Synthesis, Structure and Electrochemistry of Tetranuclear Oxygen-Centered Copper(II) Clusters with Acetylacetone and Benz-pyrazole Hydrolyzed Derivatives as Ligand

Rasoul Vafazadeh1, * and Anthony C. Willis2

1 Department of Chemistry, Yazd University, Yazd, Iran.
2 Research School of Chemistry, Australian National University, Canberra, ACT 2601, Australia.

* Corresponding author: E-mail: rvafazadeh@yazd.ac.ir and rvafazadeh@gmail.com
Tel: +98 3538214778 Fax: +98 3537250110
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Abstract

Two copper(II) clusters Cu4OCl6(pyrazole)4 (1) and Cu4OBr6(Br-pyrazole)4 (2) have been synthesized by reacting acetylacetone and benzohydrazide (1:1 ratio) with CuX2 (X = Cl for 1 and X = Br for 2) in methanol solution. The structures of both clusters have been established by X-ray crystallography. The clusters contain four Cu, one O, six μ2-X atoms, and four pyrazole ligands. The pyrazole was prepared in situ by the reaction of acetylacetone with benzohydrazide in methanol under reflux. In 2, the methine hydrogen of the pyrazole ligand has been replaced by bromine atom. The four copper atoms encapsulate the central O atom in a tetrahedral arrangement. All copper atoms are five-coordinate and have similar coordination environments with slightly distorted trigonal bipyramidal geometry. The cyclic voltammogram of the clusters 1 and 2 show a one-electron quasi-reversible reduction wave in the region 0.485 to 0.731 V, and a one-electron quasi-reversible oxidation wave in the region 0.767 to 0.898 V. In 1, one irreversible oxidative response is observed on the positive side of the voltammogram at 1.512 V and this can be assigned to Cu(II) to Cu(III) oxidation.

Keywords: Copper clusters; Pyrazole; Crystal structures; Cyclic voltammetry; Tetranuclear

1. Introduction

The synthesis of multi-metal clusters by spontaneous self-assembly of organic-inorganic ligands and transition-metal ions have attracted special attention due to their potential application in magnetic, electrochemical, catalytic studies and coordination chemistry.1–9 A feature of modern coordination chemistry is its development of metal bio-sites modeling for biology systems.10 Self-assembly is one of the few practical strategies for making such compounds. The spontaneous self-assembly of well-defined and complex molecular entities from constituent subunits occurs in solution.11 In biology systems, self-assembly occurs by weak inter- or intra-molecular interactions of non-covalent bonds, while self-assembly in coordination chemistry occurs through the formation of covalent coordinate bonds.11–15 It is well known that the constituent ligands and metals play important roles in the structures and properties of the multi-metal clusters. The synthesis and characterization of high nuclearity metal clusters with oxo bridges has been the goal of much research.15–20 Oxo-copper(II) halide clusters have been extensively studied.20–23 Bertrand reported the first structure in 1966.24 The usual arrangement in tetranuclear Cu4OX₆L₄ complexes consists of a central oxygen atom bound to four tetrahedrally arranged copper(II) atoms. At the same time, each copper(II) atom adopts a trigonal bipyramidal coordination with one terminal axial position occupied by ligand L. Many novel complexes or coordination polymers based on ligands generated in situ have been synthesized through one-pot reaction under hydrothermal or solution reaction conditions.25–27 Here we report the synthesis, characterization
and electrochemistry of tetranuclear copper(II) clusters 1 and 2, obtained by reaction of CuX₂ (X = Cl and Br) and pyrazole ligands generated in situ under hydrothermal conditions.

2. Experimental

2.1. Reagents and Physical Measurements

All chemicals were used as supplied by Merck and Fluka without further purification. 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-Visible Cintra 101 spectrophotometer with 1 cm quartz, in the range of 200–800 nm at 25 °C. Elemental analyses (C, H, N) were performed using a CHNS-O 2400II PERKIN-ELMER elemental analyzer. Cyclic voltammetry was carried out using an Autolab potentiostat/galvanostate (PGSTAT-302N) instrument. The measurements were performed at 300 K in acetonitrile solutions containing 0.1 M tetrabutylammonium perchlorate (TBAP) and 0.1 mM copper(II) complexes deoxygenated by bubbling with nitrogen. The working, counter, and reference electrodes used were glassy carbon electrode, platinum wire and Ag/AgCl (3.0 KCl), respectively.

2.2. X-ray Crystallography

Diffraction images were measured at 200 K on a Nonius Kappa CCD diffractometer using Mo Kα, graphite monochromator (λ = 0.71073 Å). Data were extracted using the DENZO/SCALEPACK package.28 Structures were solved by direct methods with the use of SIR92 and refined on F² by full matrix last-squares techniques using the CRYSTALS program package.29,30 Atomic coordinates, bond lengths and angles, and displacement parameters were deposited at the Cambridge Crystallographic Data Centre. Crystallographic details are summarized in Table 1.

