

An Investigation of Z-in Distortion in Mononuclear Cu(II) Complex with Terpyridine Ligands, $[\text{Cu}(\text{terpy})_2](\text{PF}_6)_2$

Saravani, Hamideh; Rezvani, Ali Reza

Department of Chemistry, University of Sistan and Baluchestan, P.O. Box: 98135-674 Zahedan, I.R. IRAN

Hadadzadeh, Hassan*[†]

Department of Chemistry, Isfahan University of Technology, Isfahan 84156-83111, I.R. IRAN

Safari, Nasser

Department of Chemistry, Shahid Beheshti University, P.O. Box: 198363113 Tehran, I.R. IRAN

ABSTRACT: The first crystal structure of $[\text{Cu}(\text{terpy})_2](\text{PF}_6)_2$, where terpy=2,2':6',2''-terpyridine is reported. Green crystals of $[\text{Cu}(\text{terpy})_2](\text{PF}_6)_2$ were grown by ether diffusion into an acetonitrile solution of the complex. Crystal structure of this complex is tetragonal (space group: $P\bar{4}2_1c$) with $a = 8.8916(3)$, $c = 20.0214(13)$ Å, and $z = 2$. The structure was refined by using 1828 independent reflections with $I > 2\sigma(I)$ to a R factor of 0.0809. The terpy ligands are tridentate and linked to the Cu(II) via three N atoms. The CuN_6 entities have compressed octahedral geometry with the shortest Cu-N bonds that form the axial positions. This complex represents z-in distortion at 293K and has a D_{2d} point group. The effective magnetic moment (μ_{eff}) of $[\text{Cu}(\text{terpy})_2](\text{PF}_6)_2$ was measured to be 1.95BM by Evans method. Cyclic voltammetry experiment of the complex shows that the Cu(II/I) couple is quasi-reversible.

KEY WORDS: Cu(II) complex, Terpyridine, Z-in distortion, Crystal structure, MLCT, Evans method.

INTRODUCTION

Transition metal terpyridine complexes have been studied extensively since the ligand was first reported around 30 years ago. Terpyridine complexes were originally developed as the basis of metal selective analytical techniques, but have since played a fundamental role in the development of our understanding of the ligand substitution and electron transfer creativities of

transition metal complexes and of biological systems. Furthermore, their diverse photo-chemical and photo-physical properties have led to extensive studies related to the development of photonic devices such as sensors, optical switches and photovoltaic cells [1-10].

A regular octahedral CuL_6 chromophore for the Cu(II) is very uncommon but does occur for the $[\text{Cu}(\text{NO}_2)_6]^{4+}$

* To whom correspondence should be addressed.

† E-mail: hadad@cc.iut.ac.ir

1021-9986/07/3/103

8/\$/2.80

anion when stabilized by high symmetry lattices such as the face-centered-cubic lattice of $K_2Pb[Cu(NO_2)_6]$ at 298 K [11]. All six Cu-N distances of 2.11 Å are equivalent from the copper site symmetry, with the actual symmetry of the anion lowered to T_h by the conformation of the nitro oxygen atoms. A regular trigonal octahedral CuL_6 chromophore is more common than the regular octahedral chromophore. It is most common in the tris (chelate) Cu(II) complexes such as $[Cu(en)_3](SO_4)$ [12] or $[Cu(ompha)_3](ClO_4)_2$ [13] but also occurs with tridentate chelate ligands as in $[Cu(metri)_2]$ [14]. The compressed tetragonal octahedral stereochemistry with six equivalent ligands is restricted to the $[Cu(NO_2)_6]^{4-}$ anion in the rubidium and cesium complexes [15]. The compressed rhombic octahedral stereochemistry is more common than the tetragonal form, but both together only constitute a very restricted class of Cu(II) structures [16,17].

We are interested in the question of whether the presence of the two terpy ligands will influence the structure, bond lengths and symmetry of the $[Cu(terpy)_2]^{2+}$. In the present study, we have determined the structure of $[Cu(terpy)_2](PF_6)_2$ (Fig. 1).

The structure of $[Cu(terpy)_2](PF_6)_2$ has been compared with the structures of Cu(II) and Ni(II) complexes of terpyridine ligands such as $[Cu(terpy)X_2].nH_2O$ ($X = Cl^-, Br^-, NO_2^-, NCS^-, F^-$), $[Cu_2(terpy)Cl_4]_2$ and $[Ni(terpy)_2]^{2+}$ [18-26].

