مجله بلورشناسی و کانی شناسی ایران

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انجمن بلورشناسی و کانی شناسی ایران

سنتز، شناسایی و ساختار بلوری کمپلکس دو هسته‌ای مس (II) با لیگاند پلساز ۲،۳،۵،۶ – تترا (۲-پیریدل) پیرازین $[\{CuCl\}_2(\mu - tppz)](PF_6)_2$.

حسن حدادزاده[۱]، علیرضا رضوانی[۱]، فاطمه بهزادیان اصل[۲]، حمیده سراوانی[۱]

۱- گروه شیمی، دانشگاه سیستان و بلوچستان، زاهدان، صندوق پستی ۶۷۴-۹۸۱۳۵
۲- دانشکده شیمی، دانشگاه صنعتی شریف، تهران، صندوق پستی ۹۵۱۶-۱۱۳۶۵
پست الکترونیکی: hadad@hamoon.usb.ac.ir

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چکیده: کمپلکس دو هسته‌ای جدید مس (II) با فرمول $[\{CuCl\}_2(\mu - tppz)](PF_6)_2$ که در آن tppz = tetra-2-pyridinylpyrazine است، سنتز شده و با روشهای تجزیه عنصری و طیف سنجی‌های ^{1}H-NMR, IR و UV-vis مورد شناسایی قرار گرفته است. ساختار بلوری کمپلکس دو هسته‌ای مس (II) نشان می‌دهد که هر Cu (II) به وسیلهٔ سه اتم نیتروژن مربوط به لیگاند پلساز tppz و یک اتم کلر احاطه شده است. داده‌های ساختار بلوری این کمپلکس به شرح ذیل است: سیستم بلوری، مونوکلینیک (تک میل)، گروه نقطه‌ای C_2/m

$a = ۱۳٫۳۱۴(۳)$ Å, $b = ۱۲٫۹۰۱(۲)$Å, $c = ۸٫۹۰۳۹(۱۷)$Å, $V=۱۵۰۹٫۴(۵)$Å^3
$\beta = ۹۹٫۲۶۰$ deg, $Z=۲$, $R =۰٫۰۴۱۶$

ساختار بلوری نشان می‌دهد که مس (II) به ترتیب در بالا و پایین صفحه جزء پیرازین لیگاند پلسازtppz قرار دارند و اجزای پیریدین این لیگاند پلساز نیز به Cu (II) هم‌آرایی شده‌اند. هر لیگاند کلر به صورت استوایی به یون مس در یون $[\{CuCl\}_2(\mu\text{-}tppz)]^{2+}$ و همچنین به صورت محوری با یون مجاور $[\{CuCl\}_2(\mu\text{-}tppz)]^{2+}$ پیوند داده است. این حالت یک زنجیر تک بعدی در حالت جامد ایجاد نموده است.

واژه‌های کلیدی: *مس، پیرازین، زنجیر تک‌بعدی، ساختار بلوری.*

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Synthesis, Charactrization and Crystal Structure of Dinuclear Copper(II) Complex of the Ligand 2,3,5,6-Tetra (2-pyridyl) pyrazine, $[\{CuCl\}_2(\mu - tppz)](PF_6)_2$

H. Hadadzadeh[1], A. R. Rezvani[1], F. Behzadian Assl[2], H. Saravani[1]

1- Chemistry Department, Sistan & Baluchestan University, Zahedan, P. O. Box 98135-674, Iran,
2- Chemistry Department, Sharif University of Technology, P. O. Box 11365-9516, Tehran, Iran
E-Mail: hadad@hamoon.usb.ac.ir

