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Spectroscopic, solvent influence and thermal studies of ternary copper(II) complexes of diester and dinitrogen base ligands

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ABSTRACT

New mixed-ligand copper(II) complexes containing the bidentate dinitrogen ligands [*N*,*N*,*N*',*N*'-tetramethylethylenediamine (tmen), 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen)] and the bidentate dioxygen ligands [diethylmalonate (DEM), ethylacetoacetate (EAA) and ethylbenzoylacetate (EBA)] were prepared. The complexes were characterized by elemental analysis, infrared, mass and ESR spectral data, magnetic and molar conductance measurements and thermal gravimetric analysis. From the investigation, the geometries of the complexes are square planar for perchlorate complexes and a square pyramid or octahedral for the nitrate complexes. Solvatochromic behavior of the Cu(II) complexes indicates strong solvatochromism of their solutions in polar and non-polar solvents. The observed solvatochromism is due to the solute–solvent interaction between the chelate cation and the solvent molecules.

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1. Introduction

Solvatochromism in the mixed-ligand metal complexes has received great attention because they may be used as a Lewis acid–base color indicator [1-6] and also utilizes to develop optical sensor materials to monitor pollutant levels in the environment [7-11].

The effect of the solvent on the spectral properties of molecules, generally referred as solvatochromism, has been investigated for many years, generating a copious literature [12–16].

Solvatochromism of metal complexes can be divided into three types [2,3]; the first one comprises the case where the color changes are by the direct attachment of solvent molecules onto metal center, and the solvatochromic bands could be of metal-to-ligand or ligand-to metal character and the second type is due to the attachment of solvent molecules onto ligands, while the third type of the solvatochromic bands could be of ligand-to-ligand or intra-ligand character. Among the former whose color changes are due to those of d–d transitions, copper(II) complexes with a strong Jahn–Teller effect can be anticipated to show simple and regular changes in their electronic spectra according to the strength of interactions with solvent molecules at the axial sites [7,8,18,19].

Several works have been published concerning the solvatochromism by Fukuda, Sone and others where the dioxygen ligands were taken as β -diketones [8,12,17,18].

Recently, several studies were made on the solvatochromic behavior of Cu(II) complexes using the dioxygen ligands as o-hydroxy benzoyl derivatives with dinitrogen ligands [19]. Also, the solvatochromic mixed-ligand copper(II) complexes with the general formula [Cu(Rmal)(diam)]X where Rmal=malonate derivatives and diam=diamine derivatives and X^- = ClO₄⁻or Cl⁻ were synthesized and characterized by spectroscopic, magnetic, molar conductance and electrochemical measurements [20]. The mass spectra along with the analytical data suggest a bridged binuclear structure for the chloride complexes, while perchlorate complexes showed either mononuclear or bridged binuclear structure.

The present work reports the syntheses, spectral, thermal and solvatochromic behavior of some mixed-ligand copper(II) complexes of the general formula, Cu(OO)(NN)X where (OO) = diethylmalonate, ethylacetoacetate or ethylbenzoylacetate and (NN) = N,N,N',N'-tetramethylethylenediamine (tmen), 2,2'-bipyridine (bipy) or 1,10-phenanthroline (phen) and X⁻ = NO₃⁻, ClO₄⁻ or Br⁻.

The structure of the 18 new complexes is proved using elemental analysis, infrared and electronic, mass spectra, electron spin resonance, thermal gravimetric analysis, magnetic and molar conductivity measurements.

Although all perchlorate complexes exhibit square planar geometry, the nitrate and bromide complexes exhibit either square pyramid or octahedral geometry. Fig. 1 is a representative structure

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Fig. 1. Schematic representation of the Cu(II) complexes.

of the complexes. Of these, four Cu(II) complexes show solvatochromic behavior as will be shown.

2. 2-Experimental

2.1. Materials

Copper nitrate tri hydrate Cu(NO₃)₂•3H₂O, copper perchlorate hexa hydrate Cu(ClO₄)₂•6H₂O, diethylmalonate (DEM), ethylacetoacetate (EAA), ethylbenzoylacetate (EBA), *N*,*N*,*N*',*N*'tetramethylethylenediamine (tmen), 2,2'-bipyridine (bipy), 1,10phenanthroline (phen), anhydrous sodium carbonate (Na₂CO₃) and tertiary tetrabutylammonium bromide *t*-Bu₄NBr were analytical reagent grade and obtained from either Merck or Aldrich and were used without further purification. Organic solvents used for spectral studies were nitrobenzene (PhNO₂), acetonitrile (MeCN), methanol (MeOH), ethanol (EtOH), acetone (Me₂CO), methylenechloride (CH₂Cl₂), *N*,*N*-dimethylformamide (DMF) and dimethylsulfoxide (DMSO) were spectro-grade and used without further purification.

2.2. Syntheses of Cu(OO)(NN)X complexes

These complexes were prepared by adding a mixture of 5.0 mmol of dioxygen ligand in 20 mL absolute ethanol and 10 mmol of anhydrous Na₂CO₃ to an ethanolic solution of 5.0 mmol of $CuX_2 \bullet nH_2O$ (where X⁻ = NO₃⁻ or ClO₄⁻). The mixture was stirred for about 30 min resulting in a green solution, which was then filtered. Then a solution of 5.0 mmol diam (where diam = tmen, bipy or phen) in 10 mL absolute ethanol was added dropwise to the filtrate with a continuous stirring for an additional half an hour. The nine complexes [Cu(DEM)(tmen)]NO₃ and [Cu(DEM)(tmen)]ClO₄ $[Cu(EAA)(tmen)(NO_3)]^{\bullet}2H_2O, [Cu(EAA)(tmen)]ClO_4, [Cu(EAA) (bipy)(NO_3)(H_2O)]^{\bullet}H_2O, [Cu_2(EAA)_2(phen)_2(NO_3)_2(H_2O)]^{\bullet}H_2O,$ [Cu(EBA)(tmen)(NO₃)(H₂O)], [Cu(EBA)(tmen)]ClO₄ and [Cu(EBA) (bipy)(NO₃)(H₂O)]•H₂O were freely soluble in ethanol. These complexes were filtered off and left to stand overnight and then were recrystallized from CH₂Cl₂ solvent, where dark blue crystals were obtained.

The bromide complex [Cu(OO)(tmen)Br] was prepared in solution by mixing *t*-Bu₄NBr with $[Cu(OO)(tmen)]ClO_4$ in CH₂Cl₂ solvent (molar ratio of 5:1).

