

Figure 4. Hydrogen bonds (dashed lines) in **5** (left) and **6** (right).

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PENTACOORDINATED Cu(II) COMPLEXES WITH TRICYANOMETHANIDE, OR HOW DISAPPOINTED CAN BE THE RESULTS OF STRUCTURE ANALYSIS

K. Lacková, I. Potočňák

P. J. Šafárik University in Košice, Faculty of Science, Department of Inorganic Chemistry, Moyzesova 11, 041 54 Košice, SR
 katarina.lackova@student.upjs.sk

Introduction

The molecular structures of five-coordinated $[\text{Cu}(\text{L})_2\text{X}]\text{Y}$ complexes (L = 1,10-phenantroline (phen) or 2,2'-bipyridine (bpy), X and Y = 1- anions) show an extensive variability ranging from trigonal bipyramid (TBP) to square pyramidal (TEP) stereochemistries, with majority complexes displaying a structure, which is in the range of these two extremes [1]. In our previous work we have prepared and studied complexes with $\text{X} = \text{N}(\text{CN})_2^-$ and $\text{ONC}(\text{CN})_2^-$ with the aim to characterize the shape of coordination polyhedra (SCP) around the Cu atoms [2, 3]. The obtained results showed that the preferred SCP for compounds with phen is close to TBP, whereas for SCP bpy compounds is close to TEP.

Tricyanomethanide (tcm) anion $\text{C}(\text{CN})_3^-$ can coordinate similarly as $\text{N}(\text{CN})_2^-$ and $\text{ONC}(\text{CN})_2^-$ anions [4]. Therefore we decided to prepare complexes of general $[\text{Cu}(\text{L})_2\text{tcm}]\text{Y}$ formula (L = phen or bpy and Y = ClO_4^- , NO_3^- , Br^- and Cl^-) and thus to continue in our previous work dealing with the SCP. In this paper we describe struc-

tures of ten ionic coordination compounds, which can be divided into three groups: a) $[\text{Cu}(\text{L})_2\text{tcm}]\text{tcm}$: $[\text{Cu}(\text{phen})_2\text{tcm}]\text{tcm}$ (**1**) and $[\text{Cu}(\text{bpy})_2\text{tcm}]\text{tcm}$ (**2**); b) $[\text{Cu}(\text{L})_2\text{tcm}]\text{ClO}_4$: $[\text{Cu}(\text{bpy})_2\text{tcm}]\text{ClO}_4$ (**3**), $\text{K}[\text{Cu}(\text{phen})_2\text{tcm}]_3\text{tcm}(\text{ClO}_4)_3$ (**4**) and $[\text{Cu}(\text{phen})_2\text{tcm}][\text{Cu}(\text{phen})_2\text{H}_2\text{O}]\text{tcm}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**5**) and c) $[\text{Cu}(\text{L})_2\text{Y}]\text{tcm}$: $[\text{Cu}(\text{phen})_2\text{NO}_3]\text{tcm}$ (**6**), $[\text{Cu}(\text{phen})_2\text{Cl}]\text{tcm} \cdot \text{H}_2\text{O}$ (**7**), $[\text{Cu}(\text{bpy})_2\text{Cl}]\text{tcm}$ (**8**), $[\text{Cu}(\text{phen})_2\text{Br}]\text{tcm} \cdot 0,5\text{H}_2\text{O} \cdot 0,5\text{EtOH}$ (**9**) and $[\text{Cu}(\text{bpy})_2\text{Cl}]\text{tcm} \cdot \text{H}_2\text{O}$ (**10**).

Results and discussion

Complexes **1** and **2** (Fig. 1) belong to the first group. Their structures are formed by $[\text{Cu}(\text{L})_2\text{tcm}]^+$ cations and non-coordinating tcm anions. The structure of the cations consists of two phen or bpy molecules and one tcm anion coordinated to a copper(II) atom.

The second group consists of complexes **3 - 5** (Fig. 2), which contain the same cations as the previous group, however to balance their positive charge, ClO_4^- in **3** or ClO_4^- and tcm anions in **4** and **5** are used. Moreover, structure of **4**

