, . Navia, M.G.B. Drew, C. Estareellas, A. Frontera, A. Ghosh, *Inorg. Chim. Acta* 366 (2011) 219-226.
- [2] Y. Pang, S. Cui, B. Li, J. Zhang, Y. Zhang, *Inorg. Chem.* 47 (2008) 1.317-1.324.
- [3] P. Chakraborty, S. Mohanta, *Polyhedron* 87 (2015) 98-108.
- [4] J.-W. Lu, Y.-H. Huang, S.-I. Lo, H.-H. Wei, *Inorg. Chem. Commun.* 10 (2007) 1210-1213.
- [5] S. Thakurta, P. Roy, G. Rosair, C.J. Gomez-Garcia, E. Garribba, S. Mitra, *Polyhedron* 28 (2009) 695-702.
- [6] A.D. Khalaji, S. Triki, J.M. Clemente-Juan, C.J. Gomez-Garcia, *Polyhedron* 50 (2013) 45-50.

- [7] M. Amirnasr, M. Bagheri, K. Mereiter, C. R. Chimie, 16 (2013) 1091-1097.
- [8] F. Fadaee, M. Amirnasr, K. Prsa, P. Pattison, N.E. Shaik, H.M. Ronnow, M.D. Esrafil, A.A. Omrani, A. Amiri, K. Schenk-Job, RSC Adv. 5 (2015) 59926-59934.
- [9] R. Papadakis, E. Riviere, M. Giorgi, H. Jamet, P. Rousselot-Pailley, M. Reglier, A. Jalila Simaan, T. Tron, Inorg. Chem. 52 (2013) 5824-5830.
- [10] M.S. Ray, A. Ghosh, S. Chaudhuri, M.G.B. Drew, J. Ribas, Eur. J. Inorg. Chem. (2004) 3110-3117.
- [11] Z. Puterova, J. Valentova, Z. Bojkova, J. Kozisek, F. Devinsky, Dalton Trans. 40 (2011) 1484-1490.
- [12] P. Talukder, S. Shit, A. Sasmal, S.R. Batten, B. Moubaraki, K.S. Murray, S. Mitra, Polyhedron 30 (2011) 1767-1773.
- [13] A. Ray, S. Mitra, A.D. Khalaji, C. Atmani, N. Cosquer, S. Triki, J.M. Clemente-Juan, S. Cardona-Serra, C.J. Gomez-Garcia, R.J. Butcher, E. Garribba, D. Xu, Inorg. Chim. Acta 363 (2010) 3580-3588.
- [14] A.D. Khalaji, H. Stoeckli-Evans, Polyhedron 28 (2009) 3769-3773.
- [15] S. Koner, S. Saha, K.-I. Okamoto, J.-P. Tuchagues, Inorg. Chem. 42 (2003) 4668-4672.
- [16] S. Halder, S. Dey, C. Rizzoli, P. Roy, Polyhedron 78 (2014) 85-93.
- [17] A. Ray, D. Sadhukhan, G.M. Rosair, C.J. Gomez-Garcia, S. Mitra, Polyhedron 28 (2009) 3542-3550.
- [18] S. Thakurta, C. Rizzoli, R.J. Butcher, C.J. Gomez-Garcia, E. Garribba, S. Mitra, Inorg. Chim. Acta 363 (2010) 1395-1403.
- [19] D.J. Spira-Solomon, M. Allendrof, E.I. Solomon, J. Am. Chem. Soc. 108 (1986) 5316-5318.
- [20] G.A. van Albada, I. Mutikainen, U. Turpeinen, J. Reedijk, Eur. J. Inorg. Chem. (1998) 547-549.
- [21] Y.-F. Feng, H.-Y. Wu, B.-L. Zhu, S.-R. Wang, W.-P. Huang, Acta Crystallogr. E63 (2007) m1107-m1108.

- [22] M. Dieng, I. Thiam, M. Gaye, A.S. Sall, A.H. Barry, Acta Chim. Slov. 53 (2006) 417-423.
- [23] Palatinus L, Chapuis G, *SUPERFLIP* – a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions, J. Appl. Crystallogr.40 (2007) 786-790.
- [24] Petricek V, Dusek M, Palatinus L, Crystallographic Computing System JANA2006: General features, Z. Kristallogr.229 (2014) 345-352.
- [25] Diamond - Crystal and Molecular Structure Visualization. Crystal Impact - K. Brandenburg & H. Putz GbR, Rathausgasse 30, D-53111 Bonn.
- [26] P.K. Raul, S. Senapati, A.K. Sahoo, L.M. Umolong, R.R. Devi, A.J. Thakur, V. Veer, RSC ADV. 4 (2014) 40580-40587.

