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Synthesis, crystal structure and DFT analysis of a new trinuclear complex of copper

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ABSTRACT

The new trinuclear complex $[Cu_2(\mu\text{-}L)_2CuCl_2]$ has been synthesized and characterized by elemental analysis, IR, UV–Vis and X-ray spectroscopy, where L is a dianionic tetradentate Schiff base ligand with N_2O_2 donor atoms. The molecular structure of $[Cu_2(\mu\text{-}L)_2CuCl_2]$ was determined by X-ray crystallography. In the complex, the most remarkable aspect of the trinuclear complex is that it adopts a bent structure for the three copper atoms, with a Cu1—Cu3—Cu2 intramolecular angle of approximately 90.62(2)°. All three copper atoms are five coordinate, with a slightly distorted square pyramidal geometry. In the two terminals moieties, the basal plane of the square pyramidal is formed by two oxygen atoms and two nitrogen atoms of the Schiff base ligand, and the apical position at the Cu atom is occupied by the bridging Cl1 anion. The Cu1—Cl1—Cu2 angle is 110.51(5)°. The central copper atom also has a five-coordinate, slightly distorted square pyramidal geometry, with four phenolato oxygens belonging to the Schiff base ligands from Cu(salpn) units describing the square planar base and the Cl anions being apical. The optimized structure of the complex has been studied using the B3LYP/6-31G(d)/LanL2TZf level of theory. The calculation shows that all the copper atoms are five coordinate with distorted square pyramidal structures, which is consistent with experimental data.

1. Introduction

In recent decades, much attention has been paid to synthesizing copper(II) trinuclear complexes [1–5]. These complexes have received considerable interest because of their importance as model systems for the active sites of multinuclear proteins and metalloenzymes [6–9].

Tetradentate Schiff base ligands containing imine nitrogen and alcoholic or phenolic oxygen donor atoms can be utilized to synthesize trinuclear complexes. The internal N_2O_2 cavity of the tetradentate Schiff base is a suitable complexation point for divalent metal ions; however, the Schiff base complexes can act as a bidentate chelating ligand for further coordination as a result of the interaction with other metal ions to form homo and hetero-trinuclear complexes [10,11] known as *ligand complexes*. The ability of these complexes to act as host molecules to capture guest metal ions by coordinating through cis oxygen atoms leads to the generation of trinuclear metal complexes [10–13].

Trinuclear copper(II) complexes can be classified as linear or non-linear. The number of examples of homo- and hetero-trinuclear copper(II) complexes is limited. Most of the complexes reported, however, have a linear geometry. A search of the CCDC (Cambridge Crystallographic Data Centre) data base by Samira and his group in 2010 revealed that among the 52 different copper(II) trinuclear complexes, only four trinuclear complexes have a non-linear geometry, the remaining complexes having linear structures [14].

In the present study, we have explained the synthesis and single-crystal X-ray structure of a new trinuclear copper complex, $[Cu_2(\mu\text{-}L)_2CuCl_2]$ (L = tetradentate Schiff base, salpn), in which the array of metals adopts a non-linear configuration. We also report a theoretical study of the structure of this complex and a comparison between the calculations and the experimental data.

2. Experimental

2.1. Reagents

All chemicals were used as supplied by Merck and Fluka without further purification.

2.2. Physical measurements

Infrared spectra were taken with an Equinox 55 Bruker FT-IR spectrometer using KBr pellets in the 400–4000 cm^{-1} range. Absorption spectra were determined in the solvent methanol using a GBC UV–Vis Cintra 101 spectrophotometer with 1 cm quartz, in the range 200–800 nm at 25 °C. Elemental analyses (C, H, N) were performed by using a CHNS-O 2400II Perkin Elmer elemental analyzer.

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2.3. X-ray crystallography

Diffraction images were measured on a Nonius Kappa CCD diffractometer (Mo Kα, graphite monochromator, $\lambda = 0.71073$ Å), and data were extracted using the DENZO/SCALEPACK package [15]. The structure solution was determined by direct methods (SIR92) [16], and refinement was performed using the CRYSTALS program package [17]. The crystal was a twin from a 180° rotation about the direction (0 0 1). Application of a twinning correction within CRYSTALS to allow for overlapping reflections, based on the above relationship, gave a significant improvement in the agreement factors. The twin elements refined to 0.523(5):0.477(5). A numerical absorption correction was applied, $T_{min}/T_{max} = 0.770/0.955$.

There was a region of disordered solvate molecules in the unit cell. A difference electron density map calculated prior to their inclusion showed a distorted image of three partially occupied toluene molecules [occupancies 0.607(11); 0.229(14); 0.164(15)]. For the seven C atoms restraints were applied to distances, angles and planarity as their parameters were refined. The C atom sites were refined with isotropic displacement factors, for sites C51—C57 they were individually refined but for sites C61—67 they were refined as one parameter and likewise for C71—C77. Hydrogen atoms were included at calculated positions and allowed to ride on the atom to which they are attached.

The crystallographic data for the complex are summarized in Table 1.

2.4. Syntheses

2.4.1. Synthesis of the Schiff base ligand H_2L

The tetradentate Schiff base H_2L was prepared by a general method [18,19], by the condensation reaction between 2 equivalents of salicylaldehyde and 1 equivalent of 1,3-propandiamine. The resulting bright yellow solution was heated to reflux for 1 h. Upon cooling, a yellow product was obtained. The yield was 70%.

