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Synthesis, Crystal Structure, and Quantum Mechanics Studies of Tetrapyridinecopper(I) iodide

Ehab AlShamaileh, Rawhi Al-Far and Muath Atmeh *

ABSTRACT

Tetrapyridinecopper(I) iodide, $[Cu(C_5H_5N)_4].I$, has been synthesized and characterized by single-crystal X-ray diffraction at room temperature: tetragonal with space group *I-4*, Z =2, a = 12.1801(17) Å, b = 12.1801(17) Å, c = 6.8890(14) Å, V = 1022.0(3) Å^3 and R_1 = 0.0330 at 293 K. There is one independent molecule in the unit cell and neither hydrogen-halogen interaction (minimum H--I distance= 3.67(6) Å), nor halogen-halogen interaction (minimum I--I distance= 6.8890 (14) Å), was observed, as might be expected. Only weaker π –π interactions exits between cations with centroid to centroid distance of 4.71(8) Å. The overall coordination number of copper(I) in this complex is 4 and this might explain the resistance of copper(I) in this complex to air oxidation. Density Functional Theory (DFT) calculations were carried out on the complex to simulate the lowest energy crystal structure. An excellent agreement was achieved using the B3LYP method. Tetrapyridinecopper(I) iodide shows large dipole moments which makes the complex useful for several applications such as medical imaging, catalysis and petrochemical processes. The asymmetric unit contains one Cu atom, one pyridine molecule and one I atom.

Keywords: Tetrapyridinecopper (I), Crystal Structure, Single Crystal, Pyridine Complex, Copper (I) Iodide, $[Cu(C_5H_5N)_4].I.$, DFT Calculations.

1. INTRODUCTION

The use of pyridine and its derivatives as templating agents for the self-assembly of organic-inorganic supramolecular materials has been widely studied (Matsumoto et al., 2003). There has been considerable interest in the structure of complexes of transition metals in oxidation states having the d^{10} electronic configuration. For example, the tetrakis complex of copper (I), $Cu_4I_4(C_5H_5N)_4$, was the subject of an X-ray crystallographic analysis due to its rich photoluminescence properties (Raston et al., 1976). Copper-pyridine ($Cu\text{-}NC_5H_5$) complexes have applications in areas such as catalysis and magnetism (Balogh-Hergovich et al., 1975).

Steric properties of ligands and of solvent media affect the stability and nature of complexes. Several studies investigated the thermodynamics of complex formation of metal ions with *N*-donors in aqueous (Smith et al., 1989), (Martell et al., 2005), (Bencini et al., 1992) and in non-aqueous or mixed solvents (Del Piero et al., 2006), in order to design ligands for selective complexation of metal ions.

Pyridine (C_5H_5N) is the simplest azabenzene, in which one CH group of benzene is replaced by a nitrogen atom having a lone pair of electrons. Therefore, in the binding between pyridine and a metal atom/ion, the π donation/back-donation interactions play important roles in addition to the σ-donation from the lone pair of the nitrogen.

Only two structures containing the cation $[Cu(C_5H_5N)_4]^+$ have been determined by single-crystal X-ray diffraction crystallography, namely: $[Cu(C_5H_5N)_4].ClO_4$ (Nilsson et al., 1982) and $[Cu(C_5H_5N)_4].PF_6$ (Horvat et al., 2007).

The $[Cu(C_5H_5N)_4].ClO_4$ complex has been extensively studied using various spectroscopic methods and theoretically as a model to understand the nature of the Cu-N bonding (Nilsson et al., 1982). Theoretical calculations show that this complex has a planar structure

* Department of Chemistry, Faculty of Science, The University of Jordan, Amman; Faculty of Science and Information Technology, Al-Balqa' Applied University, Salt, Jordan; and Department of Chemistry, National University of Ireland Maynooth, Maynooth, Co. Kildare, Ireland. Received on 6/4/2010 and Accepted for Publication on 23/1/2011.

