Full Length Research Paper

Synthesis, experimental and theoretical characterization of Cu(II) complex of 2-chloropyrimidine

S. Ali Beyramabadi[1]*, Hossein Eshtiagh-Hosseini[2], Mohammad R. Housaindokht[2] and Ali Morsali[1]

[1]Department of Chemistry, Faculty of Science, Mashhad Branch, Islamic Azad University, Mashhad, Iran.
[2]Department of Chemistry, Ferdowsi University of Mashhad, Mashhad, Iran.

The new dimeric [$Cu_2(OAc)_4$(2-Clpym)$_2$] complex of 2-chloropyrimidine (2-Clpym) ligand was synthesized, where 2-Clpym coordinated via the nitrogen atom and acts as monodentate ligand. The water molecules of dimeric $Cu_2(OAc)_4(H_2O)_2$ salt replaced by two 2-Clpym ligands producing the new complex. The nature of synthesized complex was determinated by elemental and spectrochemical (IR, UV-Vis) analysis. Also, the geometries of ligand and complex have been fully optimized using density functional theory (B3LYP) method. The obtained structural parameters are in good agreement with the experimental data, reported for the similar compounds. Also, the calculated and experimental wavenumbers confirm validity of the optimized structures for the ligand and Cu complex.

Key words: 2-Chloropyrimidine, copper(II), IR spectra, geometry optimization, density functional theory, B3LYP.

INTRODUCTION

Pyrimidines with high physiological importance as the components of nucleic acids are very attractive compounds (Anzellotti et al., 2008; Jacobson et al., 2002). They provide the sites that have bonding potential to the metallic ions. Also, any information about their coordinative properties can be used as a mean for explanation of the metallic role in biological systems (Löffler and Zameitat, 2004). Many complexes of transition metals with pyrimidine and its derivaties have already been synthesized and reported in the literature (Maddah et al., 2006; Blake et al., 2002; Lumme et al., 1984).

It has been confirmed that the platinum complexes have toxic effects on body organism especially on kidney tissues. The synthesis of anti-carcinogenic complexes with metallic ions involving normally in human meta-bolism seems to be advantageous, since the overdose of such elements can simply be excreted from the organism (Lumme et al., 1984). On the other hand, it has been shown that the complex formation with copper ion increases the anti-carcinogenic effects of the ligands (Gokhale et al., 2001). The copper complex of 2-aminopyrimidine ligand showed the anticancer properties (Lumme et al., 1984).

On the basis of a literature survey, the only synthesized metallic complex of 2-chloropyrimidine (2-Clpym) corresponds to that obtained by addition of a Pd(0) compound to 2,4-dichloropyrimidine (Benneche, 1990). In this work, we have succeeded in the synthesis and characterization of new dimeric complex of 2-Clpym ligand using dimeric [$Cu_2(OAc)_4(H_2O)_2$] salt (OAc = acetate) by IR, UV-Vis, and elemental analysis approaches. Also, theoretically optimized geometries of 2-Clpym ligand and [$Cu_2(OAc)_4$(2-Clpym)$_2$] complex have been reported. Because of novelity of the Cu(II) complex, determination of structural parameters is important.

EXPERIMENTAL

Materials and general methods

All chemicals and solvents obtained from Merck except 2-Clpym which was purchase from Fluka. They used without further

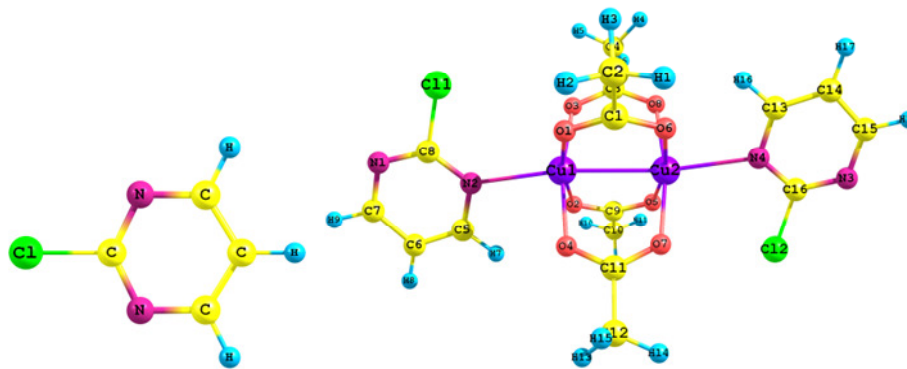Corresponding author. E-mail: beiramabadi6285@mshdiau.ac.ir. Tel/Fax: +98 511 8414182.