2.3. Syntheses of Tetranuclear Copper(II) Clusters

The cluster 1 was prepared as previously reported.36 The cluster 2 was synthesized similar to cluster 1, acetylacetone (1.05 mL, 10 mmol) was added to a methanol solution (25 mL) of benzohydrazide (1.36 g, 10 mmol), and the mixture was heated to reflux for 5 h. A solution of CuBr₂ (2.23 g, 10 mmol) in methanol was added to the above-mentioned bright yellow solution. The green solution was stirred at room temperature for 2 h.

Cluster 1: Yield 40%. Anal. Calcd. for C₂₀H₂₈Br₁₀Cu₄N₈O: C, 27.69; H, 3.72; N, 12.92. Found: C, 27.57; H, 4.01; N, 12.52%. IR (KBr, cm⁻¹): v = C–N (pyrazol ring) = 1572, vN–H = 3335. Electronic spectra in methanol: λ(max)(nm), (log ε): 813 (2.24), 311 (3.59).

Cluster 2: A green-brown precipitate was obtained upon the slow evaporation of the solvents at room temperature over two days. Dark-green block crystals were obtained by slow evaporation of the mother liquor and were washed with methanol and dried in air. Yield 25%. Anal. Calcd. for C₂₀H₂₈Br₁₀Cu₄N₈O: C, 16.57; H, 1.95; N, 7.73. Found: C, 16.72; H, 2.01; N, 7.52%. IR (KBr, cm⁻¹): v = C–N (pyrazol ring) = 1566, vN–H = 3310. Electronic spectra in methanol: λ(max)(nm), (log ε): 823 (2.07), 316 (3.42).

3. Result and Discussion

3.1. Synthesis

The synthetic route of the clusters is shown in Scheme 1. Clusters 1 and 2 were synthesized by a two-steps-one-pot reaction with the initial formation of the pyrazole (without its isolation) and then the addition of a methanolic solution of CuX₂ (X = Cl and Br). The pyrazole was prepared in situ from the reactions between acetylacetone and benzohydrazide in methanol under reflux. Initially, (3,5-dimethyl-1H-pyrazol-1-yl)(phenyl)methanone (benz-pyrazole) was obtained by the reaction of equimolar amount of acetylacetone and benzohydrazide.31 The resulting solution was refluxed for 5 h and then was used for the synthesis of the complex without further purification.

Cluster 1, Cu₄Cl₆O(pyrazole)₄, was obtained by the reaction between CuCl₂ and benz-pyrazole in association with hydrolysis at room temperature (Scheme 1). A search of the literature revealed that the cluster had been reported previously by Jacimović et al. in 2007.32 They synthesized the green crystals of the copper(II) cluster from the one...
The reaction of 3,5-dimethylpyrazole-1-carboxamide and CuCl₂ in hot ethanol solvent leads to formation of cluster 1, Cu₄Cl₆O(Br-pyrazole)₄ (Scheme 1).

3.2. Crystal Structures

The structure of cluster 1 is similar to the structure that has been previously reported. In the Jáčimović report, the space group was triclinic P1̅. This crystal structure contained a region of electron density external to the atoms of the complex molecule which suggested the presence of ethanol solvate molecules. Attempts to find a satisfactory structural model for these molecules however failed, and SQUEEZE was used to correct the data set for the electron density in this region of the cell. Our determination is in the monoclinic space group P2/n. It also contains disordered solvate species, though not ethanol. This same cell was reported to the Cambridge Structure Database as a private communication by Stibrany and Potenza in 2007. Crystallographic data for our determination of the structure of cluster 1 were given previously. Selected interatomic distances and angles for 1 are given in Table 2 to allow direct comparisons values for cluster 2. Both structures were run at the same temperature (200 K).

The molecular structures of the clusters, with selected atoms labeled, are shown in Figures 1 and 2. Selected bond lengths and angles are given in Table 2. The clusters each contains four Cu, one μ₄-O and six μ₂-X atoms (X = Cl and Br), along with four 3,5-dimethyl-1H-pyrazole ligands for 1 and four 4-bromo-3,5-dimethyl-1H-pyrazole ligands for 2. The four Cu(II) ions form a nearly ideal tetrahedral skeletal structure with the Cu–Cu–Cu angles ranging from 59.0 to 61.3° for 1 and 59.6 to 61.2° for 2 and Cu–Cu distances ranging from 3.078 to 3.145 Å, for 1 and 2 respectively, which are comparable with those found in similar cluster compounds. The four copper