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with C_{2v} symmetry where the Cu atom/ion is bound to the nitrogen atom of pyridine, indicating that the σ interaction with the lone pair electrons on the nitrogen atom is stronger than that with the π electrons (Nilsson et al., 1982). The binding energy of the ion complex Cu^{+}–NC_5H_5 has been concluded from photo-dissociation and collision induced dissociation experiments (Cassol et al., 1992).

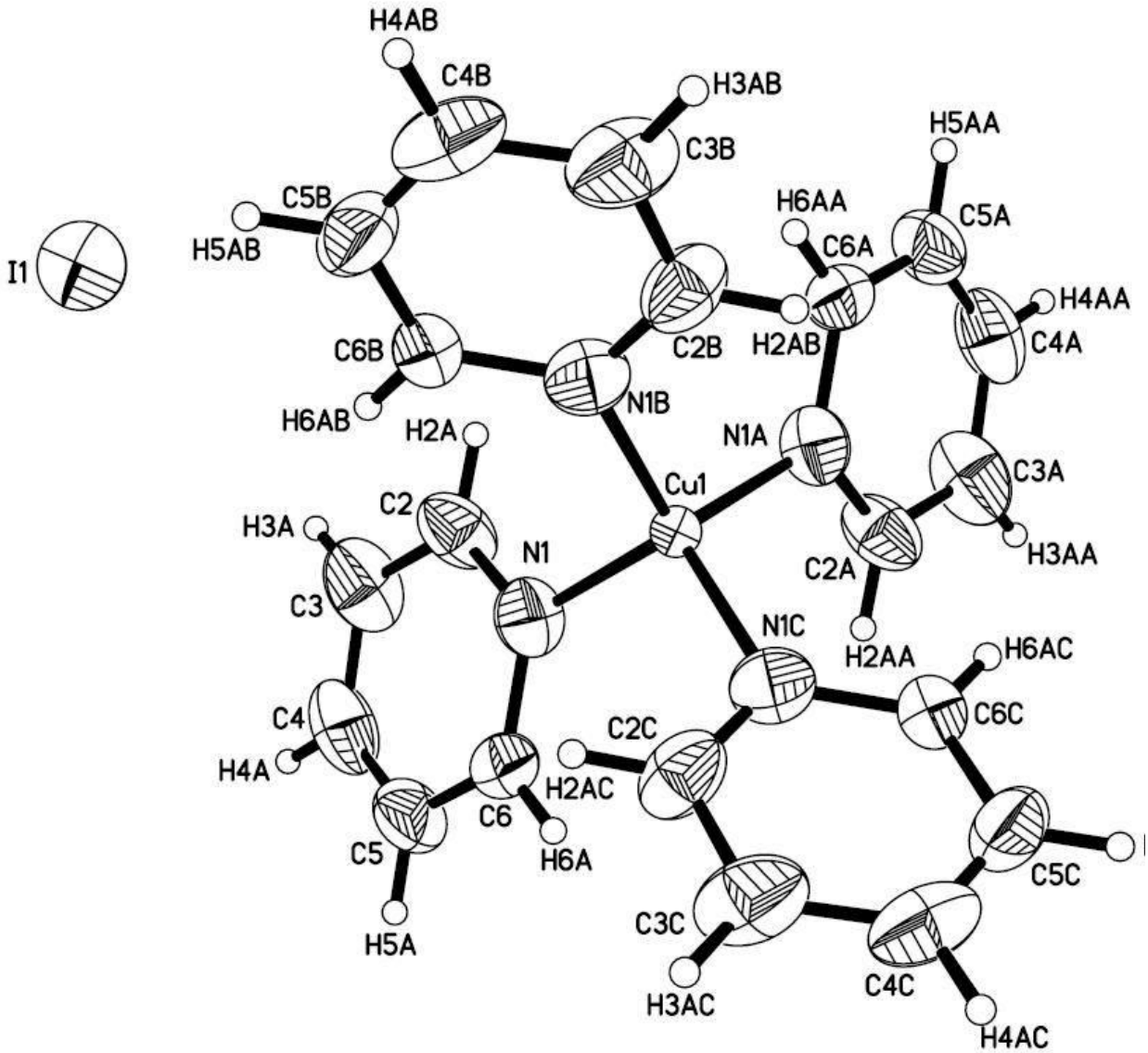

Figure 1. ORTEP diagram of Tetrapyridinecopper (I) iodide with the ellipsoids drawn at the 50% probability level, with the atomic labeling scheme, at room temperature

Recently, the structure of the closely related complex of $[Cu(C_5H_5N)_4].PF_6$ has been solved by X-ray crystallography (Horvat et al., 2007). The space group was I-4 and the anion PF_6 was located on -4 axis. The Cu-N bond length was 2.061(3) Å.

