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Synthesis, solid-state structure and supramolecularity of [Cu(pyterpy)₂](ClO₄)₂



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Copper; Terpyridine; Supramolecular chemistry; Solid-state structure; $\pi - \pi$ interaction

Abstract The copper(II) polypyridyl complex $[Cu(pyterpy)_2](ClO_4)_2$ (3) (pyterpy = 4'-(4-pyridyl)-2,2':6,2''-terpyridine) was prepared by the reaction of pyterpy (1) with stoichiometric amounts of $[Cu(ClO_4)_2 \cdot 6H_2O]$ (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 $[Cu(pyterpy)_2]^+$ 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 C_5N rings link adjacent $[Cu(pyterpy)_2]^{2+}$ 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"-terpyr-

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ELSEVIER Production and hosting by Elsevier idine (pyterpy), produces homo and heteroleptic [M(pyter $py_{2}^{2^{+}}$ (M = Fe, Ru, Os, Rh, Co, Cu, 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; Figgemeir 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 [M(pyterpy)₂]²⁺ cations. The most common geometries of π -interactions are face-to-face and edge-to-face 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 -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 [Cd(NO₃)₂·4H₂O] with 4'-(2-pyridyl)-2,2':6',2"-terpyridine (pyterpy) afforded a neutral mononuclear complex of composition $[Cd(pyterpy)(H_2O)(NO_3)_2]$ (Granifo et al., 2004a). Within this species, $\pi - \pi$ 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 [Co(pyterpy)Cl₂]·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 [Cu(pyterpy)(OH)(NO₃)] and [Cu(pyterpy)(NO₃)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 $[Cu(pyterpy)_2](PF_6)_2$. It was found in the crystal that $\pi - \pi$ interactions between adjacent $[Cu(pyterpy)_2]^{2+}$ 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 $[Cu(py-terpy)_2](ClO_4)_2$ (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 FLASHEA 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 $[Cu(pyterpy)_2](ClO_4)_2$ (3)

Complex $[Cu(ClO_4)_2:6H_2O]$ (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 | C40H28Cl4CuN8O16 | | | | |
| Formula weight | 1082.04 | | | | |
| Temperature | 100 K | | | | |
| Wavelength | 1.54184 Å | | | | |
| Crystal system, space group | Tetragonal, $I4(1)/a$ | | | | |
| 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} | | | | |
| <i>F</i> (000) | 1804 | | | | |
| Crystal size | $0.2 \times 0.2 \times 0.2$ mm | | | | |
| θ range for data collection | 3.07–60.56° | | | | |
| Limiting indices | $-9 \leqslant h \leqslant 9, \ -9 \leqslant k \leqslant 9, \ -63 \leqslant l \leqslant 64$ | | | | |
| Reflections collected/unique | 13160/1609 [R(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 <i>R</i> 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 A^{-3} | | | | |



Scheme 1 Synthesis of 3.



Figure 1 ORTEP plot of the molecular structure of 3 (50% probability level of the molecular structure). Hydrogen atoms and the $CLOP_4^-$ anions have been omitted for clarity. Symmetry transformations used to generate equivalent atoms: 'A' y + 3/4, -x + 5/4, -z + 5/4. 'B' -x + 2, -y + 1/2, z. 'C' -y + 5/4, x-3/4, -z + 5/4.