Figure 1. B3LYP optimized geometries of the 2-Clpym ligand and $[Cu_2(OAc)_4(2\text{-Clpym})_2]$ complex together with their labeling.

purification. Melting points were determinated by Electrothermal-9100 apparatus. Percentage of Cu in complex was obtained by spectrophotometry, using a Shimadzu AA-670 atomic absorption spectrophotometer. Vibrational spectra were obtained as KBr pellets by Perkin Elmer 783 infrared spectrophotometer and electronic spectra were achieved by a Cecil CE9500 UV-Vis spectrophotometer.

Synthesis of $[Cu_2(OAc)_4(2\text{-Clpym})_2]$

One mmol (0.200 g) of copper(II) acetate-monohydrate was dissolved in 60 ml methanol. A solution of ligand was also prepared by dissolving 2.5 mmol (0.286 g) of 2-Clpym in 40 ml methanol. The former solution was added into the later one at room temperature accompanied by a regular stirring. The formed green precipitate was separated by centrifuging the titled solution, washed by methanol and dried at about 60°C (Yield based on 2-Clpym : 27%).

Theory

All alculations were pereformed with the B3LYP hybrid density functional level (Becke, 1993) using the Gaussian 98 program (Hay and Wadt, 1985). In the gas phase, geometries of 2-Clpym ligand and $[Cu_2(OAc)_4(2\text{-Clpym})_2]$ complex were optimized at 6-311+G(2d,2p) basis sets expect for Cu atom where LANL2DZ basis set was used with including effective core potential functions. The optimized geometries were confirmed to have no imaginary frequency of the Hessian.

Theoretical calculations of harmonic frequencies on the fully optimized geometries of 2-Clpym ligand and its Cu complex have been performed at B3LYP level, where the used basis sets are LANL2DZ for Cu and 6-31G(d) basis sets for the other atoms. The DFT vibrational wavenumbers are usually higher than the experimental values, which can be corrected by applying the procedure of scaling the wavenumbers (Eshtiagh-Hosseini et al., 2008). Here, the scale factor of 0.9614 was used for the calculated vibrational wavenumbers (Young, 2001).

RESULTS AND DISCUSSION

Chemistry

The Cu(II) complex is melted at 246°C, while

$Cu_2(OAc)_4(H_2O)_2$ salt does not melt. Considering that 2-Clpym ligand has a melting point of 63.5 to 64°C, the formation of a new product seems evident. According to the elemental analysis results, one can find out the amount 21.07% relating to Cu. So, the suitable chemical formula for the complex may be $Cu_2(OAc)_4(2\text{-Clpym})_2$.

Electronic spectra

Electronic spectra of free 2-Clpym ligand and $Cu_2(OAc)_4(2\text{-Clpym})_2$ complex were obtained in methanol solutions. The investigation of these spectra indicates the remarkable changes of maximum absorbance relative to л-л* transition of the ligand. These peaks in complex spectrum (300.8 and 213.6 nm) are significantly different from those of ligand (309.0 and 224.0 nm), which is the sign of an interaction between metallic ion and ligand. The weak peak at 712 nm was attributed to $Eg \longrightarrow T_2g$ transition of the octahedral complex (Cotton and Wilkinson, 2006).

Geometry optimization

Theoretical studies are powerful tools for providing new insights into chemistry (Eshtiagh-Hosseini et al., 2008; Beyramabadi et al., 2008; Niu and Hall, 2000; Morsali et al., 2010). The optimized structures of 2-Clpym and $[Cu_2(OAc)_4(2\text{-Clpym})_2]$ complex with labeling of atoms are shown in Figure 1. The selected structural parameters of them together with the available experimental data for similar compounds (Blake et al., 2002; Uekusa et al., 1992; Chen et al., 2006; Lu et al., 2004; Harada et al., 1997; Xuan et al., 2003a, b) are collected in Table 1. As seen, there is a very well agreement between the theoretically determined structural parameters of the 2-Clpym ligand and its Cu(II) complex and the experimental values available in the literature.