It is important to know the influence of a substituent on the role of metal (I) ions in their complexes. Theoretical studies have been carried out to calculate the formation constants or binding energies of complexes (Hancock et al., 2005). Formation constants are very important to understand or predict the role of metal ion complexes in biology (Lippard et al., 1994) in the environment (Salbu et al., 1995) and in medicine (Bianchi et al., 2000).

It has been reported that *N*-methylated tertiary amines stabilize the 1+ oxidation state of copper in aqueous solutions, which is of great interest for its role in biological systems (Kim et al., 2004). Accordingly, pyridine as a ligand should affect the solvation, electronic and structural rigidity and the stability of copper (I)

complexes. Solvation of copper ions changes with solvent properties to such an extent that the logarithm of the disproportionation equilibrium $2Cu^{+} \rightleftharpoons Cu^{2+} + Cu_{(s)}$, which is $\log K_D = +6$ in water, becomes 0.2 in dimethyl sulfoxide (Foll et al., 1972) and is very low in pyridine ($\log K_D = -14$) (Ahrland et al., 1986), where Cu(I) exhibits significant stability which explains why most of the available data on Cu (I) complexes are limited to non-aqueous solvents. Intermolecular interactions are of particular significance in chemistry, mainly because these interactions are responsible for stabilizing many important molecules such as DNA and proteins (Desiraju et al., 2001).

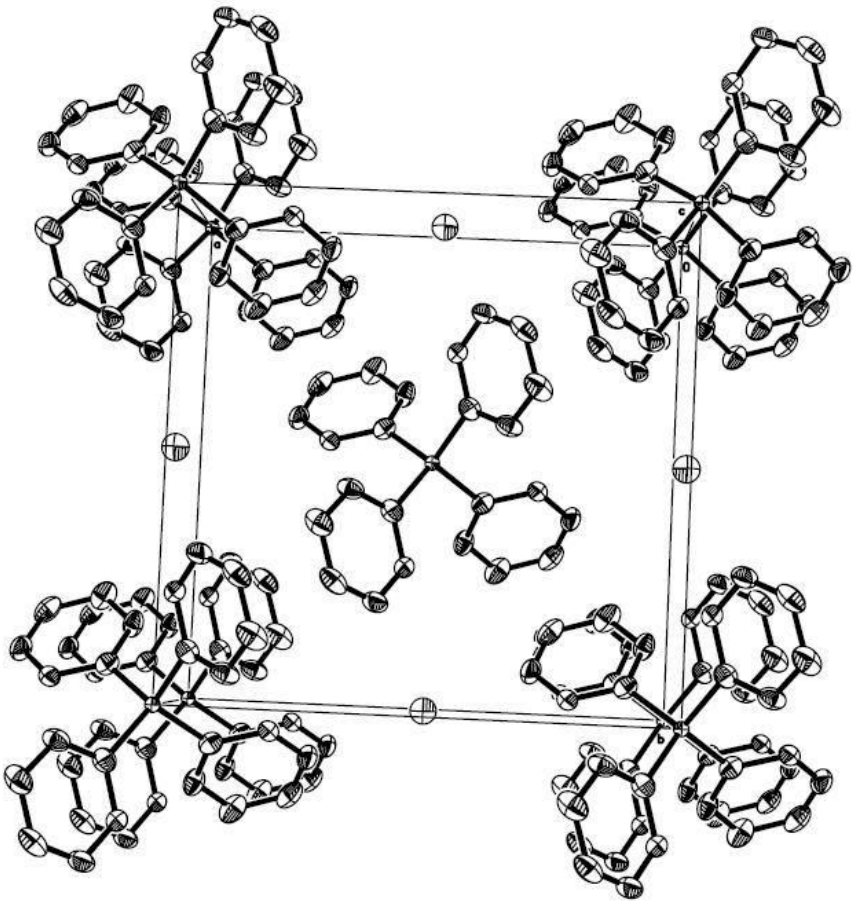

Figure 2. Crystal packing arrangement for tetrapyridinecopper(I) iodide viewed along the z-axis