EXPERIMENTAL SECTION

Materials

All the chemicals and solvents used were reagent grade. Absolute ethanol, DMF, acetonitrile, 2,2':6',2''-terpyridine, copper (II) chloride hydrate and ammonium hexafluorophosphate were purchased from Aldrich and used without further purification.

Physical Measurements

IR spectra were recorded as KBr pellets on a FT-IR Jasco 460 spectrophotometer and electronic spectra on a Jasco 7850 spectrophotometer. 1H -NMR spectra were recorded on a Bruker DRX-500 MHz, AVANCE spectrometer at ambient temperature in $DMSO-d_6$. Elemental analyses were performed by Heraeus CHN-O-Rapid elemental analyzer.

Cyclic voltammograms were recorded by using a PC PII Pentium 300 MHz microcomputer equipped with a

data acquisition board (PCL- 818 PG, PC- Labcard Co.) and a custom made potentiostat. Gold ultramicro-electrodes (25 μm , in diameter) were prepared by sealing metal microwires (Goodfellow metals Ltd., UK) into a soft glass capillary.

The capillary was then cut perpendicular to its length to expose the wire. Electrical contacts were made using silver epoxy (Johnson Matthey Ltd., UK). Before each experiment, the electrode surface was polished for 1 minute using extra fine carborundum paper and then for 10 minutes with 0.3 μm alumina. Prior to being placed in the cell, the electrode was washed with water and acetone. In all measurements an $Ag(s)|AgCl(s)|1M KCl(aq)$ reference electrode was used. The auxiliary electrode was made a Pt wire, 1 cm length and 0.5 mm in diameter.

Preparation of $[Cu(terpy)_2](PF_6)_2$

$CuCl_2.2H_2O$ (63 mg, 0.37 mmol) was dissolved in 20 mL of absolute ethanol in a 100 mL round-bottom flask. 2,2':6',2''-terpyridine (172 mg, 0.738 mmol) was added. The dark green solution was stirred and refluxed for 1 h. The solution was cooled to $-50^\circ C$ overnight and the dark green precipitate $[Cu(terpy)_2]Cl_2$ was collected by suction filtration and washed with absolute ethanol (10 mL) and diethylether (10 mL), respectively. $[Cu(terpy)_2]Cl_2$ was dissolved in 20 mL water and precipitated from solution as a hexafluorophosphate salt by the addition of excess of NH_4PF_6 (815 mg, 5 mmol). The product, $[Cu(terpy)_2](PF_6)_2$, was collected by suction filtration, washed with cold water (10 mL) and ether (10 mL), and then air dried. Diffusion of diethylether into an acetonitrile solution of the complex gave green crystals suitable for X-ray crystallography. Yield 103 mg, 76%. Found: C, 44.12; H, 2.76; N, 10.63 calculated for $C_{30}H_{22}F_{12}CuN_6P_2$ (Fw = 820.02): C, 43.90; H, 2.70; N, 10.25.

Crystallography

Green crystals of $[Cu(terpy)_2](PF_6)_2$ were grown by ether diffusion into an acetonitrile solution of the complex. Single-crystal X-ray diffraction measurements were carried out with a Bruker ApexII diffractometer equipped with a graphite monochromator for data collection at 293 (2) K. The determination of unit cell dimensions and data collection were performed with $MoK\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data reduction processing was carried

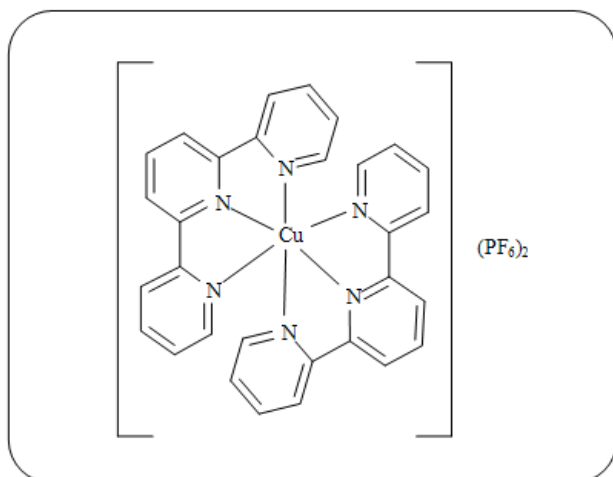


Fig. 1: $[Cu(terpy)_2](PF_6)_2$.