[N.B. Caution: the melting point, mass spectra and thermal analysis were not possible to be used in the perchlorate complexes due to its detonation effect.]

These complexes were not isolated in the solid state, and were used to study the effect of the bromide anion on the complexes in solution, in different solvents.

The following detailed preparations are given as examples and the other complexes were obtained similarly.

2.2.1. Synthesis of complex (2)

Add a mixture of (0.801 g, 5.0 mmol) of diethylmalonate (DEM) in 20 mL absolute ethanol and (1.060 g, 10.0 mmol) of anhydrous Na₂CO₃ to an ethanolic solution of (1.853 g, 5.0 mmol) Cu(ClO₄)₂•6H₂O. The mixture was stirred for about 30 min resulting in a green solution, which was then filtered. Then a solution of (0.581 g, 5.0 mmol) of *N*,*N*,*N*'.tetramethylethylenediamine (tmen) in 10 mL absolute ethanol was added dropwise to the filtrate with a continuous stirring for an additional half an hour. A solution was formed which was filtered off and left to stand overnight and then was recrystallized from CH₂Cl₂ solvent. Dark blue crystals were formed. The yield was 1.217 g (59.3%).

2.2.2. Synthesis of complex (7)

Add a mixture of (0.651 g, 5.0 mmol) of ethylacetoacetate (EAA) in 20 mL absolute ethanol and (1.060 g, 10.0 mmol) of anhydrous Na₂CO₃ to an ethanolic solution of (1.208 g, 5.0 mmol) Cu(NO₃)₂•3H₂O. The mixture was stirred for about 30 min, resulting in a green solution, which was then filtered. Then, a solution of (0.581 g, 5.0 mmol) of *N,N,N',N'*-tetramethylethylenediamine (tmen) in 10 mL absolute ethanol was added dropwise to the filtrate with a continuous stirring for an additional half an hour. A solution was formed which was filtered off and left to stand overnight and then was recrystallized from CH₂Cl₂ solvent. Violet crystals were formed. The yield was 1.660 g (79.1%) and its melting point was 200 °C.

2.2.3. Synthesis of complex (14)

Add a mixture of (0.864 g, 5.0 mmol) of ethylbenzoylacetate (EBA) in 20 mL absolute ethanol and (1.060 g, 10.0 mmol) of anhydrous Na₂CO₃ to an ethanolic solution of (1.853 g, 5.0 mmol) Cu(ClO₄)₂•6H₂O. The mixture was stirred for about 30 min resulting in a green solution, which was then filtered. Then a solution of (0.581 g, 5.0 mmol) of *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (tmen) in 10 mL absolute ethanol was added dropwise to the filtrate with a continuous stirring for an additional half an hour. A solution was formed which was filtered off and left to stand overnight and then was recrystallized from CH₂Cl₂ solvent. Violet crystals were formed. The yield was 2.332 g (77.3%).

2.3. Physical measurements

The analysis of carbon, hydrogen and nitrogen were carried out at the Microanalytical Center, Cairo University, Giza, Egypt. Copper ions were determined by EDTA solution using muroxide, as an indicator. FT-IR spectra ($4000-400 \text{ cm}^{-1}$) of the compounds were recorded as KBr discs using FT-IR (shemedzo) spectrophotometer model 4000. The UV-vis spectra of the compounds were obtained on a JASCO model V-550 UV-vis spectrophotometer. Mass spectra were carried out by a shimadzu-GC–MS–QL mass spectrometer model 1000EX using a direct inlet system. TGA curves were obtained using NETZSCH-gerateban Bestell-Nr 348472c. Thermal analyzer equipped with a thermobalance. Samples (~50 mg) were heated at a programmed rate of 5 °C min⁻¹ in a dynamic N₂ atmosphere. The sample was contained in a boat-shaped platinum pan suspended in the center of a furnace. Meting points reported in this work were not corrected. Magnetic susceptibilities were measured at room temperature using a magnetic susceptibility balance (Johnson Matthey Alfa product, Model No. MKI). ESR spectra were recorded on a Bruker Model EMX, X-band spectrometer. Diamagnetic corrections calculated from Pascal's constants [21]. Molar conductance of 10^{-3} M solutions of the complexes in CH₂Cl₂ and DMF solutions were measured on a Corning conductivity meter NY 14831 model 441 (USA)

3. Results and discussion

The ternary metal complexes were prepared in the molar ratio 1:1:1 from diethylmalonate, dinitrogen bases (tmen, bipy and phen) and copper ions associated with NO₃⁻ or ClO₄⁻ as counter-anions in absolute ethanol. The diester possesses monobasic bidentate dioxygen ligand, while all dinitrogen bases are neutral bidentate ligands. All Cu(II) complexes carried one positive charge due to the presence of α -hydrogen in the diester where the structure of the diester exists in several tautomeric forms due to the presence of α -hydrogen of the methylene group, where the deprotonated (anionic form IV) is the active form, which binds to the Cu(II) center compensating one positive charge of Cu(II). Scheme 1 represents the tautomeric forms of the diethylmalonate.

Eighteen new Cu(II) complexes were identified by infrared, electronic, mass, electron spin resonance spectra, and magnetic and molar conductivity measurements. Solvatochromic properties were studied to investigate the effect of ligands and anions on the structure of the complex and its chromotropic behavior. Based on the effect of the anion and solvents, the Cu(II) complexes exhibit different geometrical arrangements such as a square planar, square pyramidal and octahedral arrangements. Table 1 lists the physical and analytical data of the complexes.

3.1. Infrared spectra

The vibrational assignments of the Cu(II) complexes were aided by comparison with the vibrational frequencies of the starting materials [22–27]. Table 2 lists the characteristic infrared bands for 1–18 complexes. A comprehensive vibrational survey of the derivative ligands are published by other authors and the references are cited in the text.



Scheme 1. Schematic representation of the tautomeric forms (I–III) of the diester ligands ($R=OC_2H_5$ for DEM, $R=CH_3$ for EAA and $R=C_6H_5$ for EBA). Form IV is a general form.