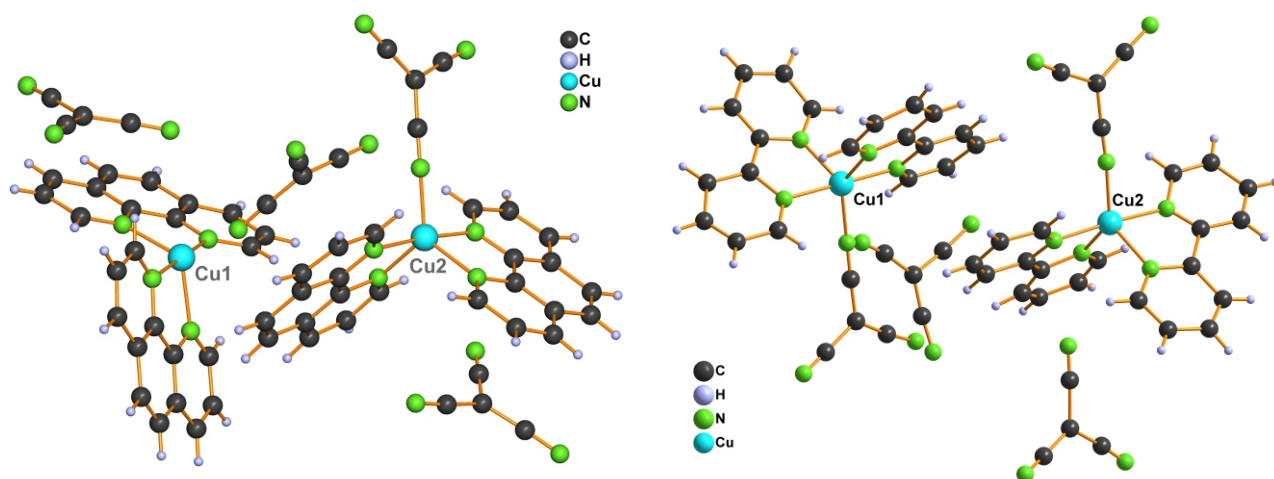


Figure 1. Structure of complexes 1 (left) and 2 (right)

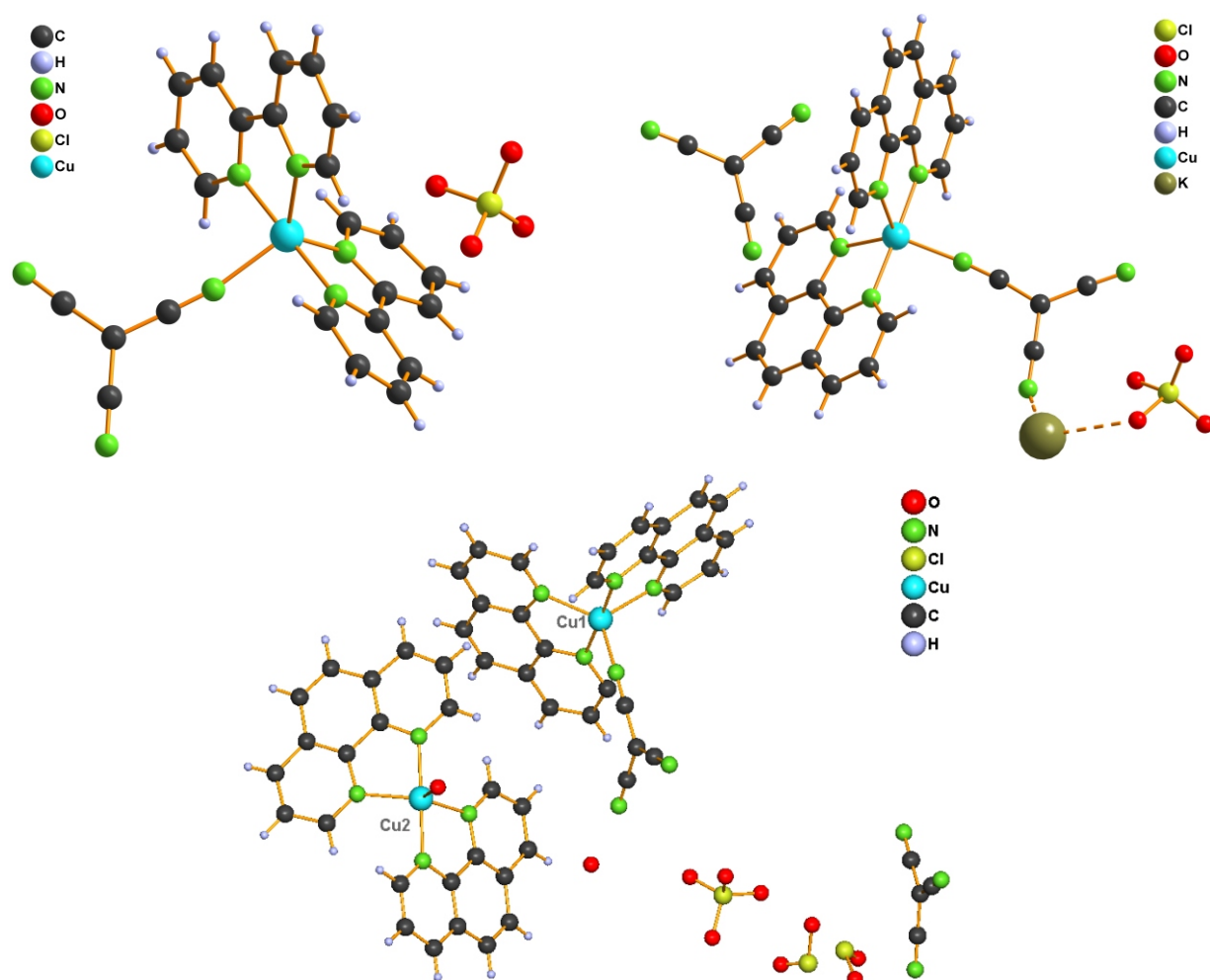


Figure 2. Structure of complexes 3 (left), 4 (right) and 5 (middle)

contains K^+ cation occupying threefold rotation axis and in the structure of **5** also $[Cu(phen)_2H_2O]^{2+}$ cation and water molecule are present.