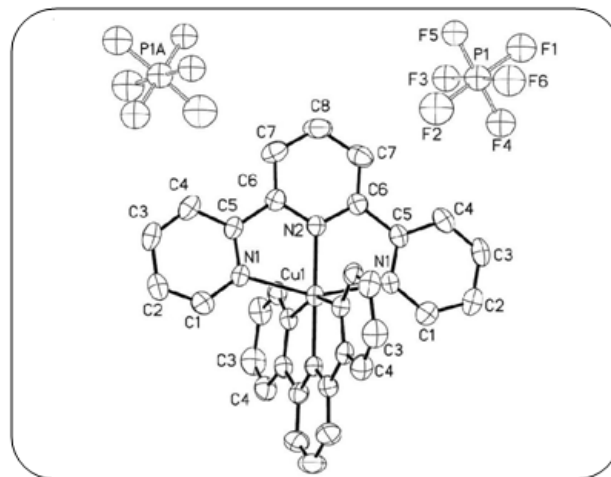


Fig. 2: ORTEP drawing for the complex $[Cu(terpy)_2](PF_6)_2$.

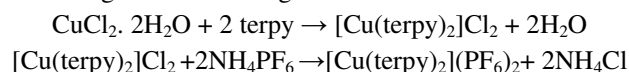
out by the use of the program Siemens SAINT, which applied Lorentz and Polarization correction to three-dimensionally integrated diffraction spots.

The program Bruker SPINT was utilized for the scaling of diffraction data, the application of a decay correction, and an empirical absorption correction based on redundant reflections. The space group was confirmed by XPREP routine in SHELXTL program. The structure was solved by direct method using SHELXS97 [27-30] and difmap synthesis using SHELXS97. Anisotropic refinement was performed for all non-hydrogen positions. All H- atoms were calculated. Further details of the structural analyses are given in table 1.

Position parameters and atomic coordinates are given in table 2, and selected bond lengths and angles are listed in table 3.

RESULTS AND DISCUSSION

The terpyridine Cu(II) complex was prepared according to the following reactions:



$[Cu(terpy)_2](PF_6)_2$ is air-stable and readily recrystallized in the tetragonal space group $P\bar{4}2_1c$. The elemental analysis of the complex is consistent with $C_{30}H_{22}F_{12}CuN_6P_2$, as are the following X-ray structure and spectroscopic characterizations. Fig. 2 shows the coordination geometry of the ligands about the Cu(II). The terpy ligands are tridentate and linked to the Cu(II) via three N atoms. Thus, the metal ion is six-

coordinate. The CuN_6 entities have compressed octahedral geometry with the shortest Cu-N bonds [Cu(1)- N(2), 1.986(5) and 1.987(5) Å] that form the axial positions. The remaining nitrogen atoms [N(1), N(1A), N(1C) and N(1B)] of terpy ligands are in the equatorial base. As shown in Fig. 2 and table 3, this complex represents z-in distortion at 293 K and has a D_{2d} point group. The mean Cu-N axial bond lengths are significantly (by 0.20 Å) shorter than the Cu-N equatorial bond distances (2.187(4) Å). In complexes of the type $[M(terpy)_2]^{2+}$, the predominant strain component of the rigid terpyridine ligand corresponds to a distinct compression along the molecular z axis of the MN_6 polyhedron. This is nicely documented by the Ni(II) complexes, because the ${}^3A_{2g}$ ground state of octahedral Ni(II) is *John-Teller* stable and the NiN_6 geometry solely reflects the strain effects imposed by the ligands and /or steric packing effects in the unit cell [19].

The bond angle formed by Cu(II) and two *cis* nitrogen atoms of each terpyridine ligand [N(1)-Cu(1)-N(2), N(1A)-Cu(1)-N(2)] is 77.44(11)°, while, the bond angle formed by two *trans* nitrogen atoms of the terpyridine ligands [N(2)-Cu(1)-N(2)] is linear (180.000(1)°). Previous studies of the structures of copper (II) complexes with terpyridine ligand have indicated structural distortions. For example, in $[Cu_2(terpy)Cl_4]_2$, all copper ions are subject to a distorted square- pyramidal coordination with typically long axial bonds [28]. In $[Cu(terpy)Cl_2]$ and $[Cu(terpy)(NO_2)_2] \cdot H_2O$, Cu(II) is found in a distorted square pyramid, with the terpyridine ligand in the

Table 1: Crystal data for [Cu(terpy)₂](PF₆)₂.