DFT calculations for structures similar to $[Cu(C_5H_5N)_4].I$ such as $[Ag(DMSO)_4]^+$ and $[Ag(H_2O)_4]^+$, are in good agreement with experimental data, confirming the reliability of this computational approach in predicting structural parameters of complexes (Del Piero et al., 2007). Single-crystal X-ray diffraction analysis of the $[Ag(DMSO)_4]ClO_4$ complex (Persson et al., 2006) shows that DMSO is oxygen bonded to Ag(I) in the solid state. Similarly, spectroscopic studies demonstrate distorted tetrahedral geometry for Ag(I) complexes even in the oxygen-donor solvent *N,N'*-dimethylpropyleneurea (DMPU) (Persson et al., 2006). Many theoretical studies have been done on copper (I) compounds involving complexes with pyridine (Wu et al., 2002). In this study, we present a combined X-ray and DFT structural determination of the complex Tetrapyridinecopper (I) iodide.

Experimental and Computational Methods

Synthesis of $[Cu(C_5H_5N)_4].I$

Copper(I) iodide (CuI) was purchased from Ridel de Haen (99.5%) and pyridine from BDH Chemicals (99.7%) and were used as received. All other analytical reagents were purchased from commercial sources and used without further purification.

Tetrapyridinecopper(I) iodide was synthesized under nitrogen atmosphere according to the following procedure (adapted from Lewin et al., 1971): CuI

(1 mmol) was added to pyridine (4 mmol). Two drops of 55% HI in order to dissolve CuI were added to the mixture and stirred vigorously at around 90 °C under continuous reflux. The slightly acidic mixture was heated for around 3 h and then filtered and allowed to evaporate undisturbed at room temperature. The salt crystallized out over 2 days as white crystals. The crystals were filtered off, washed with acetonitrile and dried. The complex formation was confirmed by FT-IR spectroscopy, elemental analysis and mass spectrometry (Lewin et al., 1971).