| Complex 1                        | Complex 2                        |
|----------------------------------|----------------------------------|
| Cu1–Cl1 2.3580 (11)              | Cu1–Br1 2.5072 (6)               |
| Cu1–Cl4 2.4386 (19)              | Cu1–Br2 2.5163 (6)               |
| Cu1–Cl2 2.4069 (12)              | Cu1–Br1 2.5807 (6)               |
| Cu1–N1 1.9620 (3)                | Cu1–Br2 2.5163 (6)               |
| Cu1–O1 1.9072 (17)               | Cu1–Cu1 3.1450 (7)               |
| Cu2–Cl1 2.3567 (10)              | Cu1–Cu1 3.1274 (8)               |
| Cu2–Cl2 2.3810 (10)              | Cu1–O1 1.9223 (4)                |
| Cu2–Cl3 2.4901 (11)              | Cu1–N1 1.967 (3)                 |
| Cu2–N3 1.9530 (3)                | Cu1–N2 1.355 (4)                 |
| Cu2–O1 1.9901 (16)               | Cu1–C4 1.342 (4)                 |
| N1–N2 1.3550 (4)                 | C3–Br3 1.871 (3)                 |
| N1–C4 1.3340 (4)                 | C2–N2 1.343 (5)                  |
| Cl1–Cu1–Cl2 116.83 (5)           | Br1–Cu1–Br2 108.83 (2)           |
| Cl1–Cu1–O1 85.46 (4)             | Br1–Cu1–Br1 118.90 (2)           |
| Cl4–Cu1–O1 82.59 (8)             | Br2–Cu1–Br1 131.17 (2)           |
| Cl1–Cu1–N1 96.12 (9)             | Br2–Cu1–O1 87.145 (17)           |
| Cl4–Cu1–N1 92.75 (10)            | Br2–Cu1–N1 92.85 (9)             |
| O1–Cu1–N1 174.33 (11)            | Br2–Cu1–O1 87.189 (18)           |
| Cl1–Cu2–Cl2 125.74 (5)           | Br1–Cu1–N1 93.14 (8)             |
| Cl1–Cu2–Cl3 117.96 (4)           | O1–Cu1–N1 179.56 (9)             |
| Cl1–Cu2–N3 175.97 (5)            | Cu1–Cu1 109.774 (12)             |
| Cu1–O1–Cu2 107.53 (17)           | Cu1–Cu1 108.87 (2)               |
| Cu1–O1–Cu1 111.06 (15)           | Cu1–Br1–Cu1 76.34 (2)            |
| Cu1–O1–Cu2 108.36 (18)           |                                  |

* symmetry codes for 1: (i) −x + 3/2, y, −z + 3/2 and for 2: (i) y + 1/4, −x + 3/4, −z + 7/4; (ii) −x + 1, −y + 1/2, z; (iii) −y + 3/4, x − 1/4, −z + 7/4.

Figure 1. The structure of the [Cu₄Cl₆O(C₆H₈N₂)_4] molecule, cluster 1, with labelling of selected atoms, showing only one location of the disordered atom (Cl4). Asterisks indicate atoms generated by symmetry operations. Anisotropic displacement ellipsoids exhibit 30% probability levels. Hydrogen atoms are drawn as circles with small radii.
atoms encapsulate a central O atom in a distorted tetrahedral arrangement (Figure 3). The Cu–O bond lengths are 1.907(2) and 1.909(2) Å for 1 and 1.9223(4) Å for 2. The Cu–O–Cu angles in 1 and 2 are 107.53(2)–114.04(2)° and 108.87(2)–109.77(1), respectively; these results are in agreement with 109.47° for an ideal tetrahedron. Between each pair of copper atoms there is a bridging chlorine atom with Cu–Cl distances of 2.3567(10)–2.4908(2) Å for 1, and a bridging bromine atom with Cu–Br distances of 2.5072(6)–2.5807(6) Å for 2. In 2, the methine hydrogen of the pyrazole ligand has been replaced by a bromine atom with a C–Br distance of 1.871(3) Å.

The four copper atoms are five-coordinate and have similar coordination environments (Fig. 3). The geometry of the copper atoms in 1 and 2 are best described as having a distorted trigonal bipyramid coordination sphere with structural parameter $\tau = 0.90$ for 1 and $\tau = 0.80$ for 2. The parameter $\tau$ is defined as $\tau = (\alpha - \beta)/60$, $\alpha > \beta$, where $\alpha$ and $\beta$ are the largest angles, so $\tau = 1$ for a regular trigonal bipyramid and $\tau = 0$ for a regular square pyramid.

The three halogen atoms lie in the equatorial positions of the trigonal bipyramid, while the central oxygen and the pyridine nitrogen from the pyrazole ligand are placed at the axial sites. The O–Cu–Cl and N–Cu–Cl bond angles in 1 are 81.18(8)–85.74(4)°, and 92.75(10)–99.03(9)°, respectively. The O–Cu–Br and N–Cu–Br bond angles in 2 are 85.106(17)–87.189(18)°, and 92.85(9)–94.48(8)°, respectively.