| | X | у | Ζ | U(eq) |
|--------|------------|----------|---------|--------|
| Cu(1) | 10,000 | 2500 | 6250 | 28(1) |
| N(2) | 12,291(4) | 3412(4) | 6331(1) | 28(1) |
| N(1) | 10,000 | 2500 | 6595(1) | 28(1) |
| C(6) | 11,229(4) | 3049(5) | 6710(1) | 33(1) |
| C(1) | 13,409(5) | 3841(5) | 6183(1) | 31(1) |
| C(5) | 12,521(5) | 3595(5) | 6559(1) | 31(1) |
| C(7) | 11,254(5) | 3067(5) | 6949(1) | 37(1) |
| C(3) | 14,996(5) | 4729(6) | 6491(1) | 41(1) |
| C(2) | 14,775(5) | 4515(6) | 6257(1) | 36(1) |
| C(8) | 10,000 | 2500 | 7071(1) | 39(2) |
| C(4) | 13,866(5) | 4270(6) | 6645(1) | 39(1) |
| C(9) | 10,000 | 2500 | 7329(1) | 46(2) |
| N(3) | 10,000 | 2500 | 7815(1) | 64(2) |
| C(10) | 10,684(7) | 3675(7) | 7456(1) | 59(2) |
| C(11) | 10,657(7) | 3612(8) | 7697(1) | 67(2) |
| Cl(1) | 11,804(8) | 7764(5) | 6978(1) | 103(2) |
| O(1) | 11,190(20) | 6862(17) | 6797(2) | 105(4) |
| O(2) | 12,770(20) | 6755(16) | 7107(2) | 141(5) |
| O(3) | 12,740(30) | 8870(20) | 6864(2) | 179(8) |
| O(4) | 10,850(30) | 8560(20) | 7150(3) | 192(8) |
| Cl(1') | 10,490(30) | 8100(20) | 6933(3) | 243(7) |
| O(1′) | 10,770(50) | 6890(40) | 6782(5) | 195(11 |
| O(2′) | 10,850(50) | 7400(40) | 7158(4) | 241(11 |
| O(3') | 11.840(30) | 9151(18) | 6913(5) | 182(9) |

U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

9040(40)

6992(7)

275(13)

9160(40)

O(4′)

of **3**: 82% (based on **1**). M.p. 378–380 °C (explosive). FT-IR (KBr, cm⁻¹): $[v_{O-H}]$ 3438 (vs), $[v_{C=N}]$ 1540, 1572, 1597, 1620 (s), $[v_{CI-O}]$ 1088 (vs). UV–vis (CH₃CN) λ (nm) 267 nm ($\epsilon = 3.81 \times 10^{2}$ cm⁻¹ mole⁻¹ L), 332 nm ($\epsilon = 1.37 \times 10^{2}$ cm⁻¹

mole⁻¹ L), 697 nm ($\varepsilon = 66 \text{ cm}^{-1} \text{ mole}^{-1}$ L). Anal. Calcd for $C_{40}H_{28}N_8Cl_2O_8Cu$ (883.256 g mol⁻¹): C, 54.39%; H, 3.20%; N, 12.69%. Found: C, 53.95%; H, 3.05%; N, 12.64%.

2.4. Solid-state structure of $[Cu(pyterpy)_2](ClO_4)_2$ (3)

Data were collected on an Oxford Gemini diffractometer at 100 K using Cu K_{α} radiation ($\lambda = 1.54184$ Å). The structure was solved by direct methods using SHELXS-97 (Sheldrick, 1990). The structure was refined by full-matrix least-square procedures on F^2 using SHELXL-97 (Sheldrick, 1997). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were added on calculated positions. The ClO₄⁻ anion, with an occupation of 0.5 within the asymmetric unit, has been refined disordered with split occupancies of 0.833 (Cl1, Ol–O4) and 0.167 (Cl1', Ol'–O3'), respectively.

A summary of data collection and structure refinement of **3** are given in Table 1. The CCDC No. 813708 contains the supplementary crystallographic data for this complex. The data can be obtained free of charge at http://www.ccdc.cam.ac.uk, or from the Cambridge Crystallographic Data Center (CCDC), 12 Union Road Cambridge CB2 1 EZ, UK. Fax: +44(0)1223-3360033; e-mail: deposit@ccdc.cam.ac.uk.

3. Results and discussion

3.1. Synthesis and characterization

Complex $[Cu(pyterpy)_2](ClO_4)_2$ (3) (pyterpy = 4'-(4'''-pyridyl)-2,2':6,2'''-terpyridine) was prepared by the treatment of pyterpy (1) with $[Cu(ClO_4)_2.6H_2O]$ (2) in a 2:1 M ratio in 30 mL of chloroform-acetonitrile mixture (ratio 1:1, v/v) at ambient temperature (Scheme 1). After appropriate work-up, complex 3 was isolated as a green-blue solid in 82% yield (Section 2). Complex 3 is air stable in solid and solution, partly dis-

| Table 3 | Selected | bond | distances ^a | (A) | and | bond | angles ^a | ' (°) | for 3 . | |
|---------|----------|------|------------------------|-----|-----|------|---------------------|-------|----------------|--|
|---------|----------|------|------------------------|-----|-----|------|---------------------|-------|----------------|--|