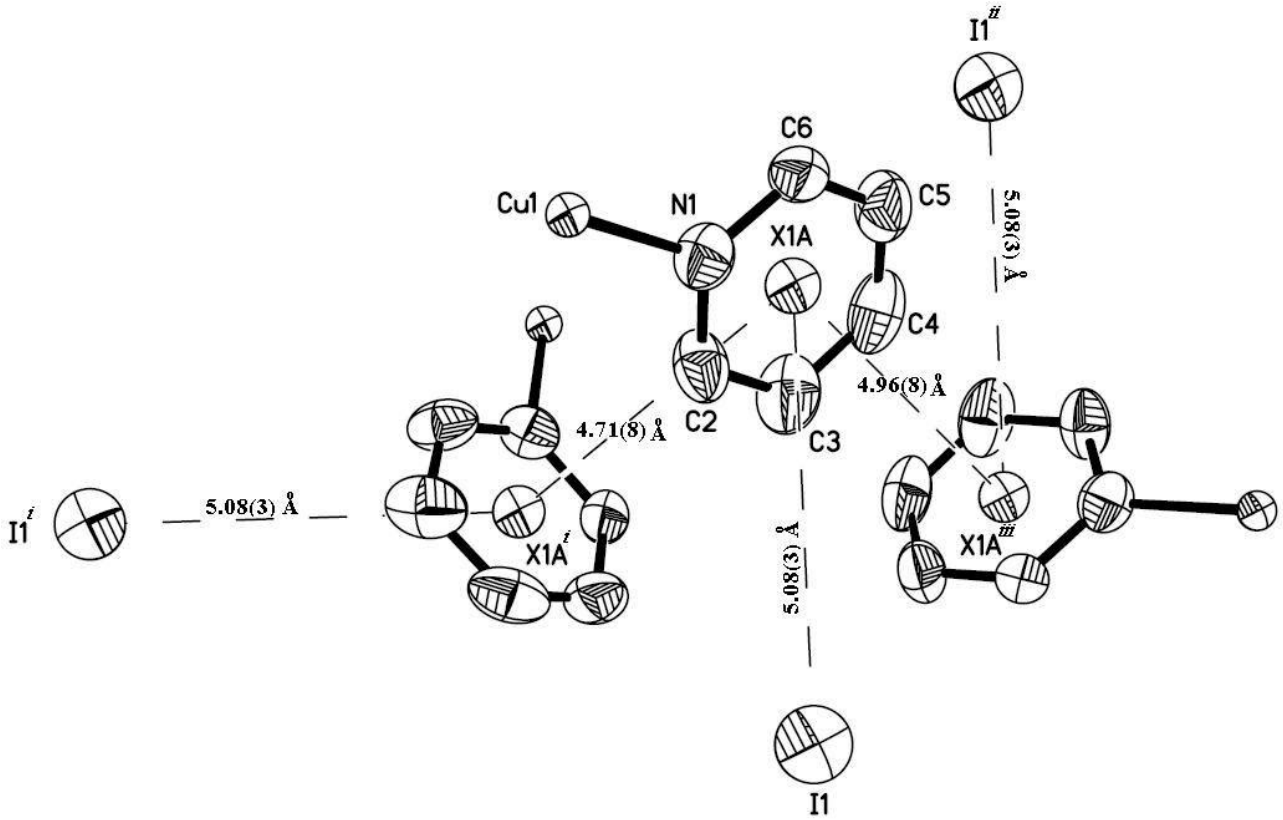

Figure 3. π- π interactions and iodine-pyridine interactions for tetrapyridinecopper (I) iodide. Symmetry transformations used to generate equivalent atoms are *i: y, 1-x, -z, ii: 3/2-x, 1/2-y, -1/2+z, iii: 3/2-x, 1/2-y, 1/2+z*

Crystal Structure Determination

A single crystal of the complex with dimensions of $0.40 \times 0.20 \times 0.10$ mm^3 was used for data collection on a Rigaku MSC Mercury CCD diffractometer (in ω scan mode) equipped with graphite monochromated Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å) at 293(2) K. A total of 5128 reflections were measured in the range of $6.73 \leq \theta \leq 25.02°$, of which 862 unique reflections with $R_{int} = 0.0451$ and with $I > 2\sigma$ (I) were used in the succeeding refinements. Cell parameters were retrieved and refined using *CrystalClear* software (Rigaku, 2000) on all observed reflections. Data reduction and correction for Lp and decay were performed using the *CrystalClear* software. Absorption corrections were applied using *CrystalClear*. The structure was solved by direct methods and refined by least squares method on F^2 using the *SHELXTL* program package (Sheldrick, 1997). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were positioned geometrically, with C—H = 0.93 Å, and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2_{eq}(C,N)$. No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 1. Further details are provided in the Supporting Information.

DFT Studies

DFT structure optimization of the complex was performed using Gaussian 03 software (Frisch et al., 2004), starting from the X-ray geometry. The calculations employed the B3LYP (Becke three-parameter Lee–Yang–Parr) exchange correlation functional, which combines the hybrid exchange functional of Becke (Becke, 1988), (Becke, 1993) with the correlation functional of Lee, Yang and Parr (Lee et

al., 1988). The 6-31*G** basis sets were used for the expansion of the Kohn–Sham orbitals (Clark et al., 1983). The final equilibrium geometry has an energy of -9510.96741053 Hartrees. Dipole moment was found to be large: -24.276 Debye. The DFT results are summarized in Table 2.

