Scientific paper

Synthesis and Crystal Structure of a Five-Coordinate Complex of Copper(II) with 4-Nitrobenzenesulfonate and 2, 2'-Bipyridine

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Abstract

$[Cu(bipy)_2Cl](nbs)$ (**1**) (bipy = 2,2'-bipyridine, nbs = 4-nitrobenzenesulfonate) was obtained from the reaction of 4-nitrobenzenesulfonyl chloride and 2-amine-4-methylopyridine with $CuCl_2$ in the presence of 2,2'-bipyridine and characterized by elemental analysis, IR spectra and X-ray single-crystal diffraction. The asymmetric unit of (**1**) contains the cationic complex $[Cu(bipy)_2Cl]^+$ and, in the outer coordination sphere, an $(nbs)^-$ counter ion.

Keywords: copper(II) complex, 2,2'-bipyridine, 4-nitrobenzenesulfonate, trigonal bipyramid

1. Introduction

The shape of five-fold coordination polyhedra, is an interesting topic in coordination chemistry. Five- fold coordination is much more uncommon than four- fold coordination. Due to the lack of higher symmetry stabilizing many chemical systems, thus five- fold coordination is more often seen in solution where symmetric restrictions are less important. There are two main five-coordinated geometries: the trigonal bipyramid (tbp) and the square pyramid (sqpy). They are closely related to each other, which can be illustrated with the so-called Berry mechanism or pseudo-rotation for a five coordinated complex, with its tbp-sqpy-tbp interconversion.[1–5] In continuation of our recent work on synthesis of new ligands with sulfur and nitrogen atoms[6–9] and proton transfer compounds,[10–12] we prepared $(C_5H_9N_2)(C_6H_4NO_5S)$ by the reaction of 2-amino-4-methylpyridine and 4-nitrobenzenesulfonyl chloride.[13] Now we are going to report on the synthesis and crystal structure of the copper(II) complex with this proton transfer compound.

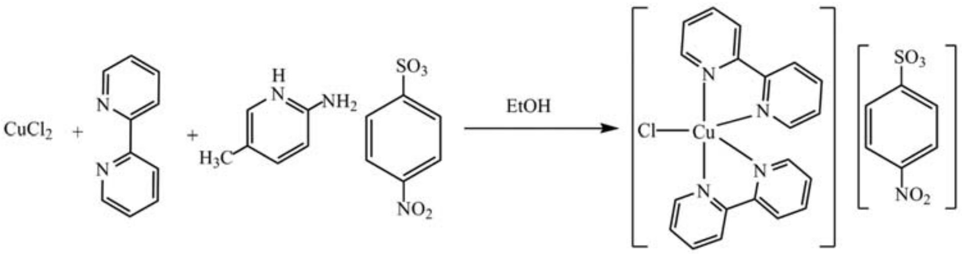
2. Experimental

2. 1. Materials and Instrumentations

$CuCl_2$, 4-nitrobenzenesulfonyl chloride, 2-amin-4-methylopyridine and 2,2'-bipyridine were purchased from Merck and used without further purification. IR spectra were recorded on a Bruker FT-IR Tensor 27 spectrometer (KBr pellets, Nujol mulls, 4000–400 cm^{-1}). X-ray structure analysis of suitable single crystals was carried out on a Bruker APEX II CCD area detector (Mo $K\alpha$ radiation, graphite monochromator, $\lambda = 0.71073$ Å at ambient temperature).

2. 2. Synthesis of Complex

A solution of $CuCl_2$ (134.45 mg, 1 mmol) and 2,2'-bipyridine(156.01m g, 1 mmol) in ethanol (20 ml) was added to a solution of (ampyH)(nbs)[13] (ampy is 2-amino-4-methylpyridine and nbs is 4-nitrobenzenesulfonate) (311.31 mg, 1 mmol, 20 ml ethanol) in a 1:1:1 molar ratio. The mixture was stirred for 6 h at room temperature, the



Scheme 1. The synthetic method for the preparation of [Cu(bipy)$_2$Cl](nbs)

resultant mixture was filtered and the filtrate was kept at room temperature. Blue crystals of (**1**) were obtained after allowing the mixture to stand for two weeks (Schem 1).

