



*Dedicated to the memory of  
Professor Ioan Silaghi-Dumitrescu (1950 – 2009)*

## A NEW EXAMPLE OF COEXISTENCE OF TWO DIFFERENT COMPLEXES IN ONE CRYSTAL: $[\{\text{Cu}^{\text{II}}(\text{acac})(\text{phen})\}_2\text{Co}^{\text{II}}(\text{NCS})_4] \cdot 2[\text{Cu}^{\text{II}}(\text{acac})(\text{phen})(\text{NCS})]$

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Herein we describe the synthesis and the structural characterization of a new heterobimetallic  $\{\text{Cu}^{\text{II}}\text{Co}^{\text{II}}\}$  system constructed using the  $[\text{Cu}^{\text{II}}(\text{acac})(\text{phen})(\text{H}_2\text{O})]^+$  mononuclear species and the  $[\text{Co}^{\text{II}}(\text{NCS})_4]^{2-}$  anion as tectons. The reaction of  $[\text{Cu}^{\text{II}}(\text{acac})(\text{phen})(\text{H}_2\text{O})](\text{ClO}_4)$  with  $(\text{Et}_4\text{N})_2[\text{Co}^{\text{II}}(\text{NCS})_4]$  in acetonitrile leads to green crystals of  $[\text{Cu}_2^{\text{II}}(\text{acac})_2(\text{phen})_2\text{Co}^{\text{II}}(\text{NCS})_4] \cdot 2[\text{Cu}^{\text{II}}(\text{acac})(\text{phen})(\text{NCS})]$ . The X-ray diffraction studies revealed a supramolecular solid-state architecture in which heterotrimeric  $[\{\text{Cu}^{\text{II}}(\text{acac})(\text{phen})\}_2\text{Co}^{\text{II}}(\text{NCS})_4]$  and mononuclear  $[\text{Cu}^{\text{II}}(\text{acac})(\text{phen})(\text{NCS})]$  entities are held together by  $\pi$ - $\pi$  stacking interactions and S...S interactions.

### INTRODUCTION

One of the aims of modern coordination chemistry is the development of new synthetic strategies leading to multimetallic complexes, due to their high interest in various fields of chemistry: molecular magnetism,<sup>1</sup> materials science (zeolite-like materials),<sup>2</sup> or in model bioinorganic chemistry.<sup>3</sup> Copper(II) complexes have a plethora of applications: catalysts in the oxidation of cyclic, aliphatic, or aromatic compounds,<sup>4</sup> enantioselective reactions,<sup>5</sup> biomimetic species,<sup>6</sup> molecular magnetism.<sup>7</sup> Another intensively studied feature of copper(II) compounds is represented by the self-assembly processes of metallic complexes into well-defined supramolecular architectures.<sup>8</sup>

The synthesis of polynuclear complexes is governed by three important synthetic strategies: (i) the rational design and use of compartmental ligands, which usually leads to oligonuclear complexes;<sup>9</sup> (ii) the building-block approach, in which complexes with potentially bridging groups

act as ligands toward a second metal ion (complexes as ligands);<sup>10</sup> (iii) the use of *exo*-bidentate ligands, in order to generate high-dimensionality systems.<sup>11</sup>

The synthesis of heteropolynuclear complexes with different nuclearities, dimensionalities or topologies of the metallic centers can be realized using several versatile anionic building-blocks, the most popular being tris-oxalato and bis-oxalato species,<sup>12</sup> hexacyanometallates,<sup>13</sup> and N,N'-bis(coordinating group substituted)oxamides of copper(II).<sup>14</sup> As cationic building-blocks, monocationic  $[\text{Cu}(\text{AA})(\text{BB})]^+$  species (AA = acetylacetonate, salicylaldehyde; BB = 2,2'-bipyridine, 1,10-phenanthroline and related ligands) can be used because the apical position at the copper(II) ion is available for the interaction with various ligands or with anionic complexes, while the aromatic ligands attached to copper(II) favor the intermolecular  $\pi$ - $\pi$  stacking interactions, which play an important role sustaining supramolecular solid-state architectures.<sup>8d,15</sup>

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In this paper, we report on the syntheses and structural characterization of a new heteropolynuclear complex,  $[\{\text{Cu}^{\text{II}}(\text{acac})(\text{phen})\}_2\text{Co}^{\text{II}}(\text{NCS})_4]\cdot 2[\text{Cu}^{\text{II}}(\text{acac})(\text{phen})(\text{NCS})]$ , obtained by reacting the  $[\text{Cu}^{\text{II}}(\text{acac})(\text{phen})(\text{H}_2\text{O})]\text{ClO}_4$  complex ( $\text{acac}^- = \text{acetylacetonate}$ ;  $\text{phen} = 1,10\text{-phenanthroline}$ ) with  $(\text{Et}_4\text{N})_2[\text{Co}^{\text{II}}(\text{NCS})_4]$ .

