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Spectral, electrochemical and molecular orbital studies on solvatochromic mixed ligand copper(II) complexes of malonate and diamine derivatives

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Abstract

Solvatochromic mixed ligand complexes of copper(II) with malonate and diamine derivatives, $Cu_n(RMal)(diam)_n X_m$ (where n = 1 or 2, m = 1-4, RMal, malonic acid (H₂Mal), diethylmalonate (HDEtMal) or diethylethoxyethylenemalonate (DEtEMal), and diam, ethylenediamine (en), 1,3-propylenediamine (1,3-pn), N,N,N'-trimethylethylenediamine (Me_3en) , N, N, N'-triethylethylenediamine (Et₃en), N, N, N', N'-tetramethylethylenediamine (Me₄en), N, N, N', N'-tetramethylpropylenediamine (Me₄pn), or N-methyl-1,4-diazacycloheptane (medach); and $X = ClO_4^-$ or Cl^-), has been synthesized and characterized by spectroscopic, magnetic, molar conductance and electrochemical measurements. The mass spectra along with the analytical data of the complexes show peaks with m/e corresponding to a bridged binuclear structure for the chloride complexes, while perchlorate complexes showed either mononuclear structure for DEtMal and DEtEMal or bridged binuclear structure for Mal complexes. These results correspond to IR spectral data, which indicated that the modes of ester and carboxylato coordination sites are mono- and/or bidentate. The d-d absorption bands in weak donor solvents suggest square-planar and distorted square pyramidal-trigonal bipyramid geometries for the perchlorate and chloride complexes; respectively. On the other hand, an octahedral structure is identified for complexes in strong donor solvents. Perchlorate complexes show a drastic color change from violet to green as the donation ability of solvent increases, whereas chloride complexes are highly affected by the acceptor properties of the solvent. Cyclic voltammetric measurements on the complexes, proposed a quasi-reversible or irreversible and mainly diffusion controlled reduction process. Such behavior has been explained according to the ECE mechanism. A linear correlation has been found between the Cu(II) reduction potential and the spectral data. Molecular orbital calculations were performed for the ligands on the bases of PM3 level and the results corresponded to the experimental data. The data are discussed in terms of chromotropic concept and its applications as a Lewis acid-base color indicator. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Solvatochromic; Copper(II); Mixed ligand; Bridged binuclear complexes; Lewis acid-base indicators; Electrochemistry

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1. Introduction

One of the decisive experimental techniques for investigating solute-solvent interactions is based on the dependence of the absorption spectra on the nature of the solvent [1,2]. This is because the variations in color are direct measures of the specific interactions between the solute and solvent molecules [3–6]. Developing environmental sensor materials has been substantially important due to the accelerating demands for monitoring pollutant levels in the environment. Such materials are chromotropic as a result of exhibiting color change when exposed to solvent or environmental pollutant molecules [7].

Recently, our research efforts have been focused on the synthesis and characterization of mixed ligand complexes of the type $[M(O-O)(N-N]^+$ [8-10], which are likely to demonstrate sensitivity to solvation or anation. Such behavior can be monitored by absorption spectra, electrochemical and quantum mechanical studies [11-15]. In this direction, there has been no systematic studies reported in literature on the solvatochromicity of the ternary Cu(II) complexes of malonate (RMal) and diamine derivatives.

Herein, we report newly synthesized solvatochromic complexes with the general formula, $Cu_n(RMal)(diam)_n X_m$, where n = 1 or 2, m =1-4, RMal, malonato (Mal), diethylmalonato (DEtMal) or diethylethoxyethylenemalonate (DEtEMal), diam, ethylenediamine (en), propylenediamine (1,3-pn), N, N, N', N'-tetramethylethylenediamine (Me₄en), N, N, N'-trimethylethylenediamine (Me₃en), N, N, N'-triethylethylenediamine (Et₃en), N, N, N', N'-tetramethylpropylenediamine (Me₄pn) or N-methyl-1,4-diazacycloheptane (medach); and $X = \text{ClO}_4^-$ or Cl^- (Scheme 1a-b). The effect of substituents at both diamine and RMal ligands, and also changing the anion on the structure and sensitivity of the complex toward solvents have been investigated using spectral and electrochemical techniques. One goal of this study is to examine the applicability of these complexes as a Lewis acid-base color indicator. As further support to our experimental work, molecular orbital calculations have been accomplished for