As shown in Figure 1, the Cl atom is in the same plane

Table 1. Selected calculated structural parameters of 2-Clpym ligand and [Cu₂(OAc)₄(2-Clpym)₂] complex.

Parameter	Experimental	Calculated	
		Ligand	Complex
Bond lengths (pm)			
Cu-Cu$_2$	262.9, 270.1, 264.7, 265.9	-	265.0
Cu-N$_2$	221.4, 226.6, 215.4, 213.1	-	237.3
N$_2$-C$_8$	134.2, 132.9, 132.0, 133.4	132.3	132.9
C$_8$-Cl	172.3, 172.3	175.0	174.1
N-C$_7$	133.1, 133.3, 132.0	133.5	133.4
C$_7$-C$_6$	137.0, 137.8, 137.3, 138.5	138.8	138.6
Cu-O	198.3, 196.9, 199.7, 198.4, 198.2	-	201.4
Cu$_2$-O$_6$	198.3, 202, 197.0, 199.7	-	203.4
O-C	125.7, 125.6, 125.8, 125.7	-	125.8
C-C$_2$	151.0, 152.0, 152.5, 153.3	-	152.3
Angles (º)			
N$_2$-Cu-Cu$_2$	175.6, 175.8, 168.2, 173.4	-	172.0
Cu-N$_2$-C$_8$	125.9, 129.1,	-	132.4
N$_2$-C$_8$-N	124.2, 125.1,	128.1	127.3
C$_8$-N-C$_7$	116.6, 116.6, 118.4, 117.6	115.5	116.0
N-C$_7$-C$_6$	123.0, 123.7, 122.8, 123.3	122.3	122.3
C$_7$-C$_6$-C$_5$	116.6, 116.3	116.4	116.6
C$_5$-N$_2$-Cu	114.5, 114.6	-	111.7
Cu-O-C	123.7, 123.5, 122.9, 122.4	-	122.9
O-C-O$_6$	128.7, 125.9, 126.0, 127.6	-	127.4
C-O$_6$-Cu$_2$	122.1, 121.8, 120.8, 120.4	-	120.8
O-Cu-O$_2$	168.1, 166.7, 167.8, 169.8	-	168.7
Dihedral angles (º)			
N$_2$-Cu-Cu$_2$-N$_4$	179.9, 179.8	-	180.0
C$_7$-N$_2$-N$_4$-C$_15$	180	-	180.0
Cl-C$_8$-N-C$_7$	178.7	180.0	179.9

with the pyrimidine ring, where the Cu(II) complex has C$_{2h}$ symmetry point group. The symmetry plane is involved two 2-Clpym ligands and two Cu atoms, where the C$_2$ symmetry axis is perpendicular to this plane, and passes through of Cu-Cu bond. As given in Table 1, both of the calculated C7-N2-N4-C15 and N2-Cu1-Cu2-N4 dihedral angles are 180.0°, hence, two aromatic rings are in the same plane with Cu atoms. The acetate groups are located at two sides of earlier mentioned plane which are opposite than each other. The short bonding distance of Cu-Cu indicates the presence of interaction between Cu atoms. This distance is similar to the reported values for the dimeric complexes of Cu (Blake et al., 2002; Uekusa et al., 1992; Chen et al., 2006; Lu et al., 2004; Harada et al., 1997).

Here, the 2-Clpym ligands act as monodentate via the nitrogen atom of pyrimidine, which are in place of the water ligands relating to the dimeric salt of Cu$_2$(OAc)$_4$(H$_2$O)$_2$. Many of structural parameters undergo

no noticeable changes when the ligand molecule is coordinated to the Cu(II) (Figure 1 and Table 1). The similar structures with the optimized geometry of [Cu$_2$(OAc)$_4$(2-Clpym)$_2$] complex have been reported, previously (Blake et al., 2002; Uekusa et al., 1992; Chen et al., 2006; Lu et al., 2004; Harada et al., 1997).

