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Synthesis and Crystal Structure of two Copper (II) Carboxylate Complexes with Ethelyenediamine

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Abstract

A new crystal of, [Cu $(OH_2)_2$ $(en)_2$] 4-oxidobenzoate and [Cu$(OH_2)_2$ $(en)_2$] (3,5-dinitrobenzoate$)_2$ Where (en = ethylenediamine) have- been synthesize, and the resulting complexes has been analyzed on the base of CHN analyses, IR spectral, Electronic spectra, single- crystal X-ray- diffraction method and magnetic susceptibility. In both complexes cations have a distorted octahedral CuN_4O_2 around copper (II), surrounded by two molecules of ethylenediamine and two water molecules. The cations [Cu (en) $_2(OH_2)_2]^{2+}$ of both complexes are associated to carboxylate anions by hydrogen bonding in addition to electrostatic forces.

Introduction

Cu (II) carboxylates are interesting compounds containing mononuclear, binuclear or polynuclear structural units ***[1-4]***. Carboxylates ligand can be coordinated to metal center as monodentate, bidentate, bridging or may lie outside the coordination sphere ***[5-8]***. Adducts of Cu(II) with carboxylate containing a variety of basic ligands and their preparation, magnetic and spectral properties have been reported ***[9,10]***.The interesting of Copper (II) carboxylate and Ethylenediamine Complexes which have been used as catalyst in organic preparation by use the Cross-Coupling Reaction ***[11,12].***the application of Copper(II) carboxylates in various areas including as anticorrosive materials, also use in the preparation of nanorods semiconductor as templates molecular ***[13-16]***. complexes containing ethylenediamine inside coordination sphere with Cu (II) and carboxylate ligands as counter anions have been reported such as 4-fluorobenzoate,3-(3-pyridyl)-propionate,2,2-dithiodinicotinate, 3-methoxybenzoate, 4-nitrobenzoate have been prepared ***[17-21]***. In this work, we prepared two different copper divalent complexes and report crystal structures of them, which containing ethylenediamine and 4-oxidobenzoate or 3,5-dnitrobenzoate (Figure 1).

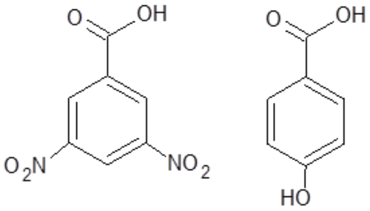


Figure-1: Structures of carboxylic acids.

Experimental

A. Material and instruments measurements.

Reagent grade ethylenediamine, 4-hydroxybenzoic acid, 3,5-dinitrobenzoic acid, sodium hydroxide, methanol, ethanol, and copper (II) sulphate pentahydrat were obtained from the British Drug House (BDH) and Aldrich Chemicals Co., and-were-used without further purification. Infrared absorption spectra were obtained from the measurement on Thermo Mattson IR 300 spectrophotometer-in the' wave number' range between 4000- and 400- cm^{-1} using' KBr discs. Electronic spectra recorded on SHIMADZU UV-1900i uv-vis spectrophotpmeter. Electro thermal-IA 9000-England melting point device was used to determined melting point of the complexes. 'Carbon', 'hydrogen' and- nitrogen- analysis were carried out on a CE-440"Elemental' Analyzer" (UK). 'X-'ray data were-collected using a Brucker APEX-II CCD 'diffractometer' using graphite' crystal and beam-monochromatic-using MoKα '(λ = 0.71073 Å) radiation. (Cambridge Crystallographic Centre, UK).

