



ORIGINAL ARTICLE

Synthesis, solid-state structure and supramolecularity of $[\text{Cu}(\text{pyterpy})_2](\text{ClO}_4)_2$



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Abstract The copper(II) polypyridyl complex $[\text{Cu}(\text{pyterpy})_2](\text{ClO}_4)_2$ (**3**) (pyterpy = 4'-(4-pyridyl)-2,2':6,2''-terpyridine) was prepared by the reaction of pyterpy (**1**) with stoichiometric amounts of $[\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}]$ (**2**). The progress of the reaction was controlled by FT-IR and UV-vis spectroscopy. The title complex crystallized in the tetragonal space group $I4(1)/a$ with unit cell dimensions of $a = 8.6277(1)$, $b = 8.6277(1)$, $c = 57.6398(10)$ Å, $V = 4290.55(12)$ Å³, and $Z = 4$. The structure of **3** in the solid-state consists of discrete $[\text{Cu}(\text{pyterpy})_2]^+$ ions with copper(II) in a distorted octahedral environment setup by two meridional coordinated tripodal 4'-(4-pyridyl)-2,2':6,2''-terpyridine ligands of which the pyridyl unit stays free. Face-to-face π -interactions between terminal coordinated terpy C₅N rings link adjacent $[\text{Cu}(\text{pyterpy})_2]^{2+}$ units resulting in the formation of a 2D-polymer. The geometrical-to-geometrical centroid distance (d) is 3.568 Å.

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1. Introduction

Metal-polypyridyl complexes are of considerable interest in terms of metal-organic supramolecular chemistry. The reaction of divalent transition metal species with polypyridyls, similar to 2,2':6',2''-terpyridine (terpy) and 4'-(2-pyridyl)-2,2':6',2''-terpyridine (pyterpy), produces homo and heteroleptic $[\text{M}(\text{pyterpy})_2]^{2+}$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}, \text{Rh}, \text{Co}, \text{Cu}, \text{Mn}$ and Cd) cations allowing the successful setup of different topologies and supramolecular architectures (Hayami et al., 2004; Lehn, 1988; Funeriu et al., 1997; Ziener et al., 2000; Breuninger et al., 2000; Vidal et al., 2000; Sauvage and Hosseini, 1996; Al-Anber et al., 2004; Lohmeijer and Schubert, 2002; Schutte et al., 1998; Salditt et al., 1999; Jennette et al., 1974; Bonse et al., 2000; Long-Xuan et al., 2004; Swiegers and Malefetse, 2000; Hofmeier and Schubert, 2004; Chelucci, 1993; Uenishi et al., 1994; Chelucci et al., 1995; Leroy-Lhez and Fages, 2005; Ward, 1995; Sauvage et al., 1994; Constable and Gargill Thompson, 1992, 1994; Constable et al., 2000; Hutchinson et al., 1999; Fig-gemeir et al., 2003; Sun et al., 2000; Chichak and Branda, 1999).

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The most common driving force for the formation of such supramolecular structures results from π – π interactions between the aromatic pyridine rings of pyterpy ligand that link the adjacent $[\text{M}(\text{pyterpy})_2]^{2+}$ cations. The most common geometries of π – π interactions are face-to-face and edge-to-face π – π interactions (Beves et al., 2008a; McMurtrie and Dance, 2005a,b). Therefore, the shape of such assemblies mainly depends on the type of the nature of π – π stacking, the appropriate metal ion, counter ion, organic ligand, solvent system, and/or the metal-to-ligand ratio (Alcock et al., 2000; Masuhara et al., 2007). Wherein, the physical and chemical properties can be influenced. Therefore, many researchers are searching for new isostructural forms to obtain new properties, wherein the crystal structure could change with changes in the reaction and crystallization conditions.

For example, the reaction of the cadmium complex $[\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}]$ with 4'-(2-pyridyl)-2,2':6',2''-terpyridine (pyterpy) afforded a neutral mononuclear complex of composition $[\text{Cd}(\text{pyterpy})(\text{H}_2\text{O})(\text{NO}_3)_2]$ (Granifo et al., 2004a). Within this species, π – π interactions between the aromatic pyridine rings and hydrogen bond gave a couple of linear strips assembled in a zipper-like motif (Granifo et al., 2004b). Also, the structure of $[\text{Co}(\text{pyterpy})\text{Cl}_2] \cdot \text{MeOH}$ in the solid-state was reported indicating that this species forms a quasi 3D-network by π – π interactions of individual 1D-chains (Hayami et al., 2004). The addition of a biphenylene tail to 2,2':6',2''-terpyridine gave rod-like structures and 2D-sheets (Alcock et al., 2000; Masuhara et al., 2007). Recently, the mononuclear structures of $[\text{Cu}(\text{pyterpy})(\text{OH})(\text{NO}_3)]$ and $[\text{Cu}(\text{pyterpy})(\text{NO}_3)_2]$ have been reported (Hou et al., 2005a,b). The crystal packing of these mononuclear complexes resulted in the formation of coordination polymers, wherein the shortest π – π intermolecular interaction between the face-to-face of pyridyl centroids was 3.37 Å (Padhi and Manivannan, 2006). In addition, the reaction of pyterpy with copper(II) produced mononuclear $[\text{Cu}(\text{pyterpy})_2](\text{PF}_6)_2$. It was found in the crystal that π – π interactions between adjacent $[\text{Cu}(\text{pyterpy})_2]^{2+}$ cations resulted in the formation of channels which run in perpendicular directions (Pitarch López et al., 2005).

