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Syntheses and crystal structure of binuclear μ -oxamido copper(II) complexes containing 1,4,7-triazacyclononane as a terminal ligand

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Two new binuclear copper(II) complexes, Cu(tacn)Cu(oxpn)(ClO₄)₂·C₂H₅OH (**1**), and Cu(tacn)Cu(oxap)(ClO₄)₂·CH₃OH (**2**), have been prepared from the planar fragment Cu(oxpn) and Cu(oxap) (tacn denotes 1,4,7-triazacyclononane, oxpn and oxap stand for the dianions of *N,N'*-bis(3-aminopropyl)oxamide, and *N,N'*-bis(2-aminopropyl)oxamide, respectively). The complexes have been characterized by means of elemental analyses and IR, and UV spectra. The crystal structure of compound **1** shows that copper(II) coordinates to the four nitrogen atoms of oxpn in a square-planar environment and the other copper(II) ion is in a distorted square-pyramidal environment.

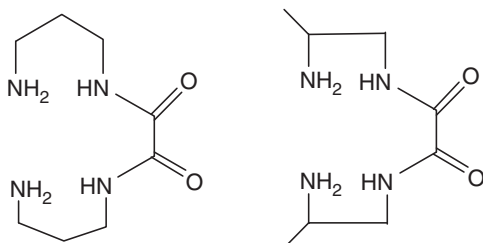
Keywords: Binuclear compounds; Copper(II) complexes; Oxamide; 1,4,7-Triazacyclononane; X-ray structure

1. Introduction

Binuclear metal complexes with extended bridging ligands are an active area of coordination chemistry, because of spin exchange between metal ions and biological significance.

Mononuclear copper(II) complexes of *N,N'*-disubstituted oxamides act as bidentate chelating ligands toward a second metal ion with formation of binuclear complexes. Through this approach, a large number of binuclear copper(II) complexes have been prepared and studied in recent years. However, for most cases reported, the terminal ligands coordinating to the other copper(II) atom were bidentate chelating agents [1–8], and in two cases linear tridentate agents [1]. In this work, two new binuclear copper(II) complexes, in which the terminal copper(II) ions are blocked with the more rigid macrocycle tacn (tacn = 1,4,7-triazacyclononane), have been prepared and characterized. These complexes have formulas Cu(tacn)Cu(oxpn)(ClO₄)₂·C₂H₅OH (**1**)

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Scheme 1. Structures of H₂oxpn and H₂oxap.

and Cu(tacn)Cu(oxap)(ClO₄)₂·CH₃OH (**2**), where oxpn and oxap are the dianions of *N,N'*-bis(3-aminopropyl)oxamide and *N,N'*-bis(2-aminopropyl), respectively. Scheme 1 shows the structures of H₂oxpn and H₂oxap. The crystal structure of compound **1** has been determined.

2. Experimental

2.1. Materials

All reagents used in the syntheses were analytical grade. The planar fragment Cu(oxpn) and Cu(oxap) were synthesized as previously described [1–9].

2.2. Syntheses of the complexes

2.2.1. Cu(tacn)Cu(oxpn)(ClO₄)₂·C₂H₅OH (1**).** To 0.3 mmol (79 mg) of Cu(oxpn) stirred in 5 mL of ethanol was added a solution of 0.3 mmol (111 mg) copper(II) perchlorate in 5 mL of ethanol. A brown solution with a little brown precipitate was formed. To the mixture was then added a solution of 0.3 mmol tacn in 3 mL of ethanol. The resulting deep green solution was filtered. Overnight green needle-like crystals formed and were separated by filtration. Finally, well-shaped single crystals were obtained through slow evaporation of the filtrate at room temperature. Anal. Calcd for C₁₆H₃₇N₇O₁₁Cl₂Cu₂ (%): C, 27.39; H, 5.28; N, 13.98; Cu, 18.12. Found: C, 27.51; H, 4.93; N, 14.24; Cu, 18.35.

2.2.2. Cu(tacn)Cu(oxap)(ClO₄)₂·CH₃OH (2**).** To 0.3 mmol (79 mg) of Cu(oxap) stirred in 5 mL of methanol was added a solution of 0.3 mmol (111 mg) copper(II) perchlorate in 5 mL of methanol. A blue solution along with a little dark blue precipitate was formed. To the mixture a solution of 0.3 mmol tacn in 3 mL of methanol was added. The resulting green solution was filtered after removal of some solvent, the solution was allowed to stand overnight. Green microcrystals formed and were separated by filtration. Anal. Calcd for C₁₅H₃₅N₇O₁₁Cl₂Cu₂ (%): C, 26.20; H, 5.09; N, 14.26; Cu, 18.49. Found: C, 25.81; H, 5.22; N, 13.53; Cu, 18.20.