Empirical formula	C ₃₀ H ₂₂ F ₁₂ CuN ₆ P ₂
Formula weight	820.02
Temperature	293(2) K
Wavelength(λ)	0.71073 Å (Mo Kα)
Crystal system, Space group	Tetragonal, $P\bar{4}2_1c$
Unit cell dimension	$a = 8.8916(3)$ Å, $c = 20.0214(13)$ Å
Volume	1582.90(13) Å ³
Z	2
Exptl crystal density diffrn	1.720 g/cm ³
Absorption coefficient	0.896 mm ⁻¹
F(000)	822
Crystal Size	0.2×0.12×0.04 mm
Theta rang for data collection	2.5-25.5
Reflections collected/ unique	2424/1828 [R(int)= 0.0314]
Goodness- of- fit on F ²	1.067
Refinement method	Full- matrix least- square on F ²
Data / restraints / parameters	2424/0/100
Final R indices (1>2σ(1))	$R_1 = 0.0809$, $WR_1 = 0.2562$
R indices (all data)	$R_2 = 0.0971$, $WR_2 = 0.2764$
Diffraction – radiation – source	Fine-focus sealed tube
Monochromator	graphite
Diffraction – measurement – device-type	Bruker Apex II
Limiting indices	-12<=h<=12, -12<=k<=12, -28<=l<=28
Refine ls extinction coef	0.009(5)
Computing – data- collection	Bruker Apex 2
Computing – cell- refinement	Bruker SAINT
Computing – data- reduction	S SAINT
Computing – structure- solution	SHELXS97 (Sheldrick, 1990)
Computing – structure- refinement	SHELXL97 (Sheldrick, 1997)
Computing – molecular- graphics	SHELXTL 5.1, XP (Sheldrick, 1994)
Computing – publication- material	SHELXL97

$$R = \sum |F_o| - |F_c| / \sum F_o, WR = \sum W(|F_o| - |F_c|)^2 / \sum W(|F_o|)^2)^{1/2}$$

equatorial plane. [Cu(terpy)(NCS)₂] and [Cu(terpy)Br₂] exhibit a quite unusual coordination geometry in the solid state. The average Cu-N distance between Cu(II) and the terpyridine ligand (≈ 2.00 Å) in both complexes are similar to those in [Cu(terpy)Cl₂]. But while the two Cu-Cl spacings in the latter compounds differ by more than 0.2 Å, corresponding to a distorted square pyramid with a very long apical bond distance, the two Cu- Br or Cu-NCS bonds are of equal length in the two complexes, [Cu(terpy)Br₂] and [Cu(terpy)(NCS)₂] [29].

The comparison of the geometries of the CuN₆ entities in [Cu(terpy)₂](PF₆)₂ with the corresponding Ni(II) polyhedron in [Ni(terpy)₂]²⁺ (space group P4₂/n) [24, 30, 36] is quite informative. In [Ni(terpy)₂]²⁺, the Ni(II) coordination is also tetragonal. Though the ionic radii of Ni(II) and Cu(II) are nearly identical, the average Ni- N bond length (2.09 Å) is slightly smaller than the comparable Cu-N distance (2.12 Å). In previous studies, the force field for the cellular ligand field stabilization energy/ molecular mechanics (CLFSE/MM) method [32-45]

**Table 2: Atomic coordinates and equivalent isotropic displacement parameters for [Cu(terpy)₂](PF₆)₂.
U_(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.**

Atom	x	y	z	U(eq)
Cu(1)	0.5000	0.5000	0.5000	0.0483(3)
N(1)	0.7208(4)	0.4057(4)	0.4762(2)	0.0483(8)
N(2)	0.5000	0.5000	0.5000	0.0468(9)
C(1)	0.8309(7)	0.3622(6)	0.5174(3)	0.0613(12)
C(2)	0.9631(6)	0.3020(7)	0.4977(4)	0.0723(14)
C(3)	0.9838(6)	0.2823(7)	0.4271(4)	0.0775(15)
C(4)	0.8737(6)	0.3281(7)	0.3844(3)	0.0692(15)
C(5)	0.7430(5)	0.3901(5)	0.4097(2)	0.0516(10)
C(6)	0.6202(6)	0.4472(6)	0.3674(3)	0.0545(10)
C(7)	0.6255(9)	0.4434(8)	0.2998(3)	0.0768(16)
C(8)	0.5000	0.5000	0.2635(4)	0.086(3)
P(1)	0.9827(5)	0.5089(6)	0.19042(13)	0.0849(9)
F(1)	1.1082(7)	0.4393(8)	0.1448(3)	0.110(4)
F(2)	0.8642(7)	0.5818(10)	0.2375(3)	0.142(4)
F(3)	0.8770(7)	0.3747(7)	0.1858(4)	0.093(3)
F(4)	1.0492(7)	0.4195(9)	0.2502(3)	0.105(3)
F(5)	0.9170(8)	0.5969(9)	0.1312(3)	0.084(2)
F(6)	1.0881(8)	0.6442(7)	0.1996(4)	0.129(5)