There are five conceptual features in the infrared spectra of the complexes. In case of the free perchlorate, ClO_4^- , there are four vibrational bands observed at 935, 460, 1050–1170 and 630 cm^{-1} . The third and fourth bands appear strongly in the infrared spectra. The strong bands observed in the perchlorate Cu(II) complexes 2, 4, 6, 8, 10, 12, 14, 16 and 18 at the range 1084-1117 cm⁻¹ (antisymmetric stretch) and the sharp band at $621-625 \text{ cm}^{-1}$ (antisymmetric bend) suggest uncoordinated perchlorate anions [23]. The free nitrate, NO₃⁻, ions exhibited two bands which are observed at 1384 and 856 cm⁻¹. Three strong vibrational bands for the nitrate groups were observed at 1357-1383, 1272-1277 and 952-972 cm⁻¹ which indicate that it is coordinated in complexes 1, 3, 5, 7, 9, 11, 13, 15 and 17. Unidentate nitrate groups show C_{2V} symmetry, with three non-degenerate modes of vibration $(\nu_s, \nu_s' \text{ and } \nu_{as})$, where $\nu_s(NO_3^{-1})$ is in the range 1357–1383 cm⁻¹, $\nu_{\rm s}'({\rm NO_3}^-)$ 1272–1296 cm⁻¹ and $\nu_{\rm as}({\rm NO_3}^-)$ 905–1026 cm⁻¹ [24]. The $v_{\rm s}({\rm NO}_3^-)$ of the unidentate ${\rm NO}_3^-$ is markedly shifted to lower frequency compared to that of the free nitrate (1384 cm^{-1}) [24] providing a measure of the covalent bond strength due to transfer of electron density from NO₃⁻ to the metal ion.

The second feature is related to the ethyl groups which appeared at the range $2801-3118 \text{ cm}^{-1}$. This indicates that it still persist in the complexes compared with their precursors [25].

The third feature is the dioxygen (OO) ligand in the ternary complexes exhibited two partially resolved bands at 1602–1665 and 1514–1586 cm⁻¹, which assigned to v_{as} (COO) and a single band at 1457–1484 cm⁻¹ for v_s (COO). Generally, the free dioxygen ligand showed a strong broad band at 1739 cm⁻¹ [26]. This band was shifted to lower frequencies which appeared at 1602–1628 and 1565–1586 cm⁻¹. This lowering shift may be due to the chelation of the oxygen atoms of the carbonyl group in the dioxygen ligand.

The fourth feature is about the characteristic bands of the dinitrogen base ligands. Changes are observed in the infrared spectrum of bipy, when it is coordinated with the metal centers. The characteristic band of the C=N group in complexes 3, 4, 9, 10, 15 and 16 are shifted to lower frequencies compared with the free ligand at 1570 cm^{-1} [27]. This suggests that both nitrogens of 2,2′bipy are coordinated to the metal ion [28]. Similar behavior has been observed for the C=N vibration of phen, which has a band at 1560 cm^{-1} . This band shifts on coordination to lower frequencies in complexes 5, 6, 11, 12, 17 and 18; respectively, presumably because of coordination to the metal [29].

The last feature is the weak to medium bands in the two ranges 411–518 and 512–593 cm⁻¹, which could be assigned to the stretching frequencies of the ν (Cu–O) and ν (Cu–N) bands [30], respectively, supporting that the bonding of the ligands to the metal ions is achieved by the oxygen of the carbonyl group of the dioxygen ligands and nitrogen atoms of the base ligands.

3.2. Electronic spectra, magnetic and molar conductivity measurements

The electronic spectra for the complexes [Cu(DEM) $(tmen)(NO_3)]^{\bullet}2H_2O$ (1), [Cu(DEM)(tmen)]ClO₄ (2), [Cu(EAA) $(tmen)NO_3]^{\bullet}2H_2O$ (7), [Cu(EAA)(tmen)]ClO₄ (8), [Cu(EAA)(bipy) $(NO_3)(H_2O)]^{\bullet}H_2O$ (9), [Cu₂(EAA)₂(phen)₂(NO₃)₂(H₂O)]^{\bullet}H₂O (11), [Cu(EBA) $(tmen)(NO_3)(H_2O)$] (13), [Cu(EBA)(tmen)]ClO₄ (14) and [Cu(EBA) $(bipy)(NO_3)(H_2O)$]^ H_2O (15) were obtained in CH₂Cl₂ solutions, while the other complexes were insoluble in most common organic solvents and were not possible to get electronic spectra in solution. The electronic spectra were obtained by reflectance within the range 450–800 nm. It is possible to draw up the electronic transitions and predict the geometry with the aid of the magnetic moment and molar conductivity measurements. Table 3 lists the characteristic electronic spectral bands and the

Table 1 The physical and analytical data of the Cu(DEM)(diam)X complexes.