B. Preparation-of complex-1 [Cu (OH$_2$)$_2$ (en) $_2$] 4-oxidobenzoate

4-hydroxybenzoic'-acid Sodium'salt'was synthesis-by dissolving (1.1 g, 8 mmol) of 4 hydroxybenzoic"acid and (0.34 g, 8 mmol) of sodium hydroxide in (20 ml)-water. Solution $CuSO_4.5H_2O$ was prepared by dissolving' (0.50 g, 2 mmol) in (10 ml) water' then' added-to the first' solution, the precipitated product filtered' and washed-several time, with water and dried-at room-temperature. The' above copper-complexes suspended' by' dissolved in (40 ml) of water, and added (0.3 g, 5 mmol) of ethylenediamine to give clear dark blue colored solution. Evaporated the solvent and the precipitate was dissolved in water. The' solution-was kept' at room-temperature for 7' day-, dark-deep blue colored crystals appeared. M.p = 205-207 ºC (dec.). Anal. calc. for $C_{11}CuH_{24}N_4O_5$: Carbon (37.22%); Hydrogen (6.90%); Nitrogen (15.53%). Found: Carbon (37.3%); Hydrogen (6.20%); Nitrogen (15.80 %). The important IR bands (cm^{-1}): 2964, 1395, 1342, 548, 476.

C. Preparation of complex -2- [Cu (OH$_2$)$_2$ (en) $_2$] 3,5-dinitrobenzoate

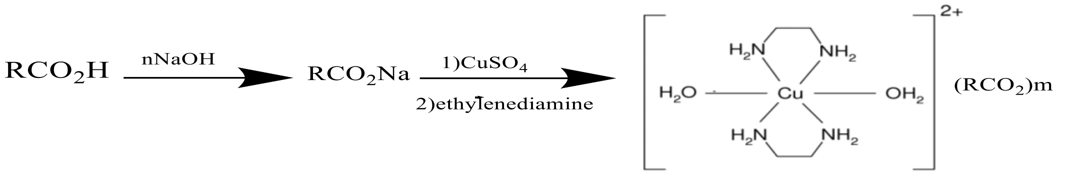
3,5-dinitrobenzoic' acid -(1.7 g, 8 mmol,) and NaOH' (0.32 g ,8 mmol) were"dissolved in (20 ml) of 'water to prepare-sodium salt of 3,5-dinitrobenzoic acid, $CuSO_4.5H_2O$ solution" prepared' by dissolving (1.0 g ,4 mmol) in (20 ml) water then-added to the first' solution. The precipitated" product filtered and washed' several time with water and dried at room temperature. The above copper-complexes, suspended by dissolved in (40 ml) of water, and added (0.3g, 5 mmol) of ethylenediamine- to give clear' dark' blue colored' solution. Evaporated the solvent and the precipitate was dissolved in water. The' solution' was kept' at room-temperature for 7 day-, dark" deep blue' colored crystals appeared, M.p=254-256 ºC (dec.). Anal. calc. for $C_{18}CuH_{26}N_8O_{14}$: Carbon (33.75%); Hydrogen (3.75%); Nitrogen (17.50%). Found: Carbon, (33.49%); Hydrogen (4.09%); Nitrogen (17.06 %). The important IR bands (cm^{-1}): 2936, 1373, 1302 524,453.

D. X-ray' crystallographic' study-

Diffraction data' for' two complexes' compounds –were' collected by using Brucker APEX-II CCD diffract meter equipped at 100.0 and 100.15 K, respectively using graphite crystal and beam monochromatic using MoKα (λ = 0.71073 Å) radiation. For both complexes compound The crystal data solved by using SHELXT program as direct methods, Crystal structures data for both complexes were solved by substantial phasing methods and repeated 'on' F2- by' full-matrix' least-squares"techniques with-anisotropic non-hydrogen atoms ***[22,23]***. The H atoms positions were, inserted' at their' calculated positions.

Results and discussion

Reaction of copper sulfate pentahydrate with sodium salt of 4-hydroxybenzoic acid or 3,5-dinitrobenzoic acid and ethylenediamine afforded their corresponding ionic complexes. The' synthesized-complexes are' stable' in air also they are soluble' in common-solvents like water ethanol and methanol.