| Atom | Distances | Atom | Distances |
|-------------------|------------|-------------------|------------|
| Cu(1)–N(1) | 1.978(4) | Cu(1)-N(1+)A | 1.978(4) |
| Cu(1)–N(2) | 2.174(3) | Cu(1)–N(2)B | 2.174(3) |
| Cu(1)–N(2)C | 2.174(3) | Cu(1)–N(2)A | 2.174(3) |
| Atom | Angles | Atom | Angles |
| N(1)-Cu(1)-N(1)A | 180.0 | N(2)-Cu(1)-N(2)B | 155.17(16) |
| N(1)-Cu(1)-N(2) | 77.59(8) | N(1)-Cu(1)-N(2)A | 102.41(8) |
| N(1)A-Cu(1)-N(2) | 102.41(8) | N(1)A-Cu(1)-N(2)A | 77.59(8) |
| N(1)-Cu(1)-N(2)B | 77.59(8) | N(2)-Cu(1)-N(2)A | 92.65(3) |
| N(1)A–Cu(1)–N(2)B | 102.41(8) | N(2)B-Cu(1)-N(2)A | 92.65(3) |
| N(1)-Cu(1)-N(2)C | 102.41(8) | N(1)A-Cu(1)-N(2)C | 77.59(8) |
| N(2)-Cu(1)-N(2)C | 92.65(3) | N(2)B-Cu(1)-N(2)C | 92.65(3) |
| N(2)A-Cu(1)-N(2)C | 155.17(16) | | |

The estimated standard deviations of the last significant digits are shown in parentheses.

^a Symmetry transformations used to generate equivalent atoms: 'A' y + 3/4, -x + 5/4, -z + 5/4. 'B' -x + 2, -y + 1/2, z. 'C' -y + 5/4, x-3/4, -z + 5/4.



Figure 2 Left: Representation of a part of the 2D-polymer formed by $[Cu(pyterpy)_2](ClO_4)_2$ (3) due to π -interactions. Thereby, *d* refers to the geometrical-to-geometrical centroid distance indicated by dashed lines, and \angle to the interplanar angle of interacting C₅N aromatic rings. Open lines refer to the shortest C···C distances (e.g., $d(C1 \cdots C2/) = 3.319$ Å) and dashed open lines to the longest C···C distances (e.g., $d(C4 \cdots C4/) = 3.627$ Å) of interacting C₅N rings. All hydrogen atoms and the ClO₄⁻ anions were omitted. Right: Interaction of adjacent C₅N aromatic rings in larger detail. The distance between the rings amounts to 3.422(2) Å. Symmetry transformations used to generate equivalent atoms: '/ 1-x, $\frac{1}{2}-y$, z.

solves in acetonitrile, whereas in all other common organic solvents it is insoluble. Elemental analysis for **3** is consistent with the proposed formula in Scheme 1.

The reaction progress of **1** with **2** could be monitored by FT-IR spectroscopy. The characteristic bands of non-coordinated pyterpy ($1580-1536 \text{ cm}^{-1}$) are shifted to higher wavenumbers during the course of the reaction ($1620-1572 \text{ cm}^{-1}$) (Section 2) (Saravani et al., 2007). The non-coordinated ClO₄ anions show one v_{Cl-O} vibration at 1085 cm^{-1} indicating the

non-coordinating character of these groups. No shift is found upon coordination of the copper ion by pyterpy ligands.

In the UV-vis spectrum of **1** the bands at 240, 277 and 317 nm can be assigned to ligand-based $(\pi \rightarrow \pi^*)$ transitions (Zhang et al., 2008). During the formation of **3** the 1st and 2nd bands appeared as broad absorptions with a maximum at 267 nm $(3.81 \times 10^2 \text{ cm}^{-1} \text{ mole}^{-1} \text{ L})$, while the band at 317 nm was shifted to lower energy (332 nm, $1.37 \times 10^2 \text{ cm}^{-1} \text{ mole}^{-1} \text{ L})$. The very broad *d*-*d* transition for **3** was observed at 697 nm



Figure 3 Representation of selected parts of adjacent 2-dimensional polymers of 3 in three different views along the unit cell.

(66 cm⁻¹ mole⁻¹ L), while for [Cu(ClO₄)₂·6H₂O] (2) it was found at 674 nm (2.61 × 10² cm⁻¹ mole⁻¹ L) (Lever, 1984). During the course of the reaction a new band of low intensity appeared at 486 nm (22.3 cm⁻¹ mole⁻¹ L) which can be assigned to Cu(d)→pyterpy(π^*) MLCT transitions. This observation is in agreement with other Cu(II) polypyridyl complexes (Trivedi et al., 2009).