Complex		Weight; g (mmol)		Empirical formula	M.wt.	Wt. (g) (yield %)	Color	m.p. (°C)	Elemental analysis Found (Calc.) %					
		00 ligand	NN ligand	Metal Salt						С	Н	Ν	Cl	Cu
1	DEM + tmen + Cu(NO ₃) ₂ •3H ₂ O	0.801 (5.0)	0.755 (5.0)	1.208 (5.0)	CuC ₁₃ H ₃₅ N ₃ O ₉	436.5	1.624 (39.6)	Dark blue	245	35.83 (35.74)	6.60 (6.84)	9.63 (9.62)	-	14.65 (14.54)
2	$\rightarrow [Cu(DEM)(tmen)(NO_3)]^{\bullet}2H_2O$ DEM + tmen + Cu(ClO_4)_2^{\bullet}6H_2O $\rightarrow [Cu(DEM)(tmen)]ClO_4$	0.801 (5.0)	0.755 (5.0)	1.853 (5.0)	CuC ₁₁ H ₂₃ N ₂ ClO ₈	410.0	1.217 (59.3)	Dark blue	-	32.10 (32.20)	5.66 (5.61)	6.63 (6.83)	8.90 (8.70)	15.41 (15.48)
3	$DEM + bipy + Cu(NO_3)_2 \bullet 3H_2O$	0.801 (5.0)	0.781 (5.0)	1.208 (5.0)	$\mathrm{CuC_{15}H_{21}N_3O_8}$	476.5	1.065 (37.4)	Bluish-violet	330	37.86 (37.78)	8.76 (8.81)	7.65 (7.39)	-	13.46 (13.33)
4	$\rightarrow [Cu(DEM)(Dipy)(NO_3)(H_2O)] H_2O$ DEM + bipy + Cu(ClO ₄) ₂ •6H ₂ O $\rightarrow [Cu(DEM)(bipy)]ClO_4$	0.801 (5.0)	0.781 (5.0)	1.853 (5.0)	CuC ₁₇ H ₁₉ N ₂ ClO ₈	478.0	1.752 (73.2)	Bluish-violet	-	42.48 (42.67)	4.07 (3.97)	5.31 (5.90)	7.61 (7.43)	13.12 (13.30)
5	$DEM + phen + Cu(NO_3)_2 \bullet 3H_2O$	0.801 (5.0)	0.991 (5.0)	1.208 (5.0)	$Cu_2C_{38}H_{40}N_6O_{15}$	947.0	3.181 (67.1)	Bluish-violet	320	47.86 (48.15)	4.55 (4.22)	8.79 (8.87)	-	13.55 (13.41)
6	$\rightarrow [Cu_2(DEM)_2(phen)_2(NO_3)_2(R_2O)]$ DEM + phen + Cu(ClO ₄)_2 • 6H ₂ O $\rightarrow [Cu(DEM)(phen)]ClO_4$	0.801 (5.0)	0.991 (5.0)	1.853 (5.0)	CuC ₁₉ H ₂₂ N ₂ ClO ₉	520.0	1.172 (45.0)	Bluish-violet	-	45.98 (45.40)	3.93 (3.80)	5.52 (5.58)	7.10 (7.07)	12.00 (12.20)
7	EAA + tmen + Cu(NO ₃) ₂ • 3H ₂ O	0.651 (5.0)	0.755 (5.0)	1.208 (5.0)	$CuC_{12}H_{29}N_3O_8$	406.5	1.660 (79.1)	Violet	200	39.57 (41.33)	7.18 (7.63)	10.41 (10.33)	-	16.03 (15.62)
8	$\rightarrow [Cu(EAA)(tmen)(NO_3)]^2 H_2 O$ EAA + tmen + Cu(ClO ₄) ₂ • 6H ₂ O $\rightarrow [Cu(EAA)(tmen)]ClO_4$	0.651 (5.0)	0.755 (5.0)	1.853 (5.0)	CuC ₁₂ H ₂₅ N ₂ ClO	408.0	1.790 (87.0)	Violet	-	35.10 (35.29)	6.66 (6.13	6.63 (6.86)	8.90 (8.70)	15.04 (15.56)
9	$= \frac{(cu(EAA)(ch(eh))coo_4}{(cu(EAA)(ch(eh))coo_4}$ $= \frac{(cu(EAA)(ch(eh))coo_4}{(cu(EAA)(ch(eh))coo_4)(ch(eh))coo_4}$	0.651 (5.0)	0.781 (5.0)	1.208 (5.0)	$\mathrm{CuC_{16}H_{21}N_{3}O_{8}}$	446.5	1.412 (63.2)	Green	250	43.41 (43.00)	4.26 (4.70)	9.83 (9.41)	-	13.97 (14.22)
10	$= [Cu(EAA)(bipy)(RO_3)(H_2O)] H_2O$ EAA + bipy + Cu(ClO ₄) ₂ •6H ₂ O $\rightarrow [Cu(EAA)(bipy)]ClO_4$	0.651 (5.0)	0.781 (5.0)	1.853 (5.0)	$\rm CuC_{16}H_{17}N_2ClO_7$	448.0	1.270 (56.5)	Bluish-violet	-	42.48 (42.86)	4.07 (3.79)	6.31 (6.25)	7.61 (7.93)	14.00 (14.18)
11	EAA + phen + Cu(NO ₃) ₂ •3H ₂ O \rightarrow [Cu ₂ (EAA) ₂ (phen) ₂ (NO ₂) ₂ (H ₂ O)]•H ₂ O	0.651 (5.0)	0.991 (5.0)	1.208 (5.0)	$\rm Cu_2C_{36}H_{38}N_6O_{14}$	905.0	3.221 (71.0)	Green	340	46.68 (46.80)	4.01 (4.33)	9.35 (9.10)	-	13.97 (13.76)
12	$EAA + phen + Cu(ClO_4)_2 \cdot 6H_2O$ $\rightarrow [Cu(EAA)(phen)]ClO_4$	0.651 (5.0)	0.991 (5.0)	1.853 (5.0)	$\rm CuC_{18}H_{17}N_2ClO$	472.0	1.940 (81.9)	Bluish-violet	-	45.98 (45.76)	3.93 (3.60)	5.52 (5.93)	7.10 (7.52)	13.22 (13.45)
13	$EBA + tmen + Cu(NO_3)_2 \bullet 3H_2O$ $\rightarrow [Cu(EBA)(tmen)(NO_2)(H_2O)]$	0.864 (5.0)	0.755 (5.0)	1.208 (5.0)	CuC ₁₇ H ₂₉ N ₃ O ₇	450.5	2.682 (82.4)	Violet	155	45.63 (45.28)	6.25 (6.45)	9.64 (9.32)	-	14.01 (14.09)
14	$EBA + tmen + Cu(ClO_4)_2 \cdot 6H_2O$ $\Rightarrow [Cu(EBA)(tmen)]ClO_4$	0.864 (5.0)	0.755 (5.0)	1.853 (5.0)	$\mathrm{CuC_{17}H_{27}N_2ClO_8}$	486.0	2.332 (77.3)	Violet	-	41.86 (41.97)	5.61 (5.56)	5.56 (5.36)	7.51 (7.31)	12.99 (13.07)
15	$EBA + bipy + Cu(NO_3)_2 \circ 3H_2O$ $\Rightarrow [Cu(EBA)(bipy)(NO_2)(H_2O)] \circ H_2O$	0.864 (5.0)	0.781 (5.0)	1.208 (5.0)	$CuC_{21}H_{23}N_3O_8$	508.5	2.313 (67.9)	Green	200	49.64 (49.56)	4.47 (4.52)	8.26 (8.17)	-	12.49 (12.36)
16	$EBA + bipy + Cu(ClO_4)_2 \bullet 6H_2O$ $\Rightarrow [Cu(EBA)(bipy)]ClO_4$	0.864 (5.0)	0.781 (5.0)	1.853 (5.0)	$\rm CuC_{17}H_{19}N_2ClO_8$	446.0	1.703 (57.0)	Blue	-	56.37 (56.50)	4.33 (4.26)	6.41 (6.28)	7.73 (7.96)	14.24 (14.43)
17	$EBA + phen + Cu(NO_3)_2 * 3H_2O$	0.864 (5.0)	0.991 (5.0)	1.208 (5.0)	$\mathrm{CuC}_{23}\mathrm{H}_{21}\mathrm{N}_{3}\mathrm{O}_{8}$	514.5	2.230 (59.4)	Bluish-green	180	54.26 (53.65)	4.15 (4.08)	10.01 (10.11)	-	12.47 (12.34)
18	$EBA + phen + Cu(ClO_4)_2 \bullet GH_2O$ $\rightarrow [Cu(EBA)(phen)]ClO_4$	0.864 (5.0)	0.991 (5.0)	1.853 (5.0)	CuC ₃₂ H ₁₉ N ₂ ClO ₉	534.0	2.829 (79.1)	Blue	-	51.69 (51.08)	3.41 (3.56)	5.12 (5.24)	6.95 (6.65)	11.95 (11.89)

Table 2

Infrared frequencies of the characteristic bands of Cu(II) complexes (cm⁻¹).

