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Research paper

# Influence of the counterion on the geometry of Cu(I) and Cu(II) complexes with 1,10-phenanthroline

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ABSTRACT

The influence of the counterions on the geometry of Cu(I) and Cu(II) unsubstituted *phen*-based (*phen* = 1,10-phenanthroline) complexes was investigated. The synthetic strategy used afforded the synthesis of both the tetracoordinated Cu(I) and pentacoordinated Cu(II) species with general formula $[(phen)_2Cu]^+Y^-$ ($Y^-$ = $ClO_4^-$, $I^-$, $SCN^-$ and $BF_4^-$) and $[(phen)_2CuX]^+Y^-$ (X = $Cl^-$, $I^-$, $NCS^-$, and $Y^-$ = $ClO_4^-$, $I^-$, $SCN^-$ and $BF_4^-$), respectively. The firstly isolated Cu(I) complexes were characterized by IR, $^1H$ NMR and UV-Vis spectroscopies, their proposed structures being confirmed by elemental analysis, atomic absorption spectroscopy (AAS) and thermogravimetric analysis (TGA). The molecular structure of Cu(II) complexes was determined by single crystal X-ray diffraction analysis. While for Cu(I) complexes, the coordinating nature of the counterions seems to have a strong influence (observed in the solid state and concentrated solution) on the flattening distortion ($D_{2d} \rightarrow D_2$) of the geometry about the Cu(I) ion, in the Cu(II) derivatives, the size, shape, number and type of intermolecular interactions established by the counterions, drive not only the overall cations supramolecular organization, but also the molecular stereochemistry around the Cu(II) ion.



## 1. Introduction

The chemistry of copper coordination complexes in its common oxidation states (+1 and +2) was intensively investigated because of their widespread use in a range of application fields, from catalysis [1], to medicinal chemistry [2,3] or electrooptics [4,5]. The properties of the copper complexes are related to the oxidation state of the metal centre and the nature of coordinating ligands and donor atoms bounded, directing the coordination geometries, and further the supramolecular packing. With aromatic diimine ligands, Cu(I) strongly prefers tetrahedral coordination, whereas Cu(II) complexes allows several coordination numbers and modes, with a preference to pentacoordination [6–8].

In particular, Cu(I) coordination complexes based on phenanthroline (*phen*) ligands are intensively researched in solar energy conversion as cheaper alternatives to Ru(II) complexes, having strong metal-to-ligand charge transfer (MLCT) absorption in the visible and relatively long excited-state lifetimes [9–12]. Moreover, the couple $Cu(phen)_2^{+/2+}$ was shown to be important in medicinal chemistry, having excellent nuclease properties [13] and being potent cytotoxic agents already in the submicromolar range [2]. By insertion of sterically active substituents on the *phen* ligand, Cu(I) species are stabilized and their photophysical properties optimized by the reduction of the geometry distortion of both ground and excited states, enhancing the energy, intensity, and lifetime of the emission from the MLCT excited state [8,14–17]. Thus, the majority of photochemical research has been focused on Cu(I) derivatives containing substituted *phen* ligands. The nuclease activity of Cu-*phen* species was shown to be influenced by the ligand environment geometries, planar species being more effective DNA intercalators [2,18,19]. Studies on the different factors affecting the stability of copper complexes was considered essential for the development of the derived molecular materials. Extensive research has been conducted on the influence of the ligands substituent nature and position on the molecular geometry of the ground and excited states [20–24], as well as on the influence of Lewis bases and coordinating solvents on the excited states of

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substituted *phen*-based copper(I) complexes [25–29]. Moreover, the influence of the counterion was only studied on complexes with substituted *phen* and mostly with non coordinating ions [30–33]. Although mostly of the desired properties derive from the complex cation $[Cu(N^N)_2]^+$, counterions play an important role on the photophysical properties of their relative complexes in solution and/or in packing forces and stacking interactions particularly in the solid state related to the stereochemistry of the metal ion [34–37].

Regarding copper species with non substituted *phen* ligands, large structural reorganization may occur because minimum steric demand could permit significant rearrangements. To this end, it is known that the role of copper compounds in some biological systems relies on their kinetic lability and versatile coordination environment [17]. Thus, the synthesis and characterization of several Cu(I) and Cu(II) coordination complexes with unsubstituted *phen* ligands bearing counterions with different coordination strengths ($ClO_4^-$, $I^-$, $SCN^-$, $BF_4^-$) are reported. Differently than the syntheses reported in literature, targeted to obtain copper complexes in a unique oxidation state, herein, the synthetic strategy presented is such that both Cu(I) and Cu(II) derivatives are obtained and isolated on the base of their different solubility properties from the same reaction batch, in an attempt to link the stereochemical preferences of the copper ions. The influence of the counterion on the geometry of Cu(I) species will be discussed, as well as its importance in the molecular engineering of the Cu(II) derivatives.

## 2. Experimental

### 2.1. Materials and methods

$CuSO_4{\cdot}5H_2O$, hydroxylamine hydrochloride, aqueous ammonia, 1,10-phenanthroline monohydrate were purchased from Aldrich; $NaClO_4$, KI, KSCN and $KBF_4$ were purchased from Fluka or Merck. All reagents were of analytical grade and used without further purification. IR spectra were recorded on a Cary 630 FT-IR spectrophotometer, as KBr pellet, in the 400–4000 $cm^{-1}$ range. $^1H$ NMR spectra were run on a Bruker Furier 300 MHz spectrometer. To determine the copper content the samples were digested using Digesdahl® Digestion Apparatus Models 23130-20, −21 by HACH (USA). The concentration of copper ions was then measured using a Flame Atomic Absorption Spectrometer (SensAA, GBC Scientific Equipment, Australia) equipped with a copper hollow cathode lamp (detection limit: 1–5 μg/mL, integration time 3 s). The flame used was an air-acetylene mixture. For each complex, two determinations were made and the average absorbance value was further used. Molar electrical conductivities were measured with a Mettler Toledo FiveEasy plus (FP30) conductivity meter equipped with a Lab conductivity sensor LE740. Electronic spectra were recorded using a V-650 double-beam spectrophotometer with a photomultiplier tube detector, 60 mm integrating sphere coated with barium sulfate.

