

## Spectral, Electrochemical and Molecular Orbital Studies on a New Solvatochromic Binuclear Mixed Ligand Copper(II) Complexes

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### Abstract

A new series of solvatochromic binuclear mixed ligand complexes with the general formula:  $\text{Cu}_2(\text{DMCHD})(\text{Am})_2\text{X}_3$  (where, DMCHD: 5,5-Dimethyl cyclohexanate 1,3-dione, Am=N,N,N',N'-trimethylethylenediamine (Me3en), N,N,N',N'-tetramethylethylenediamine (Me4en), or N,N,N',N',N''-penta-methyldiethylenetriamine (Me5dien) and X=ClO<sub>4</sub>- or Cl- have been synthesized and characterized by the analytical, spectral methods, magnetic and molar conductance as well as electrochemical measurements. The formation constant values for HDMCHD ligand with various metal ions are much lower than expected for similar β-diketones revealing a monobasic unidentate nature of this ligand. The d-d absorption bands of the prepared complexes in weak donor solvents suggest square-planar, distorted octahedral and/or distorted trigonal bipyramid geometries for the perchlorate and chloride of diamine in addition to triamine complexes, respectively. However, an octahedral structure was identified for the complexes in strong donor solvents. Perchlorate of diamine complexes show a remarkable color change from violet to green as the Lewis basicity of the donor solvent or anions increases, whereas chloride complex is mainly affected by the Lewis acidity of the acceptor solvent. Specific and non-specific interactions of solvent molecules with the complexes have been investigated using the unified solvation model. Band's oscillator strength of the d-d transition has been calculated and discussed. Cyclic voltammetric measurements on the prepared complexes in different solvents showed a quasi-reversible or irreversible and mainly diffusion controlled reduction process. Such behavior has been explained according to the EECE mechanism. A linear correlation has been found between the Cu(II) reduction potential and the spectral data. Structural parameters of the free ligands and their Cu(II)- complexes have been calculated on the basis of semiempirical PM3 level and correlated with the experimental data.

**Keywords:** Formation constant; pH-metric; Solvatochromic; Red shift; Oscillator strength; Cyclic voltammetry; Semiempirical; Molecular modeling; Biological activity

### Introduction

Solvatochromism is widely used in many fields of chemical and biological research to study bulk and local polarity in macro-systems (membranes, etc.), even though its wide use, solvatochromism (a color change as a result of solvent effect) still remains a largely unknown phenomenon due to the enormously complex coupling of many different interactions and dynamical processes which describe it. Metal- chelates with O<sub>2</sub>N<sub>2</sub> as Schiff-base or mixed ligands have been studied as solvatochromic indicators [1-5]. In view of the limited information available regarding the spectroscopic properties of mixed ligand metal complexes containing 5,5-dimethyl cyclohexane1,3-dione (HDMCHD) the present study which is a continuation of our studies on chromotropic of the metal chelates with mixed ligands containing O-O and N-N in various solvents [6-10]. In the preceding communication detailed structural, molecular orbital and optical characterizations of solvatochromic mixed ligand copper(II) complex of 5,5-dimethyl cyclohexanate 1,3-dione and N,N,N',N',N''-penta-methyldiethylenetriamine,  $\text{Cu}(\text{DMCHD})(\text{Me}_5\text{dien})\text{NO}_3$ , the structure elucidated as mononuclear and HDMCHD ligand acted as mono-basic monodentate [11].

Thus, the purpose of the current work was to achieve a microscopic understanding of the intermolecular effects which govern the absorption spectral properties of solvated complex probes, such as solubility, Lewis-acid base, and specific and non-specific interactions. Thus, the present investigation includes: (a) effect of solvent anion and secondary ligand (polyamine) on energetic shifts of d-d bands and change the color of solution, (b) solvation effect on the structure and stability of the resulting complexes. For this intention a new series of copper(II) complexes abbreviated as  $\text{Cu}_2(\text{DMCHD})(\text{Am})_2\text{X}_3$  (where DMCHD=5,5-dimethyl cyclohexanate1.3-dione, Am=N,N,N',N'-trimethylethylenediamine (Me<sub>3</sub>en), N,N,N',N'-tetramethylethylenediamine (Me<sub>4</sub>en), or

N,N,N',N',N''-pentamethyldiethylenetriamine (Me<sub>5</sub>dien) and X=ClO<sub>4</sub><sup>-</sup> or Cl<sup>-</sup> have been synthesized and characterized by spectral, conductivity and magnetic as well as electrochemical techniques. The main goal of this study is to examine the applicability of the current complexes as a Lewis acid-base color indicator. As further support to our experimental work, molecular orbital calculations have been accomplished using Hyperchem 7.52 for the ligands and their complexes, the structural parameters data are correlated with the experimental results.

### Experimental

#### Materials

All chemicals used were of the analytical reagent grade and obtained from either Merck or Aldrich and were used without further purification. Solvents used, nitromethane (CH<sub>3</sub>NO<sub>2</sub>), acetonitrile (MeCN), acetone (Me<sub>2</sub>CO), methanol (MeOH), pyridine (py), N,N-dimethylformamide (DMF) and dimethylsulfoxide (DMSO), propylenedicarbonate (PDC), formamide (Fa) were "Spectro-grade" and further purified using standard methods [12].

#### Physical measurements

The infrared spectra in KBr (400-4000 cm<sup>-1</sup>) were recorded using Shimadzu FTIR 8101 spectrometer. Electronic spectra were obtained on UV-2101 pc w/full spectrophotometer using 10 mm quartz cells

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thermostated at 25°C. Magnetic moments were obtained using a MSB-AUTO magnetic susceptibility balance by the Gouy method. The molar conductance was measured with Metrohm 660 conductor in DMF solutions at 25°C. The potentiometric titrations were carried out by means of a digital 520 WTW pH-meter with a conventional pH-electrode. Titrations and calculations of the proton-dissociation and stepwise formation constants were performed as described earlier [12]. Cyclic voltammetric measurements were performed as reported elsewhere [8,13].

### Syntheses of Cu<sub>n</sub>(DMCHD)(Am)<sub>n</sub>X<sub>m</sub> complexes

These complexes were prepared by adding a mixture of 10 mmol of the HDMCHD ligand in 25 mL absolute EtOH and solid anhydrous Na<sub>2</sub>CO<sub>3</sub> (20 mmol) to an ethanolic solution of 20 mmol appropriate copper(II) salt. The mixture was continuously stirred for about 30 minutes resulting in a green solution, which was then filtered. Then a solution of 20 mmol diamine or triamine derivative (Am) in 20 mL EtOH was added dropwise to the filtrate with a continuous stirring for an additional 45 min. After that, the resulting solution was filtered off and left to stand overnight. The complexes obtained were re-crystallized from dichloromethane and stored over silica gel.