## EXPERIMENTAL

### Materials

The chemicals and the solvents used were purchased from commercial sources and all manipulations were performed using materials as received.

### Syntheses

The  $[\text{Cu}^{\text{II}}(\text{acac})(\text{phen})(\text{H}_2\text{O})]\text{ClO}_4$  and  $(\text{Et}_4\text{N})_2[\text{Co}^{\text{II}}(\text{NCS})_4]$  mononuclear complexes were prepared using the methods previously described in the literature.<sup>15</sup>

In order to obtain the  $[\{\text{Cu}^{\text{II}}(\text{acac})(\text{phen})\}_2\text{Co}^{\text{II}}(\text{NCS})_4]\cdot 2[\text{Cu}^{\text{II}}(\text{acac})(\text{phen})(\text{NCS})]$  **1** system, two solutions were mixed under stirring: a solution containing 0.4 mmol  $[\text{Cu}^{\text{II}}(\text{acac})(\text{phen})(\text{H}_2\text{O})]\text{ClO}_4$  in 20 mL acetonitrile and a second one containing 1 mmol  $(\text{Et}_4\text{N})_2[\text{Co}(\text{NCS})_4]$  in 10 mL acetonitrile. Green crystals of **1** were obtained after several days through the slow vaporization of the solvent, at room temperature. IR data for **1** (KBr,  $\text{cm}^{-1}$ ): 2112vs, 2094vs, 1601m, 1569m, 1515m, 1468m, 1441m, 1379m, 1308w, 1246w, 1163w, 1106w, 1031w, 935w, 772w, 728w, 649w, 589w.

### X-ray data collection and structure refinement

X-ray diffraction measurements were performed on a Nonius Kappa CCD diffractometer, using graphite monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71070 \text{ \AA}$ ). The structure was solved by direct methods and refined by full-matrix least-squares techniques based on  $F^2$ . The non-H atoms were refined with anisotropic displacement parameters. Calculations were performed using SHELX-97 crystallographic software package. A summary of the crystallographic data and the structure refinement is given in Table 1. CCDC reference number: 769609.

Table 1

Crystallographic data, details of data collection and structure refinement parameters for **1**

Compound	<b>1</b>
Chemical formula	$\text{C}_{74}\text{H}_{60}\text{CoCu}_4\text{N}_{14}\text{O}_8\text{S}_6$
$M$ ( $\text{g mol}^{-1}$ )	1778.81
Temperature, (K)	293(2)
Wavelength, ( $\text{\AA}$ )	0.71070
Crystal system	<i>Monoclinic</i>
Space group	<i>C2/c</i>
$a$ ( $\text{\AA}$ )	31.156(2)
$b$ ( $\text{\AA}$ )	11.9631(10)
$c$ ( $\text{\AA}$ )	21.6016(13)
$\alpha$ ( $^\circ$ )	90.00
$\beta$ ( $^\circ$ )	104.208(8)
$\gamma$ ( $^\circ$ )	90.00
$V$ ( $\text{\AA}^3$ )	7805.0(10)
$Z$	4
$D_c$ ( $\text{g cm}^{-3}$ )	1.514
$\mu$ ( $\text{mm}^{-1}$ )	1.504
$F(000)$	3620
Goodness-of-fit on $F^2$	1.010
Final $R1$ , $wR2$ [ $I > 2\sigma(I)$ ]	0.0683, 0.0955
$R1$ , $wR2$ (all data)	0.1856, 0.1197
Largest diff. peak and hole ( $\text{e}\text{\AA}^{-3}$ )	0.529, -0.359

## RESULTS AND DISCUSSION

The easily accessible axial positions of the monocationic  $[\text{Cu}(\text{AA})(\text{BB})]^+$  complexes and the aromatic chelating ligands which favour intermolecular  $\pi$ - $\pi$  stacking interactions make them attractive starting materials for building interesting heterometallic compounds.<sup>15</sup> The objective of this work was to obtain heterometallic complexes using

the preformed  $[\text{Cu}^{\text{II}}(\text{acac})(\text{phen})(\text{H}_2\text{O})]^+$  cationic building block and the  $[\text{Co}(\text{NCS})_4]^{2-}$  anionic complex as a ligand.

The crystallographic investigation of **1** reveals the presence of two neutral complexes: a trinuclear  $[\text{Cu}^{\text{II}}_2(\text{acac})_2(\text{phen})_2\text{Co}^{\text{II}}(\text{NCS})_4]$  (Fig. 1a), and a mononuclear one,  $[\text{Cu}^{\text{II}}(\text{acac})(\text{phen})(\text{NCS})]$  (Fig. 1b), in a molar ratio of 1:2.