Scheme 1. Chemical structure and the coordination mode of the new symmetric tetradentate N_2O_2 Schiff base ligand.

Fig. 1. The TG curve of $[\{\text{Cu}(\mu\text{-L})(\text{H}_2\text{O})(\mu\text{-NO}_3)\}_2\text{Cu}]\cdot\text{H}_2\text{O}$

Fig. 2. The trinuclear copper(II) complex $[\{\text{Cu}(\mu\text{-L})(\text{H}_2\text{O})(\mu\text{-NO}_3)\}_2\text{Cu}]\cdot\text{H}_2\text{O}$ with an inversion centre at the Cu2 atom. The uncoordinated lattice water molecule has been omitted for clarity; the atoms related by the inversion centre (symmetry operation $2-x, 1-y, 1-z$) are distinguished with a light blue border. (a) Overall view of the molecule where only atoms coordinated at the equatorial plane are shown; (b) details of the structure also showing NO_3 and disordered water molecules coordinated at axial positions.

Fig. 3 XRD pattern of the as-prepared CuO particles

Fig. 4. SEM micrographs of the CuO particles at different scales

Table 1. Crystallographic data and structural refinement details of the title complex

Formula weight	C ₆₆ H ₆₄ Cu ₃ N ₆ O ₁₇
Formula weight	1400.5
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	14.0482(5)
<i>b</i> , Å	10.2191(3)
<i>c</i> , Å	22.1764(8)
β , deg	98.003(3)
<i>V</i> , Å ³	3152.64(19)
μ , mm ⁻¹	1.79
<i>Z</i>	2
<i>S</i>	1.56
<i>R</i> _{int}	0.021
Measured reflections	12047
Measured independent	5499
Reflections with <i>I</i> > 3 σ (<i>I</i>)	4628
Parameters	426
<i>R</i> (<i>F</i> ² > 2 σ (<i>F</i> ²))	0.045
<i>wR</i> (<i>F</i> ²)	0.118
$\Delta\rho_{\text{max}}$, e Å ⁻³	0.52
$\Delta\rho_{\text{min}}$, e Å ⁻³	-0.72

Table 2. Selected bond distances (Å) and angles (°) of [$\{\text{Cu}(\mu\text{-L})(\text{H}_2\text{O})(\mu\text{-NO}_3)\}_2\text{Cu}\}\cdot\text{H}_2\text{O}$]

Cu1 O1	1.9501(18)	Cu1 O3	1.9287(19)
Cu1 N1	1.964(2)	Cu1 N2	1.967(2)
Cu2 O1	1.9820(18)	Cu2 O3	1.9664(16)
N1 C2	1.466(4)	N1 C6	1.297(3)
N2 C3	1.471(4)	N2 C20	1.302(4)
O5 N3	1.261(3)	O6 N3	1.257(4)
O7 N3	1.235(4)	O1 C14	1.334(3)
O2 C16	1.364(3)	O2 C19	1.434(4)
O3 C28	1.345(3)	O4 C30	1.366(4)
O4 C33	1.432(3)		
O1 Cu1 O3	79.93(8)	O1 Cu1 N1	89.84(8)
O1 Cu1 N2	170.77(9)	O3 Cu1 N1	169.63(9)
O3 Cu1 N2	90.84(9)	N1 Cu1 N2	99.40(9)
O1 Cu2 O1	180.0(5)	O1 Cu2 O3	101.75(7)
Cu1 O1 Cu2	98.56(8)	Cu1 N2 C20	124.23(19)
Cu1 N2 C3	115.35(17)	Cu1 N1 C6	123.9(2)
Cu1 N1 C2	114.68(17)	N2 C3 C1	114.9(2)
N1 C2 C1	114.5(2)	N1 C6 C13	122.6(3)
N1 C6 C7	121.9(3)	N2 C20 C27	123.3(2)
N2 C20 C21	121.6(3)		

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