### Results and Discussion

The analytical and physical data of the mixed ligands solid complexes with Cu(II) ion are given in Table 1. It is well known that most of β-diketones are mixtures of keto-enol forms. Their keto-enol tautomerism is responsible for the formation of inner complexes with metal ions; so they behave in general as monobasic bidentate nature [14]. This statement cannot apply to characterize the current mixed ligands complexes of copper(II) with 5,5-dimethylcyclohexane-1,3dione (HDMCHD) and polyamine ligands (Am). This motivated us to study the complexation equilibrium of HDMCHD ligand with various metal ions in solution to focus the light on the dentate nature of HDMCHD ligand. Thus, potentiometric titration studies were carried out for HDMCHD ligand with various metal ions in 50% (v/v) aqueous solution.

### Potentiometric studies

Potentiometric titration curves of free HDMCHD ligand ( $2.5 \times 10^{-3}$  M) in the absence and presence of different metal ions ( $5 \times 10^{-4}$  M) in a ratio 5:1(L:M) revealed: (i) divalent metal ions showed a distinct inflection point at  $m=2$ , ( $m$ =number of moles of base added per mole of metal ion), indicating the formation of ML<sub>2</sub>, (ii) however an inflection at  $m=3$  for trivalent metal ions corresponding to the formation of ML<sub>3</sub> or ML<sub>2</sub>OH complexes.

The titration curve of the free ligand against KOH solution shows one ionizable proton as expected with the value of  $pK^H=6.29$  and 6.16, in 50% (v/v) dioxane-water and isopropanol-water, respectively which agrees with the value obtained in pure water ( $pK^H=5.22$ ) [15]. The trend of deprotonation constant is in the opposite of increasing dielectric constant of the medium. The lower basicity of HDMCHD compared to acetylacetone arises from the existence of 95.3% of HDMCHD in enol form [15,16].

Formation constants values given in Table 2, evident that  $\log K_1$  and  $K_2$  values are too low compared to the basicity of HDMCHD ligand [17]. Moreover allied complexes derived from 2-acylcyclohexanone have sufficiently large formation constant values supporting its bidentate nature. These facts in addition to the small ratio of the two successive formation constants would lead to suggest monodentate nature of HDMCHD. Furthermore, the half-chair boat [18] conformation of the enol form of HDMCHD clearly depicts that due to imposition of the planar configuration of the cyclohexane ring bearing the groupings -C(OH)=C-C=O the proximity of the C-OH and C=O groups (the positions of which are non-flexible) are so wide that intramolecular hydrogen bonding is precluded in HDMCHD. Thus chelation is not possible, rather complex formation would take place typically by the replacement of the hydrogen ion of the enolic-OH group [15]. Thus, HDMCHD ligand behaves as monobasic mono-dentate or binuclear bidentate ligand.

The values in Table 2 reveal that, the formation constants increase in the following order: Cd(II)<Mn(II)<Co(II) ~ Ni(II)<Cu(II)<<Fe(III). This order except Fe(III) (owing to the higher oxidation state) is largely reflects the change in the heat of complex formation across the series, which arises from a combination of the influence of the polarizing ability of metal ion and crystal field stabilization energies [12]. The formation constant values of some lanthanides (Ln<sup>3+</sup>) -DMCHD complexes increase in the order of increasing  $1/r$  ( $r$ =ionic radii of Ln(III) ions): Pr(III)<Sm(III)<Yb(III).

### Infrared spectra

The main characteristic IR absorption frequencies of the free ligand (HDMCHD) and its Cu(II)-mixed ligand complexes are given in Table 3. The observed bands may classified into those originating from the ligands, those emanating from the counter-balancing anions and those arise from the bonds formed between copper(II) and coordinating sites. The bands are assigned in comparison with similar Cu(II)-complexes [7-11,19]. The broad band observed in the range 3225-3520 cm<sup>-1</sup> for complex (1) assigned to  $\nu_{NH}$  of the unsymmetrical alkylated diamine Me<sub>3</sub>en- ligand. The blue shift of the observed IR absorption bands at

No.	Complex/ Empirical Formula	Formula weight	Color	Anal, Found (Calc)				M.P	λ/S.cm <sup>2</sup> Mol <sup>-1</sup>	μ <sub>eff.</sub> (B.M)
				M%	C%	H%	N%			
1	Cu <sub>2</sub> (DMCHD)(Me <sub>3</sub> en) <sub>2</sub> (ClO <sub>4</sub> ) <sub>3</sub> .2C <sub>2</sub> H <sub>5</sub> OH C <sub>22</sub> H <sub>51</sub> N <sub>4</sub> O <sub>16</sub> Cl <sub>3</sub> Cu <sub>2</sub>	861	Bluish violet	15.25 (14.75)	31.42 (30.69)	5.98 (5.97)	6.46 (6.51)	196	199	1.65
2	Cu <sub>2</sub> (DMCHD)(Me <sub>4</sub> en) <sub>2</sub> (ClO <sub>4</sub> ) <sub>3</sub> .2C <sub>2</sub> H <sub>5</sub> OH C <sub>24</sub> H <sub>53</sub> N <sub>4</sub> O <sub>16</sub> Cl <sub>3</sub> Cu <sub>2</sub>	889	Reddish-violet	17.80 (14.30)	32.5 (32.39)	5.90 (5.96)	6.21 (6.29)	154	245	1.74
3	Cu <sub>2</sub> (DMCHD)(Me <sub>4</sub> en) <sub>2</sub> Cl <sub>3</sub> .2C <sub>2</sub> H <sub>5</sub> OH C <sub>24</sub> H <sub>53</sub> N <sub>4</sub> O <sub>4</sub> Cl <sub>3</sub> Cu <sub>2</sub>	697	Green	19.02 (18.22)	41.70 (41.35)	7.68 (7.95)	7.43 (8.04)	110	90	2.67
4	Cu <sub>2</sub> (DMCHD)(Me <sub>5</sub> dien) <sub>2</sub> (ClO <sub>4</sub> ) <sub>3</sub> 2C <sub>2</sub> H <sub>5</sub> OH C <sub>30</sub> H <sub>69</sub> N <sub>6</sub> O <sub>16</sub> Cl <sub>3</sub> Cu <sub>2</sub>	1003	Reddish-violet	12.01 11.61	37.25 (37.22)	8.19 (7.66)	7.78 (7.66)	157	155	1.62

Table 1: Physical and analytical data of Cu<sub>2</sub>(DMCHD)(am)<sub>2</sub>X<sub>m</sub> complexes.