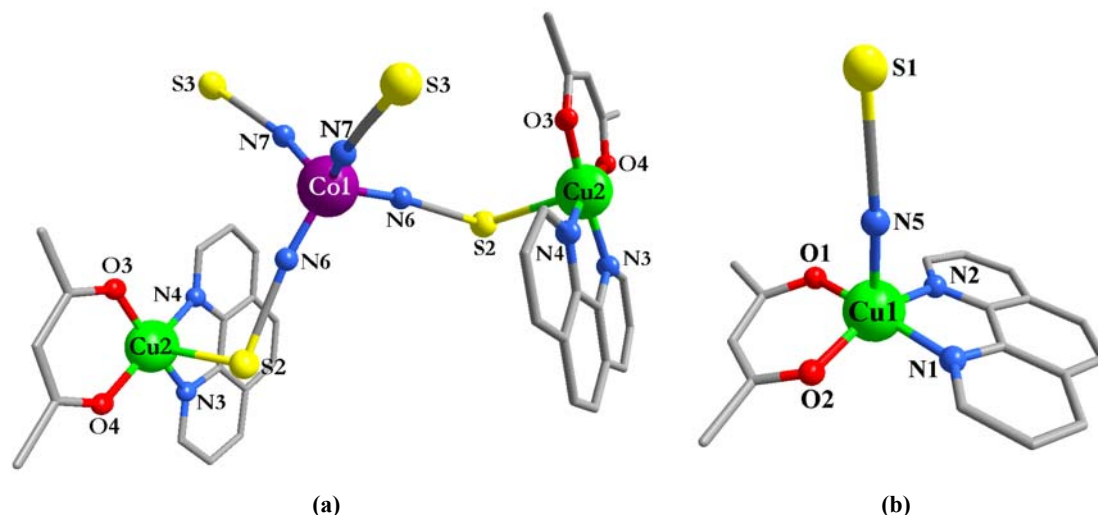


Fig. 1 – View of the trinuclear (a) and of the mononuclear (b) units found in the structure of  $[\text{Cu}^{\text{II}}_2(\text{acac})_2(\text{phen})_2\text{Co}^{\text{II}}(\text{NCS})_4] \cdot 2[\text{Cu}^{\text{II}}(\text{acac})(\text{phen})(\text{NCS})]$  **1**.

The  $[\{\text{Cu}^{\text{II}}(\text{acac})(\text{phen})\}_2\text{Co}^{\text{II}}(\text{NCS})_4]$  heterotrimeric units can be described as resulting from the coordination of the  $[\text{Co}(\text{NCS})_4]^{2-}$  anion, through two NCS groups, to two  $[\text{Cu}^{\text{II}}(\text{acac})(\text{phen})]^+$  cations, into the apical position of the copper ion. The  $\text{Cu}^{\text{II}}$  ions are pentacoordinated and exhibit a square pyramid geometry, in which the basal plane is formed by the chelating ligands, acac and phen, with  $\text{Cu}^{\text{II}} - \text{O}$  distances around 1.9 Å and  $\text{Cu}^{\text{II}} - \text{N}$  slightly longer than 2.0 Å [ $\text{Cu}2 - \text{O}3 = 1.890(5)$ ;  $\text{Cu}2 - \text{O}4 = 1.891(5)$ ;  $\text{Cu}2 - \text{N}3 = 2.013(5)$ ;  $\text{Cu}2 - \text{N}4 = 2.001(5)$  Å]. The apical position is occupied by the sulfur atom of one of the thiocyanato ligands from the anionic  $[\text{Co}^{\text{II}}(\text{NCS})_4]^{2-}$  complex, at a distance much longer than those formed in the basal plane of the pyramid [ $\text{Cu}2 - \text{S}2 = 2.784(2)$  Å]. The stereochemistry around the  $\text{Co}^{\text{II}}$  ion is tetrahedral, with practically the same  $\text{Co}^{\text{II}} - \text{N}$  bond length in the bridging thiocyanato groups [ $\text{Co}1 - \text{N}6 = 1.938(7)$  Å] and the terminal ones [ $\text{Co}1 - \text{N}7 = 1.937(7)$  Å].