Table 1. Crystal data and structure refinement for Tetrapyridinecopper(I) iodide

CCDC No.	665843	Largest diff. peak and hole	0.535 and −0.359 e.Å^3
Identification code	*I-4*	Absorption coefficient	2.589 mm^{-1}
Empirical formula	C_{20} H_{20} Cu I N_4	*F*(000)	500
Formula weight	506.85	Crystal size	0.40 × 0.20 × 0.10 mm^3
Temperature	293(2) K	θ range for data collection	6.73–25.02°
Wavelength	0.71073 Å	Index ranges	$-14 \le h \le 14$, $-14 \le k \le 14$, $-7 \le l \le 8$
Crystal system	Tetragonal	Reflections collected	5128
Space group	*I-4*	Independent reflections	862 [$R_{(int)}$ = 0.0451]
Unit cell dimensions	a = 12.1801(17) Å	Completeness to θ = 25.02°	98.7%
	b = 12.1801(17) Å	Absorption correction	Numerical
	c = 6.8890(14) Å	Max. and min. transmission	0.813 and 0.614
	α = 90°	Refinement method	Full-matrix least-squares on F^2
	β = 90°	Data/restraints/parameters	862/0/61
	γ = 90°	Goodness-of-fit on F^2	1.099
Volume	1022.0(3) Å^3	Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0291, wR_2 = 0.0677
Z	2	R indices (all data)	R_1 = 0.0301, wR_2 = 0.0686
Density (calculated)	1.647 mg/m^3	Extinction coefficient	*0.018(5)*

Table 2. Selected bond lengths (Å) and angles (°) for the Tetrapyridinecopper (I) iodide complex as determined by X-ray diffraction and DFT calculations

Bond	Length (Å)		Bond	Angle (°)	
	X-ray	DFT		X-ray	DFT
Cu(1)-N(1)#1*	1.904 (4)	1.900	N(1)#1-Cu(1)-N(1)#2	110.15(10)	109.5
Cu(1)-N(1)#2*	1.904 (4)	1.900	N(1)#1-Cu(1)-N(1)#3	108.1(2)	109.5
Cu(1)-N(1)#3*	1.904 (4)	1.900	N(1)#2-Cu(1)-N(1)#3	110.15(11)	109.5
Cu(1)-N(1)	1.904 (4)	1.900	N(1)#1-Cu(1)-N(1)	110.15(11)	109.5
N(1)-C(6)	1.389 (5)	1.390	N(1)#2-Cu(1)-N(1)	108.1(2)	109.5
N(1)-C(2)	1.378 (6)	1.379	N(1)#3-Cu(1)-N(1)	110.15(10)	109.5
C(6)-H(6A)	0.930 (0)	1.105	C(2)-N(1)-C(6)	119.7(4)	115.4
C(5)- C(6)	1.392 (7)	1.395	C(2)-N(1)-Cu(1)	118.9(3)	122.2
C(2)- C(3)	1.373 (9)	1.393	C(6)-N(1)-Cu(1)	121.4(3)	122.4
C(5)- H(5A)	0.930 (0)	1.097	C(3)-C(2)-N(1)	121.1(4)	123.4
C(4)- C(5)	1.354 (8)	1.396	C(2)-C(3)-C(4)	118.9(5)	119.4
C(4)- H(4A)	0.930 (0)	1.099	C(4)-C(5)-H(5A)	119.5	121.5
C(3)- C(4)	1.404 (8)	1.396	C(5)-C(6)-H(6A)	120.4	121.5
C(3)- H(3A)	0.930 (0)	1.097			
Cu(1) — I(1)	6.32 (9)	6.280			

* Symmetry transformations used to generate equivalent atoms: #1:-y+1,x,-z+1; #2:-x+1,-y+1,z; #3:y,-x+1,-z+1.

2. RESULTS AND DISCUSSION

Crystal Structure of the Complex

The molecular unit structure of the complex $[Cu(C_5H_5N)_4]$.I together with the atom-numbering scheme is illustrated in Figure 1 as refined at room temperature.

There is one independent molecule of the type tetrapyridinecopper(I) iodide in the unit cell . The asymmetric unit of Tetrapyridinecopper(I) iodide was found to contain one pyridine molecule coordinated to Cu atom through N atom and iodide ion .The Cu1 atom lies

on a special position at (0.5, 0.5, 0.5) and I1 also lies on a special position (0.5, 0, 0.25). Cu1 coordinated is coordinated to 4 pyridinic N atoms at four different symmetry operations (x, y, z), (-x+1, -y+1, z), (y, -x+1, -z+1) and (-y+1, x, -z+1) as shown in Figure 1. Typical Cu—N distances of 1.904(4) are found.