Cation	HDMCHD						Hacac		
	Dioxane-water			Isopropanol-water			LogK1	LogK2	logβ
	LogK1	LogK2	logβ	LogK1	LogK2	logβ	LogK1	LogK2	logβ
H <sup>+</sup>	6.29	-	-	6.16	-	-	11.78	-	7.27
Mn <sup>2+</sup>	3.45	3.11	6.56	-	-	-	4.18	3.07	-
Co <sup>2+</sup>	3.64	3.22	6.86	3.52	3.13	6.65	5.40	4.40	-
Ni <sup>2+</sup>	3.62	3.21	6.83	3.62	3.21	6.83	6.69	6.73	-
Cu <sup>2+</sup>	3.62	3.33	6.95	3.49	3.15	6.64	8.22	8.23	-
Cd <sup>2+</sup>	3.43	3.07	6.50	3.51	3.11	6.62	3.82	2.76	-
Fe <sup>3+</sup>	6.12	5.87	11.99	5.62	5.41	11.03	-	-	-
Pr <sup>3+</sup>	3.58	3.20	6.78	3.39	3.07	6.46	-	-	2.64
Sm <sup>3+</sup>	3.69	3.28	6.97	3.48	3.13	6.61	5.59	4.46	2.86
Yb <sup>3+</sup>	3.74	3.34	7.08	3.65	3.26	6.91	5.18	4.86	-

**Table 2:** Stability constants of metal ccomplexes of 5,5-dimethyl cyclohexane 1,3-dione (HDMCHD) 25°C (□=0.10 in 50 (v/v)% solvent –water)

1613 and 1582 cm<sup>-1</sup> in the spectrum of free HDMCHD ligand which assigned to ν(C=O) to 1624-1674 and 1598-1618 cm<sup>-1</sup>, respectively suggest the involvement of the carbonyl group in the coordination sphere of Cu(II) [19].

The coordination modes of perchlorate anion have been implied from the IR data. Two intense stretching vibrational bands at 1140 and 625 cm<sup>-1</sup> are observed for the perchlorate complexes 1, 2 and 4. The weak splitting observed for the strong broad band of ν(ClO<sub>4</sub><sup>-</sup>) at 1140 cm<sup>-1</sup> indicates a mixture modes for perchlorate anions, properly one being partially contributing to the coordination sphere of Cu(II) as bidentate, and the other being free [7-11,19].

### Conductance measurements

The molar conductance values, in DMF (10<sup>-3</sup> mol/L), of all complexes are given in Table 1. These values indicate that all complexes in DMF showed an electrolyte behavior, which might arise to the Lewis basicity of DMF that drive out the coordinating anions, especially when the Lewis basicity of anion (such as ClO<sub>4</sub><sup>-</sup>) is much weaker than DMF solvent [20]. Complexes 1, 2 and 4 have molar conductance values 199, 245 and 155 ohm<sup>-1</sup>cm<sup>2</sup> mol<sup>-1</sup>, respectively indicating 1:3 electrolyte [21]. Whereas, complex 3 has molar conductivity value 90 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>, suggesting the ionic nature of complex 3 (1:1 electrolytes).

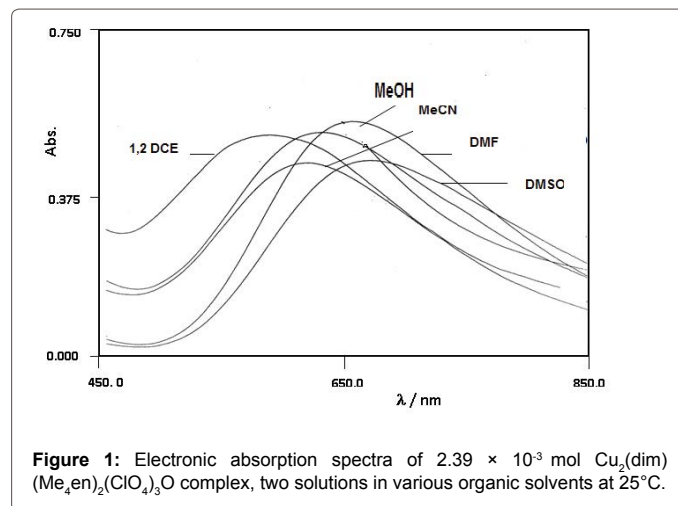
### Electronic spectra

The prepared complexes are freely soluble in most organic solvents and their UV/Vis spectra were measured at room temperature in a variety of solvents, selected to give a wide spread of donor and acceptor strengths as possible; the data obtained are collected in Table 4. The positions of the d-d absorption band of the Cu<sub>2</sub>(DMCHD)(Am)<sub>2</sub>X<sub>3</sub>, where X=perchlorate or chloride anions in weak donor solvent (such as CH<sub>3</sub>NO<sub>2</sub>) are observed in the range 19.05 × 10<sup>3</sup> and 14.47-13.97 × 10<sup>3</sup> cm<sup>-1</sup>. These values could be assigned to the following d-d transitions: dxy → dx<sup>2</sup>-y<sup>2</sup> (<sup>2</sup>B<sub>1g</sub> → <sup>2</sup>B<sub>2g</sub>), dx<sup>2</sup>-y<sup>2</sup> → dz<sup>2</sup> (<sup>2</sup>E<sub>g</sub> → <sup>2</sup>T<sub>2g</sub>), and/or dz<sup>2</sup> → dx<sup>2</sup>-y<sup>2</sup> [22,23]. These transitions suggest a square planar for diamine perchlorate complexes 1 and 2; distorted octahedral for triamine perchlorate complex 4 and/or square based pyramidal distorted trigonal bipyramide (SBRDTBP) geometries for chloride complex 3 [24,25]. This could be attributed to the polyamine, which varies between diamine for complexes 1-3 and triamine in complex 4, and coordination abilities of anions towards Cu(II). This interpretation further confirmed by the strong effect of anions on the d-d bands of perchlorate complexes 1 and 2 in weak donor solvents such as MeNO<sub>2</sub> (Table 5). The red shift of ν<sub>max</sub> versus the donor strength of these anions (DN<sub>X, MeNO<sub>2</sub></sub>) [20] yield the following linear correlations: ν<sub>max</sub>/cm<sup>-1</sup>=20340-168.44 DN<sub>X, MeNO<sub>2</sub></sub> r=0.99, and ν<sub>max</sub>/cm<sup>-1</sup>=18640-

12528, DN<sub>X, CH<sub>3</sub>NO<sub>2</sub></sub> r=0.95, for Cu<sub>2</sub>(Me<sub>3</sub>en)<sub>2</sub>(DMCHD)(ClO<sub>4</sub>)<sub>3</sub> and Cu<sub>2</sub>(Me<sub>4</sub>en)<sub>2</sub>(DMCHD)(ClO<sub>4</sub>)<sub>3</sub>, respectively.

