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X-ray structural study of aqua bis (Thymine-N^1, N^3) ethylenediamine copper (ii) dihydrate

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The new complex formulated as [Cu $(Thy)_2(en)(H_2O)]2(H_2O)$, (en = ethylenediamine, Thy = thymine) is synthesized according the reaction between the spices of copper(II) nitrate, ethylenediamine and thymine. The complex has been characterized by the methods of elemental, spectroscopic (IR and UV-Visible) and X-Ray diffraction. The complex crystallizes in the triclinic space group P-1. The cell dimensions are a = 6.1648(6) A°, b = 9.5515(9) A°, c = 15.8251(16) A°, α = 81.282(8) °, β = 79.513(9) °, γ = 82.921(8) °, V = 901.28(15) $A°^3$, Z = 2, D_{cal} = 1.577 Mg/m^3, F(000) = 412, Final R indices [I > 2σ (I)], R_1 = 0.0387, wR_2 = 0.1008.

1 Introduction

The study of coordination chemistry of copper has been intensively studies in recent years. ethylenediamine chelator act as a potential antitumor agent, it can show better antitumor activity and form water-soluble neutral complexes with transition metal ion [1]. Thymine and Uracil are among bases derived from nucleic acids. The metal complexes of pyrimidine nucleotides play an important role in biochemical processes namely molecular biology [2]. Gupta and Srivastava reported the synthesis of some mixed ligand Cu (II), Ni (II) and Co (II) complexes with uracil, 2-thiouracil or thymine [3]. However, a very few well defined metal complexes with thymine have been isolated and characterized by X-Ray.

2 Experimental

2.1 Materials and methods

The ligands thymine (thy), ethylenediamine (en) and the metal ion Cu (II) used in the form sulphate were obtained from PHYWE.

IR spectra was recorded (as KBr disc) on infrared spectrophotometer FTIR-8400 Shimadzu in the 4000-400 cm^{-1} region. Conductivity measurement was performed using a Digisun Digital conductivity bridge model Consort C3030 and a dip-type cell calibrated with KCl solution. The electronic spectrum of the complex was recorded in DMSO on Shimadzu UV-160PC spectrophotometer. The X-Ray crystal structure analysis was obtained on "service commun d'analyse par diffraction des rayons-X, Université de Brest". Elements C, H, N were carried out in "service de microanalyse" I.C.S.N-C.N.R.S. Gif-sur-Yvette Cedex.

2.2 Synthesis of [Cu (Thy)2(en)(H2O)].2(H2O)

A solution of thymine (6 mmol) in water (20 ml) was neutralised with NaOH (6 mmol). The $CuSO_4.5H_2O$ (3 mmol) in water (10 ml) was added to this solution (PH=8). The resulting solution was stirred for 2 h and ethylenediamine (3mmol) was added dropewise. The final solution was stirred for 8h at 60C°, and the cooling to room temperature. A blue crystal was obtained. Analysis; Found: C, 34.12; H, 5.59; N, 20.27; Cu, 14.91. Calc.: C, 33.65; H, 5.60; N, 19.63, Cu, 14.84. Conductivity in DMSO: 12.62 $\Omega^{-1}.cm^2.mol^{-1}$.

3 Results and discussion

The IR spectrum of the complex was determined within 4000-400cm-1 frequency range. ν(OH), H_2O (hydratation): 3540, 3451 cm^{-1}; H_2O(coordinated): 3411 cm^{-1}. $\nu(NH_2)$, ethylenediamine: 3289, 3249 cm^{-1}; ν(NH) thymine: 3163 cm^{-1} [4], ν(C=O) thymine: 1746, 1621 cm^{-1}, ν(Cu-N): 409, 487 cm^{-1}[5].

The Cu (II) ion is coordinated to the two monoanions of thymine through the two nitrogen atoms N^1, N^3 and two the éthylènediamine by the N^5, N^6 nitrogen atoms.

Transition d-d: 21330 cm^{-1}. This feature is characteristic for five-coordinate Cu (II) complex [6]. The bands observed at 41660cm-1, 40078cm-1 and 38080cm-1 can be attributed to a charge transfer. Those multiples bands are characteristics of the d^9 system.

Crystallographic data

Compound crystallized in asymmetric unit, space group P-1 (Figure 1, Table 1).

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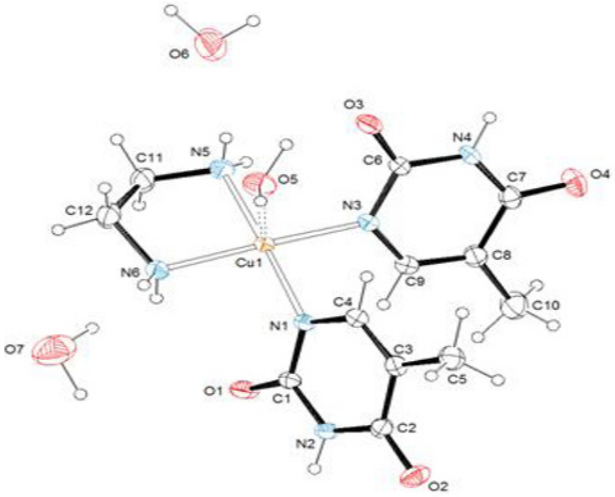

Figure 1. [Cu (Thy)$_2$(en)(H$_2$O)].2(H$_2$O) at 296 K in P-1, asymmetric unit.