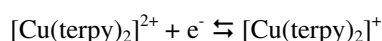
has been applied to Ni(II) and Cu(II) polypyridyl complexes [30]. For [Cu(terpy)₂]²⁺ and [Ni(terpy)₂]²⁺ the limiting geometries of tetragonally elongated and compressed octahedral are within a few kcal mol⁻¹, although the set of parameters overestimates the ligand contribution and predicts a compressed geometry [25,31].

The ¹H-NMR of [Cu(terpy)₂](PF₆)₂ was recorded in DMSO-d₆. The ¹H-NMR spectrum with broad resonance of this complex indicates paramagnetic behavior at room temperature. The effective magnetic moment (μ_{eff}) of [Cu(terpy)₂](PF₆)₂ was measured to be 1.95 BM by Evans method [46]. The magnitude of μ_{eff} is consistent with magnetic moment for six-coordinated Cu(II) complexes (1.7-2.2 BM) [47]. The IR spectrum of [Cu(terpy)₂](PF₆)₂ shows a absorption pattern in 4000 - 400 cm⁻¹ region similar to terpy ligand.

Electronic spectrum of the complex was taken in DMF. The intense absorption bands seen in the UV region (264, 279 and 329 nm with logε = 4.8, 4.6 and 4.01, respectively) are assigned to ligand-centered (π→π*) transitions [48-50]. For six-coordinated Cu(II) with z-in

distortion, three ligand field transitions are expected. However, the intensity of the absorption at visible region suggests a more accurate assignment may be metal- to-ligand charge transfer (MLCT) with minor contribution to band intensity due to underlying ligand field transitions. The intense absorption band at visible region (683, logε = 3.6) is assigned to metal- to-ligand charge transfer (MLCT) (dπ→π*) by analogy to other Cu(II) polypyridyl complexes [48].

Cyclic voltammetry was performed on an acetonitrile solution of [Cu(terpy)₂](PF₆)₂ with 0.1 M TBAH as a supporting electrolyte. The Cu (II/I) couple was observed at -1128 mV vs SCE. As shown in Figs. 3 and 4, Cu (II/I) couple is quasi-reversible and generally possesses invariant anodic to cathodic peak separation of 78 mV at scan rates from 50 to 400 mV/s.



The four quasi-reversible reduction couples at negative potential are assigned to the sequential reductions of terpy ligands as shown in following reactions [49,51-54].

Table 3: Bond lengths [\AA] and Angles [deg] for $[\text{Cu}(\text{terpy})_2](\text{PF}_6)_2$.