	Complexes	ν (CH ₃ CH ₂), ν (CH ₃) and ν (CH) _{aromatic}	ν(CO ⁻)	$\nu(NO_3)$	$\nu(ClO_4)$	ν(Cu-N)	ν(Cu-O)
1	$[Cu(DEM)(tmen)(NO_{2})]$ 2H-O	2020_3016	1612 1567 1/65	1357 1272 052		503	518
2	$[Cu(DEM)(tmen)]ClO_{\ell}$	2020-2080	1626 1586 1460	1557 1272 552	-	512	145
2	[Cu(DEM)(hint)]Clo4	2021 2100	1602 1565 1475	1220 1206 1026	1201 1050 1021 024	522	445
1	[Cu(DEM)(Dipy)(NO3)(1120)] 1120	2521-5105	1602 1505 1475	1380 1290 1020	-	525	444
4	$[Cu(DEW)(DIPY)]CIO_4$	2924-3118	1005 15/1 14/5	-	1100 1084 1011 021	515	411
5	$[Cu_2(DEM)_2(pnen)_2(NO_3)_2(H_2O)]$	2927-3113	1628 1586 1484	1383 1277 972	-	588	430
6	[Cu(DEM)(phen)]ClO ₄	3067	1625 1584 1457	-	1146 1089 1020 622	544	424
7	[Cu(EAA)(tmen)(NO ₃)]•2H ₂ O	2806-3008	1610 1564 1465	1383 1273 989	-	516	477
8	[Cu(EAA)(tmen)]ClO ₄	2807-2993	1613 1517 1472	-	1179 1089 1016 623	513	454
9	[Cu(EAA)(bipy)(NO ₃)(H ₂ O)]•H ₂ O	2933-3109	1607 1521 1474	1381 1286 987	-	585	419
10	[Cu(EAA)(bipy)]ClO ₄	2934-3116	1608 1567 1473	-	1174 1095 1061 622	486	420
11	$[Cu_2(EAA)_2(phen)_2(NO_3)_2(H_2O)]^{\bullet}H_2O$	2937-3055	1607 1514 1477	1383 1282 972	-	488	429
12	[Cu(EAA)(phen)]ClO ₄	2914-3086	1606 1566 1475	-	1150 1117 1064 622	494	433
13	$[Cu(EBA)(tmen)(NO_3)(H_2O)]$	2801-2984	1613 1576 1479	1357 1272 952	-	554	484
14	[Cu(EBA)(tmen)]ClO ₄	2850-2990	1609 1574 1470	-	1200 1092 1021 625	556	486
15	[Cu(EBA)(bipy)(NO ₃)(H ₂ O)]•H ₂ O	2983-3113	1665 1577 1446	1364 1293 1023	-	513	478
16	[[Cu(EBA)(bipy)]ClO ₄	2934-3015	1608 1566 1497	-	1161 1093 1011 621	518	482
17	[Cu(EBA)(phen)(NO ₃)]•H ₂ O	2900-3046	1648 1586 1475	1363 1277 1014	-	597	480
18	[Cu(EBA)(phen)]ClO ₄	3086-3118	1610 1568 1475	-	1146 1089 1020 622	544	477

magnetic moments of the Cu(II) ions in their complexes in the solid state, and the molar conductance measurements.

The electronic transitions due to the organic ligands are not mentioned in the tables, where in all electronic transitions of the Cu(II) complexes, the absorption bands due to the organic ligands were appeared and compared with the electronic transition of the free ligands. Generally, the intensities of the electronic transition bands due to the d–d transitions in the metal complexes are lower than the electronic transitions due to the organic ligands.

Electronic spectral data of the ligands in the Cu(II) complexes were predicted in CH₂Cl₂ solution. In the electronic spectrum of the ligands, five absorption bands at 272–290, 307–319, 363–373, 390–410 and 428–430 nm were characterized. The former two bands correspond to ¹L_a \rightarrow ¹A₁ and ¹L_b \rightarrow ¹A₁ transitions of the aromatic ring of the 1,10-phenanthroline, 2,2'-bipyridine and ethylbenzoylacetate ligands [31]. The third band corresponds to the $\pi \rightarrow \pi^*$ transition of the carbonyl group of the dioxygen ligands (diethylmalonate, ethylacetoacetate and ethylbenzoylacetate) and also, the phenyl rings of 1, 10-phenanthroline, 2,2'-bipyridine and ethylbenzoylacetate. The last two bands correspond to the $n \rightarrow \pi^*$ transitions of the oxygen and nitrogen atoms which are overlapped with the intermolecular charge transfer from the aromatic ring.

The one unsymmetrical band for 2, 4, 6, 8, 10, 12, 14, 16, and 18 complexes at 564, 584, 521, 609, 597, 587, 567, 578 and 589 nm due to ${}^{2}A_{1g} \leftarrow {}^{2}B_{1g}$, ${}^{2}B_{2g} \leftarrow {}^{2}B_{1g}$, ${}^{2}E_{g} \leftarrow {}^{2}B_{1g}$ transitions in a square planar geometry [32]. The one band for 1 and 7 complexes at 656 and 573 nm due to ${}^{2}T_{2g} \leftarrow {}^{2}E_{g}$ transition in square pyramid geometry. The observed one band for 3, 5, 9, 11, 13, 15 and 17 complexes at 708, 693, 678, 702, 645, 678 and 614 nm due to ${}^{2}T_{2g} \leftarrow {}^{2}E_{g}$ transition in octahedral geometry.