Thermal decomposition was carried out using a TGA/SDTA 851-LF 1100 Mettler Toledo thermo-gravimetric analyzer. The samples with mass of about 10–20 mg were placed in alumina crucible of 150 μL. The experiments were conducted in air flow of 50 mL $min^{-1}$, in the temperature range of 25–800 °C with a heating rate of 10 °C $min^{-1}$ and a final isothermal heating at 800 °C for 30 min. Complex **4b-*powder*** was analyzed following the same procedure, but under nitrogen flow for the non-isothermal heating and under synthetic air flow for the isothermal heating. The gas was supplied from Linde gas of 4.6 (nitrogen) purity classes.

Powder X-ray diffraction patterns were acquired on a Bruker D2-Phaser equipped with a Cu Kα radiation (λ = 1.5418 Å) and a Lynxeye detector, at 30 kV and 10 mA, with a step size of 0.01°(2θ) between 5 and 50°(2θ).

### 2.2. Crystal structure analyses

Single crystal X-ray data of complexes **1b**, **3b** and **4b-*crystal*** were collected at room temperature with a Bruker-Nonius X8APEXII CCD area detector system equipped with a graphite monochromator with radiation Mo Kα radiation (λ = 0.71073 Å). The data were processed through the SAINT [38] reduction and SADABS [39] absorption software. The structures were solved by direct methods through the *SIR92* structure determination package and refined by full-matrix least-squares based on $F^2$ with *SHELXL* [40,41]. Details of data collection and structure refinements for are reported in Table 1. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were included as idealized atoms riding on the respective carbon atoms with C—H and O—H bond lengths appropriate to the carbon and nitrogen atom hybridization. Due to the disorder of the perchlorate and the tetrafluoroborate anions found in both **1b** and **4b-*crystal*** crystal structures, two positions of the oxygen and fluorine atoms were introduced in the crystal structure refinements with the main occupancy factors of 0.83 and 0.76, respectively. Details of data collection and structure refinements are reported in Table 1.

**CAUTION.** Though while working with **1a** and **1b** we have not met with any incident, care should be taken in handling, since perchlorates are potentially explosive. They should not be prepared and stored in large amounts.

### 2.3. Synthesis

**$ClO_4^-$ complexes**: The synthesis of copper complexes was carried out using the synthesis method reported by Schilt and Taylor for complex $[(phen)_2Cu]ClO_4$, **1a** [42], as follows: 0.20 g (2.9 mmol) $NH_2OH$.HCl and 1 mL aqueous ammonia 25% (dropwise) were added to a hot solution of 0.25 g (1 mmol) $CuSO_4{\cdot}5H_2O$ in 100 mL water. After the mixture has reached the boiling point, 0.40 g (2 mmol) 1,10-phenanthroline monohydrate in 25 mL ethanol was added dropwise, resulting a dark red solution. The mixture was treated with a slight excess of $NaClO_4$ (0.14 g, 1.1 mmol) and boiled for 1 h. Cu(I) species, obtained as dark purple precipitates,

**Table 1**
Details of data collection and structure refinements for complex **1b, 3b** and **4b-*crystal***.

| Complex | **1b** | **3b** | **4b-*crystal*** |
|---|---|---|---|
| Formula | $C_{24}H_{16}Cl_2N_4O_4Cu{\cdot}H_2O$ | $C_{26}H_{16}S_2N_4Cu$ | $C_{24}H_{17}BF_4N_4O_4Cu$ |
| *Mr* | 576.86 | 512.09 | 527.76 |
| Crystal system | Triclinic | Monoclinic | Monoclinic |
| Space group | *P*-1 | $P2_1/c$ | $C2/c$ |
| *a* [Å] | 9.884(2) | 15.198(2) | 19.161(5) |
| *b* [Å] | 11.964(3) | 17.422(3) | 8.121(2) |
| *c* [Å] | 12.243(3) | 9.0356(15) | 16.226(4) |
| α [°] | 63.955(12) | 90 | 90 |
| β [°] | 69.442(12) | 105.042(6) | 100.47(2) |
| γ [°] | 69.767(12) | 90 | 90 |
| *V* [$Å^3$] | 1185.8(5) | 2310.4(6) | 2482.8(11) |
| *Z* | 2 | 4 | 4 |
| $\rho_{calcd}$ [$gcm^{-3}$] | 1.616 | 1.472 | 1.409 |
| μ [$mm^{-1}$] | 1.191 | 1.148 | 0.993 |
| θ range [°] | 2.18–25.24 | 2.34–25.24 | 2.16–25.24 |
| Data collected | 15553 | 27059 | 18083 |
| Unique data, $R_{int}$ | 4965, 0.0306 | 4976, 0.0461 | 2643, 0.0347 |
| No. parameters | 348 | 319 | 199 |
| $R_1$ [obs. data] | 0.0410 | 0.0519 | 0.0548 |
| w$R_2$ [all data] | 0.1184 | 0.1614 | 0.1636 |
| GOF | 1.002 | 1.035 | 1.073 |