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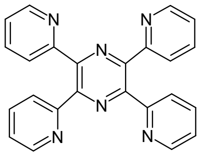
Abstract: The Dinuclear Cu (II) complex $[\{CuCl\}_2(\mu - tppz)](PF_6)_2$, where tppz represents tetra-2-pyridinylpyrazine, has been prepared and characterized by elemental analysis, ^{1}H-NMR, IR and UV-vis spectroscopies. A crystal structure of the complex showed the Cu (II) are surrounded by three N atoms of tppz bridging ligand and one Cl atom. Crystal structure data are as follows: crystal system monoclinic, space group *C2/m*, a= 13.314(3), b= 12.901(2), c= 8.9039(17) Å, β= 99.260º, V=1509.4(5) Å^3 and Z=2. The structure was refined to a final R factor of 0.0416. The crystal structure revealed that the Cu(II) are respectively above and below the plane of the pyrazine moiety of the bridging tppz ligand with the pyridine moieties moving out of the pyrazine plane in order to coordinate to Cu(II). Each chloride ligand bonds equatorially to Cu(II) in a $[\{CuCl\}_2(\mu\text{-tppz})]^{2+}$ ion and axially to a neighboring $[\{CuCl\}_2(\mu\text{-tppz})]^{2+}$ ion so as to form a one-dimensional chain in the solid state.

Keywords: *Pyridinylpyrazine, Copper, One-dimensional chain, Crystal Structure.*

Introduction

Based on coordination complexes, electronic and magnetic materials, that composed of metal centers connected by bridging ligands of some description, are of interest e.g. for their potential as molecular wires, magnets and switches. Understanding the factors controlling metal-metal coupling is central to the purposeful synthesis of such materials and to the tuning of their properties. In such system, the electronic of metal centers are mediated by the orbital of the bridge, and the interplay between metal and bridge orbitals are thus central in determining the behavior of the resultant system [1-6].



tppz

Some mono-,di-, and even trinuclear complexes of Fe^{II}, Co^{III}, Rh^{III}, Ru^{II}, Ir^{III} and Os^{II}[7-11] with tppz ligand have been prepared. The study of electron transfer in the mixed-valence dinuclear $[(tpy)Ru^{II}$ $(\mu\text{-tppz})Ru^{III}$ $(tpy)]^{5+}$has shown[12] that strong electronic coupling was observed in this complex (V_{ab} = 0.05 eV). However, in these dinuclear tppz complexes, steric repulsion of the 3 and 3' hydrogen atoms induces a twisting of the pyridine rings, which reduces the planarity of the bridging ligand [13].

In this study, the dinuclear Cu(II) complex $[\{CuCl\}_2(\mu - tppz)](PF_6)_2$ where tppz is tetra-2-pyridinylpyrazine has been prepared to examine the effect of the nature of metal centers and bridging ligand on the metal-metal coupling via Cu- tppz -Cu linkages. The properties of this complex will be compared with $[(tpy\ )Ru^{II}$ $(\mu\text{-tppz})$ Ru^{III} $(tpy)]^{5+}$ complexes.

Experimental Section

Materials

All of the chemicals and solvents used were reagent grade. Acetonitrile, diethylether, DMF and toluene were purchased from Merck. Copper (II) chloride hydrate, tetra-2-pyridinylpyrazine (tppz) and alumina (WA-1, 150 meshes), were purchased from Aldrich and used without further purification.

Physical Measurements

UV-vis was taken on a JASCO VSP-575 spectrophotometer. The spectra were measured in acetonitrile solution at room temperature. The IR spectra (KBr disks) were obtained on a BOMEM Michelson-100 FT-IR spectrometer. ^{1}H-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 analyzed.

Preparation of $[\{CuCl\}_2(\mu - tppz)](PF_6)_2$

$CuCl_2.6H_2O$ (0.269g, 2 mmol) was dissolved in 50 mL of DMF in a 250 mL round-bottom flask. Tetra-2-pyridinylpyrazine (tppz) (0.388g, 1 mmol) was added, and the green solution was stirred with gentle heating (55-60^{o}C) for 48 h. The reaction mixture was then chilled to room temperature. The green–brown precipitate $[\{CuCl\}_2(\mu - tppz)]Cl_2$ was collected and washed with 3×10 mL acetone and 3×10 mL diethylether. Due to the poor solubility of $[\{CuCl\}_2(\mu - tppz)]Cl_2$ in organic solvent (acetonitrile), the chloride salt of the complex was dissolved in 50 mL of water and then excess of NH_4PF_6 (1.5g) was added to the solution. The green – brown precipitate $[\{CuCl\}_2(\mu\text{–}tppz)](PF_6)_2$ was filtered off, washed with water, and dried at room temperature in air. The crude product was dissolved in 10 mL 3:1 MeCN/toluene, filtered, and purified by chromatography on a 50 cm × 2 cm diameter column containing ~200 g grade V alumina (Brockmann I, weakly acidic, 150 mesh). One band containing mononuclear complex was eluted with 1:1 MeCN/toluene. A second band was eluted with 100 mL 3:1 MeCN/toluene and contained the target complex, which crystallized from the solution upon evaporation of the MeCN by rotary evaporator. Recrystallization was achieved by the slow diffusion of ether into a saturated solution of the complex in MeCN. Yield: 0.46g (53%). Anal. Calcd for $C_{24}H_{16}Cl_2F_{12}N_6P_2Cu_2$: C, 32.90; H, 1.84; N, 9.59. Found: C, 33.08; H, 1.90; N, 9.66.