We also tried to prepare $[Cu(L)_2tcm]Y$ ($L = phen, bpy$ and $Y = Br^-, Cl^-$ and NO_3^-) complexes within our study. Infrared spectroscopy and elemental analysis were consistent with expected composition, however X-ray structure anal-

ysis disappointed us because it revealed that the prepared complexes are with exchanged anions and their formulae are $[Cu(L)_2Y]tcm$ **6 – 10** (Fig. 3).

Besides the ionic forces, the structures of the prepared complexes are stabilized by π - π interactions and, moreover, hydrogen bonds were also observed in the structures containing water molecules.

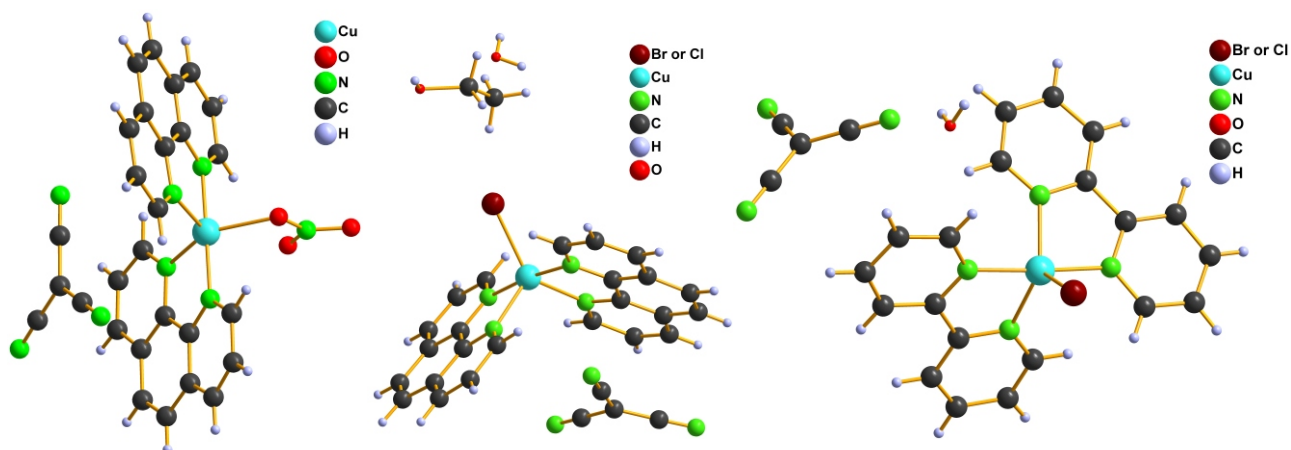


Figure 3. Structure of complexes 6 (left), 7, 9 (middle) and 8, 10 (right)

SCP of cations in all prepared complexes can be characterized as more or less deformed trigonal bipyramids as evidenced by the parameters [5] and [6] (Tab. 1). Thus we can conclude that contrary to the compounds with $\text{N}(\text{CN})_2^-$ or $\text{ONC}(\text{CN})_2^-$ anions, the SCP in compounds with $\text{C}(\text{CN})_3^-$ are unaffected by the different ligands L (phen or bpy) coordinated to the Cu(II) atom.

Table 1. Summary of parameters and (TBP)

Complex		(TBP) [°]
[Cu(phen) ₂ tcm]tcm (1)	78,9 (Cu1) 84,7 (Cu2)	58,2 53,7
[Cu(bpy) ₂ tcm]tcm (2)	77,9 (Cu1) 71,5 (Cu2)	67,0 71,1
[Cu(bpy) ₂ tcm]ClO ₄ (3)	92,5	50,0
K[Cu(phen) ₂ tcm] ₃ tcm (ClO ₄) ₃ (4)	76,9	61,7
[Cu(phen) ₂ tcm] [Cu(phen) ₂ H ₂ O]tcm(ClO ₄) ₂ ·H ₂ O (5)	80,9 (Cu1) 90,0 (Cu2)	59,9 44,1
[Cu(phen) ₂ NO ₃]tcm (6)	92,8	75,0
[Cu(phen) ₂ Cl]tcm·H ₂ O (7)	72,5	63,7
[Cu(bpy) ₂ Cl]tcm (8)	69,5	80,9
[Cu(phen) ₂ Br]tcm·0,5H ₂ O· 0,5EtOH (9)	95,1	70,4

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