Vibrational spectroscopy

Theoretical description of vibrational spectra is a valuable tool for identification of the chemical compounds. The IR spectra of 2-Clpym ligand and its Cu(II) complex are presented in Figure 2. These spectra were investigated by comparing the calculated vibrational modes with those reported in the literatures (Dey et al., 1999; Pui et al., 2007; Ünver et al., 2006). The selected vibrational wavenumbers computed by the B3LYP/6-31G(d) approach and the corresponding experimental values are
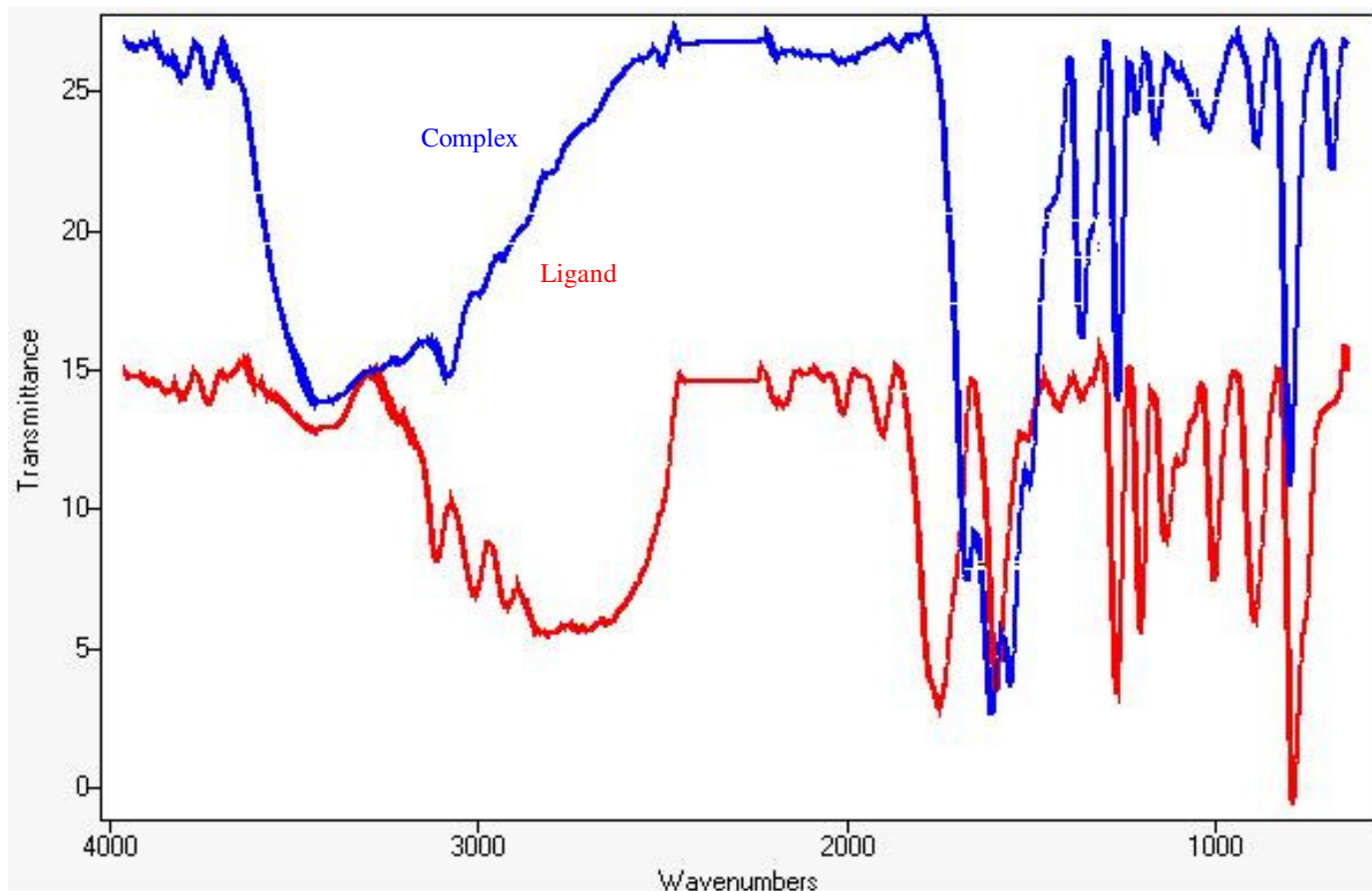
Figure 2. The IR spectra of 2-Clpym and [Cu$_2$(OAc)$_4$(2-Clpym)$_2$] complex.

listed in Table 2.