The position of the d-d transition band of diamine perchlorate complexes 1 and 2 exhibits a red shift forming a wide range of color solutions (violet → blue → green) as the Lewis basicity of solvent increases revealing a positive solvatochromic [9]. Figure 1 shows the visible absorption spectra of the Cu<sub>2</sub>(DMCHD)(Me<sub>2</sub>en)<sub>2</sub>(ClO<sub>4</sub>)<sub>3</sub> complex 2, in different organic solvents. There is only one broad band observed in the visible region that assigned to the promotion of an electron from dz<sup>2</sup> orbital of the Cu(II) ion to the hole in dx<sup>2</sup>-y<sup>2</sup> orbital of the Cu(II) ion (d<sup>9</sup>) forming different distorted tetragonal depending on the Lewis basicity (DN) of the donor solvent or anion [23]. This red shift could be attributed to the strong repulsion of the electrons in dz<sup>2</sup> orbital by the lone pair of the incoming Lewis base such as solvent molecules or anion species, those are axially coordinated to the central copper (II) ion, consequently, a less energy will be required to transfer the electron to dx<sup>2</sup>-y<sup>2</sup>. In view of the fact that all the d<sub>xy</sub>, d<sub>yz</sub> and d<sub>xz</sub> orbitals of the Cu(II) ion are raised up by its interaction with the lone pair of electron on the solvent molecules approaching from above and below of the molecular plane, the broad d-d transition band of complexes moves gradually to the red with the increase of the Lewis basicity (DN) of the solvent. This originates in variation of Lewis acid-base interaction between the complex ion and the respective solvent molecules or anion.

Some remarks on the solute-solvent interaction resolved from the data in Table 4 are of immediate notes with discussing, (a) the λ<sub>max</sub>



**Figure 1:** Electronic absorption spectra of 2.39 × 10<sup>-3</sup> mol Cu<sub>2</sub>(dim)(Me<sub>2</sub>en)<sub>2</sub>(ClO<sub>4</sub>)<sub>3</sub>O complex, two solutions in various organic solvents at 25°C.

of the present complexes in 1,2-dichloroethane (DCE) occur at longer wavelength than in nitro methane ( $\text{CH}_3\text{NO}_2$ ), although the donor number of DCE (DN=0) is lower than that of  $\text{CH}_3\text{NO}_2$  (DN=2.7). This anomaly was ascribed to the formation of ion pairs by mean of an axial coordination of  $\text{ClO}_4^-$  anion in DCE. As the relative dielectric constant of nitromethane 28.5 versus 8.9 for DCE at room temperature; facilitating the dissociation of cationic complex and minimizes the axial interactions of  $\text{ClO}_4^-$  with the central copper(II) ion [26]. (b) Finally, although donor strength (DN), of acetone is higher than that of acetonitrile, the solutions of the present perchlorate of diamine-complexes 1 and 2 in acetone show a slightly lower  $\nu_{\max}$  values than acetonitrile solution. This discrepancy was recognized to the effect of steric and  $\pi$ -bonding in acetone and acetonitrile, since they are acting in opposite directions [27].

The extraction of chemical information from the data in Table 4 can be carried out by statistical method of Multiple Linear Regression Analysis (MLRA). In this method, a dependent variables Y ( $\nu_{\max}$ ) is described in terms of a series of explanatory variables X. In this respect, the well known Gutmann's and Mayer's donor-acceptor numbers (DN and AN) [28] and the unified solvation model of Drago [29-31] were used, according to Equations 1 and 2; respectively.

$$\nu_{\max}/10^3 \text{ cm}^{-1} = \nu^0 + a(\text{DN}) + b(\text{AN}) \quad (1)$$

$$\nu_{\max}/10^3 \text{ cm}^{-1} = W + P(S) + E_B E_A + C_B C_A \quad (2)$$

It is assumed that all the explanatory variables are independent of each other and truly additive as well as relevant to the problem under study [30,31] where DN and AN refer to the solvent Lewis basicity and acidity; respectively [28]. S is the solvent bipolarity term; P is a measure of the susceptibility of the complex to solvation.  $E_B$ ,  $C_B$  and  $E_A$ ,  $C_A$  quantify the electrostatic and covalent contributions to the Lewis basicity and acidity; respectively [29-31]. For acceptor probes, (complexes 1 and 2),  $E_B$  and  $C_B$  solvent parameters are used in Equation 2. Nevertheless,  $E_A$  and  $C_A$  reflect the physicochemical acceptor parameters of the complex under investigation. However  $E_A$  and  $C_A$  solvent parameters were used as an alternative in case of complex 3.

The following discussion examines the data of the current complexes. The overall picture which emerges from the MLRA based on Guttmann's donor-acceptor concept is considered followed by the unified solvent model proposed by Drago. The frequencies of d-d absorption transition band ( $\nu_{\max}$ ) of the current complexes in various solvents (Table 4) are fitted in Equations 1 and 2. The Regression

coefficients and constant values are shown in Table 6.

Fitting spectral data of the current complexes (Table 4) in Equation 1 indicates dependence of the d-d absorption transitions on the DN and AN parameters. The relative percentage of the influences of DN and AN parameters on the  $\nu_{\max}$  values were calculated from the coefficients a and b, and found in the ranges 16.23-96.7% and 3.23-83.77%; respectively. The data in Table 6 suggests that, the DN parameter of the solvent has the dominant contribution (61.30-96.77%) in the shift of d-d absorption band of the perchlorate complexes 1, 2 and 4. However, the AN parameter (83.77%) is more pronounced than the DN parameter (16.23%) in case of chloride complex 3. The negative signs of the coefficients a and b for the current complexes indicate a red shift as the Lewis acid- base interactions increases. Complexes 1 and 2 are highly sensitive towards the Lewis basicity of solvent than complex 4 as indicated from their contribution percentage of DN (89.7-96.8) for the former and 61.3% for the later.

Fitting the  $\nu_{\max}$  data (Table 4) in Equation 2 indicates dependence of the observed spectral shifts on the dipolarity/polarizability parameter P(S) and both components of the Lewis acid-base quantification, E and C parameters. The regression coefficients reported in Table 6 indicate that, the shift of the d-d absorption transitions of the chloride complex 3 is mainly influenced by the specific term of solute-solvent interaction (contribution percentages, 96%); in which the contribution of the covalency part (C) is more pronounced than the electrostatic part (E). However the contributions of E (67.65 and 56.00%) are more pronounced than C (11.7 and 3.3%) for the perchlorate complexes 1 and 4, respectively; whereas in case of perchlorate complex 2, E smaller than C (22.40 and 33.51%). In the same way the non-specific term plays a significance role on the d-d transition of complexes 2 and 4 than complex 1.