Bond Lengths, (\AA)			
Cu(1)-N(2)	1.986(5)	N(2)-C(6)	1.345(5)
Cu(1)-N(2)	1.987(5)	N(2)-C(6)	1.345(5)
Cu(1)-N(1)	2.187(4)	C(2)-C(3)	1.435(11)
Cu(1)-N(1A)	2.187(4)	C(3)-C(4)	1.363(9)
Cu(1)-N(1C)	2.187(4)	C(4)-C(5)	1.383(7)
Cu(1)-N(1B)	2.187(4)	C(5)-C(6)	1.427(7)
N(1)-C(1)	1.337(7)	C(6)-C(7)	1.356(9)
N(1)-C(5)	1.333(6)	C(7)-C(8)	1.424(9)
C(1)-C(2)	1.350(8)	C(8)-C(9)	1.424(9)
Bond Angles (deg)			
N(2)-Cu(1)-N(2)	180.00(1)	N(1)-Cu(1)-N(1)	154.9(2)
N(2)-Cu(1)-N(1)	77.44(11)	C(1)-N(1)-C(5)	118.1(4)
N(2)-Cu(1)-N(1)	102.56(11)	C(1)-N(1)-Cu(1)	129.4(4)
N(2)-Cu(1)-N(1)	77.44(11)	C(5)-N(1)-Cu(1)	112.6(3)
N(2)-Cu(1)-N(1)	102.56(11)	N(1)-Cu(1)-N(1)	124.8(6)
N(1)-Cu(1)-N(1)	154.9(2)	C(6)-N(2)-C(6)	120.5(2)
N(2)-Cu(1)-N(1)	102.56(11)	C(6)-N(2)-Cu(1)	119.8(3)
N(2)-Cu(1)-N(1)	77.44(11)	N(1)-C(5)-C(4)	121.7(5)
N(1)-Cu(1)-N(1)	92.71(5)	N(1)-C(5)-C(6)	115.0(4)
N(1)-Cu(1)-N(1)	92.71(5)	C(4)-C(5)-C(6)	123.3(5)
N(2)-Cu(1)-N(1)	102.56(11)	N(2)-C(6)-C(7)	122.1(5)
N(2)-Cu(1)-N(1)	77.44(11)	N(2)-C(6)-C(5)	115.1(4)
N(1)-Cu(1)-N(1)	92.71(5)	C(7)-C(6)-C(5)	122.7(5)

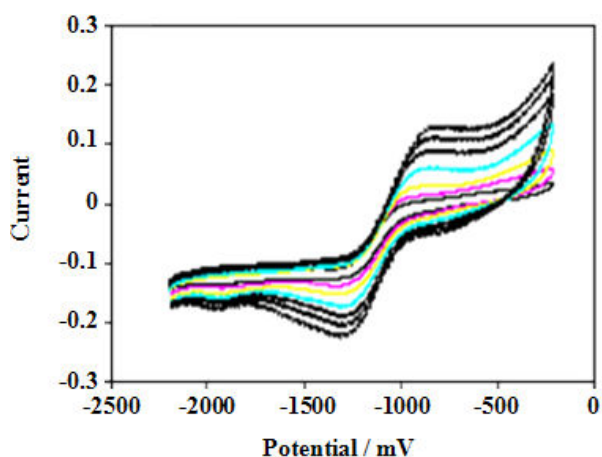


Fig. 3: Cyclic voltammograms of $[\text{Cu}(\text{terpy})_2](\text{PF}_6)_2$, 10^{-3}M in acetonitrile show Cu (II/I) couple in the range 0 to -2500 mV, between scan rates of 50-400 mV/s (I-VII).

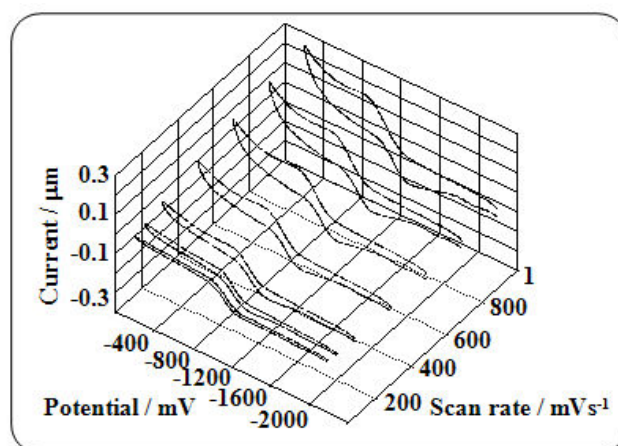
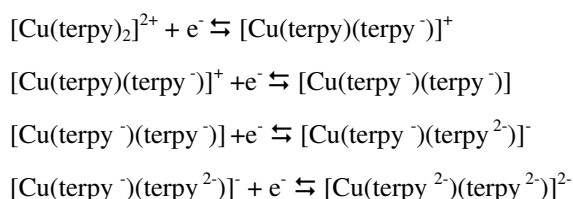


Fig. 4: Three-dimensional voltammograms (current-potential-scan rate) of $[\text{Cu}(\text{terpy})_2](\text{PF}_6)_2$, 10^{-3}M in acetonitrile shows a quasi-reversible behavior for the Cu(II/I) couple.



CONCLUSIONS

$[\text{Cu}(\text{terpy})_2](\text{PF}_6)_2$ represents a static *Jahn-Teller* distortion (z-in) at 293 K and the Cu-N axial bond lengths are significantly shorter than the Cu-N equatorial bond distances.