The strong bonds in the 1660-1500 cm^{-1} region, commonly could be assigned to υ(C=N) and υ(C=C) vibrations (Eshtiagh-Hosseini et al., 2008; Dey et al., 1999; Pui et al., 2007). These bands are interest since their wavenumbers is diagnostic of the mode of coordination of the ligands. The very strong bands of 2-Clpym ligand at 1267 and 1594 cm^{-1} were assigned to the symmetrical stretching modes of C=N and C=C bonds which are shifted to 1263 and 1607 cm^{-1} in the IR spectrum of Cu complex, respectively. The asymmetrical stretching vibrations of C=N and C=C bonds are appeared as a strong band in the IR spectra, at 1751 cm^{-1} (for the ligand) and 1675 cm^{-1} (for the complex). On complexation, the υ(C=N) bands are shifted slightly to lower frequencies in the IR spectrum of Cu complex (Eshtiagh-Hosseini et al., 2008; Dey et al., 1999; Pui et al., 2007; Ünver et al., 2006).

For the 2-Clpym ligand and Cu complex, the stretching C-Cl vibration is appeared at 1135 and 1263 cm^{-1}, respectively. This is an extra reason for coordination of the ligand to the metal ion in via the nitrogen atom of pyrimidine ring, rather than the chlorine atom. Formation of the Cu-N bond results in the appearance of new bands at 632 cm^{-1} region of the IR spectrum of Cu(II) complex, which is absent in the IR spectrum of free ligand (Pui et al., 2007; Ünver et al., 2006).

The new strong band at 1555 cm^{-1} in the IR spectrum of complex was attributed to the C-O and C-C stretching vibrations of acetate group. This band together with ones appeared at 1362, 2801 and 2883 cm^{-1} of the IR spectrum of complex confirm the coordination of acetate groups.

The C-H stretching vibrations of both the methyl group of acetate (at 2800-3000 cm^{-1}) and the pyrimidine ring (at 2900 to 3200 cm^{-1}) provide remarkable changes in 2700 to 3300 cm^{-1} region of the IR spectra.

Conclusion

The [Cu$_2$(OAc)$_4$(2-Clpym)$_2$] complex has been synthesized and characterized by the atomic absorbtion, UV-Vis and IR spectroscopies. The geometry of the 2-Clpym ligand and [Cu$_2$(OAc)$_4$(2-Clpym)$_2$] complex were optimized with the B3LYP functional. The frequency

Table 2. Selected experimental and calculated IR vibrational frequencies (cm^{-1}) of 2-Clpym ligand and its Cu(II) complex.

Experimental frequencies		Calculated frequencies		Vibrational assignment
Ligand	Cu(II) complex	Ligand	Cu(II) complex	
-	-		192	u_{sym}(Cu-N)
-	-	-	244	u_{asym}(Cu-N)
-	-	-	251	u_{sym}(Cu-O)
			305	u_{asym}(Cu-O)
-	-	424	431	u(C-Cl)
-	632 ^{w}	-	618	$\delta_{in\text{-}plane}$(ring^a)+ u_{asym}(Cu-N)
792 ^{vs}	797 ^{s}	742	747	$\delta_{out\text{-}of\text{-}plane}$(ring^a)
894 ^{s}	887 ^{w}	791	789	$\delta_{wagging}$(aromatic hydrogens)
1003 ^{m}	1100 ^{w}	1056	1061	u_{sym}(C=C)
1135 ^{m}	1160 ^{w}	1153	1161	u_{sym}(C=N) + u(C-Cl)
1201 ^{s}	1214 ^{m}	1255	1258	u_{asym}(C=N) + $\delta_{rocking}$(aromatic hydrogens)
1267 ^{vs}	1263 ^{m}	1382	1389	u_{sym}(C=N)
-	1335 ^{sh}	-	1345	$\delta_{scissoring}$(CH$_3$)
-	1362 ^{m}	-	1358	u_{asym}(C-O)
-	1555 $^{vs,\ sh}$	-	1417	u_{sym}(C-O)+ u(C-C)$_{acetate}$
1594 ^{vs}	1607 ^{vs}	1546	1551	u_{sym}(C=N) + u_{sym}(C=C)
1751 ^{vs}	1675 ^{vs}	1623	1565	u_{asym}(C=N) + u_{asym}(C=C)
-	2801 ^{w}	-	2945	u_{sym}(C-H)$_{methyl}$
-	2883 ^{w}	-	3012	u_{asym}(C-H)$_{methyl}$
-	2990 ^{w}	-	3069	u(C-H$_9$,H$_{18}$)
2917 ^{sh}	-	3066	-	u_{sym}(C-H) meta^b
3011 ^{sh}	-	3068	-	u_{asym}(C-H) meta^b
3113 ^{sh}	3077 ^{m}	3110	3110	u(C-H) para^c
-	3152 ^{m}	-	3126	u(C-H$_7$,H$_{16}$)