The d-d transition band in the visible region of the electronic absorption spectrum of the investigated complexes is completely resolved, which allows an accurate determination of the band's oscillator strength (f) as described earlier [8]. The oscillator strength, f, is a dimensionless quantity that is used to express the electronic transition probability [23]. Table 7 collects f-values of the present complexes, in several solvents.

Once more, the data in Table 7 reveals the dependence of the d-d transitions on the Lewis acid base interactions of the current Cu(II)-complexes with the solvent molecules as indicated from the

No	Complex	$\nu(\text{C=O})$		C=C	$\nu(\text{ClO}_4^-)$ or			$\nu(\text{Cu-O})$	$\nu(\text{Cu-N})$
	HDMCHD	1613	1582	1474	-	-	-	-	-
1	$\text{Cu}_2(\text{DMCHD})(\text{Me}_3\text{en})_2(\text{ClO}_4)_3 \cdot 2\text{C}_2\text{H}_5\text{OH}$	1624 (m)	-	1468 (w)	1141	1085	626	515	458 (w)
2	$\text{Cu}_2(\text{DMCHD})(\text{Me}_4\text{en})_2(\text{ClO}_4)_3 \cdot 2\text{C}_2\text{H}_5\text{OH}$	1638	1570	1410 (s)	1144	1090	627	525	478
3	$[\text{Cu}_2(\text{DMCHD})(\text{Me}_2\text{en})_2\text{Cl}_2] \cdot \text{Cl} \cdot 2\text{C}_2\text{H}_5\text{OH}$	1674	1602 (s)	1528 (m)	-	-	-	568	500
4	$\text{Cu}_2(\text{DMCHD})(\text{Me}_5\text{dien})_2(\text{ClO}_4)_3 \cdot 2\text{C}_2\text{H}_5\text{OH}$	1637	1618	1572	1143	1089	-	574	478

Table 3: Characteristic infrared frequencies ( $\text{cm}^{-1}$ ) and their tentative assignments of free HDMCHD ligand and its mixed ligand complexes

No	Complex	Py	DMSO	DMF	MeOH	$\text{Me}_2\text{CO}$	MeCN	1.2DCE	MeNO <sub>2</sub>
1	$\text{Cu}_2(\text{DMCHD})(\text{Me}_3\text{en})_2(\text{ClO}_4)_3 \cdot 2\text{C}_2\text{H}_5\text{OH}$	670	646	633	605	571	596	590	525
2	$\text{Cu}_2(\text{DMCHD})(\text{Me}_4\text{en})_2(\text{ClO}_4)_3 \cdot 2\text{C}_2\text{H}_5\text{OH}$	664	646	632	614	576	588	595	525
3	$[\text{Cu}_2(\text{DMCHD})(\text{Me}_2\text{en})_2\text{Cl}_2] \cdot \text{Cl} \cdot 2\text{C}_2\text{H}_5\text{OH}$	749	709	696	661	678	685	620	691
4	$\text{Cu}_2(\text{DMCHD})(\text{Me}_5\text{dien})_2(\text{ClO}_4)_3 \cdot 2\text{C}_2\text{H}_5\text{OH}$	695	692	675	655	645	625	640	630

Table 4: Absorption maxima bands,  $\lambda_{\max}/\text{nm}$  for the  $\text{Cu}_2(\text{DMCHD})(\text{am})_2\text{X}_3$  complexes solutions in various solvents at 25°C.

Chelate	ClO <sub>4</sub> <sup>-</sup>	I <sup>-</sup>	Br <sup>-</sup>	Cl <sup>-</sup>	N <sub>3</sub> <sup>-</sup>	CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>-2</sup>
DN <sub>x</sub> (anion)/MeNO <sub>2</sub>	8.44	28.9	33.7	36.2	34.3	16.9	13.3
Cu <sub>2</sub> (DMCHD)(Me <sub>3</sub> en) <sub>2</sub> (ClO <sub>4</sub> ) <sub>3</sub> ·2C <sub>2</sub> H <sub>5</sub> OH	525	670	677	690	684	-	-
Cu <sub>2</sub> (DMCHD)(Me <sub>4</sub> en) <sub>2</sub> (ClO <sub>4</sub> ) <sub>3</sub> ·2C <sub>2</sub> H <sub>5</sub> OH	567	647	707	705	608	635	573

Table 5: Absorption maxima bands, λ<sub>max</sub>/nm for the Cu<sub>2</sub>(DMCHD)(diam)<sub>2</sub>(ClO<sub>4</sub>)<sub>3</sub> complexes with various anions in MeNO<sub>2</sub> solution at 25°C.

Complex	MLRA using Gutmann parameter, Eqn. 2				MLRA using Drago parameter, Eqn.					Relative contrib.%		
	V <sub>s</sub> <sup>0</sup> /10 <sup>3</sup>	a	b	r	W	P	E	C	r	Non-specific	Specific	
Cu <sub>2</sub> (DMCHD)(Me <sub>3</sub> en) <sub>2</sub> (ClO <sub>4</sub> ) <sub>3</sub> ·2C <sub>2</sub> H <sub>5</sub> OH	19.86	-3.50 (94.59) <sup>*</sup>	-0.20 (5.41) <sup>*</sup>	0.97	18.40	0.468	-1.533	-0.265	0.99	20.65	67.65	11.70
Cu <sub>2</sub> (DMCHD)(Me <sub>4</sub> en) <sub>2</sub> (ClO <sub>4</sub> ) <sub>3</sub> ·2C <sub>2</sub> H <sub>5</sub> OH	19.72	-3.69 (95.35) <sup>*</sup>	-0.18 (4.65) <sup>*</sup>	0.99	14.39	0.745	-0.378	0.566	0.97	44.1	22.4	33.51
[Cu <sub>2</sub> (DMCHD)(Me <sub>4</sub> en) <sub>2</sub> Cl <sub>2</sub> ]Cl·2C <sub>2</sub> H <sub>5</sub> OH	15.72	-0.62 (16.23) <sup>*</sup>	-3.20 (83.77) <sup>*</sup>	0.998	15.32	-0.23	2.18	-3.10	0.99	4.0	39.50	56.30
Cu <sub>2</sub> (DMCHD)(Me <sub>5</sub> dien) <sub>2</sub> (ClO <sub>4</sub> ) <sub>3</sub> ·2C <sub>2</sub> H <sub>5</sub> OH	16.47	-2.075 (61.30) <sup>*</sup>	-1.031 (38.70) <sup>*</sup>	0.98	13.78	0.50	0.69	-0.041	0.97	40.70	56.00	3.30

\*Relative contribution percentage.

Table 6: Solvatochromic parameters of the Cu<sub>2</sub>(DMCHD)(am)<sub>2</sub>X<sub>3</sub> complexes, using Gutmann's and Drag's models (Equations 1 and 2).

