Crystal Structure of Bis-(2,2'-bipyridine-N,N')-(dicyanamide-N)-copper(II) Tricyanomethanide. Electronic and Structural Parameters Describing the Shape of Coordination Polyhedra in Five-Coordinated Copper(II) Compounds

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Summary. The structure of the new compound [Cu(bpy)₂N(CN)₂]C(CN)₃ (6) is compared with the structures of six copper(II) coordination compounds with phenanthroline or bipyridine ligands and N-donor pseudohalide anions: [Cu(phen)₂NCS]C(CN)₃ (1), [Cu(bpy)₂NCS]C(CN)₃ (2), [Cu(phen)₂NCS]ONC(CN)₂ (3), [Cu(phen)₂N(CN)₂]C(CN)₃ (4), [Cu(bpy)₂C(CN)₃]C(CN)₃ (5), and [Cu(bpy)₂NCO]C(CN)₃ (7). The Cu(II) atoms in all above compounds are five-coordinated with an N-donor atom of the pseudohalide anion located in the equatorial plane of a deformed trigonal bipyramid. The shape of the coordination polyhedra and the degree of trigonal bipyramidal distortion towards a tetragonal pyramid are discussed and described using one electronic and several structural criteria which are discussed and compared.

Keywords. Copper(II) complexes; Polyhedron shape; Pseudohalide; UV/Vis spectroscopy; X-Ray structure determination.

Introduction

The study of the shape of coordination polyhedra (SCP) is one of the problems of coordination chemistry. The SCP in five-coordinated compounds is trigonal-bipyramidal (TBP stereochemistry) with some degree of distortion towards a tetragonal pyramid (TEP stereochemistry). To describe this distortion, the criteria of Harrison and Hathaway [1] concerning the values of three equatorial angles αᵢ (i = 1, 2, 3; Fig. 1) can be used. The angle α₃ is the angle opposite to the N⁵ atom, i.e., to the N-donor atom of the coordinated anion X. Of the other two equatorial angles, α₁ is always assigned to the larger one. According to these criteria, compounds can be divided into three groups of different SCP. Recently, eight different modes of distortion of TBP have been reported [2–5], but it is rather difficult to

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describe the degree of a TBP polyhedron distortion towards TEP quantitatively using the above criteria. Moreover, a number of structural approaches have been used in the past to describe the geometries of five-coordinated compounds [6–11], all of them based on the results of crystal structure analyses and mostly using the values of bond angles around the central atom. On the other hand, criteria have been suggested which are based on spectroscopic results [12, 13] and do not include the results of crystal structure analyses.

In previous investigations we have studied the structures of five-coordinated copper(II) coordination compounds of the general formula $[\text{Cu}L_2X]Y$ where $L$ = 1,10-phenanthroline ($\text{phen}$) or 2,2'-bipyridine ($\text{bpy}$) and $X, Y$ = pseudohalide anions: $[\text{Cu(phen)_2NCS}C(CN)_3]$ (1), $[\text{Cu(bpy)_2NCS}C(CN)_3]$ (2), $[\text{Cu(phen)_2NCS}-\text{ONC(CN)_2}]$ (3), $[\text{Cu(phen)_2N(CN)_2}]C(CN)_3$ (4), $[\text{Cu(bpy)_2C(CN)_3}]C(CN)_3$ (5) and $[\text{Cu(bpy)_2NCO}]C(CN)_3$ (7) [14–19]. The shape of the coordination polyhedra in these compounds is distorted trigonal-bipyramidal. To describe the distortion of TBP towards TEP we have used criteria according to Ref. [1]. Now we have successfully prepared a new compound, $[\text{Cu(bpy)_2N(CN)_2}]C(CN)_3$ (6). We decided to use an electronic criterion from Ref. [12] and compare it with the structural criteria with the aim to verify whether this electronic criterion is reliable in describing the coordination polyhedron and to choose the criterion that best describes the actual shape of the coordination polyhedron of the studied compounds. Reports on compounds with the ($\text{CuN}_4X$) chromophore ($X = \text{Br, Cl, I, O}$) in this context has already been performed [2–5, 20]; we therefore set out for compounds with the ($\text{CuN}_5$) chromophore for our analysis. To exclude possible small differences in the structures of the cations which can result from the small differences in the crystal field of the different counter-anions, we included only compounds with the same $[\text{C(CN)_3}]$ counter-anion in our study with the exception of the closely related $[\text{ONC(CN)_2}]^-$ anion.

**Results and Discussion**

Figure 2 shows the labelling scheme of one formula unit of the compound 6; the fractional coordinates of the atoms are given in Table 1. The Cu atom is five-