Abbreviation: w, weak; m, medium; s, strong; vs, very strong; sh, shoulder; a: pyrimidine ring; b,c: meta and para positions on pyrimidine ring with respect to Cl ligand, respectively.

calculations were computed at the same computational method.

A melting point of 246°C for the complex, in comparison with a value of 64°C for the 2-Clpym ligand, is the indicative of Cu complex formation. The comparison of UV spectrum of the ligand with that of the Cu(II) complex, could be a good sign of interaction between the metal and 2-Clpym ligand, and the appearance of a peak at 300.8 nm can be considered as a change in coordination sphere. According to the results obtained from atomic absorbtion spectroscopy and the comparison of the experimental and theoretical IR spectra of the ligand and its complex, a conclusion central to our study proves a dimeric structure with a formula of [Cu$_2$(OAc)$_4$(2-Clpym)$_2$] for the synthesized complex, in which monodentate 2-Clpym ligand is coordinated to copper ion *via* the N atom of pyrimidine ring. Important IR bands were identified, which can be used as a data bank for explanation of the IR spectra of similar compounds.

The calculated structural parameters for 2-Clpym and its Cu(II) complex are in good agreement with the experimental data for the similar compounds, confirming suitability of the proposed octahedral geometries for the complex. The two 2-Clpym ligands act as monodentate ligand in such manner that the pyrimidine rings are in the same plane. Hence, the point group of [Cu$_2$(OAc)$_4$(2-Clpym)$_2$] complex is C$_{2h}$.

REFERENCES

Anzellotti AI, Bayse CA, Farrell NP (2008). Effects of Nucleobase Metalation on Frontier Molecular Orbitals: Potential Implications for π-Stacking Interactions with Tryptophan. Inorg. Chem., 47: 10425-10431.

Becke AD (1993). Density-functional thermochemistry. III. The role of exact exchange. J. Chem. Phys. 98(7): 5648-5662.

Benneche T (1990). Pyrimidinylpalladium(II) Complexes in the Synthesis of Alkenylpyrimidines. Acta Chem. Scand., 44: 927-931.

Beyramabadi SA, Eshtiagh-Hosseini H, Housaindokht MR, Morsali A (2008). Mechanism and Kinetics of the Wacker Process: A Quantum. Mechanical Approach. Organometallics, 27: 72-79.

Blake AJ, Hubberstey P, Sampson CL (2002). Catena-Poly[[tetrakis(μ-acetato-ĸO:ĸO')dicopper(II)]-μ-2-aminopyrimidine-ĸ ^{2}N:N'] at 150 K. Acta Cryst. E58: m99-m101.

Chen JM, Sun JJ, Huang WW, Lao YN, Yang SP (2006). Tetra-μ-acetato-bis[(9,10-dihydrobenzo[de]imidazo[2,1-a]isoquinolin-7-one-ĸ

N[11])copper(II)]. Acta Cryst. E62: m2573-m2574.