No.	Solvent/Complex	F × 10 <sup>3</sup>							F=f <sub>0</sub> +aDN+bAN					el.con	
		PY	DMSO	DMF	MeOH	Me <sub>2</sub> CO	MeCN	CH <sub>2</sub> Cl <sub>2</sub>	f <sub>0</sub>	a	b	r	n	DN	AN
1	Cu <sub>2</sub> (DMCHD)(Me <sub>3</sub> en) <sub>2</sub> (ClO <sub>4</sub> ) <sub>3</sub> ·2C <sub>2</sub> H <sub>5</sub> OH	24.827	24.523	25.027	25.531	27.745	25.916	28.194	28.16	-0.112	-	0.93	6	100	0
2	Cu <sub>2</sub> (DMCHD)(Me <sub>4</sub> en) <sub>2</sub> (ClO <sub>4</sub> ) <sub>3</sub> ·2C <sub>2</sub> H <sub>5</sub> OH	24.634	25.321	22.00	25.308	28.398	30.600	29.553	32.4	-7.37	-4.64	0.99	5	61.4	38.6
3	[Cu <sub>2</sub> (DMCHD)(Me <sub>4</sub> en) <sub>2</sub> Cl <sub>2</sub> ]Cl·2C <sub>2</sub> H <sub>5</sub> OH	14.126	14.018	14.280	15.521	14.659	15.445	16.548	16.2	-3.24	1.33	0.92	7	70.9	29.1
4	Cu <sub>2</sub> (DMCHD)(Me <sub>5</sub> dien) <sub>2</sub> (ClO <sub>4</sub> ) <sub>3</sub> ·2C <sub>2</sub> H <sub>5</sub> OH	11.3	9.581	8.706	9.586	9.734	9.242	8.633	8.3	3.25	-0.68	0.99	5	84.3	15.7

Table 7: Oscillator strength (f) of d-d transition absorption bands of the Cu<sub>2</sub>(DMCHD)(am)<sub>2</sub>X<sub>3</sub> complexes.

linear plots of the f-values versus the Lewis basicity (DN) and Lewis acidity (AN) of solvent:  $f=f_0+aDN+bAN$ , the multi-parametric linear regression data were collected in Table 7. The intercept (f<sub>0</sub>) represent the extrapolated oscillator strength, which was found to be higher for square planar diamine complexes 1 and 2 than the five coordinated, chloro of diamine and the perchlorate of triamine, complexes 3 and 4. For the same complex cation, [Cu<sub>2</sub>(DMCHD)(Me<sub>4</sub>en)<sub>2</sub>]<sup>3+</sup>, as the coordination ability of Lewis base increases f-values decreases.

### Electrochemical studies

Cyclic voltammetric studies were performed for some copper(II) complexes 2 and 3 using a platinum microelectrode, of 1.0 mM L<sup>-1</sup> complex solutions in different solvents and 0.1M L<sup>-1</sup> Bu<sub>4</sub>ClO<sub>4</sub> as supporting electrolyte at scanning rate of 100 mV s<sup>-1</sup>, ferrocene/ferrocinium (Fc/Fc<sup>+</sup>) and bis(biphenyl)chromium (I)/(0) were used

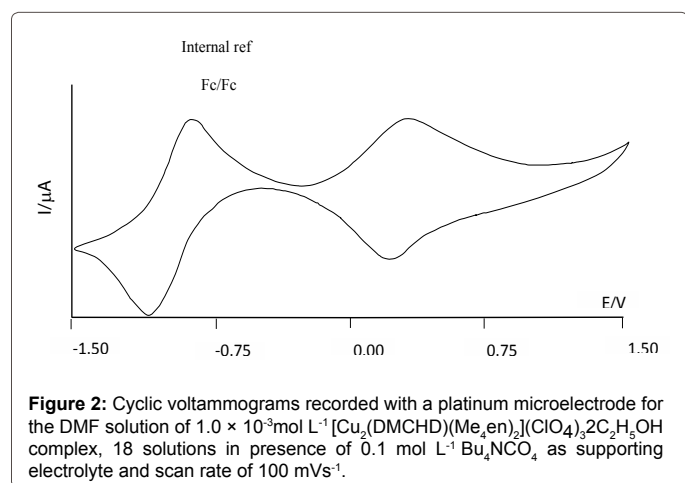
as internal standards for assignment of the potential values, the experimental data are given in Table 8. Since the ligands used in this work are not reversibly oxidized or reduced at the applied potential range values, the redox processes are assigned to the metal centers only. The reduction process of the investigated complexes in all solvents exhibited a quasi-reversible or quasi-irreversible, redox associated with a two-electron reduction, and mainly diffusion controlled as indicated from the linear dependence of the current peak on the square root of the scan rate [32-34].

Taking into account the cyclic voltammetric behavior of [Cu<sub>2</sub>(DMCHD)(Me<sub>4</sub>en)<sub>2</sub>Cl<sub>2</sub>]Cl complex 3, in DMF solution (Figure 2) one can propose the following mechanism consisting of electrode and chemical reactions:

(a) the cathodic peak can be assigned to the cathodic reduction

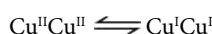
Solvent	$\text{Cu}_2(\text{DMCHD})(\text{Me}_4\text{en})_2(\text{ClO}_4)_3$				$\text{Cu}_2(\text{DMCHD})(\text{Me}_4\text{en})_2(\text{Cl})_3$			
	$E_{pc1}$	$E_{pc2}$	$E_{pa1}$	$E_{pa2}$	$E_{pc1}$	$E_{pc2}$	$E_{pa1}$	$E_{pa2}$
MeNO <sub>2</sub>	0.83	—	0.52	—	0.80	0.87	0.015	—
MeCN	0.48	—	0.149	—	0.49	0.58	0.12	—
Fa	0.62	0.91	0.225	0.62	0.61	—	0.62	—
DMF	0.914	0.742	0.127	-	0.632	—	0.567	0.262
DMSO	0.933	0.723	0.713	0.328	0.728	0.908	0.377	0.327

**Table 8:** Electrochemical data for the redox processes of  $\text{Cu}_2(\text{DMCHD})(\text{diam})_2\text{X}_3$  in various solvents potentials E/V vs. bis(biphenyl)-chromium(1) at (pt) ref electrode



**Figure 2:** Cyclic voltammograms recorded with a platinum microelectrode for the DMF solution of  $1.0 \times 10^{-3} \text{ mol L}^{-1} [\text{Cu}_2(\text{DMCHD})(\text{Me}_4\text{en})_2](\text{ClO}_4)_3 \cdot 2\text{C}_2\text{H}_5\text{OH}$  complex, 18 solutions in presence of  $0.1 \text{ mol L}^{-1} \text{ Bu}_4\text{NCO}_4$  as supporting electrolyte and scan rate of  $100 \text{ mVs}^{-1}$ .