R1=4-hydroxybenzoic acid ,n=2, m=1

R2=3,5-dinitrobenzoic ,n=1 ,m=2

A. *Description of the X-ray structures of complex(1)*

Figure 2 show molecular structure of complex 1. Thermal ellipsoids are drawn at 50% probability level. The' asymmetric' units-consist' of one' complex-cation of a $[Cu'(OH_2)_2\ (en)_{2'}]^{2+}$ and' one' uncoordinating" 4-oxidocarboxylate anion. Cu' divalent' ions are located" at the inversion' centre and surrounding by two molecules of chelating ethylenediamine, and in axial positions coordinated to the two water molecules by oxygen atoms. The complex has octahedral structure with tetragonal elongation due to effect of Jahn–Teller ***[24]***. The distances between Copper-Nitrogen vary between 2.0439 (7) and 2.0211(7) Å. Bond distances between copper-oxygen are 2.5274(6)Å, Because of effect of Jahn-Teller [24], the bond length between copper-oxygen is longer than expected. In the prepared complex number (1) the' bond' distances-are in agreement to those'found'in related-complexes ***[17, 21]***. The N-Cu-N bond angles are 176.00(3)-84.85 (4)° while the N-Cu-O are 94.25(2) - 87.86(2)°, respectively. The complex has a center of inversion. In the' crystal-structure, the' $[Cu'(OH_2)_2\ (en)_2]^{2+}$ coordination' cations' and-counter anions 4-oxidocarboxylate bonded by nitrogen(1)-hydrogen(1B)···oxygen(3)^2 hydrogen-bond with angle and length of 158.4° and 3.0087 Å (7), respectively and O(1W)-H(1WB)···O(3) bond with 172.4(14) angle and 2.6820(8) length (Table 2, Figure '3). Crystal 'data and' details-of 'refinements "for both prepared complex compounds-are given' in Table 1. Coordination bond lengths-and'angles'are listed'in Table 2.

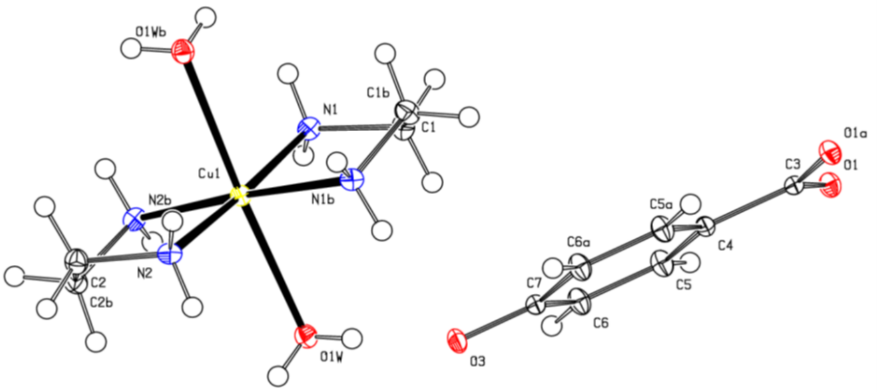


Figure-2: View of the molecular structure for [Cu (OH2)2 (en) 2] 4-oxidobenzoate complex.

Table-1: Crystal data, data collection and structure refinement parameters for complexes 1 and 2.

Parameters	Complex 1	Complex 2
Chemical formula	$C_{11}CuH_{24}N_4O_5$	$C_{18}CuH_{26}N_8O_{14}$
M_r	355.88	642.01
Cell system	Monoclinic	Monoclinic
Space group	P2/n	$P2_1/c$
a (Å)	6.9895(7)	11.625(10)
b (Å)	10.5366(10)	9.428(7)
c (Å)	10.9621(10)	11.907(10)
α (°)	90°	90
β (°)	102.144(5)	105.05(4)
γ (°)	90°	90
V (Å^3)	789.24(13)	1260.2(18)
Z	2	2
θ range (°)	5.422 - 72.158	5.588 - 64.828
D_{calc} (Mg m^{-3})	1.498	1.692
μ(mm^{-1})	1.410	0.955
F(000)	374.0	662.0
R_1 [I > 2σ]	0.0210	0.0278,
wR_2 [I > 2σ]	0.0559	0.0714
R_1 (all data)	0.0237	0.0344
wR_2 (all data)	0.0568	0.0741