3. Results and Discussions

3. 1. IR Spectra

IR spectroscopy of the complex (**1**) shows a strong, broad and branched band at 3550–2980 cm^{-1} attributed to aromatic C-H's of coordinated 2, 2'-bipyridine and benzene ring of nbs. Sharp and relatively strong bands in 1104 cm^{-1} are attributed to stretching C-N vibration. The bands around 1480 and 1420 cm^{-1} are due to the C=C and C=N stretching modes of the coordinated 2,2'-bipyridine molecules. Another remarkable feature of the IR spectrum is strong bands at 1517 and 1342 cm^{-1}, which is explained by the presence of the N=O bonds with different strengths. Other strong bands in 1216 and 655 cm^{-1} are related to resonance of $(SO_3)^-$, in fact, ν(S=O) and ν(S-O) bands are transformed into the symmetric and asymmetric stretching vibrations of the sulphonate group.

3. 2. Crystal structure

The molecular structure of [Cu(bipy)$_2$Cl](nbs), **1** with atom numbering and a view of the crystal packing are presented in Figures 1 and 2. The crystallographic data, selected bond lengths, bond angles and torsion angles are listed in Tables 1 and 2, respectively.

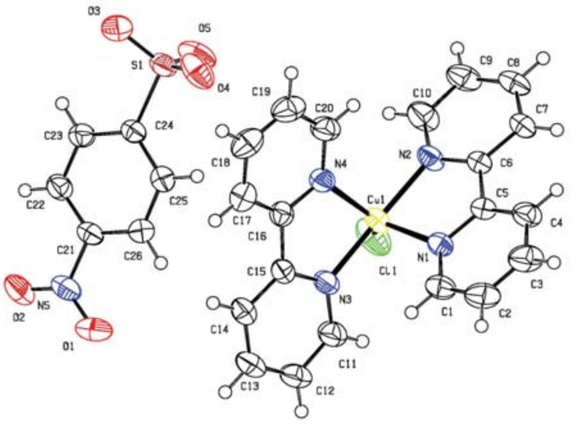


Fig. 1 The molecular structure of [Cu(bipy)$_2$Cl](nbs), showing the atom-numbering scheme.

Table 1. Crystal and Structure Refinement Data for Compound **1**

Crystal data	
Empirical Formula	$C_{26}H_{20}ClCuN_5O_5S$
Formula weight	613.54
Cell setting, Space group	Monoclinic, $P2_1/c$
Unit cell dimensions	a = 7.0435(12) Å
	b = 10.6811(12) Å
	c = 33.731(6) Å
	β = 91.186(14)°
Unit cell volume	2537.1(7) Å^3
Temperature (K)	293 (2)
Absorption coefficient	1.098 mm^{-1}
Z, Density [g/cm^3]	4, 1.606Mg/m^3
F(000)	1252
Crystal size (mm)	0.50× 0.45× 0.30
R value	0.041
Rw value	0.050
θ range (°)	2.00 → 29.47°
h range	–9 → 7
k range	–13 → 14
l range	–46 → 46
Reflections collected / unique	15873/ 5615 [R (int) =]
Completeness to θ_{max}	96.7%
Goodness-of-fit on F^2	1.085
Large diff. peak and hole	0.79 and –0.56 e. Å^{-3}
Wavelength	0.71073 Å
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0624P)^2 + 1.1103P]$ where $P = (F_o^2 + 2F_c^2)/3$

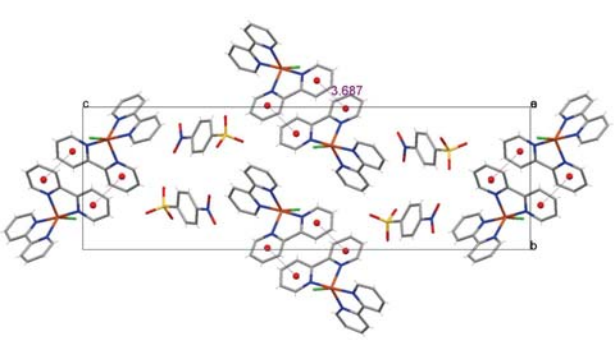


Fig. 2 The crystal packing diagram of [Cu(bipy)$_2$Cl](nbs)

In compound **1** the asymmetric unit is composed of the cationic complex $[Cu(bipy)_2Cl]^+$ and, in the outer coordination sphere, an $(nbs)^-$ counter ion. The copper atom in **1** is five coordinated to the four 2,2'-bipyridine nitrogen atoms and to one atom of chlorine. However, the protonated 2-amino-4-methylpyridine is lost and the nbs^- anion does not enter the inner coordination sphere.