2.3. Physical measurements

Analyses for C, H and N were performed on a Perkin-Elmer 240 analyser and metal content was determined by EDTA titration. Infrared spectra were recorded on

Table 1. Crystallographic data for $\text{Cu}(\text{tacn})\text{Cu}(\text{oxpn})(\text{ClO}_4)_2 \cdot \text{C}_2\text{H}_5\text{OH}$ (**1**).

Formula	$\text{C}_{16}\text{H}_{37}\text{N}_7\text{O}_{11}\text{Cl}_2\text{Cu}_2$
Formula weight	701.50
Temperature (K)	299 (1)
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	12.186 (2)
b (Å)	17.783 (4)
c (Å)	13.286 (3)
β (°)	99.38 (3)
V (Å ³)	2841 (1)
Z	4
Density (Calcd, g cm^{-3})	1.640
μ (Mo $K\alpha$) (mm^{-1})	1.7518
Crystal size (mm)	$0.25 \times 0.35 \times 0.40$
Instrument	Enraf-Nonius CAD-4
Radiation	Monochromated $\text{MoK}\alpha$ ($\lambda = 0.71073$ Å)
Scan mode	$\omega/2\theta$
2θ range (°)	4.5–50
Scan range (°)	$0.6 + 0.35 \tan \theta$
Index ranges	$-14 \leq h \leq 14, 0 \leq k \leq 21,$ $0 \leq l \leq 15$
Reflections collected	5411
Independent reflections	4402
Observed reflections ($I \geq 3\sigma(I)$)	2899
Absorption correction	Empirical
Parameters	379
R, wR	0.062, 0.070
Goodness-of-fit on F	1.15
Largest difference peak and hole ($\text{e} \text{Å}^{-3}$)	0.73, -0.63

a Shimadzu IR-408 spectrometer using KBr pellets. The electronic spectra were measured with acetonitrile solutions on a Shimadzu UV-2101 PC UV-Vis scanning spectrophotometer.

2.4. X-Ray structural characterization

A summary of the crystallographic data and structure refinement parameters are given in table 1. The crystal structure was solved by direct methods and refined by full-matrix least-squares on F . The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/(\sigma^2(F) + 0.0001F^2)$. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were added in calculated positions and refined with riding model position parameters and fixed isotropic thermal parameters. The final R factor was 0.062 ($wR = 0.070$) for all observed reflections.

3. Results and discussion

3.1. Syntheses

In preparation of complex **1**, when copper(II) perchlorate solution was added to $\text{Cu}(\text{oxpn})$ suspension, some brown precipitate formed. Lloret and co-workers [10] have demonstrated that the mixing of copper(II) nitrate with an equivalent of

Cu(oxpn) leads to formation of binuclear species in which the oxamido ligand exhibits a trans conformation; thus the precipitate should be analogous binuclear species. The IR spectrum for the precipitate exhibited peaks corresponding to amino groups (3150 cm^{-1}), oxamido ligands (1600 cm^{-1}) and perchlorate anions (1100 cm^{-1}). In the preparation of complex **2**, similar product was formed in the same step. When tacn was added to the mixtures, the conformations of oxamido ligands changed from *trans* to *cis* resulting in the formation of the target complexes.