In our research group we are searching for new forms of such complexes using different reaction and crystallization conditions. In this context, we report the synthesis of $[\text{Cu}(\text{pyterpy})_2](\text{ClO}_4)_2$ (pyterpy: 4'-(4-pyridyl)-2,2':6',2''-terpyridine) as well as its electronic and structural features.

2. Experimental

2.1. General remarks

All chemicals were commercially purchased and were used as received. Molecule pyterpy (**1**) was synthesized according to the literature procedure (Constable and Gargill Thompson, 1992).

2.2. Physical measurements

Infrared spectra were recorded using a Perkin-Elmer FT-IR 1000 spectrometer. The melting point was determined using an analytically pure sample on a Gallenkamp MFB 595 010 M melting point apparatus. Microanalyses were performed using a Thermo FLASH EA 1112 Series instrument. The electronic absorption was measured in acetonitrile solution using a

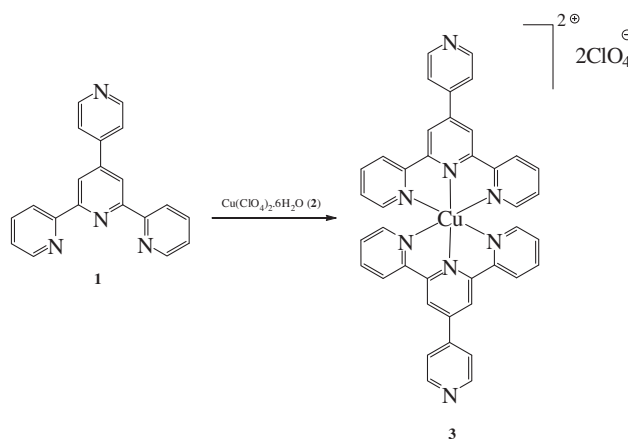
Perkin-Elmer Lambda 650 UV–vis spectrophotometer, working in the wavelength range 190–900 nm.

2.3. Synthesis of $[\text{Cu}(\text{pyterpy})_2](\text{ClO}_4)_2$ (**3**)

Complex $[\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}]$ (46.6 mg, 0.15 mmol) was dissolved in 15 mL of acetonitrile. To this solution 4'-(4-pyridyl)-2,2':6',2''-terpyridine (**1**: pyterpy) (93.11 mg, 0.30 mmol) in 30 mL of chloroform was added gradually at ambient temperature, whereby a green-blue solution formed after 3 h. After 3 days green-blue single crystals suitable for single X-ray structure measurement were formed. After separation of the single crystals of **3**, all volatiles were removed in oil-pump vacuum and the remaining bulk solid was washed with chloroform and diethyl ether (3×5 mL) and was dried in oil-pump vacuum for 24 h to give further **3**. Yield

Table 1 Crystal and structure refinement data for **3**.

Empirical formula	$\text{C}_{40}\text{H}_{28}\text{Cl}_4\text{CuN}_8\text{O}_{16}$
Formula weight	1082.04
Temperature	100 K
Wavelength	1.54184 Å
Crystal system, space group	Tetragonal, $I4(I)/a$
Unit cell dimensions	$a = 8.6277(1)$ Å $b = 8.6277(1)$ Å $c = 57.6398(10)$ Å
V	4290.55(12) Å ³
Z , calculated density	4, 1.367 mg cm ^{−3}
Absorption coefficient	2.366 mm ^{−1}
$F(000)$	1804
Crystal size	0.2 × 0.2 × 0.2 mm
θ range for data collection	3.07–60.56°
Limiting indices	$-9 \leq h \leq 9$, $-9 \leq k \leq 9$, $-63 \leq l \leq 64$
Reflections collected/unique	13160/1609 [$R(\text{int}) = 0.0181$]
Completeness to $\theta = 60.56$	98.8%
Absorption correction	Semi-empirical from equivalents
Max., min. transmission	1.00000, 0.92693
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1605/72/198
Goodness-of-fit on F^2	1.064
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0694$, $wR_2 = 0.1989$
R indices (all data)	$R_1 = 0.0746$, $wR_2 = 0.2050$
Extinction coefficient	0.0019(4)
Largest diff. peak and hole	0.729 and -0.305 e Å ^{−3}



Scheme 1 Synthesis of **3**.

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