The structure of **3** in the solid-state was determined by single X-ray structure analysis. The result thereof is shown in Fig. 1 together with the atomic-labeling scheme. Crystal and experimental data are given in Table 1, atomic coordinates for non-hydrogen atoms are listed in Table 2, and selected bond distances (Å) and angels (°) are given in Table 3 (Section 2).

From Fig. 1 it can be seen that the Cu1 atom is hexa-coordinated by two *meridional* η^3 -chelate bonded of pyterpy (1) to form a distorted octahedron. [Cu(pyterpy)₂](ClO₄)₂ (3) crystallizes in the I4(1)/a space group and the Cu(II) center lies on the

special position 4-bar inversion axis (Wyckoff letter b). A similar structure was reported for $[Cu(pyterpy)_2](PF_6)_2$ (Pitarch López et al., 2005). This complex is isostructural to **3**, however, it is not isomorphic, wherein the space group of the reported complex $(P4_1)$ is different from that of **3** (I4(1)/a).

Further insight can be directed to the distortion around the Cu(II) center, wherein the distortion arises from the bite angles of the 2,2':6',2"-terpyridine (terpy) unit being N(1)–Cu(1)–N(2) = 77.59(8), N(1A)–Cu(1)–N(2B) = 102.41(8), and N(2)–Cu(1)–N(2B) = 155.17(16)°. These values are far away from ideal octahedral bond angles, which most probably are the result of the tridentate binding motif (Alcock et al., 2000; Masuhara et al., 2007). A typical behavior was also reported for [Rh(pyterpy)_2](PF_6)_2 (Paul et al., 2004), [Co(pyterpy)_2](ClO₄)₂ (Indumathy et al., 2007), [Fe(pyterpy)_2](PF₆)₂ (Beves et al., 2008a; McMurtrie and Dance, 2005a,b), and [Cu(terpy)]²⁺ (terpy = 2,2':6',2"-terpyridine) (Saravani et al., 2007).

Also Jahn–Teller contribution is added to the distortion (Folgado et al., 1990), which influences the Cu–N bond lengths (Saravani et al., 2007). In this respect, the inner nitrogen atom N(1) and symmetry-generated N(1A) are strongly binding to Cu1 with a Cu–N distance of 1.978(4) Å. The outer nitrogen atoms from the terminal pyridyl rings are datively bonded to Cu1 with quite long equatorial Cu–N bonds (Cu(1)–N(2), Cu(1)–N(2B), Cu(1)–N(2A), Cu(1)–N(2C): 2.174(3) Å). The axial bond distances are comparable with those of [Cu(pyterpy)₂](PF₆)₂ (Pitarch López et al., 2005) and [Cu(terpy)₂](PF₆)₂ (1.987(5) Å), respectively, while the equatorial Cu–N distances are with 2.174(3) Å quite shorter (2.187(4) Å) (Saravani et al., 2007; Narr et al., 2003).

The 2,2':6',2"-terpyridine (terpy) rings in **3** are essentially planar (root mean square deviation from planarity 0.042 Å). This plane is precisely perpendicular oriented to the plane of the second coordinated terpy unit. The free 4'-4'''-pyridyl rings in **3** are non-coordinated as shown in Fig. 1. These free rings are twisted by the same amount out of the plane of the coordinated terpy unit (tilted by 36.3°). They exhibit the staggered conformation, in contrast to the eclipsed conformation observed in [Fe(pyterpy)₂]-(NO₃)₂:3H₂O·MeCN (Constable et al., 2000), [Co(pyterpy)₂](ClO₄)₂:4H₂O·MeCN, respectively (Indumathy et al., 2007). The staggered conformation was observed in [Ni(pyterpy)₂](NO₃)₂:2H₂O·2MeOH (Beves et al., 2008b), [Cu(pyterpy)₂](PF₆)₂·MeOH·0.5CH₂Cl₂ (Pitarch López et al., 2005), and [Ru(pyterpy)₂]PF₆·NO₃·DMSO (Constable et al., 2006).