Table-2: Coordination Bond Lengths (Å), Angles (°) and H-bond Geometry for complex (1)

1			
Cu1-N1	2.0439(7)	Cu1-N(2)#1	2.0211(7)
Cu1-N2	2.0212(7)	Cu1-OW1	2.5274(6)
N1-Cu1-N(1)#1	84.85(4)	N2-Cu1-N1	176.00(3)
N1-Cu1-N(1W)#1	88.14(2)	N(2)#1-Cu1-N2	85.09(4)
N(1)#1-Cu1-N(1W)#1	89.75(2)	N(2)#1-Cu1-O1W	87.86(2)
N2-Cu1-N(1)#1	95.17(3)	N2-Cu1-O(1W)#1	94.25(2)
O1W-Cu1-O(1W)#1			177.13(3)

D-H···A	D-H	H···A	<(DHA)	D···A
N1-H1A···O1^{I}	0.91	2.27	155.1	3.1224(9)
N1-H1B···O3^{II}	0.91	2.14	158.4	3.0087(7)
N2-H2A···O1^{III}	0.91	2.12	162.5	2.9992(9)
O1W-H1WB···O3	0.775(14)	1.912(14)	172.4(14)	2.6820(8)

Symmetry codes: (I) 1-X, 1-Y, 1-Z; (II) 1+X, +Y, +Z; (III) 1/2-X, 1+Y, 3/2-Z

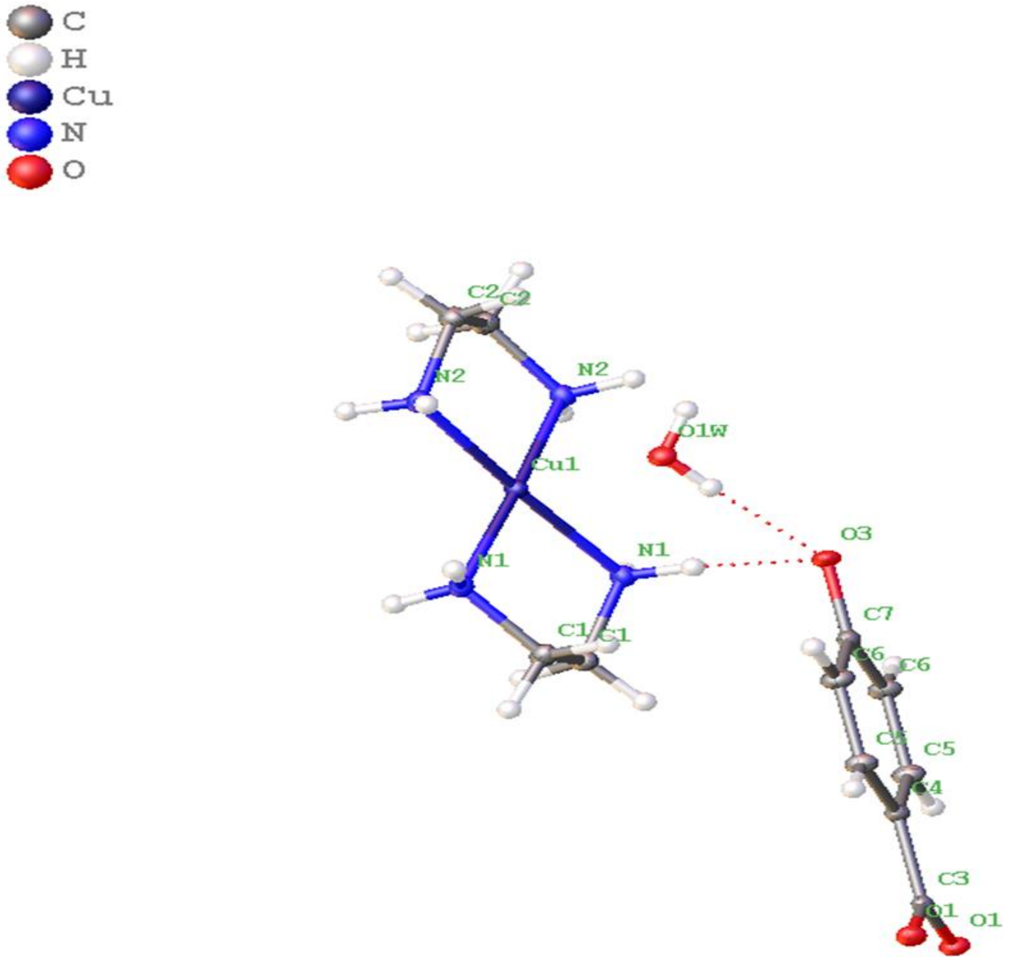


Figure-3: view of molecule Structures [Cu (OH$_2$)$_2$ (en)$_2$] 4-oxidobenzoate complex. Dotted lines denote the hydrogen bonds between complex cation and anions.

B. Description of the X-ray Structures of Complex Compound (2)