The  $[\text{Cu}^{\text{II}}(\text{acac})(\text{phen})(\text{NCS})]$  mononuclear species contain a  $\text{Cu}^{\text{II}}$  ion in a square pyramid surrounding, with the two oxygen atoms from the acetylacetonato ligand, and the two nitrogen atoms of 1,10-phenanthroline in the basal plane, at distances slightly longer than the ones encountered in the heterotrimeric unit [ $\text{Cu}1 - \text{O}1 = 1.925(4)$ ;  $\text{Cu}1 - \text{O}2 = 1.930(4)$ ;  $\text{Cu}1 - \text{N}1 = 2.025(5)$ ;  $\text{Cu}2 - \text{N}2 = 2.022(5)$  Å]. The thiocyanato ligand is coordinated, through its nitrogen atom as a terminal ligand, into the apical position [ $\text{Cu}1 - \text{N}5 = 2.161(6)$  Å]. Selected bond distances are collected in table 2.

At supramolecular level, the sulfur atoms belonging to the terminal thiocyanato ligands interact and give rise to pentanuclear entities (Fig. 2) in which one trinuclear and two mononuclear units are held together by  $\text{S} \cdots \text{S}$  interactions [ $\text{S}1 \cdots \text{S}3 = 3.7414(3)$  Å].

Table 2

Selected bond distances (Å) for <b>1</b>	
Cu1-O1	1.925(4)
Cu1-O2	1.930(4)
Cu1-N2	2.022(5)
Cu1-N1	2.025(5)
Cu1-N5	2.161(6)
Cu2-O4	1.891(5)
Cu2-O3	1.890(5)
Cu2-N4	2.001(5)
Cu2-N3	2.013(5)
Cu2-S2	2.784(2)
Co1-N6	1.938(7)
Co1-N7	1.937(7)

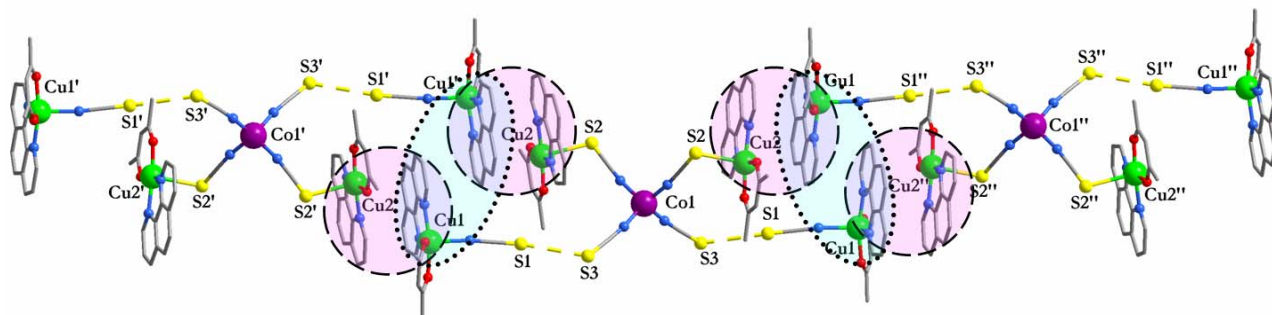


Fig. 2 – Pentanuclear supramolecular entities formed through S...S interactions between one trinuclear and two mononuclear entities.  $\pi - \pi$  interactions involving two mononuclear units (light blue, on the web version of this paper) and between trinuclear and mononuclear units (light magenta, on the web version of this paper) yield supramolecular chains.

Besides the S...S interactions, significant  $\pi - \pi$  stacking interactions between the  $[\{\text{Cu}^{\text{II}}(\text{acac})(\text{phen})\}_2\text{Co}^{\text{II}}(\text{NCS})_4]$  and  $[\text{Cu}^{\text{II}}(\text{acac})(\text{phen})(\text{NCS})]$  molecular units give rise to the solid-state supramolecular architecture of the compound. The  $\pi - \pi$  stacking interactions are established between: (a) the 1,10-phenanthroline ligands belonging to two neighbouring  $[\text{Cu}^{\text{II}}(\text{acac})(\text{phen})(\text{NCS})]$  units (3.46 – 3.6 Å) (Fig. 2); (b) the 1,10-phenanthroline ligands of one  $[\{\text{Cu}^{\text{II}}(\text{acac})(\text{phen})\}_2\text{Co}^{\text{II}}(\text{NCS})_4]$  trinuclear species and two 1,10-phenanthroline ligands coming from two neighbouring  $[\text{Cu}^{\text{II}}(\text{acac})(\text{phen})(\text{NCS})]$  units (3.47 – 3.72 Å) (Fig. 2).

## CONCLUSION

The heterobimetallic compound described in this paper, as well as the complexes previously reported by our group,<sup>15</sup> illustrate the rich chemistry generated by the  $[\text{Cu}(\text{AA})(\text{BB})]^+$  building-blocks. The synthetic strategy is based on the easily accessible apical position of the square pyramidal precursors.

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