Dey DK, Saha MK, Das MK, Bhartiya N, Bansal RK, Rosair G, Mitra S (1999). Synthesis and characterization of diorganotin(IV) complexes of tetradentate Schiff bases: crystal structure of n-Bu$_2$Sn(Vanophen). Polyhedron, 18(20): 2687-2696.

Eshtiagh-Hosseini H, Housaindokht MR, Beyramabadi SA, Beheshti S, Esmaeili AA, Javan Khoshkholgh M, Morsali A (2008). Synthesis, experimental and theoretical characterization of tetra dentate N,N′-dipyridoxyl (1,3-propylenediamine) salen ligand and its Co(III) complex. Spectrochim. Acta part A 71(4): 1341-1347.

Gokhale N, Padhye S, Rathbone D, Billington D, Lowe P, Schwalbe C, Newton C (2001). The crystal structure of first copper(II) complex of a pyridine-2-carboxamidrazone - a potential antitumor agent. Inorg. Chem. Commun., 4: 26-29.

Harada A, Tsuchimoto M, Ohba S, Iwasawa K, Tokii T (1997). Structures and magnetic properties of dimeric copper(II) benzoylformates. Acta Cryst., B53: 654-661.

Hay PJ, Wadt WR (1985). Ab initio effective core potentials for molecular calculations. Potentials for main group elements Na to Bi. J. Chem. Phys., 82: 284-298.

Jacobson KA, Jarvis MF, Williams M (2002). Purine and pyrimidine (P2) receptors as drug targets. J. Med. Chem. 45(19): 4057-4093.

Löffler M., Zameitat E. (2004). Pyrimidine Biosynthesis. Encyclopedia of Biological Chemistry 600-606.

Lu ZZ, Gao S, Huo LH, Zhao H, Zhao JG (2004). Tetrakis(μ-acetato-κ^{2}O:O′)bis[(4-pyridone-κO)copper(II)]. Acta Cryst. E60: m976-m978.

Lumme P, Elo H, Jänne J (1984). Antitumor activity and metal complexes of the first transition series. Trans-bis(salicylaldoximato)copper(II) and related copper(II) complexes, a novel group of potential antitumor agents. Inorg. Chim. Acta, 92(4): 241-251.

Maddah B, Alizadeh K, Shamsipur M, Moghimi A, Ganjali MR (2006). Differential Pulse polarographic Study of Mercury Complexes with Some Substituted Pyrimidines in Binary Acetonitrile-Dimethylformamide Mixtures. Polish J. Chem., 80: 737-744.

Morsali A, Beyramabadi SA, Bozorgmehr MR, Raanaee M, Keyvani B, Jafari GR (2010). Prediction of gas chromatography retention of BTEX and other substituted benzenes based on quantum chemical parameters. Sci. Res. Essays, 5(3): 349-351.

Niu S, Hall MB (2000). Theoretical studies of reactions of transition-metal complexes. Chem. Rev., 100: 353-405.

Pui A, Policar C, Mahy JP (2007). Electronic and steric effects in cobalt Schiff bases complexes: Synthesis, characterization and catalytic activity of some cobalt(II) tetra-halogens-dimethyl salen complexes. Inorg. Chim. Acta, 360(6): 2139-2144.

Uekusa H, Ohba S, Tokii T, Muto Y, Kato M, Husebye S, Steward OW, Chang SC, Rose JP, Pletcher JF, Suzuki I. (1992). Magneto-structural corrections of dimeric copper(II) trichloroacetates. Acta Cryst., B48: 650-667.

Ünver H, Elmali A, Karakaş A, Kara H, Donmez E (2006). Synthesis, spectroscopic studies and nonlinear optical behavior of N,N′-bis(2-hydroxy-1-naphthylmethylidene)-1-methyl-1,2-diaminoethane-N,N′,O,O′-nickel(II). J. Mol. Struct., 800(1-3): 18-22.

Xuan RC, Li MC, Wan YH (2003b). Bis(2-chloro-5-methylpyridine-κN)bis(nitrato-κ^{2}O,O′)copper(II). Acta Cryst. C59: m462-m464.

Xuan RC, Hu WX, Yang ZY, Xuan RR (2003a). Dichlorobis(2-chloro-5-methylpyridine-κN)copper(II). Acta Cryst. C59: m112-m114.