Table 2. Bond lengths (Å), bond angles and torsion angles (°) for Compound **1**

Distances (Å)			
Cu1–N3	1.9775 (18)	Cu1–N1	2.1106 (18)
Cu1–N2	1.9903 (18)	Cu1–Cl1	2.2805 (8)
Cu1–N4	2.1045 (18)		
Angles (°)			
N3–Cu1–N2	174.86 (8)	N4–Cu1–N1	100.34 (7)
N3–Cu1–N4	80.26 (7)	N3–Cu1–Cl1	92.45 (6)
N2–Cu1–N4	97.62 (8)	N2–Cu1–Cl1	92.44 (6)
N3–Cu1–N1	96.05 (7)	N4–Cu1–Cl1	131.78 (5)
N2–Cu1–N1	79.68 (7)		
Torsion angles (°)			
N4–Cu1–N1–C1	78.97 (19)	N1–Cu1–N3–C11	–79.4 (2)
N4–Cu1–N1–C5	–96.66 (14)	N1–Cu1–N3–C15	101.66 (16)
N4–Cu1–N2–C10	–82.6 (2)	N1–Cu1–N4–C20	80.16 (19)
N4–Cu1–N2–C6	104.53 (16)	N1–Cu1–N4–C16	–94.26 (14)

The Cu-N and Cu-Cl distances are within the usual ranges for this kind of copper(II) complex.[14–16] The coordination polyhedron cannot be described as either a square pyramid or a trigonal bipyramid, having a trigonality index $\tau = 0.718$ ($\tau = (\beta - \alpha)/60$, where β and α are the largest angles in the coordination sphere;[17] its value is zero for a perfect square pyramid and one for a perfect trigonal bipyramid). Thus Complex **1** displays a distorted trigonal bipyramidal geometry around the Cu(II) center. Two sets of Cu–N distances were observed. The axial distances are short compared to the equatorial ones. The axial Cu–N distances are 1.988(2) and 1.991(2) Å and the equatorial distances are 2.105(2) and 2.109(2) Å. The axial directions, Cu-N2 and Cu-N3, define the largest N–Cu–N angle of 174.85(8)°, which shows 5.14° deviation from linearity and N4Cu1N1C5 and N1Cu1N4C16 torsion angles are -96.66 (14) and -94.26 (14)° respectively (see table 2). Thus, it can be concluded that two 2,2'-bipyridine ligands are almost perpendicular to each other.

The longest in-plane distance, Cu–N1 is opposite to the largest in-plane angle. While the observed Cu–Cl distances are longer because of larger covalent radii[18] of the Cl atom relative to the nitrogen atom, *i.e.* 0.99 and 0.70 Å, respectively. Our results compare well with those reported for $[Cu(bipy)_2Cl][(CH_3)_2C_6H_3SO_3] \cdot H_2O$.[19]

As expected, the individual pyridine rings of the bpy ligands are all planar. The bpy ligand as a whole is almost planar in **1**, but there are dihedral angles between the pyridyl rings of each bipy: 10.21(11) between N1/C1-C5 and N2/C6-C10 rings and 7.01(11)° between N3/C11-C15 and N4/C16-C20 rings. Twisting around the 2-2' bond is normal in coordinated bpy.[20]

The non-covalent interactions have an important role in self-association of the crystal system. As can be seen from the packing diagram (Fig. 2) there are two kinds of the non-covalent interactions: the intermolecular π-π stacking interaction with centroid-centroid distance 3.687(2) Å (Fig. 3) and Cu–Cl···π stacking interaction, with Cl···π distance and angle of 3.726(2) Å and 157.72(4)° (Fig. 4) seem to be effective in the stabilization of the crystal structure, resulting in the formation of an interesting supramolecular structure.

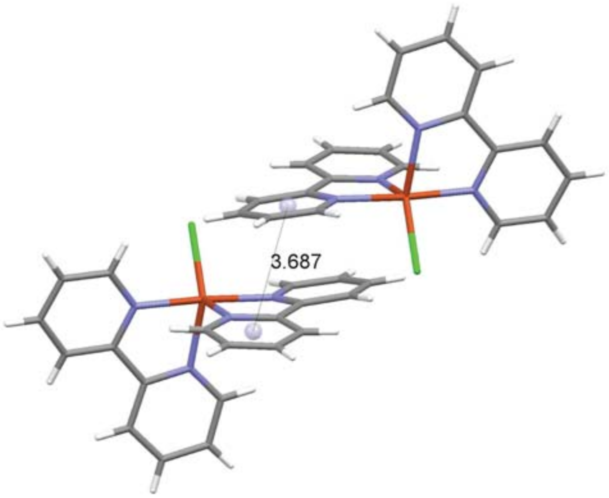


Fig. 3. A view of the π–π stacking interaction between two aromatic rings. The distance between the planes of the rings (N1/C1–C5) and (N2/C6–C10) is 3.687(2) Å [symmetry code: 1-*x*, 1-*y*, -*z*].