The obtained complexes are violet, dark blue, bluish-violet and green crystals. The analytical and molar conductance data suggest the mononuclear structure of the complexes except for $[Cu_2(DEM)_2(phen)_2(NO_3)_2(H_2O)]$ (5) and $[Cu_2(EAA)_2(phen)_2$ $(NO_3)_2(H_2O)]^{\bullet}H_2O$ (11) complexes. The molar conductance values obtained for solutions of these complexes in CH₂Cl₂ were in the range 10, 83, 43, 85, 15, 19, 11, 83 and 14 Ohm⁻¹ cm² mol⁻¹ for complexes 1, 2, 7, 8, 9, 11, 13, 14 and 15; respectively, while in

Table 3

Electronic absorption bands (nm) in CH₂Cl₂ solutions, molecular ion peak, magnetic moment and molar conductance of the copper(II) complexes and their assignments.

	Complex	λ_{max} (nm)	_x (nm) Molecular ion peak ^b Magnetic mome		Molar conductance (Λ	
			m/z (intensity%)		CH ₂ Cl ₂	DMF
1	$[Cu(DEM)(tmen)(NO_3)]$ •2H ₂ O	656 (102)	438(0.5)	1.98	10	97
2	[Cu(DEM)(tmen)]ClO ₄	564 (71)	_	2.17	83	102
3	[Cu(DEM)(bipy)(NO ₃)(H ₂ O)]•H ₂ O	708 ^a	477(4.0)	1.92	-	91
4	[Cu(DEM)(bipy)]ClO ₄	584 ^a	_	2.09	-	105
5	$[Cu_2(DEM)_2(phen)_2(NO_3)_2(H_2O)]$	693 ^a	480(7.0)	2.43 ^c	-	140
6	[Cu(DEM)(phen)]ClO ₄	521 ^a	_	2.14	-	95
7	[Cu(EAA)(tmen)(NO ₃)]•2H ₂ O	573 (84)	411(14.7)	1.99	43	98
8	[Cu(EAA)(tmen)]ClO ₄	609 (74)	_	2.10	85	110
9	[Cu(EAA)(bipy)(NO ₃)(H ₂ O)]•H ₂ O	678 (91)	447(11.9)	1.91	15	91
10	[Cu(EAA)(bipy)]ClO ₄	597ª	_	2.04	-	106
11	$[Cu_2(EAA)_2(phen)_2(NO_3)_2(H_2O)]^{\bullet}H_2O$	702 (88)	471(1.9)	3.07 ^c	19	135
12	[Cu(EAA)(phen)]ClO ₄	587 ^a	_	2.11	-	96
13	$[Cu(EBA)(tmen)(NO_3)(H_2O)]$	645 (69)	453(15)	1.99	11	97
14	[Cu(EBA)(tmen)]ClO ₄	567 (42)	_	2.20	83	103
15	[Cu(EBA)(bipy)(NO ₃)(H ₂ O)]•H ₂ O	678 (77)	509(18.9)	1.94	14	91
16	[[Cu(EBA)(bipy)]ClO ₄	578 ^a	_	2.11	-	104
17	[Cu(EBA)(phen)(NO ₃)]•H ₂ O	614 ^a	563(7.2)	1.93	-	96
18	[Cu(EBA)(phen)]ClO ₄	589 ^a	-	2.13	-	95

Electronic spectra in the visible region were recorded in CH_2Cl_2 solvent and the values (ε_{max}) are in parentheses (mol⁻¹ cm⁻¹). The electronic transitions for the ligands were observed in all copper(II) complexes within the range 200–450 nm, and is not cited in this table.

Molar conductivities (Ohm⁻¹ cm² mol⁻¹) were measured in 10⁻³ mol⁻¹ cm⁻¹ in CH₂Cl₂ and DMF solvents.

^aValues were measured in Nujol mull in the solid state.

^bMass spectra for the perchlorate complexes were not performed due to its detonation effect.

 $^{c}\mu_{eff}$ is the magnetic moment of one Cu(II) ion in the complex.

DMF the values were in the range $91-130 \text{ Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ for the same complexes; respectively.

In CH₂Cl₂ solvent, the values of the perchlorate complexes are in the range of 1:1 electrolytes, while the values of the nitrate complexes are in the non-electrolytic range. In DMF solution, the molar conductance values are in the range 1:1 or 1:2 electrolytes of both the perchlorate and nitrate counter-anions; respectively. This may be due to the fact that the DMF solvent replaced the NO₃⁻ anion in the complexes, which results in the 1:1 or 1:2 electrolytes due to the uncoordinated nitrate ions [33].

The molar conductance for 3, 4, 5, 6, 10, 12, 16, 17 and 18 complexes were measured only in DMF and gave values in the range $91-140 \text{ Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$; respectively. In these complexes DMF replaced the NO₃⁻ anion and all the complexes are in the range 1:1 electrolyte except complexes 5, 11 which are 1:2 electrolyte.

The magnetic moments data of the investigated Cu(II) complexes are found in the range 1.91–2.20 B.M. In general, moments of magnetically dilute complexes are in the range 1.9–2.2 B.M., with compounds whose geometries approach octahedral having moments at the lower end, and those with geometries approaching square planar or tetrahedral having moments at the higher end [34]. This indicates that all the perchlorate complexes are square planar while the nitrate complexes have octahedral geometry except 1, 7 and 17 complexes which are square pyramid.

3.3. Mass and ESR spectra

The mass spectra of the Cu(II) complexes of the nitrate were performed and the molecular ion peak were recorded in Table 2. The molecular ion peaks are coincident with the formula weight of the complexes (See Table 1). This supports the identity of the structure. Schemes 2 and 3 illustrate the fragmentation patterns of the complexes, where complexes 5 and 9 showed the fragmentation of the mononuclear pattern only. The



Scheme 2. Fragmentation patterns of the [Cu₂(DEM)₂(phen)₂(NO₃)₂(H₂O)] complex (5).



Scheme 3. Fragmentation patterns of the [Cu(EAA)(bipy)(NO₃)(H₂O)]•H₂O (9).

mass spectra $[Cu(DEM)(bipy)(NO_3)(H_2O)]^{\bullet}H_2O$ complex (3) and $[Cu(EAA)(tmen)(NO_3)]^{\bullet}2H_2O$ complex (7) were depicted in Fig. 2. The mass spectra of the perchlorates were not performed due to the detonation of the perchlorate compounds.