Complexation of Cu(II) by substituted terpyridine and other polypyridyl ligands opens up a convenient pathway to a multitude of well-defined supramolecular architectures.

Acknowledgmen

We wish to acknowledge financial support by the University of Sistan and Baluchestan and Isfahan University of Technology. The authors thank Professor Marilyn M. Olmstead for the collection X-ray diffraction data at University of California, Davis, USA.

Received : 13th May 2006 ; Accepted : 28th August 2006

REFERENCES

- [1] DeRosa, M. C., Al-mutlaq, F. and Crutchley, R.J., *Inorg. Chem.*, **40**, 1406 (2001).
- [2] Liegghio, R., Potvin, P. G. and Lever, A. B. P., *Inorg. Chem.*, **40**, 5485 (2001).
- [3] Diaz, D.J., Bernhard, S., Storrier, G. D. and Abruna, H. D., *J. Phys. Chem. B*, **105**, 8746 (2001).
- [4] Dong, T. Y., Shih, H. W. and Chang, L. S., *Langmuir*, **20**, 9340 (2004).
- [5] Arm, K. J., Leslie, W., Gareth Williams, J.A., *Inorg. Chim. Acta*, **359**, 1222 (2006).
- [6] Corral, E., Hotze, A.C.G., Tooke, D.M., Spek, A. L., Reedijk, J., *Inorg. Chim. Acta*, **359**, 830 (2006).
- [7] Benniston, A. C., Chapman, G. M., Harriman, A., Sams, C. A., *Inorg. Chim. Acta*, **359**, 753 (2006).
- [8] Lima, R. G., Sauaia, M. G., Bonaventura, D., Tedesco, A. C., Lopez, V. R. F., Bendhack, L. M., Silva, R. S., *Inorg. Chim. Acta*, **358**, 2643 (2005).
- [9] Meier, M. A. R., Wouters, D., Ott, C., Guillet, P., Fustin, C. A., Gohy, J. F. and Schubert, U. S., *Macromolecules*, **39**, 1569 (2006).
- [10] Aamer, K. A., and Tew, G. N., *Macromolecules*, **37**, 1990 (2004).
- [11] Isaacs, N. W. and Kennard, C. H. L., *J. Chem. Soc. (A)*, 386 (1969).
- [12] Cullen, D. L. and Lingafelter, E. C., *Inorg. Chem.*, **9**, 1858 (1970).
- [13] Joesten, M. D., Hussain, M. S. and Lenhert, P. G., *Inorg. Chem.*, **9**, 151 (1970).
- [14] Sheldon, R.I., Jircitano, A.J., Beno, M. A., Williams, J. M. and Mertes, K.B., *J. Am. Chem. Soc.*, **105**, 3028 (1983).
- [15] Takagi, S., Joesten, M. D. and Lenhert, P., *J. Am. Chem. Soc.*, **97**, 444 (1975).
- [16] Allrann, R., Henke, W. and Reinen, D., *Inorg. Chem.*, **17**, 378 (1978).
- [17] Arriortua, M. I., Rojo, T., Amigo, J. M., Germain, G. and Declereq, J. P., *Acta Crystallogr., Sect. B*, **38**, 1323 (1982).
- [18] Cini, R. and Pifferi, C., *J. Chem. Soc., Dalton Trans.* 699 (1999).
- [19] Folgado, J.V., Henke, W., Allmann, R., Stratemeier, H., Beltran-Poter, D., Rojo, T. and Reinen, D., *Inorg. Chem.*, **29**, 2035 (1990).
- [20] Kremer, H. and Reinen, D., *Inorg. Chem.*, **22**, 2858 (1983).
- [21] Allmann, R., Henke, W., Reinen, D., *Inorg. Chem.*, **17**, 378 (1978).
- [22] Bresciani-Pahor, N., Nardin, G., Bonomo, R. P., Nardin, G., *J. Chem. Soc. Dalton Trans.*, 2625 (1984).
- [23] Folgado, J. V., Gómez-Romero, P., Sapiña, F., Beltrán-Porter, D., *J. Chem. Soc. Dalton Trans.*, 2325 (1990).
- [24] Arriortua, I.M., Mesa, J.L., Rojo, T., Debaerdemaeker, T., Beltrán-Porter, D., Stratemeier, H., *Inorg. Chem.*, **27**, 2976 (1988).
- [25] Deeth, R.J., Paget, V. J., *J. Chem. Soc. Dalton Trans.*, 537 (1997).
- [26] Castro, I., Faus, J., Julve, M., Gleizes, A., *J. Chem. Soc. Dalton Trans.*, 1937 (1991).
- [27] Sheldrick, G.M. SADABS, Bruker Area Detector Absorption Correction, Bruker Axs Inc., Madison, (1996).
- [28] SHELXTEL Release 5.03, The Complete Software Package for Single Crystal Structure Determination, Bruker AXS Inc., Madison, (1997).
- [29] Sheldrick, G.M. SHELX &, Program for Crystal Structure Solution, University of Göttingen,