Crystallography

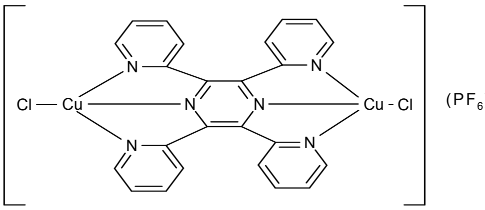
Dark green crystals of $[\{CuCl\}_2(\mu\text{–}tppz)](PF_6)_2$ were grown by ether diffusion into an acetonitrile solution of the complex. The data were collected on a 1K Siemens smart CCD using Mo Kα radiation (λ= 0.71073Å) at 203(2) K using an ω-scan technique and corrected for absorptions using equivalent reflections[14]. No symmetry higher than monoclinic was observed, and solution in the centric space group option yielded chemically reasonable and computationally stable results of refinement. The structure was solved by direct methods and refined with full-matrix least-squares procedures. Anisotropic refinement was performed for all non-hydrogen positions. All hydrogen atoms were calculated. Scattering factors are contained in the SHELXTL 5.1 program library.

Results and Discussion

The dinuclear Cu(II) complex was synthesized in good yield according to the following reactions:

$$2CuCl_2 + tppz \xrightarrow{\text{DMF, } 60\,^oC} [\{CuCl\}_2(\mu\text{-}tppz)]Cl_2 \xrightarrow{NH_4PF_6\text{ , }H_2O} [\{CuCl\}_2(\mu\text{-}tppz)](PF_6)_2$$

Some purification by column chromatography was required. The complex is air-stable and can be readily recrystallized.



The hexafluorophosphate complex is readily soluble in polar organic solvents and, after purification by chromatography using alumina and recrystallization from acetonitrile/ether solution, was isolated as dark green crystals in 74% yield. The complex appeared stable in solution for days at a time and no evidence of decomposition was seen in the solid state.

The IR spectrum of the complex shows absorption patterns like tppz in 500-1600 cm^{-1} region, indicating the existence of tppz as the bridging ligand. In the electronic spectrum of the complex, the absorption bands seen in the UV region are assigned to ligand-centered transition ($\pi \rightarrow \pi^*$) and two ligand field transition ($d_{yz} \rightarrow d_{xy}$, $d_{xz} \rightarrow d_{xy}$) for $Cu(II)N_3Cl$ unit with C_{2v} microsymmetry [16] at 460 and 390 nm. Deep green crystals of the dinuclear Cu(II) complex $[\{CuCl\}_2\ (\mu - tppz)]\ (PF_6)_2$ that were suitable for crystallography were grown by diffusion of ether into a solution of the complex in acetonitrile. Crystallography data, atomic coordinate and bond lengths and angles are reported in Tables 1, 2 and 3, respectively. An ORTEP drawing of the complex cation is shown in Figure 1.

Table 1 Crystal Data for $[\{CuCl\}_2(\mu - tppz)](PF_6)_2$.