Fig. 2 shows the 2D setup formed by π - π interactions between adjacent [Cu(pyterpy)₂]²⁺ spheres. As analogs to [Cu(pyterpy)₂](PF₆)₂·MeOH·0.5CH₂Cl₂ (Pitarch López et al., 2005), the face-to-face π - π interactions between terminal coordinated C_5N terpy units link adjacent $[Cu(pyterpy)_2]^{2+}$ cations forming a 2D-polymer. Consequently, the geometrical-to-geometrical centroid distance (d) is 3.568 Å. Thereby the geometrical-to-geometrical centroid distance (d) of π -interacting C₅N units resembles 3.568 Å. In this π -interaction, the shortest $C \cdots C$ distance of interacting C₅N rings (e.g., $d(C1 \cdots C2/)$) is 3.319 Å, while the longest C···C distance (e.g., $d(C4 \cdot \cdot C4/)$) is 3.627 Å. The centroids–centroids distance is found shorter than the similar distances in polymeric $Cu(pyterpy)_2(PF_6)_2$. MeOH·0.5CH₂Cl₂ polymers (Pitarch López et al., 2005), while it is longer than the calculated π - π interaction distance between the pyridine dimer (3.25 Å) (Mishra et al., 2010). The interplanar angle (\angle) of interacting C₅N aromatic rings is 7.0°.

In general, the packing mode of $[Cu(pyterpy)_2](PF_6)_2$ (Pitarch López et al., 2005) is compared with that of **3** identical. However, the cavities in $[Cu(pyterpy)_2](PF_6)_2$ are filled with PF_6^- anions and packing solvent molecules, while in the case of **3** they are filled with the disordered CLO_4^- anions only. The absence of any solvent molecules inside the structure of **3** and, for example, $[Ru(pyterpy)_2]PF_6 \cdot NO_3$ (Constable et al., 2006) can express the following: (i) no further intermolecular hydrogen bond interactions can be setup by solvent molecules as a characteristic for $[Ru(pyterpy)_2]PF_6 \cdot NO_3 \cdot DMSO$ (Constable et al., 2006) and $[Cu(pyterpy)_2]PF_6 \cdot NO_3 \cdot DMSO$ (Constable et al., 2006) and $[Cu(pyterpy)_2](PF_6)_2 \cdot MeOH \cdot 0.5CH_2Cl_2$ (Pitarch López et al., 2005), respectively and (ii) it allows the cations $M(pytrpy)^{2+}$ to approach more closely to each other giving rise to centro-symmetric pairs of π -stacking (Pitarch López et al., 2005).

In addition, adjacent 2D-polymers of **3** possess tail-to-tail interactions due to π - π interactions between non-coordinated C₅N aromatic rings producing vacant alternating perpendicu-

lar channels (see Fig. 3). In contrast, the solvent molecules were located inside the cavity of $[Cu(pyterpy)_2](PF_6)_2$ (Pitarch López et al., 2005). This pattern of interaction and vacant channels is observed in similar structures, i.e., Ru(pyter-py)_2](PF_6)(NO_3) (Constable et al., 2006), Ru(pyterpy)_2](PF_6)(Reves et al., 2008b), [Co(pyterpy)(NCS)_2] (Masuhara et al., 2007), and [Co(pyterpy)_2](CIO_4)_2 (Constable et al., 2006).

4. Conclusion

Complex $[Cu(pyterpy)_2](ClO_4)_2$ (3) (pyterpy = 4'-(4'''-pyridy))-2,2':6,2"-terpyridine) has been prepared by the treatment of pyterpy (1) with $[Cu(ClO_4)_2 \cdot 6H_2O]$ (2) in a 2:1 molar ratio. The structure of 3 in the solid-state is determined by single crystal X-ray analysis. The Cu1 atom is hexa-coordinated by two merid*ional* η^3 -chelates bonded of pyterpy (1) forming a distorted octahedron. The 4'-4"'-pyridyl ring is non-coordinated and hence can serve as a bridging system to bind another metal fragment. The face-to-face π -interactions of C5N aromatic rings between the terminal coordinated terpyridine entities link adjacent [Cu($pyterpy)_2]^{2+}$ cations into 2D-polymers. The adjacent 2D-polymers of 3 are also π stacked through π -interactions between the non-coordinating 4'-4"'-pyridyl rings producing vacant sites between adjacent 2D-polymers of 3. In contrast with the previous studies, the complexes given in reference (Pitarch López et al., 2005) are isostructural with 3.