- Germany, (1997).
- [30] Wada, A., Sakabe, N. and Tanaka, J., *Acta Crystallogr. Sect. B*, **32**, 1121 (1976).
- [31] Arriortua, M.I., Rojo, T., Amigo, J. M., Germain, G., Declercq, J. P., *Bull. Soc. Belg.*, **91**, 337 (1982).
- [32] Burton, V. J., Deeth, R. J., Kemp, C. M., Gilbert, P. J., *J. Am. Chem. Soc.* **117**, 8407 (1995).
- [33] Comba, P. H., Hambley, T. W., *Molecular Modeling of Inorganic Compounds*, VCH, Weinheim, (1995).
- [34] Bernhardt, P. V., Comba, P., *Inorg. Chem.*, **33**, 2638 (1992).
- [35] Bernhardt, P. V., Comba, P., Hambley, T. W., Massoud, S. S., Stebler, S., *Inorg. Chem.*, **31**, 2644 (1992).
- [36] Adam, R.K., Antolovich, M., Brigden, L.G., Lindoy, L. f., *J. Am. Chem. Soc.*, **113**, 3346 (1991)
- [37] Hay, B. P., *Coord. Chem. Rev.*, **126**, 177 (1993).
- [38] Comba, P., Hambley, T. W., Zipper, L., *Helv. Chim. Acta*, **71**, 1875 (1988).
- [39] Hambley, T. W., *Inorg. Chem.*, **27**, 1073 (1988).
- [40] Hambley, T. W., *J. Chem. Soc. Dalton Trans.*, 565 (1986).
- [41] Hambley, T. W., Hawkins, C. J., Palmer, J. A., Snow, M. R., *Aust. J. Chem.*, **34**, 45 (1991).
- [42] Hancock, R. D., Dobson, S. M., Evers, A., Wade, P. W., Ngwenya, M. p., Boeyens, J.C.A., *J. Am. Chem. Soc.*, **110**, 2788 (1988).
- [43] Burton, V. J., Deeth, R. J., *J. Chem. Soc. Chem. Commun.*, 573 (1995).
- [44] Gerloch, M., *Magnetism and Ligand Field Analysis*, Cambridge University Press, New York (1983).
- [45] Gelloch, M., Harding, J. H., Woolley, R. G, *Struct. Bonding* (Berlin), **46**, 1 (1981).
- [46] Mackey, D.J. and Evans, S.V., *J. Chem. Soc. Dalton Trans.*, 2004 (1976).
- [47] Drago, R. S., "Physical Methods for Chemists," (Second Edition), Saunders, Philadelphia, (1992).
- [48] Lever, A. B. P., "Inorganic Electronic Spectroscopy" (Second Edition), Elsevier, (1984).
- [49] Hadadzadeh, H., Rezvani, A. R., *Iran. J. Chem. & Chem. Eng.* **24** (2), 21 (2005).
- [50] Rezvani, A. R., Hadadzadeh, H., Patrick, B., *Inorg. Chim. Acta*, **336**, 125 (2002).
- [51] Rezvani, A.R., Evans, C. E. B., Crutchley, R., J., *Inorg. Chem.*, **33**, 170 (1994).
- [52] Evans, C. E. B., Yap, G. P. A., Crutchley, R. J., *Inorg. Chem.*, **37**, 6167 (1998).
- [53] Johansson, O., Borgstro1m, M., Lomoth, R., Palmblad, M., Bergquist, J., Hammarstro1m, L., Sun, Licheng. and Akermark, B., *Inorg. Chem.*, **42**, 2908 (2003).
- [54] Drew, M. G. B., Foreman, M. R. S. J., Geist, A., Hudson, M. J., Marken, F., Norman, V., Weigl, M., *Polyhedron*, **25**, 888 (2006).