Figure 4 shown molecular*****crystal structure'of complex'(2). Coordination geometry around Cu (II) ions in complex (2) are distorted octahedral, with-tetragonal"elongation, due'to Jahn-Teller-distortion ***[24]***. Square base consists of four nitrogen atoms of the two molecular of ethylenediamine CuN$_4$, and oxygen atom of two water-molecules in the apical-position (Table-3). The distances-between Copper-Nitrogen in range from 2.0322(15) to 2.0268(15) Å. bond lengths between Copper-Oxygen are 2.458(2) Å ***[17-21]***. Complex cation in both synthesis compound observed similar-to the equivalent-values'for"Copper-Nitrogen and Cu-O bond lengths. As well as-electrostatic"forces', the cation and anion species"in complex (**2)** interact'by'Nitrogen (2)-Hydrogen (2B)···Oxygen(1)^{1} hydrogen-bond with 175.9 angle and 2.954(2) length and Oxygen(1W)-Hydrogen (1WA)···Oxygen(2) bond with 178 (2) angle and 2.710(2) length (Table 3, Figure 5). Table 3 includes-Coordination"bond-lengths'(Å), Angles' (°) and-H-bond"Geometry for, Complex-(2).

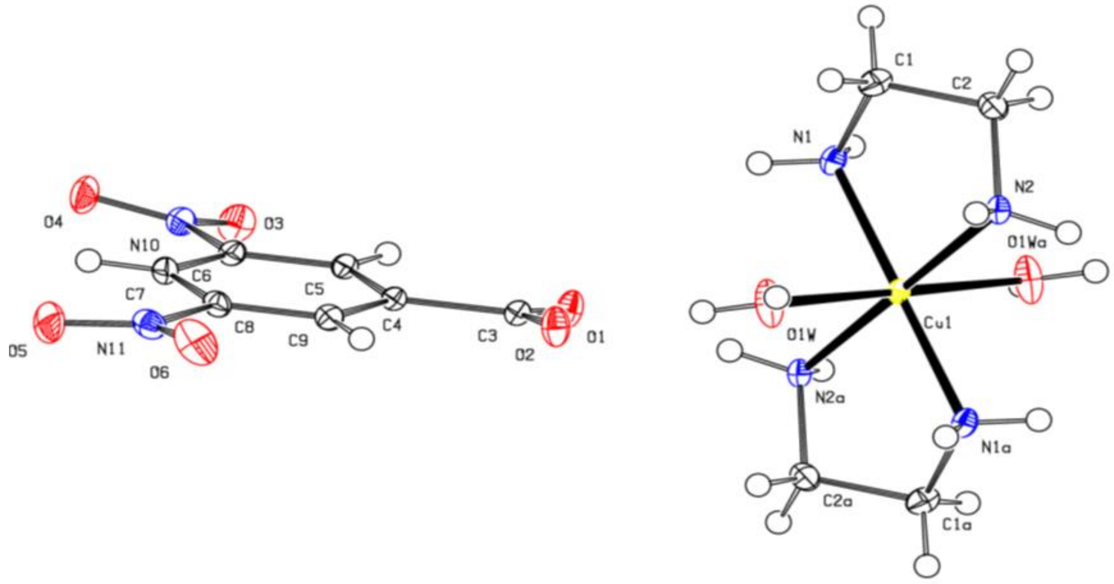


Figure-4: View of the molecular structure for [Cu (OH$_2$)$_2$ (en) $_2$] 3,5-dinitrobenzoate.