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References

- Al-Anber, M., Walfort, B., Vatsadze, S., Lang, H., 2004. Inorg. Chem. Commun. 7, 799.
- Alcock, N.W., Barker, P.R., Haider, J.M., Hannon, M.J., Painting, C.L., Pikramenou, Z., Plummer, E.A., Rissanen, K., Saarenketo, P., 2000. J. Chem. Soc., Dalton Trans., 1447.
- Beves, Jonathon E., Dunphy, Emma L., Constable, Edwin C., Housecroft, Catherine E., Kepert, Cameron J., Neuburger, Markus, Price, David J., Schaffner, Silvia, 2008a. Dalton Trans., 386– 396.
- Beves, J.E., Bray, D.J., Clegg, J.K., Constable, E.C., Housecroft, C.E., Jolliffe, K.A., Kepert, C.J., Lindoy, L.F., Neuburger, M., Price, D.J., Schaffner, S., Schaper, F., 2008b. Inorg. Chim. Acta 361, 2582.
- Bonse, S., Richards, J.M., Ross, S.A., Lowe, G., Krauth-Siegel, R.L., 2000. J. Med. Chem. 43, 4812.
- Breuninger, E., Ruben, M., Lehn, J.-M., Renz, F., Garcia, Y., Ksenofontov, V., Gutlich, P., Wegelius, E., Rissanen, K., 2000. Angew. Chem. Int. Ed. 39, 2504.
- Chelucci, G., 1993. Synth. Commun. 23, 1897.
- Chelucci, G., Cabras, M.A., Saba, A., 1995. J. Mol. Catal. A 95, L7.
- Chichak, K., Branda, N.R., 1999. Chem. Commun., 523.
- Constable, E.C., Gargill Thompson, A.M.W., 1992. J. Chem. Soc., Dalton Trans., 2947.
- Constable, E.C., Gargill Thompson, A.M.W., 1994. J. Chem. Soc., Dalton Trans., 1409.
- Constable, E.C., Housecroft, C.E., Neuburger, M., Phillips, D., Raithby, P.R., Schoffeld, E., Sparr, E., Tocher, D.A., Zehnder, M., Zimmermann, Y., 2000. J. Chem. Soc., Dalton Trans., 2219.

- Constable, E.C., Housecroft, C.E., Neuburger, M., Schaffner, S., Schper, F., 2006. Inorg. Chem. Commun. 9, 616.
- Figgemeir, E., Merz, L., Hermann, B.A., Zimmermann, Y.C., Housecroft, C.E., Guuntherodt, H.-J., Constable, E.C., 2003. J. Phys. Chem. B 107, 1157.
- Folgado, J.V., Henke, W., Allmann, R., Stratemeir, H., Beltran-Poter, D., Rojo, T., Reinen, D., 1990. Inorg. Chem. 29, 2035.
- Funeriu, D.J., Lehn, J.-M., Baum, G., Frenske, D., 1997. Chem. Eur. J. 3, 99.
- Granifo, Juan, Garland, Marna T., Baggio, Ricardo, 2004a. Inorg. Chem. Commun. 7 (1), 77–81.
- Granifo, J., Garland, M.T., Baggio, R., 2004b. Inorg. Chem. Commun. 7, 77.
- Hayami, S., Hashiguchi, K., Juhász, G., Ohba, M., Ohkawa, H., Maeda, Y., Kato, K., Osaka, K., Takata, M., Inoue, K., 2004. Inorg. Chem. 43, 4124.
- Hofmeier, H., Schubert, U.S., 2004. Chem. Soc. Rev. 33, 373.
- Hou, L., Li, D., Shi, W.J., Yin, Y.G., Ng, S.W., 2005a. Inorg. Chem. 44, 7825.
- Hou, L., Li, D., Yin, Y.G., Ng, S.W., 2005b. Acta Crystallogr. E61, 21.
- Hutchinson, K., Morris, J.C., Nile, T.A., Walsh, J.L., Thompson, D.W., Petersen, J.D., Schoonover, J.R., 1999. Inorg. Chem. 38, 2516.
- Indumathy, R., Radhika, S., Kanthimathi, M., Weyhermuller, T., Nair, B.U., 2007. J. Inorg. Biochem. 101, 434–443.
- Jennette, K., Lippard, S.J., Vassiliades, G., Bauer, W., 1974. Proc. Natl. Acad. Sci. USA 71, 3839.
- Lehn, J.-M., 1988. Angew. Chem. Int. Ed. 27, 89.
- Leroy-Lhez, S., Fages, F., 2005. C. R. Chim. 8, 1204.
- Lever, A.B.P., 1984. Inorganic Electronic Spectroscopy. Elsevier, Amsterdam.
- Lohmeijer, B.G.G., Schubert, U.S., 2002. Angew. Chem. Int. Ed. 41, 3825.
- Long-Xuan, Z., Moon, Y.S., Basnet, A., Kim, E.K., Jahng, Y., Park, J.G., Jeong, T.C., Cho, W.J., Choi, S.U., Lee, C.O., Lee, S.Y., Lee, C.S., Lee, E.S., 2004. Bioorg. Med. Chem. Lett. 14, 1333.
- Masuhara, N., Hayami, S., Motokawa, N., Shuto, A., Inoue, K., Maeda, Y., 2007. Chem. Lett. 36 (1), 90.
- McMurtrie, J., Dance, I., 2005a. Cryst. Eng. Comm. 7, 216.
- McMurtrie, J., Dance, I., 2005b. Cryst. Eng. Comm. 7, 230.