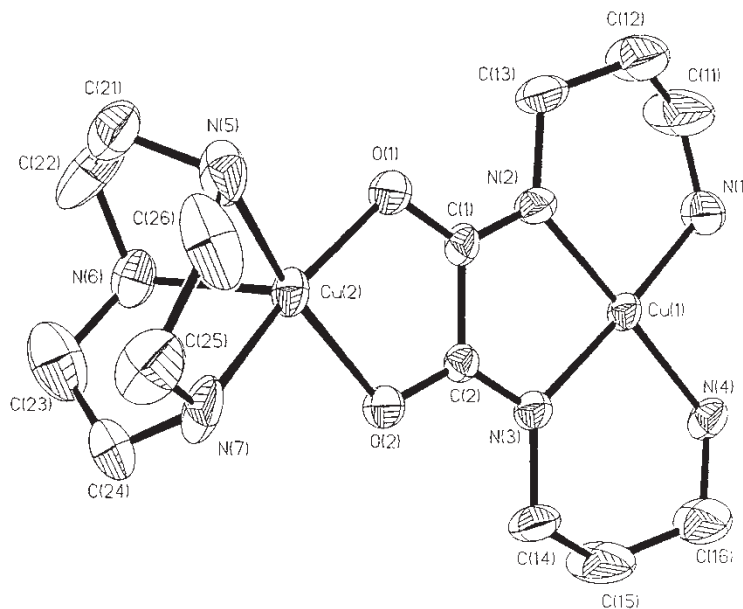
3.2. General characterization

Elemental analyses and spectral data for the products indicate that the reaction of Cu(oxpn) or Cu(oxap) with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and tacn yielded binuclear copper(II) complexes. In the IR spectra, the complexes both exhibit a strong, broad band centered at 1100 cm^{-1} characteristic of the perchlorate anions, a weak band at 2900 cm^{-1} attributable to C–H bonds as well as a broad band in the range $3100\text{--}3600\text{ cm}^{-1}$ due to the presence of co-crystallized methanol or ethanol molecules and hydrogen bonds. The strong, broad bands centered at 1625 cm^{-1} for **1** and **2** are assigned to the bridging oxamido ligands. These bands shift toward higher frequencies in comparison to the corresponding copper(II) precursors (Cu(oxpn), 1590 cm^{-1} ; Cu(oxap), 1590 cm^{-1}), indicating coordination of the oxamido carbonyl groups to another copper(II) [2]. In the electronic spectra, weak bands in the visible region (**1**, 606 nm ; **2**, 594 nm) may be attributed to the superposition of the d–d transitions of two copper(II) chromophores and the strong, broad bands centered at 238 nm for **1** and 230 nm for **2** are attributed to charge-transfer absorptions.

3.3. Description of the structure: $\text{Cu}(\text{tacn})\text{Cu}(\text{oxpn})(\text{ClO}_4)_2 \cdot \text{C}_2\text{H}_5\text{OH}$ (**1**)

A perspective view of the cation $[\text{Cu}(\text{tacn})\text{Cu}(\text{oxpn})]^{2+}$ with the atom-labeling scheme is showed in figure 1. Selected bond lengths and angles are listed in table 2.

In the binuclear cation, the two copper(II) ions are linked by a *cis*-configuration μ -oxamido ligand with separation of 5.235 \AA . On the oxpn side, the copper(II) ion (Cu(1)) is in a square-planar environment with coordination of four nitrogen atoms of oxpn. The bond lengths of Cu(1)–N(1) (2.003 \AA) and Cu(1)–N(4) (2.004 \AA) are slightly longer than those of Cu(1)–N(2) (1.972 \AA) and Cu(1)–N(3) (1.974 \AA), due to the amido nitrogen atoms (N(2), N(3)) being negatively charged. The Cu(1) coordination environment can also be viewed as a square pyramid considering an oxygen atom (O(14)) of one perchlorate anion weakly coordinates to Cu(1) at the vertex (Cu(1)···O(14), 2.831 \AA). Cu(1) deviates by only 0.009 \AA from the mean plane (denoted as P1) through the four nitrogen atoms toward O(14). On the tacn side, the copper(II) ion (Cu(2)) is in a distorted square pyramidal environment with two oxamido oxygen atoms (O(1), O(2)) and two nitrogen atoms (N(5), N(7)) of the tacn ligand in the basal plane and the other nitrogen atom (N(6)) at the apical position. The distortion can be evaluated by the structural index (τ) defined by J. Reedijk *et al.* [11]. Here for the coordination environment of Cu(2), τ is 0.14, which indicates it is more of a square pyramid ($\tau=0$) than a trigonal bipyramid ($\tau=1$). The axial Cu–N bond length (Cu(1)–N(6), 2.142 \AA) is a little longer than the basal ones (Cu(1)–N(5), 2.004 \AA ; Cu(1)–N(7), 2.015 \AA). Cu(2) is displaced by 0.250 \AA from the O(1)O(2)N(5)N(7) least-squares basal plane (denoted as P2) toward N(6). As a result of the

Figure 1. Perspective view of the cation $[\text{Cu}(\text{tacn})\text{Cu}(\text{oxpn})]^{2+}$ with the atom-labeling scheme.Table 2. Selected bond lengths (Å) and bond angles (°) for **1**.