Table-3: Coordination Bond lengths (Å), Angles (°) and H-bond Geometry for Complex (2)

2			
Cu1-N1	2.0322(15)	Cu1-O1W	2.458(2)
Cu1-N2	2.0268(15)		
N(1)#1-Cu1-N1	180.0	N2-Cu1-O1)	89.03(5)
N2-Cu1-N(1)#1	94.58(7)	N(1)#1-Cu1-O1W	89.39(5)
N2-Cu(1)-N(1)	85.42(7)	N(2)#1-Cu1-O1W	90.97(5)
N1-Cu1-O1W	90.61(5)		

D-H···A	D-H	H···A	<(DHA)	D···A
N2-H2B···O1^{I}	0.91	2.05	175.9	2.954(2)
O1W-H(1WA)···O2	0.85(2)	1.87(2)	178(2)	2.710(2)
O1W-H1WB···O4^{II}	0.79(2)	2.45(2)	168(2)	3.225(3)

Symmetry codes: (I) -X, 1-Y,-Z ;(II) +X, +Y,-1+Z

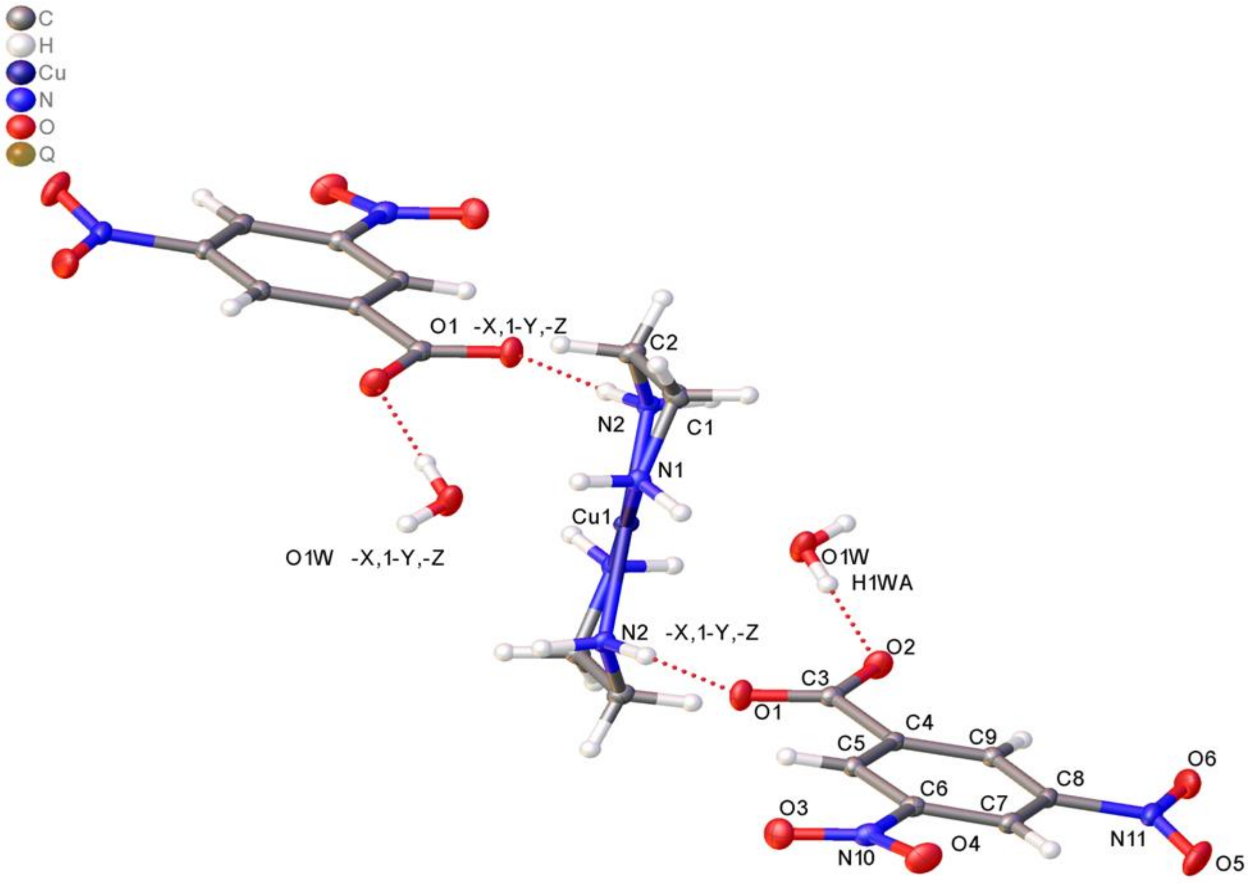


Figure-5: H-bonds system in the lattice of complex [Cu (OH2)2 (en) 2] 3,5-dinitrobenzoate. The hydrogen bonds are drawn as dashed lines

C. Infrared spectroscopy

The most significant Infrared spectra bands for both complexes are presented in the experimental section. In the range 3500-3000 cm^{-1} appears a broad band may be referred to the ν(OH) of the coordinated water molecule, C–H stretching vibrations of ethylenediamine in both prepare complexes were observed sharp bands and weak intensity in the wave numbers 2964–2936 cm^{-1}. The bands in the region 1395–1373, 1342–1302cm^{-1} were attributed to ν_{asym}(COO) and ν_{sym}(COO), respectively. The bands at 548–524 and 476–453 cm^{-1} ascribed to ν(Copper–Nitrogen) and ν(Copper–Oxygen), respectively.

D. Electronic spectra and Magnetic susceptibility study.