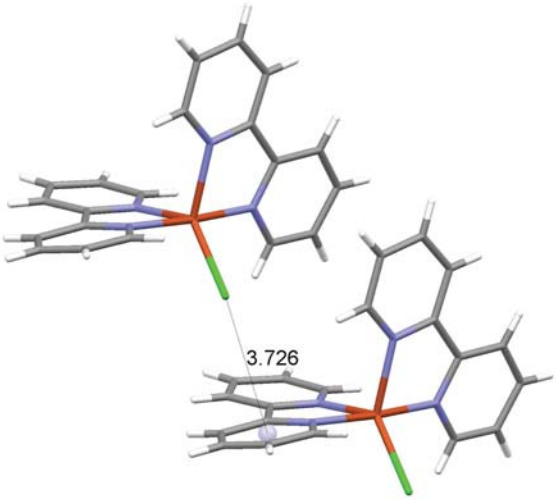


Fig. 4. Cu–Cl···π stacking interaction between the chloro ligand and centroid of the N2/C6-C10 aromatic ring of coordinated 2,2'-bipyridine [symmetry code: –1+*x*, *y*, *z*]. The distance between Cl atom and the ring centroid is 3.726(2) Å.

As shown in Table 3, a number of inter and intramolecular weak C–H·E·E·EO hydrogen bonds with D·E·E·A in the range of 2.935(3) to 3.447(3) A can be observed in crystal packing as effective factors in expanding the supramolecular network.

Table 3 Hydrogen-bond geometry (Å, °).

D–H···A	D–A	H···A	D···A	D–H···A
C13–H13···O2^{i}	0.93	2.54	3.261(3)	134
C14–H14···O4^{ii}	0.93	2.52	3.411(3)	160
C17–H17···O4^{ii}	0.93	2.50	3.343(3)	150
C18–H18···O5	0.93	2.44	3.254(3)	146
C22–H22···O1^{iii}	0.93	2.59	3.338(3)	138
C23–H23···O3	0.93	2.60	2.935(3)	102
C26–H26···O3^{iv}	0.93	2.57	3.447(3)	157

Symmetry Codes: (i) -x,-1/2+y,1/2-z (ii) -1+x,y,z
(iii) 1-x,1/2+y,1/2-z (iv) 2-x,-1/2+y,1/2-z

4. Acknowledgment

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Appendix A. Supplementary data

The selected crystal of (**1**) was covered with a per fluorinated oil and mounted on the tip of a glass capillary under a flow of cold gaseous nitrogen. The orientation matrix and unit cell dimensions were determined from 8000 (Stoe IPDS II (1), (graphite-monochromated Mo-Kα radiation in all cases; $\lambda = 71.073$ pm). In addition, absorption corrections were applied for (**1**) (numerical). The structure was solved by the direct methods (SHELXS-97 [21]) and refined against F^2 by full-matrix least-squares using the program SHELXL-97 [22], ORTEP-3 (Farrugia, 1997) [23], Mercury CSD 2.0 – New Features for the Visualization and Investigation of Crystal Structures [24], software used to prepare material for publication: WinGX (Farrugia, 1999) [25].

Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited at the Cambridge Crystallographic Center, CCDC No. 749881. Copies of the data can be obtained free of charge on http:www.ccdc.cam.ac.uk.

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Povzetek

[Cu(bipy)2Cl](nbs) (**1**) (bipy = 2,2'-bipiridin, nbs = 4-nitrobenzensulfonat) smo sintetizirali z reakcijo med 4-nitrobenzensulfonil kloridom in 2-amino-4-metilopiridinom s $CuCl_2$ v prisotnosti 2,2'-bipiridina. Spojino smo karakterizirali z elementno analizo, IR spektroskopijo in rentgensko difrakcijo na monokristalih. Asimetrična enota (**1**) vsebuje kationski kompleks [Cu(bipy)2Cl]+ in v zunanji koordinacijski sferi (nbs)- ion.