- Mishra, B.K., Arey, J.S., Sathyamurthy, N., 2010. J. Phys. Chem. A 114, 9606.
- Narr, E., Zimmermann, H., Godt, A., Goldforb, D., Jeschke, G., 2003. Phys. Chem. Chem. Phys. 5, 3959.
- Padhi, S.K., Manivannan, V., 2006. Inorg. Chem. 45, 7994.
- Paul, J., Spey, S., Adams, H., Thomas, J.A., 2004. Inorg. Chim. Acta 357, 2827.
- Pitarch, López, Jesús, Kraus, Werner, Reck, Günter, Thünemann, Andreas, , Kurth, Dirk G., 2005. Inorg. Chem. Commun. 8, 281– 284.
- Salditt, T., An, Q., Plech, A., Peisl, J., Eschbaumer, C., Weidl, C.H., Schubert, U.S., 1999. Thin Solid Films 354, 208.
- Saravani, H., Rezvani, A.R., Hadadzadeh, H., Safari, N., 2007. Iran J. Chem. Eng. 26, 103.
- Sauvage, J.P., Hosseini, M.W., 1996. In: Atwood, J.L., Macnicol, D.M., Voegtle, F., Lehn, J.-M. (Eds.), Comprehensive Supramolecular Chemistry, vol. 9. Elsevier, Amsterdam.
- Sauvage, J.-P., Collin, J.P., Chambron, J.C., Guillerez, S., Coudret, C., Balzani, V., Barigelletti, F., De Cola, L., Flamigni, L., 1994. Chem. Rev. 94, 993.
- Schutte, M., Kurth, D.G., Linford, M.R., Cölfen, H., Möhwald, H., 1998. Angew. Chem. Int. Ed. 37, 2891.
- Sheldrick, G.M., 1990. Acta Crystallogr., Sect. A, 46, 467.
- Sheldrick, G.M., 1997. SHELXL-97, Program for Crystal Structure Refinement. University of Göttingen.
- Sun, S.-S., Silva, A.S., Brinn, I.M., Lees, A.J., 2000. Inorg. Chem. 39, 1344.
- Swiegers, G.F., Malefetse, T.J., 2000. Chem. Rev. 100, 3483.
- Trivedi, M., Pandey, D.S., Rath, N.P., 2009. Inorg. Chim. Acta 362, 284.
- Uenishi, J., Nishiwaki, K., Hata, S., Nakamura, K., 1994. Tetrahedron Lett. 35, 7973.
- Vidal, P.L., Divisia-Blohorn, B., Didan, G., Hazemann, J.L., Kern, J.M., Sauvage, J.P., 2000. Chem. Eur. J. 6, 1663.
- Ward, M.D., 1995. Chem. Soc. Rev. 24, 121.
- Zhang, C.F., Huang, H.X., Liu, B., Chen, M., Qian, D.J., 2008. J. Luminescence 128, 469.
- Ziener, U., Breunung, E., Lehn, J.-M., Wegelizs, E., Rissanen, K., Baum, G., Frenske, D., Vaughan, G., 2000. Chem. Eur. J. 6, 4132.