Empirical Formula	$C_{24}H_{16}Cl_2Cu_2F_{12}N_6P_2$
Formula weight	876.35
Temperature	203(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, *C2/m*
Unit cell dimensions	a = 13.314 (3) Å b = 12.901 (2) Å beta = 99.260 deg c =8.9039(17) Å
Volume	1509.4(5) $Å^3$
Z, calculated density	2, 1.928 Mg/m^3
Absorption coefficient	1.796 mm^{-1}
F (000)	864
Crystal size	0.10 × 0.10 × 0.10 mm
Theta range for data collection	2.21 to 28.47 deg
Limiting indices	$-17<=h<=16, 0<=k<=17, 0<=l<=11$
Reflections collected / unique	3828 / 1805 [*R*(int) =0.0416]
Completeness to theta = 28.47	90.5%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000000 and 0.817274
Refinement method	Full –matrix Least-squares on F^2
Data / restraints / parameters	1805 / 0 /121
Goodness – of- fit on F ^2	1.049
Final *R* indices [*I>2sigma (I)]*	$R_1 = 0.0416$, $wR_2 = 0.1065$
R indices (all data)	$R_1 = 0.0499$, $wR_2 = 0.1129$
Largest diff. peak and hole	0.967 and -0.573 e A^{-3}

$R_1 = \Sigma \| F_0| - |F_c| / \Sigma F_0 |$, $WR_2 = \Sigma W(|F_0| - |F_c|)^2 / \Sigma W(|F_0|^2)^{1/2}$

The ORTEP drawing of the complex cation (Figure 1) shows identical tetragonally distorted coordination spheres of nitrogen and chloride donor atoms about the Cu(II). The two Cu(II) are respectively above and below the plane of the pyrazine moiety of the bridging tppz ligand with the pyridine moieties moving out of the pyrazine plane in order to coordinate to Cu(II). This tppz coordination mode has been observed in the crystal structures of dinuclear complexes of other first-row transition metal tppz complexes [2, 3]. The unit cell drawing in Figure 2 shows that $[\{CuCl\}_2(\mu\text{-tppz})]^{2+}$ cations interact with neighboring cations through a bridging chloride ligand to form a distorted square pyramidal Cu(II) coordination sphere and as a result the complex forms a one-dimensional chain in the solid state. The axial coordination of chloride atoms involves larger Cu-Cl bond lengths (in Figure 2, for Cu2-Cl1 and Cu1-Cl2 bond lengths are 2.7196(13) Å) compared to equatorial Cu-Cl bond lengths (in Figure 2, for Cu2-Cl2 and Cu1-Cl1 bond lengths are 2.2431(12) Å), suggesting that the interaction between dimers is tenuous.

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotopic displacement parameters ($A^2 \times 10^3$) for $[\{CuCl\}_2(\mu - \text{tppz})](PF_6)_2$. *U*(eq) is defined as one third of the trace of the orthogonalized *Uij* tensor.

	x	*y*	*z*	*U(eq)*
Cu	755(1)	0	8691(1)	18(1)
P(1)	3399(1)	0	6964(2)	33(1)
N(1)	793(2)	1554(2)	8287(3)	20(1)
N(2)	426(3)	0	6446(4)	16(1)
C(1)	1150(2)	2284(3)	9305(4)	26(1)
C(2)	1409(3)	3271(3)	8870(4)	35(1)
C(3)	1358(3)	3489(3)	7339(5)	41(1)
C(4)	957(3)	2744(2)	6262(4)	31(1)
C(5)	652(2)	1798(2)	6780(3)	20(1)
C(6)	240(2)	924(2)	5765(3)	17(1)
F(1)	3417(4)	1217(3)	7013(6)	125(2)
F(2)	2482(4)	0	5641(5)	150(4)
F(3)	4154(3)	0	5742(5)	58(1)
F(4)	4312(3)	0	8346(5)	89(2)
F(5)	2620(2)	0	8198(4)	47(1)
Cl	1277(1)	0	11216(1)	23(1)

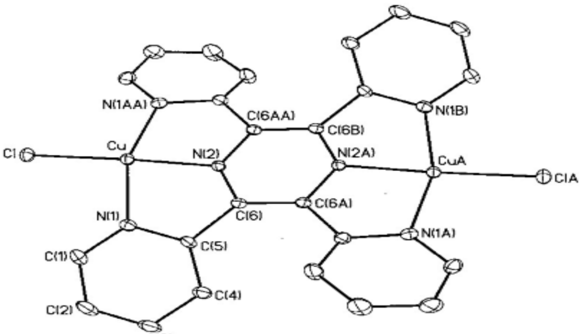


Figure 1 ORTEP of the complex, $[\{CuCl\}_2(\mu\text{-tppz})](PF_6)_2$, the counter anions have been excluded for clarity.