These values are in good agreement with those reported for Cu–N containing compounds (Reddy et al., 2003). The bond angles for N–Cu–N are in the range from 108.1(2)° to 110.15(10)°, while those for C–N–Cu and C—N—C are close to 120°. The pyridine rings are essentially planar with their planes being twisted. Representative geometrical parameters are given in Table 2.

Compared to the recently determined structure of the closely related complex of $[Cu(C_5H_5N)_4].PF_6$, $[Cu(C_5H_5N)_4].I$ shows very similar resemblance. The space group was I-4 in both complexes and the anions (PF_6 and I) were located on the -4 axis. The Cu-N bond length in the $[Cu(C_5H_5N)_4].PF_6$ was 2.061(3) Å which is slightly longer (8%) than the Cu-N bond length in the $[Cu(C_5H_5N)_4].I$ of 1.904(8). This difference may be attributed to the slightly larger interaction between the Cu^+ and the anion in the $[Cu(C_5H_5N)_4].PF_6$ compared to the $[Cu(C_5H_5N)_4].I$ complex. On the other hand, the N-Cu-N angles in both complexes were almost identical (within the error bars of the measurement).

Crystal Packing

The molecules of tetrapyridinecopper(I) iodide pack in three-dimensions with no hydrogen bonding (the nearest distance between any two hydrogens was found to be 3.63(2) Å or halogen-halogen interaction observed in the packing arrangement (nearest iodine-iodine distance = 6.889(14) Å) as illustrated by figure 2.

A weak π –π interactions exists between cations with centroid to centroid distance of 4.71(8) Å as shown in Figure 3. Also, a weak X-π electrostatic interaction with I atom to centroid of pyridine ring distance of 5.08(3) Å was found. Spatial details of these interactions are illustrated in Figure 3.

Pyridine moieties were found to be twisted with the angle between planar pyridine rings being 31.3°. The root mean square residual of the atoms in pyridine molecule, from plane is 0.012(1) Å which implies an almost planar pyridine ring.

The present complex structure shows no signs of hydrogen-hydrogen bonding. The absence of hydrogen bonding in this article is explained by that when a pyridine moiety substitutes an aliphatic amine in a ligand, the whole structure acquires extra rigidity and less affinity to hydrogen bonding.

Although weaker than amines, pyridine behaves as a σ-donor group with several monovalent metal ions which makes pyridine-containing ligands are less basic than that of alkyl amines. The pK_a values of ethylamine and triethylamine in aqueous solution are 10.66 (Hancock et al., 1980), and 10.68 (Frenna et al., 1985) but that of pyridine is only 5.42 (Capone et al., 1986).

Pyridine forms only 1:1 and 1:2 complexes with Ag(I). The stability constants of pyridine of Ag(I) ($\log \beta_{11} = 2.00$ and $\log \beta_{12} = 4.11$) (Paoletti et al., 1966). In aqueous solution, Ag(I) complexes of pyridine are considered to be linear, as found for monoamines, although in pure pyridine EXAFS experiments demonstrate that Ag(I) is tetracoordinated (Yamaguchi et al., 1988). In the solid state, both linear and tetrahedral Ag(I)- pyridine complexes are reported (Nilsson et al., 1982) , (Chen et al., 2007).

Little data is available for the stability of Cu(I)-pyridine system in water. Due to its ability to form five-membered chelate complexes, bipyridine forms more stable complexes than pyridine with both Ag(I) (Canani et al., 1958) and Cu(I) (James et al., 1961).

Stability constants for complexes of Cu(I) with pyridine in aniline ($\log \beta_{11} = 1.85$, $\log \beta_{12} = 2.52$, $\log \beta_{13} = 3.26$, at 293 K and $I = 0.1$ mol dm^{-3}) are very low with respect to those found in water, reflecting the stronger solvation of Cu(I) in aniline (Dachraoui et al., 1987). The literature reveals that no data exist for complexation reactions of Cu (I) by pyridine ligands in the other most common organic solvents.