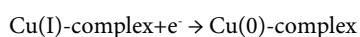
of the dicopper (II) complex to the dicopper (I) complex in a quasi-irreversible mechanism.



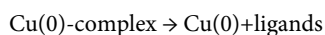
or

(b) Dissociation of the dicopper (II) into a mononuclear complex in solution first, followed by a reduction process for the product; according to the following sequences:

The anodic peak can be assigned to the anodic oxidation of the complex Cu(0), if this one could exist for very short time, to complex Cu(I):

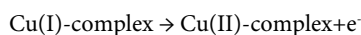


The decomplexation reaction is a chemical reaction occurring because the Cu(0) atom is unable to keep the ligands in a coordination arrangement:



This chemical reaction is fast enough in order to decrease the height of the corresponding anodic peak in which complex Cu(0) is involved.

The very prominent anodic peak, probably due to the anodic oxidation of the complex Cu(I) to complex Cu(II).



So that one may conclude that the mechanism of the single cyclic voltammetry behaviour of the complex Cu(II) is described by an EECE or EEC mechanism. (C=chemical complication following the charge transfer E), rather than a simple EE mechanism. It is more

likely that, according to the Marcus theory, the activation barrier to electron transfer is increased, slowing down the rate of heterogeneous charge transfer, i.e., causing distinct deviation from the pure reversible character of the charge transfer [35].

The potential values of the redox peaks ( $E_{pc}$  and  $E_{pa}$ ) of the investigated complexes in different solvents are given in Table 8. The  $E_{pc}$  potentials for the binuclear perchlorate and chloride Cu(II) complexes depend again on the Lewis acid-base solvent's properties. The trend of data also agrees well with the visible absorption spectral results in various solvents where, complex 2:  $E_{pc1}/v = 6.562 - 3.63 \times 10^{-4} v/\text{cm}^{-1}$ ,  $r = 0.94$  (4 points, except MeNO<sub>2</sub>); and  $E_{pa1}/v = 1.716 + 1.16 \times 10^{-4} v/\text{cm}^{-1}$ ,  $r = 0.93$  (4 points, except DMSO)

However complex 3  $\text{Cu}_2(\text{DMCHD})(\text{Me}_4\text{en})_2\text{Cl}_3$ :  $E_{pc1}/v = 7.778 - 4.78 \times 10^{-4} v/\text{cm}^{-1}$ ,  $r = 0.99$  (3 points, except MeNO<sub>2</sub> and Fa); and  $E_{pa1}/V = 8.26 + 5.73 \times 10^{-4} v/\text{cm}^{-1}$ ,  $r = 0.99$  (3 points, except DMF and DMSO)

The combination of electrochemical and spectroscopic studies enables one to investigate the axial ligation of the solvatochromic complexes in detail that can be utilized to achieve a microscopic understanding of the specific and non-specific Lewis-acid base interactions of the current Cu(II)-complexes with solvent molecules.

### Molecular orbital calculations

Table 9 shows the structural parameters data of the free ligands and their Cu(II)-complexes as calculated by means of a semi-empirical molecular orbital calculations at the PM3 level provided by the hyperchem 7.52 program. The calculated energies of the Frontier orbitals, lowest unoccupied ( $E_{LUMO}$ ) and highest occupied molecular orbitals ( $E_{HOMO}$ ) and  $E_{gap}$  ( $E_{gap} = E_{LUMO} - E_{HOMO}$ ) of the ligands and their complexes are correlated with the current experimental data (Tables 3 and 4):  $E_{gap}/eV = 9.597 - 0.0157 \Delta(\nu_{C=O-C=C})/\text{cm}^{-1}$ ,  $r = 0.92$ , and  $E_{HOMO}/eV = 8.558 - 0.0131 \Delta(\nu_{C=O-C=C})/\text{cm}^{-1}$ ,  $r = 0.92$  except complex 1. The negative slope of these linear relationships reveals increasing of both  $E_{gap}$  and  $E_{HOMO}$  accompanied by decreasing the separation in frequencies between the carbonyl group,  $\nu_{C=O}$  and adjacent  $\nu_{C-C}$ . This finding is further emphasized by the negative slope of the linear relationship of the calculated  $E_{HOMO}$  (Table 9) versus the d-d transition  $\nu_{max}$ :  $E_{HOMO}/eV = 14.127 - 4.54 \times 10^{-4} \nu_{max}/\text{cm}^{-1}$ ,  $r = 0.92$ , except complex 1. The negative slope recommends again increasing of  $E_{HOMO}$  was accompanied by red shift of d-d band. Figure 3 shows the optimized structure of the current complex 1 as an example.

**Biological activity studies:** Table 10, summarized the biological activity of  $\text{Cu}_2(\text{DMCHD})(\text{Me}_5\text{dien})_2(\text{ClO}_4)_2$  complex. Investigation

was carried out against the sensitive organisms *Staphylococcus aureus* (ATCC 25923) and *Bacillus subtilis* (ATCC 6635) as Gram-positive bacteria, *Escherichia coli* (ATCC 25922) and *Salmonella typhimurium* (ATCC 14028) as Gram-negative bacteria, yeast; *Candida albicans* (ATCC 10231) and fungus; *Aspergillus fumigates* as described elsewhere [36]. Inspection of the data reveals that the metal complex exhibited intermediate activity towards the Gram- positive bacteria *Bacillus subtilis* (ATCC 6635), also intermediate activity towards the Gram-negative bacteria *Salmonella typhimurium* (ATCC 14028). However, low antimicrobial activity was observed against Yeasts and Fungi; similar to that observed earlier for  $\text{Cu}(\text{DMCHD})(\text{Me}_3\text{dien})(\text{NO}_3)$  [11].

## Conclusion

A newly compounds have been synthesized and characterized on the basis of spectral, conductance, magnetic and electrochemical studies on the complexes were carried out in solution and in solid state; UV-visible spectra on the solution of the complexes in various solvents are found to be depending upon the type of solvent. The absorption coefficient spectrum in the UV-Vis region shows absorption bands and generally interpreted in terms of  $\pi-\pi^*$  excitation. The metal complex  $\text{Cu}_2(\text{DMCHD})(\text{Me}_3\text{dien})_2(\text{ClO}_4)_2$  showed intermediate activity toward the Gram- positive and Gram-negative bacteria, and low antimicrobial activity against yeasts and fungi.