Electronic spectra of the both ‘complexes-salt 1-and 2-were recorded in DMSO solution. The visible absorption spectra of the Cu (II) complexes 1 and 2 showed a strong band around (29411 cm^{-1}) and (29625 cm-1) assigned to n→π*, and anther band in (20746 cm^{-1}) and (20825 cm^{-1}) was appeared due to charge transfer (LMCT). At (17452 cm-1) and (17675 cm-1) a broad spectrum showed d-d electronic transition which assigned to (^{2}Eg → ^{2}T$_{2}$g) ***[25]***. The broadness of the band is due to the "Jahn'-"Teller- effect ***[24]***. Therefore, the predicated structure of both Cu (II) complexes is “distorted 'octahedral -geometry and supported by d^{9} electronic configuration ***[26]***. Moreover, the magnetic moment value of each complex is (1.76 and 1.79) B.M. which within the expected value for one unpaired electron ***[27, 28]***.

Conclusions

In the above study, we have scout about *the "synthesis- and "crystal X-ray diffraction "of "two- new "copper divalent complexes-with ethylenediamine and carboxylate ligand. The X-ray crystal structure analysis revealed that in both complexes cations have a distorted octahedral CuN_4O_2 around copper (II), surrounded by two molecules of ethylenediamine and 'two-molecules 'of "water. 3,5-dintrobenzoate acted as a counter anion while 4-oxidobenzoate showed unusual counter dianion. Elemental analyses and IR spectroscopy are in agreement with compositions of the complexes.

Supplementary material

CCDC 1569254, 1569255 include the supplementary crystallographic data for both synthesis complexes respectively. The above data can be gained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/deposit or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Telephone: +44-01223-762910; Fax: +44-01223-336033; E-mail: deposit@ccdc.cam.ac.uk

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