Table 3 Selected bond lengths (Å) and angles(^{o}) for [{CuCl}$_2$ (μ – tppz)](PF$_6$)$_2$.

Bond Lengths, (Å)			
Cu- Cl #2	2.7196(13)	N(1)- C(1)	1.341(4)
Cu-N(2)	1.977(3)	N(1)- C(5)	1.362(4)
Cu-N(1) #1	2.038(3)	N(2)- C(6)#1	1.342(3)
Cu-N(1)	2.038(3)	N(2)- C(6)	1.342(3)
Cu-Cl	2.2431(12)	C(1)- C(2)	1.391(5)
P(1)-F(2)	1.554(5)	C(2)- C(3)	1.382(6)
P(1)- F(1)	1.571(4)	C(3)- C(4)	1.401(5)
P(1)- F(1)#1	1.571(4)	C(4)- C(5)	1.388(4)
P(1)- F(4)	1.585(5)	C(5)- C(6)	1.493(4)
P(1)- F(3)	1.596(3)	C(6)- C(6)#3	1.409(6)
P(1)- F(5)	1.627(3)	Cl- Cu #2	2.7196(13)
Bond Angles (deg)			
N(2)-Cu-N(1)#1	80.16(7)	F(2)-P(1)-F(1)	91.6(2)
N(2)-Cu-N(1)	80.16(7)	F(2)-P(1)-F(1)#1	91.6(2)
N(1)#1-Cu-N(1)	159.00(15)	F(1-P(1)-F(1)#1	176.6(4)
N(2)-Cu-Cl	174.85(10)	F(2)-P(1)-F(4)	178.4(3)
Cl-Cu-Cl #2	96.80(4)	F(1)-P(1)-F(4)	88.4(2)
N(1) #1-Cu-Cl	99.47(7)	F(1)#1-P(1)-F(4)	88.4(2)
N(1)-Cu-Cl	99.47(7)	F(2)-P(1)-F(3)	89.3(2)
N(2)-Cu-Cl#2	88.35(10)	F(1)-P(1)-F(3)	90.61(15)
N(1) #1-Cu-Cl#2	93.35(7)	F(1)#1-P(1)-F(3)	90.61(15)
N(1)-Cu-Cl#2	93.35(7)	F(4)-P(1)-F(3)	92.3(2)
F(3)-P(1)-F(5)	179.4(2)	F(2)-P(1)-F(5)	90.2(2)
C(1)-N(1)-C(5)	118.8(3)	F(1)-P(1)-F(5)	89.41(15)
C(1)-N(1)-Cu	126.0(2)	F(1)#1-P(1)-F(5)	89.41(15)
C(5)-N(1)-Cu	113.46(19)	F(4)-P(1)-F(5)	88.2(2)
C(6)#1-N(2)-C(6)	125.3(4)		

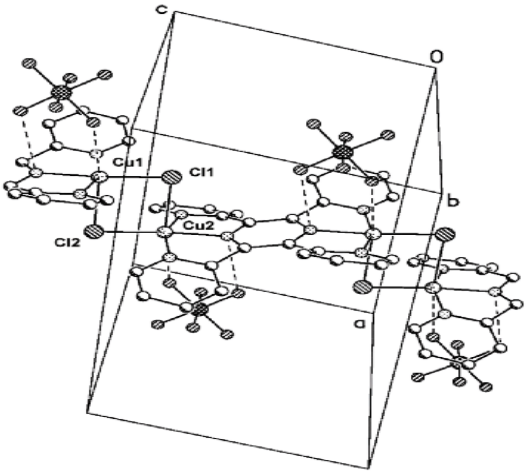


Figure 2 Cell drawing of the complex, [{CuCl}$_2$(μ-tppz)]([PF$_6$)$_2$. Selected bond lengths (Å) and bond angles (deg): Cu2-Cl2, 2.2431(12); Cu1-Cl2, 2.7196(13); Cu1-Cl2-Cu2, 83.20(4); Cl1-Cu1-Cl2, 96.80(4).

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