Table 1. Crystal data and structure refinement for [Cu(Thy)$_2$(en)(H$_2$O)].2(H$_2$O) at 296 K.

Complex	
Empirical formula	C_{12} H_{24} Cu N_6 O_7
Formula weight	427.91
Temperature (K)	170(2)
Wavelength/A°	0.71073
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions (A°,deg)	a = 6.1648(6) b = 9.5515(9) c = 15.8251(16) α = 81.282(8) β = 79.513(9) γ = 82.921(8)
Volume (A°^{3})	901.28(15)
Z	2
Calculated density (Mg/m^3)	1.577
Absorption coefficient (mm^{-1})	1.260
F(000)	446
Crystal size (mm)	0.46 x 0.21 x 0.10
Theta range for data collection(deg)	3.19 to 28.28
Limiting indices	-8≤h≤7, -12≤k≤12, -21≤l≤20
Reflections collected / unique	8006 / 4416 [R(int) = 0.0174]
Completeness to θ = 28.28	99.0 %
Absorption correction	Analytical
Max. and min. transmission	0.8843 and 0.5949
Refinement method	Full-matrix least-squares onF^2
Data/restraints/parameters	4416 / 38 / 273
Goodness-of-fit on F^2	1.055
Final R indices [I>2σ(I)]	R1=0.0387, wR2=0.1008
R indices (all data)	R1=0.0520, wR2=0.1054
Largest diff. peak and hole (e.A°$^{-3}$)	0.434 and -0.454

Table 2. Selected bond lengths [A°] and angles [deg] for [Cu(Thy)$_2$(en)(H$_2$O)].2(H$_2$O) at 296 K.

N(1)-Cu(1)	2.0067(18)	C(1)-N(1)-Cu(1)	121.75(15)
N(3)-Cu(1)	2.0048(19)	C(4)-N(1)-Cu(1)	119.96(15)
N(5)-Cu(1)	2.004(2)	C(6)-N(3)-Cu(1)	123.18(16)
N(6)-Cu(1)	2.003(2)	C(9)-N(3)-Cu(1)	118.82(15)
O(5)-Cu(1)	2.418(2)	C(11)-N(5)-Cu(1)	109.92(16)
C(1)-O(1)	1.255(3)	Cu(1)-N(5)-H(5M)	107.7(18)
C(1)-N(1)	1.346(3)	Cu(1)-N(5)-H(5N)	110.0(18)
C(1)-N(2)	1.372(3)	C(12)-N(6)-Cu(1)	109.45(16)
C(2)-O(2)	1.239(3)	Cu(1)-N(6)-H(6M)	100.2(19)
C(2)-N(2)	1.366(3)	Cu(1)-N(6)-H(6N)	116.0(18)
C(2)-C(3)	1.437(3)	Cu(1)-O(5)-H(5O)	119.2(16)
C(3)-C(4)	1.349(3)	Cu(1)-O(5)-H(5P)	128.3(16)
C(3)-C(5)	1.494(3)	N(6)-Cu(1)-N(5)	83.59(9)
C(4)-N(1)	1.358(3)	N(6)-Cu(1)-N(3)	166.82(9)
C(6)-O(3)	1.248(3)	N(5)-Cu(1)-N(3)	91.67(8)
C(6)-N(3)	1.339(3)	N(6)-Cu(1)-N(1)	94.95(8)
C(6)-N(4)	1.381(3)	N(5)-Cu(1)-N(1)	176.65(9)
C(7)-O(4)	1.248(3)	N(3)-Cu(1)-N(1)	89.10(8)
C(7)-N(4)	1.366(3)	N(6)-Cu(1)-O(5)	92.51(9)
C(7)-C(8)	1.419(3)	N(5)-Cu(1)-O(5)	88.79(9)
C(8)-C(9)	1.351(3)	N(3)-Cu(1)-O(5)	99.69(8)
C(8)-C(10)	1.498(4)	N(1)-Cu(1)-O(5)	94.29(8)
C(9)-N(3)	1.367(3)		
C(11)-N(5)	1.467(3)		
C(11)-C(12)	1.481(4)		
C(12)-N(6)	1.476(4)		

4 Conclusion

In this work, we report the isolation and characterization of a new complex of thymine with Cu (II) where two thymine acts as monodate ligand. The complex has been characterized by elemental analysis, conductance studies, electronic, IR spectral studies and X-Ray structural Study. On the basis of crystallographic data, we have noted that the coordination of the two monoanions of thymine tacking place via the nitrogen N(1) for one and N(3) for the other. Ethylenediamine chelate Cu(II) ion by the nitrogen atoms. The hydrogen bonds stabilize the structure.

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