2.4.2. Synthesis of the CuL complex

The copper(II) complex was prepared by a general method [19,20], using the reaction between $Cu(CH_3COO)_2{\cdot}H_2O$ and the Schiff base ligand, H_2L (1:1 ratio) in methanol. The resulting solution was heated to reflux for 1 h. The resulting green precipitates were collected by filtration and washed with methanol. The yield was 50%. *Anal.* Calc. for $C_{17}H_{16}CuN_2O_2$: C, 59.38; H, 4.69; N, 8.15. Found: C, 59.12; H, 4.63; N, 8.21%. IR (KBr, cm^{-1}): $\nu_{C=N}$ 1607, $\nu_{C—O}$ 1327. Electronic spectra in CH_3OH: d–d, λ_{max} (log ε) 607 nm (2.39).

Table 1
Crystallographic data for the $[Cu_2(\mu\text{-}L)2CuCl_2]$ complex.

Compound	$Cu_2(\mu\text{-}L)_2CuCl_2$
Chemical formula	$C_{34}H_{32}Cl_2Cu_3N_4O_4{\cdot}C_7H_8$
Formula weight	914.33
T (K)	200
Space group	triclinic, $P\bar{1}$
Z	2
Unit cell dimensions	
a (Å)	10.2143(4)
b (Å)	11.3714(4)
c (Å)	16.5214(4)
α (°)	82.0156(18)
β (°)	88.512(2)
γ (°)	87.0567(14)
V ($Å^3$)	1897. 52(11)
F(0 0 0)	933.996
D_{calc} ($g\ cm^{-3}$)	1.600
Crystal dimension (mm)	0.20 × 0.15 × 0.03
μ (mm^{-1})	1.86
θ Range for data collection (°)	2.6–25.0
Limiting indices	$-12 \leqslant h \leqslant 12$, $-13 \leqslant k \leqslant 13$, $-19 \leqslant l \leqslant 19$
R_1/wR_2 [observed data: $I > 2\sigma(I)$]	0.0529/0.1460
R_1/wR_2 (all data)	0.0735/0.1578*

* $w = 1/[\sigma^2(F^2) + (0.09P)^2 + 2.52P]$, where $P = (\max(F_o{}^2,0) + 2F_c{}^2)/3$.

2.4.3. Synthesis of $[Cu_2(\mu\text{-}L)_2CuCl_2]$

A solution of $CuCl_2{\cdot}6H_2O$ (0.403 g, 3 mmol) in methanol (40 mL) was added to a solution of H_2salpn ligand (0.564 g, 2 mmol) in methanol (10 mL). The mixture was refluxed for 3 h, and green precipitates were obtained by evaporation of the solvent. The green solid product was recrystallized from methanol/2-propanol/toluene (2:1:1 v/v). Green block-shaped crystals appeared at the bottom of the vessel upon slow evaporation of the solvents, which were washed with acetone and dried in air. After drying, the block-shaped crystals turned to powder. The yield was 87%. *Anal.* Calc. for $C_{34}H_{32}Cu_3N_4O_4Cl_2$: C, 49.82; H, 3.94; N, 6.84. Found: C, 51.14; H, 4.41; N, 6.41%. IR (KBr, cm^{-1}): $\nu_{C=N}$ 1621, $\nu_{C>—O}$ 1293. Electronic spectra in CH_3OH: d–d, λ_{max} (log ε) 595 nm (2.19).

3. Theoretical calculations

The geometry of the complex has been optimized using the B3LYP level of theory [21]. The 6-31G(d) basis set was used for C, H, N, and O atoms, while the basis set of LanL2TZf was used for Cu atoms [22,23]. We previously showed that LanL2TZf is a suitable choice for the geometry optimization of an organometallic compound of the transition element of Fe [24]. Care was taken to select the (global) minimum energy conformation via systematic conformational searching at this level. The nature of each stationary point was established by B3LYP/6-31G(d)/LanL2TZf frequency calculations. The geometry optimization has been completed in the absence of solvent molecules and other impurities, and the optimized structure was compared with the crystalline structure. All DFT calculations were carried out using the GAUSSIAN 03 software [25].

4. Results and discussion

4.1. Synthesis

The trinuclear metal complex was synthesized by a one-pot reaction of $CuCl_2{\cdot}6H_2O$ and H_2L in a 3:2 molar ratio in methanol at reflux, giving the trinuclear Cu(II) complex, $[Cu_2(\mu\text{-}L)_2CuCl_2]$. The purity of the complex was checked by C, H, N elemental analyses, which led to our postulated $[Cu_3L_2Cl_2]$ empirical formula for this complex.

4.2. Description of the crystal structure

The crystal structure of the trinuclear complex of $[Cu_2(\mu\text{-}L)_2CuCl_2]{\cdot}C_7H_8$ was determined by single-crystal X-ray diffraction. The molecular structure of the copper complex is shown in Figs. 1 and 2. The selected main bond lengths and angles are summarized in Table 2. X-ray quality dark green crystals of $[Cu_2(\mu\text{-}L)_2CuCl_2]{\cdot}C_7H_8$ were obtained freshly by the evaporation of the solvents (methanol/2-propanol/toluene). The unit cell contains two distinct entities of $[Cu_2(\mu\text{-}L)_2CuCl_2]$ moieties. The most remarkable aspect of the trinuclear complex is that it adopts a bent structure of the three copper atoms, with a Cu1—Cu3—Cu2 intra-atomic angle of approximately 90.62(2)°. The three copper atoms are five coordinate with a distorted square pyramidal geometry. The geometry of the terminal moieties are best described as a distorted square pyramidal with Addison parameters $\tau = 0.024$ for Cu1 and $\tau = 0.046$ for Cu2.The parameter τ is defined as $\tau = (\alpha–\beta)/60$, $(\alpha > \beta)$, where α and β are the largest angles; $\tau = 1$ for a regular