## References

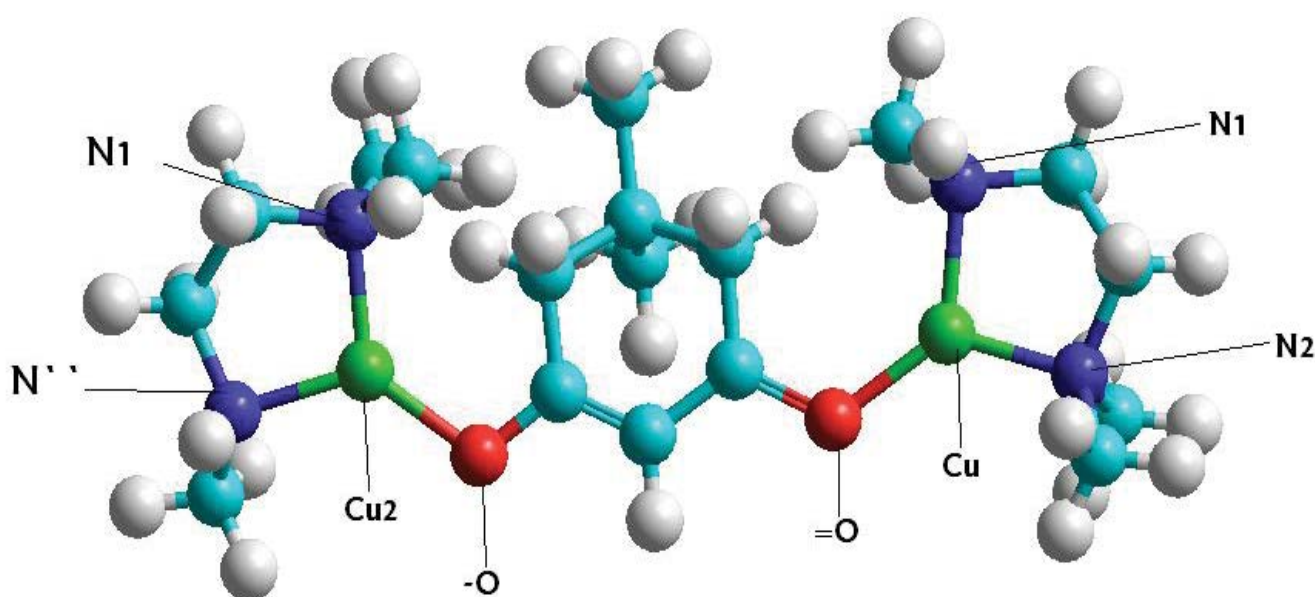


Figure 3: Optimized structure of complex 1  $\{\text{Cu}_2(\text{DMCHD})(\text{Me}_3\text{en})_2(\text{ClO}_4)_3 \cdot 2\text{C}_2\text{H}_5\text{OH}\}$ .

No	Organic ligand and complex	$E_{\text{tot}}$ Kcal/mol	Dipole moment	$\Delta H_f$ Kcal/mol	Electr E Kcal/mol	Nuclear E Kcal/mol	Binding E Kcal/mol	$E_{\text{homo}}$ ev	$E_{\text{lumo}}$ ev	$\Delta E_{\text{gap}}$
A	$\text{Me}_4\text{en}$	-29581.82	1.20	-13.30	-158075.95	128494.13	-2098.27	-8.981	2.388	11.369
B	$\text{Me}_3\text{en}$	-26136.84	1.74	-11.45	-128743.73	102606.88	-1821.32	-9.092	2.422	11.514
C	Dimedone free (HDMCHD)	-39685.20	4.94	-90.39	-204106.53	164421.32	-2201.85	-9.712	-0.014	9.698
D	$\text{Me}_3\text{dien}$	-44015.22	2.40	-16.52	-284075.25	240059	-30092.00	-8.850	2.270	11.12
1	$[\text{Cu}_2(\text{DMCHD})(\text{Me}_3\text{en})_2\text{ClO}_4]$	-146288.39	6.90	-219.03	-1130492.39	984204.5	-6059.55	-0.661	1.971	2.632
2	$\text{Cu}_2(\text{DMCHD})(\text{Me}_4\text{en})_2(\text{ClO}_4)_3$	-153186.66	3.715	-231.38	-1264009.33	1110822.65	-6622.08	-5.314	1.026	6.34
3	$[\text{Cu}_2(\text{DMCHD})(\text{Me}_4\text{en})_2\text{Cl}_2\text{Cl}]$	-175811.37	15.85	-255.50	-1576159.37	1400348.00	-6837.38	-7.190	-0.5448	6.646
4	$\text{Cu}_2(\text{DMCHD})(\text{Me}_3\text{dien})_2(\text{ClO}_4)_3$	-110636.36	5.871	-107.24	-943728.00	833091.93	-5322.66	-7.439	1.467	8.906

Table 9: Structural parameters of the organic ligands and their metal complexes using hyperchem 7.5 at pm3 level.

Organism	Gram-positive bacteria				Gram-negative bacteria				Yeasts and Fungi <sup>††</sup>			
	<i>Staphylococcus aureus</i> (ATCC 25923)		<i>Bacillus subtilis</i> (ATCC 6635)		<i>Salmonella typhimurium</i> (ATCC 14028)		<i>Escherichia coli</i> (ATCC 25922)		<i>Candida albicans</i> (ATCC 10231)		<i>Aspergillus fumigatus</i>	
Concentration	1 mg/ml	0.5 mg/ml	1 mg/ml	0.5 mg/ml	1 mg/ml	0.5 mg/ml	1 mg/ml	0.5 mg/ml	1 mg/ml	0.5 mg/ml	1 mg/ml	0.5 mg/ml
Sample	10 L	7 L	13 I	9 I	12 L	8 L	15 I	11 I	9 L	7 L	10 L	6 L
<b>Cu(DMCHD)(Me<sub>3</sub>dien)(NO<sub>3</sub>)</b>	10 L	7 L	13 I	9 I	12 L	8 L	15 I	11 I	9 L	7 L	10 L	6 L
<b>Control<sup>#</sup></b>	35	26	35	25	36	28	38	27	35	28	37	26

<sup>††</sup>Identified on the basis of routine cultural, morphological and microscopical characteristics.

L: Low activity=Mean of zone diameter  $\leq 1/3$  of mean zone diameter of control.

I: Intermediate activity=Mean of zone diameter  $\leq 2/3$  of mean zone diameter of control.

H: High activity=Mean of zone diameter  $> 2/3$  of mean zone diameter of control.

<sup>#</sup>Chloramphenicol in the case of Gram-positive bacteria, cephalothin in the case of Gram-negative bacteria and cycloheximide in the case of fungi.

**Table 10:** Antimicrobial activity of Cu<sub>2</sub>(DMCHD)(Me<sub>3</sub>dien)<sub>2</sub>(ClO<sub>4</sub>)<sub>3</sub>·2C<sub>2</sub>H<sub>5</sub>OH

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