Cu(1)–N(1)	2.003 (7)	Cu(2)–N(6)	2.142 (6)
Cu(1)–N(2)	1.972 (6)	Cu(2)–N(7)	2.015 (7)
Cu(1)–N(3)	1.974 (5)	O(1)–C(1)	1.286 (8)
Cu(1)–N(4)	2.004 (6)	O(2)–C(2)	1.298 (8)
Cu(2)–O(1)	1.948 (6)	C(1)–C(2)	1.482 (10)
Cu(2)–O(2)	1.973 (5)	C(1)–N(2)	1.289 (9)
Cu(2)–N(5)	2.004 (7)	C(2)–N(3)	1.296 (8)
N(1)–Cu(1)–N(2)	93.9 (3)	N(5)–Cu(2)–N(6)	83.0 (3)
N(1)–Cu(1)–N(3)	176.7 (3)	O(1)–Cu(2)–N(7)	169.6 (2)
N(2)–Cu(1)–N(3)	83.6 (2)	O(2)–Cu(2)–N(7)	92.8 (2)
N(1)–Cu(1)–N(4)	88.7 (3)	N(5)–Cu(2)–N(7)	83.6 (3)
N(2)–Cu(1)–N(4)	177.2 (3)	N(6)–Cu(2)–N(7)	80.6 (3)
N(3)–Cu(1)–N(4)	93.8 (2)	O(1)–C(1)–C(2)	117.4 (6)
O(1)–Cu(2)–O(2)	84.4 (2)	O(1)–C(1)–N(2)	126.9 (7)
O(1)–Cu(2)–N(5)	95.9 (3)	C(2)–C(1)–N(2)	115.6 (5)
O(2)–Cu(2)–N(5)	161.3 (3)	O(2)–C(2)–C(1)	115.4 (5)
O(1)–Cu(2)–N(6)	109.6 (2)	O(2)–C(2)–N(3)	127.3 (6)
O(2)–Cu(2)–N(6)	114.7 (2)	C(1)–C(2)–N(3)	117.2 (6)

rigidity of tacn ligand, the three angles formed by Cu(2) and N(6), N(5), N(7) are all acute, being 80.6, 83.0, 83.6°, respectively. The dihedral angle between P1 and P2 is 14.3°.

Starting from Cu(oxpn), Kahn *et al.* [1] prepared two binuclear copper(II) complexes and determined their structures, $[\text{Cu}(\text{oxpn})\text{Cu}(\text{bpy})](\text{ClO}_4)_2$ (**4**; bpy = 2,2'-bipyridyl) and $[\text{Cu}(\text{oxpn})\text{Cu}(\text{petdien})](\text{ClO}_4)_2$ (**5**; petdien = N,N,N',N'',N''-pentamethyldiethylenetriamine). The structure differences between complexes **1**, **4** and **5** mainly exist in the terminal copper(II) moieties. Though the polyhedra around the copper(II) ions

can all be described as distorted square pyramids, the extents of distortion are different. The polyhedron in complex **4**, including the bidentate ligand bpy in the basal plane and an oxygen atom of a perchlorate group at the apex, is the least distorted. This is clear in that the angles around the copper(II) ion are close to the corresponding values of the regular square pyramid (deviations less than 8°). In complexes **1** and **5**, the distortions for the terminal copper(II) polyhedra, both containing two equatorial nitrogen atoms and one apical belonging to a tridentate ligand, are more pronounced in comparison to that in complex **4** and the polyhedron in complex **1** represents the most distorted. Indeed, for the polyhedron in complex **1**, the four bond angles in the basal plane are 83.6, 84.4, 92.8, 95.9°, respectively, while in complex **5**, those angles are 83.3, 87.5, 92.8, 93.8°, respectively. On the other hand, in complex **1**, the angles at the terminal copper(II) involving the apical atom vary between 80.6 and 114.7° (80.6, 83.0, 109.6, 114.7°), while in complex **5**, those angles between 84.3 and 114.3° (84.3, 91.3, 100.8, 114.3°). Considering that the petdien ligand is linear and more flexible than tacn, the structural differences between the terminal copper(II) polyhedra in complexes **1** and **5** are clearly due to the constraints within the cyclic ligand.

Supplementary material

Crystallographic data for the structure analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 190416 for complex **1**.

Acknowledgement

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