X-band ESR spectrum of $[Cu(DEM)(bipy)]ClO_4$ complex (4) and $[Cu_2(DEM)_2(phen)_2(NO_3)_2(H_2O)]$ complex (5) were recorded in the solid state at 25 °C. The spectrum of the later complex (4) exhibited one band with g value 2.0811, which is in consistent with the square planar geometry around the Cu(II) ion in the complex. The spectrum

of the later complex (5) exhibited two bands, one of them is sharp with g = 2.1948 and the other is very weak at g = 2.0514. The shape of the spectrum is consistent with the octahedral geometry around each Cu(II) center in the complex.

3.4. Thermal gravimetric analysis

Thermal gravimetric analysis (TGA) was used as a probe to proof the associated water or solvent molecules to be in the



 $\label{eq:Fig.2.} Fig. 2. \ Mass spectra of (A) \ [Cu(DEM)(bipy)(NO_3)(H_2O)]^\bullet H_2O \ complex \ (3) \ and \ (B) \ [Cu(EAA)(tmen)(NO_3)]^\bullet 2H_2O \ complex \ (7).$



Fig. 3. TGA-DrTGA of (A) [Cu(DEM)(tmen)(NO₃)][•]2H₂O (1) and (B) [Cu(EAA)(bipy)(NO₃)(H₂O)][•]H₂O (9).

Table 4

Thermal behavior of the mixed-ligand Cu(II) nitrate complexes.

	Compound	DrTGA peak (°C)	Temperature range (°C)	Decomposition product lost (formula Wt.)	Wt. loss% Found (Calcd.)
1	[Cu(DEM)(tmen)(NO ₃)]•2H ₂ O	70.9	50-89	2H ₂ O (36)	7.874 (8.248)
		184.3	118-205	DEM (159)	37.110 (36.426)
		214.1	210-520	$tmen + NO_2$ (162)	35.964 (37.113)
3	[Cu(DEM)(bipy)(NO ₃)(H ₂ O)]•H ₂ O	80.0	32-142	H ₂ O (18)	3.500 (3.778)
		242.4	148–249	$tmen + H_2O + NO_2$ (223)	47.110 (46.799)
		405.4	255-413	bipy (156)	32.423 (32.739)
5	$[Cu_2(DEM)_2(phen)_2(NO_3)_2(H_2O)]$	146.3	140–165	bipy (156)	32.423 (32.739)
		268.2	214–277	H ₂ O (18)	2.359 (1.901)
		292.7	280-314	$2NO_2 + 4C_2H_4$ (204)	20.992 (21.540)
		461.5	328-490	2CO ₂ (82)	8.281 (9.290)
7	[Cu(EAA)(tmen)(NO ₃)]•2H ₂ O	193.0	145–267	$EAA + 2H_2O(165)$	42.922 (40.291)
		334.1	314-410	tmen (116)	28.135 (28.536)
		442.2	437–524	NO ₂ (46)	11.233 (11.316)
9	[Cu(EAA)(bipy)(NO ₃)(H ₂ O)]•H ₂ O	75.4	41-106	H ₂ O(18)	5.225 (4.032)
		132.2	117–176	$H_2O + C_2H_6$ (46)	9.904 (10.302)
		212.1	179–221	bipy (156)	35.221 (34.938)
		258.3	226-323	NO ₂ (46)	11.092 (10.301)
		474.2	339–534	CH ₃ COCHCOOH (101)	21.277 (22.620)
11	$[Cu_2(EAA)_2(phen)_2(NO_3)_2(H_2O)]^{\bullet}H_2O$	51.6	33-114	H ₂ O(18)	2.525 (1.989)
		137.5	121–157	$C_2H_4(28)$	3.255 (3.094)
		216.9	168–234	$2NO_2 + C_2H_6$ (122)	12.963 (13.481)
		308.4	246-313	$2CO_2 + C_2H_4 + H_2O(134)$	14.703 (14.807)
		372.6	321-426	2phen+2CH ₂ CHO (446)	48.317 (49.282)
13	$[Cu(EBA)(tmen)(NO_3)(H_2O)]$	211.6	175–347	$EBA + H_2O + tmen (325)$	71.588 (72.142)
		442.5	425-504	NO ₂ (46)	8.882 (10.211)
15	[Cu(EBA)(bipy)(NO ₃)(H ₂ O)]•H ₂ O	75.6	65–106	H ₂ O(18)	3.509 (3.355)
		231.1	145-302	$EBA + H_2O + NO_2$ (255)	50.551 (50.148)
		417.1	349-484	bipy (156)	31.558 (30.678)
17	[Cu(EBA)(phen)(NO ₃)]•H ₂ O	87.8	106–179	H ₂ O (18)	3.470 (3.498)
		235.2	209–319	phen (180)	31.994 (34.985)
		468.9	395-563	NO ₂ + EBA (237)	50.00 (46.069)



Fig. 4. Electronic absorption spectra of 4.0 × 10⁻³ mol L⁻¹ of (A) [Cu(DEM)(tmen)]ClO₄ complex (2) and (B) [Cu(EAA)(tmen)(NO₃)]•2H₂O complex (7) solutions at 25 °C.



Fig. 5. Electronic absorption spectra of 4.0 × 10⁻³ mol L⁻¹ of (A) [Cu(EAA)(tmen)]ClO₄ complex (8) and (B) [Cu(EBA)(tmen)]ClO₄ complex (14) solutions at 25 °C.

coordination sphere or in the crystalline form [35]. Thermogravimetric (TGA) was carried out for the nitrate complexes only (complexes 1 and 9 chosen as examples), since the perchlorate ones expected to be explosive if dried. TGA–DrTGA curves of the [Cu(DEM)(tmen)(NO₃)]•2H₂O (1) and [Cu(EAA)-(bipy)(NO₃)(H₂O)]•H₂O (9) were depicted in Fig. 3.

The stages of decomposition, temperature ranges, decomposition product loss as well as the found and calculated weight loss percentages of the complexes are given in Table 4.

The thermal decomposition process of the [Cu(DEM)(tmen) (NO₃)][•]2H₂O complex 1 involves three decomposition steps (Fig. 3(A)). Decomposition of the complex started at 50 °C and finished at 520 °C with three stages. The first stage of decomposition involves the removal of two H₂O molecules in the 50–89 °C temperature range, and is accompanied by a weight loss of 7.874%. The second stage of decomposition occurs in the 118–205 °C temperature range, corresponding to the loss of the DEM ligand, and is accompanied by a weight loss of 37.110%. While the third stage involves the removal of the tmen and the nitrate group a form of NO₂ in the 210–520 °C temperature range, and is accompanied by a weight loss of 35.964%.