In cluster 1, the planes of the pyrazole rings are angled about 78° to each other, while in 2 the angles are about 57°.

3.3. Cyclic Voltammetry

The electrochemical behavior of the Cu(II) complexes has been studied by cyclic voltammetry (CV) in CH$_3$CN solution. Tetrabutylammonium perchlorate (TBAP, 0.1 M) was used as the supporting electrolyte. The electrochemical data are summarized in Table 3 and the cyclic voltammograms of the copper(II) complexes are depicted in Fig. 4. As shown in figure 4a, cluster 1 shows a pair of redox peaks with a cathodic peak potential ($E_{pc}$) at 0.485 V and an anodic peak potential ($E_{pa}$) at 0.767 V. The half-wave potential ($E_{1/2} = 1/2(E_{pa} + E_{pc})$) and the peak-to-peak potential separation ($\Delta E_{p}$) were obtained as 0.626 V and 0.282 V, respectively, indicating that the electrochemical behavior of 1 is quasi-reversible corresponding to the redox process of all four copper (Cu(II)/Cu(I)). The crystal structures of complex 1
shows the presence of four similar Cu(II) centers in the tetrannuclear cluster, so we can assume that in solution the four copper ions exhibit similar coordination environments as in the solid state. One irreversible oxidative response is observed on the positive side of voltammogram at 1.512 V and this can be assigned to Cu(II) to Cu(III) oxidation.

The cyclic voltammogram for copper(II) complex 2 was recorded at anodic potential in the range –0.2 to +1.6 V. The cyclic voltammogram for 2 is shown in Fig. 4b. On changing the halogen from Cl to Br more redox peaks are observed. This usually happens when Cl is changed to Br or I in similar core structures.42–44 The cyclic voltammetry of 2 shows two anodic peaks potential at 0.716 and 0.898 V and two cathodic peaks at 0.731 and 0.530 V. We could not get any wave for the oxidation of copper(II) to copper(III) in the potential range up to 1.6 V.

Table 3. Cyclic voltammetric data for complexes 1 and 2 (versus Ag/AgCl)

| complex | $E_{pc}$ (V) | $E_{pa}$ (V) | $E_{1/2}$ (mV) |
|---------|-------------|-------------|---------------|
| 1       | 0.485       | 0.767, 1.512| 0.626         |
| 2       | 0.530, 0.731| 0.716, 0.898| 0.623, 0.815  |

4. Conclusion

The present work describes the synthesis by a two-steps-one-pot reaction, characterization, and electrochemical behavior of copper(II) clusters 1 and 2. Single crystal X-ray diffraction studies revealed that the two complexes have similar structures, namely a tetrannuclear cluster containing four Cu, one μ4-O, six μ2-X atoms (X = Cl, 1 and Br, 2), and four pyrazole ligands. The electrochemical behavior of clusters 1 and 2 are quasi-reversible corresponding to the redox process of all four copper (Cu(II)/Cu(I)).

5. Supplementary Material

The deposition number of the studied cluster 2 is CCDC 1404320. These data can be obtained free-of-charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data-request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033.

6. Acknowledgments

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7. References

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Figure 4. Cyclic voltammograms of the complexes 1 and 2 in a 0.1 M TBAP acetonitrile solution at 300 K and 100 mV/s.
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Sintetizirali smo dva bakrova(II) klastra Cu₄OCl₆(pirazol)₄ (1) in Cu₄OBr₆(Br-pirazol)₄ (2) z reakcijo acetilacetona z benzohidrazidom (razmerje 1:1) in CuX₂ (X = Cl (1) in X = Br (2)) v metanolu. Strukturi obeh klastrov sta bili določeni z rentgensko difrakcijo. Klastra sta zgradjena iz štirih Cu, enega O, šestih μ₂-X atomov in štirih pirazolskih ligandov. Pirazol je bil pripravljen in situ z reakcijo acetilacetona z benzohidrazidom v metanolu pri refluku. V 2 se je metinski vodik na pirazolu substituiral z bromovim atomom. Štirje bakrovi atomi obdajajo centralni O atom v tetraedrični razporeditvi. Vsi bakrovi atomi so pentakoordinirani in imajo podobno koordinacijsko razporeditev ligandov v obliki nekoliko popačene trigonalne bipiramidalne geometrije. Ciklični voltamogram klastrov 1 in 2 kaže enoelektroski kvazi-reverzibilni redukcijski signal v območju 0,485 do 0,731 V ter enoelektroski kvazi-reverzibilni oksidacijski signal v območju 0,767 do 0,898 V. Pri 1 je opaziti tudi en ireverzibilni oksidacijski signal na pozitivni strani voltamograma pri 1,512 V, ki bi ga lahko pripisali oksidaciji Cu(II) do Cu(III).