On the other hand, the complexation reaction entropy for pyridine ligands is systematically less negative than for amines of similar environment, partly attributed to the lower conformational freedom of pyridine. An important factor which may explain such negative entropy for polyamines is the increase in local order around the complex through the formation of new hydrogen bonds with surrounding solvent molecules. Hence, hydrogen bonding for complexes pyridines is not possible and the negative entropic contribution associated with it is missing. Pyridinic ligands show behaviour similar to tertiary amines, even if their structure is more rigid, while amino-pyridines clearly display intermediate features between primary polyamines and pyridines.

DFT Studies

The energy-optimized structure using the DFT at the B3LYP/6-31*G** level of theory is in very good agreement with the structure determined by X-ray crystallography as summarized in Table 2.

The value of the dipole moment found in this study for the complex molecule in the gas phase using DFT at the B3LYP/6-31*G** level is -24.276 Debye. This value might explain the absence of halogen-halogen interactions in the X-ray results. DFT results show no hydrogen-hydrogen bonding in agreement with the X-ray results and the expectations due to the missing negative entropic contribution associated with complexed pyridines.

3. CONCLUSION

Single-crystal X-ray diffraction and DFT calculations were applied successfully to determine the structure of the complex: tetrapyridinecopper (I) iodide, $[Cu(C_5H_5N)_4].I$. The asymmetric unit contains one Cu atom, one pyridine molecule and one I atom. Weak $\pi - \pi$ interactions exist between cations and neither hydrogen bonding nor halogen-halogen interactions were detected. The large magnetic moment makes the complex useful.

Supplementary Material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC 665843. Copies of this information may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK *(Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).*

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دراسات التحضير والتركيب البلوري وميكانيكا الكم لأيوديد رابع بيريدين النحاس (1)

ايهاب الشمايلة وروحي الفار ومعاذ عتمة*

ملخص

تم تحضير أيوديد رابع بيريدين النحاس (1) وتشخيصه باستخدام طريقة حيود الأشعة السينية للبلورة المفردة في درجة حرارة الغرفة. تبين أن الخلية الأحادية هي رباعية الزوايا ومجموعتها I-4 وz=2 وأبعاد وحدة الخلية هي: أ = 12.1801 أنغستروم (17، (ب) = 12.1801 (17) أنغستروم، ج= 6.8890 (14) أنغستروم و V = 1022.0(3) Å3 and R1 = 0.0330 عند 293 كلفن. وجد أن وحدة الخلية تحتوي على جزيء واحد مستقل دون ترابط بين الهيدروجين والهالوجين (أقل مسافة بين I-H وجدت = (6) 3.67 أنغستروم، ولم يلاحظ ترابط بين الهالوجين والهالوجين (أدنى مسافة بين I-I = 6.8890 (14) أنغستروم. لوحظ كذلك أن هناك ترابطاً في ال π-π بين الأيونات الموجبة بمسافة من المركز إلى المركز بمسافة مقدارها (8) 4.71 أنغستروم. كان عدد التنسيق الشامل للنحاس في هذا المعقد = 4، وهذا قد يفسر مقاومة النحاس في هذا المعقد لأكسدة الهواء. أجريت حسابات النظرية الوظيفية للكثافة (DFT) على المعقد لمحاكاة الهيكل ذي الطاقة الأدنى للبلورة ووجد أن التطابق كان ممتازا باستخدام مجموعة الأساس (B3LYP). أظهر المعقد قطبية عالية مما يجعله مفيدا لتطبيقات عدة. احتوت الوحدة غير المتماثلة على ذرة نحاس واحدة وجزيء بيريدين واحد وذرة يود واحدة.

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* قسم الكيمياء، كلية العلوم، الجامعة الأردنية، عمان؛ وكلية العلوم وتكنولوجيا المعلومات، جامعة البلقاء التطبيقية، السلط، الأردن؛ وقسم الكيمياء، جامعة ايرلندا الوطنية، ماينوث، ايرلندا تاريخ استلام البحث 2010/4/6، وتاريخ قبوله 2011/1/23.