The thermal decomposition process of $[Cu(EAA)(bipy)(NO_3)(H_2O)]^{\bullet}H_2O$ complex (9) involves five decomposition

steps (Fig. 3(B)). Decomposition of the complex started at 41 °C and finished at 524 °C with five stages. The first stage of decomposition involves the loss of uncoordinated H_2O molecule in the 41–106 °C temperature range, and is accompanied by a weight loss of 5.225%. The second stage of decomposition occurs in the



Fig. 6. Solvation free energy relationship (DN vs $\nu_{max}/1000$).



Fig. 7. Electronic absorption spectra of $4.0 \times 10^{-3} \text{ mol } L^{-1}$ of (A) [Cu₂(DEM)(tmen)Br] complex (19), (B) [Cu(EAA)(tmen)Br] complex (20) and (C) [Cu(EBA)(tmen)Br] complex (21) solutions at 25 °C.

117–221 °C temperature range, corresponding to the loss of C_2H_4 and coordinated H_2O molecule, and is accompanied by a weight loss of 9.904%. While the third stage involves the removal of bipy ligand in the 179–221 °C temperature range, and is accompanied by a weight loss of 35.221%. The fourth stage occurs in the 226–323 °C temperature range, corresponding to the loss of the nitrate group in the form of NO₂. The last stage of decomposition occurs in the 339–534 °C temperature range, corresponding to the removal of CH₃COCHCOOH molecule, and is accompanied by a weight loss of 21.277%.

3.5. Electronic spectra of the complexes in various solvents

The absorption spectra of complexes 1, 2, 7, 8, 9, 11, 13, 14 and 15 were measured in different organic solvents with different donor numbers (DN), while the complexes 3, 4, 5, 6, 10, 12 and 16 are sparingly soluble in most organic solvents thus the d–d bands of these complexes were recorded in Nujol mulls. These electronic spectra show only one broad band in the visible region due to the promotions of the electron in the lower energy orbital to the hole in d_{x2-y2} orbital of the copper(II) ion (d⁹). The position of this band is shifted to longer wavelength (red shift) as the donor number of solvent increases. Assuming that the approach of the solvent occurs along with *z*-axis, the solvent molecules are repelled by the two electrons in d_z^2 orbital of copper(II) and only the more species can force their way to form strong bonds. Upon coordination, they exert a *z*-component field proportional to their position in the spectrochemical series.

The donor number proposed by Gutmann [26–38] is a measure of the donor ability or Lewis basicity of a solvent molecule measured on the basis of the amount of heat evolved when the same solvent is added to a solution of $SbCl_5$ in DCE.

Thus, while a solvent of low donor number (basicity) has less effect in the band maxima, others with higher values induce larger red shift.

The positions of the d–d absorption bands of the perchlorate complexes were in the range 521–597 nm, while for the nitrate complexes these absorption band ranges from 614 to 708 nm. These absorption bands suggest a square planar geometry for all perchlorate complexes and square pyramid (complexes 1 and 7) or octahedral geometry for the nitrate complexes.

Solvatochromism appeared in $[Cu(DEM)(tmen)]ClO_4$ (2), $[Cu(EAA)(tmen)(NO_3)]^{\bullet}2H_2O$ (7), $[Cu(EAA)(tmen)]ClO_4$ (8) and $[Cu(EBA)(tmen)]ClO_4$ (14) complexes. These complexes exhibit a color change from violet or bluish-violet through blue to green according to the donor number (DN) of the solvent used. Figs. 4 and 5 confirm the solvatochromic behavior in complexes 2, 7, 8 and 14.

Solvatochromic behavior was studied quantitatively by applying the linear solvation free energy relationship [39],

 $\nu_{max}/10^3 = \nu^\circ + a$ (DN). Where ν_{max} is the measured d–d absorption frequency, ν° is the extrapolated frequency and (*a*) is the slope, represents the sensitivity of the complex toward solvent. Linearity of the ν_{max} vs DN, confirms the solvatochromic behavior in perchlorate complexes. Solvation free energy relationship (DN vs $\nu_{max}/1000$) was depicted in Fig. 6.

The slope values (*a*) are in the order ([Cu(EAA)(tmen)]ClO₄ < [Cu(EBA)–(tmen)]ClO₄ < [Cu(EAA)(tmen)(NO₃)]•2H₂O < [Cu(DEM) (tmen)(NO₃)]•H₂O The effect of the anion was studied using *t*-Bu₄NBr. The bromide complexes were prepared in solution in the molar ratio 5:1 (*t*-Bu₄NBr: perchlorate complexes) by replacing the perchlorate anion by the bromide anion.

The different anions (NO₃⁻, ClO₄⁻ or Br⁻) used in the present study chosen in such away, since the large size of the perchlorate anion makes it so difficult to coordinate to the Cu(II) ion, which lead to the formation of mainly square planar complexes, while the bromide anion with the small size and less electronegativity than the perchlorate anion make it so easy for the bromide to coordinate to the Cu(II) ion changing the geometry form square planar to mainly octahedral Fig. 7. Electronic absorption spectra of [Cu₂(DEM)(tmen)Br] complex (19), [Cu(EAA)(tmen)Br] complex (20) and [Cu(EBA)(tmen)Br] complex (21) solutions at 25 °C were depicted in Fig. 7. The nitrate anion may be inside or outside the coordination sphere leading to the formation of square planar, square pyramid or octahedral geometry.

4. Conclusions

Mixed-ligand Cu(II) complexes derived from three dioxygen ester ligands (diethylmalonate, ethylacetoacetate and ethylbenzoylacetate), and dinitrogen ligands (tmen, bipy and phen) with nitrate, perchlorate and bromide anions, were prepared and characterized by different spectroscopic techniques and TGA and molar conductance and magnetic measurements. The perchlorate complexes are square planar while the nitrate ones are either square pyramidal or octahedral structure. In solution, four mixed-ligand copper complexes showed solvatochromism. This behavior was confirmed by applying the linear salvation free energy relationship. The effect of anion was studied using t-Bu₄N⁺Br⁻ as a source of bromide anion that replaced the perchlorate anions converting the geometry of the complexes from mainly square planar to mainly octahedral.

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