| (a) | | R ₃ | | R ₁ | |
|----------------------------|---------|-----------------|-------------------------------------|--------------------|-----------------|
| | | R ₄ | • (CH ₂) _x N | \gg_{R_2} | |
| diam Lig | x | R ₁ | R ₂ | R ₃ | R ₄ |
| 1,3-pn | 3 | Н | Н | Н | Н |
| Me ₄ pn | 3 | CH ₃ | CH_3 | CH_3 | CH ₃ |
| en | 2 | Н | Н | Н | Н |
| Me ₃ en | 2 | CH ₃ | CH_3 | CH_3 | Н |
| Et ₃ en | 2 | C_2H_5 | C_2H_5 | C_2H_5 | Н |
| Me ₄ en | 2 | CH3 | CH_3 | CH_3 | CH3 |
| medach | 2 | CH ₃ | —(CH | (2)3— ^a | Н |
| ^a bridging sube | tituent | | | | |

^a bridging substituen

(b)



Scheme 1. (a) Position of the substituents at the diamine ligands (diam) in the investigated $Cu_n(RMal)(diam)_n X_m$ complexes.(b) Position of the substituents in the RMal ligands: H₂Mal; R₁ = R₂: OH and HDEtMal: R₁ = R₂: OC₂H₅, however, the two hydrogen atoms of the methylene group are replaced by: = COC₂H₅ in DEtEMal ligand.

the ligands and the data are correlated with the experimental results.

2. Experimental

2.1. 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 for spectral and cyclic voltammetric studies, nitromethane (MeNO₂), acetonitrile (MeCN), acetone (Me₂CO), methanol (MeOH), formamide (FA), N,N-dimethylformamide (DMF) and dimethylsulfoxide (DMSO), were 'Spectro-grade' and further purified using standard methods [16].

2.2. Physical measurements

The mass spectra were recorded on AX 500 Jeel GC-mass spectrometer using fast atom bombardment (fast/ms) method. The infrared spectra in KBr (400–4000 cm⁻¹) and in polyethene (50–650 cm⁻¹) were recorded using Shimadzu FTIR 8101 and Nicolet 20F Far-IR spectrometers. Electronic spectra were obtained on UV-2101 pc w/full spectrophotometer using 10 mm quartz cells 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 conductivity bridge in water and DMF solutions at 25 °C. Cyclic voltammetric measurements were performed as reported elsewhere [11,17].

2.3. Syntheses of $Cu_n(RMal)(diam)_n X_m$ complexes

These complexes were prepared by adding a mixture of either 5 or 10 mmol of the malonate derivative (RMal) in 25 ml absolute EtOH and solid anhydrous Na₂CO₃ (20 mmol) to an ethanolic solution of 10 mmol CuX₂·nH₂O. The mixture was continuously stirred for about 30 min resulting in a green solution, which was then filtered. Then a solution of 10 mmol diamine derivative (diam) in 10 ml EtOH was added dropwise to the filtrate with a continuous stirring for an additional 25 min. After that, the resulting solution was filtered and left to stand overnight. The complexes obtained were re-crystallized from dichloromethane.

Preparation of mixed ligand complexes of Cu(II)–DEtMal and Cu(II)–DEtEMal with nonalkylated diamine ligands (en and 1,3-pn) was not possible due to the formation of template schiffbase complexes.

2.4. Results and discussion

Perchlorate complexes (1-11) were successfully synthesized. The color of complexes varied from bluish for 4 and 7 and reddish-violet for the other perchlorate complexes, while a greenish crystals were isolated for all chloride complexes, 12-15. The elemental analyses data suggest the formation of binuclear and mononuclear structures for perchlorate complexes 1-5 and 6-11, respectively. On the other hand binuclear are established for the chloride complexes, 12-15 (Table 1). These findings, are supported by the molar conductance (Λ /S cm² mol⁻¹) values for aqueous solutions of the complexes. These values are in the range expected to 1:1 for the perchlorate of DEtMal complexes, and 1:2 for the rest perchlorate complexes [18].

Nevertheless, aqueous solutions of the chloride complexes showed molar conductance values higher than expected. This result might be attributed, at least in part, to the effect of ion-pair dissociation [19-21]. This suggestion is confirmed by the white precipitate that appears when AgNO₃ solution is added to aqueous solutions of these complexes. This phenomenon, is more pronounced in the case of the chloride complex of DEtMal, 15. It exhibited much higher molar conductance value than expected for 1:1 electrolyte. This implies dissociation of the bridged binuclear (as suggested for the complex in solid state) into mononuclear species in aqueous solution. This interpretation could be due to the higher acceptor properties of water (AN = 54.8) [22], which will strongly solvate the chloride anion [23,24], and also to the weak preferences of the ester group to act as a bridged bidentate ligand. Measuring the molar conductance of the chloride complexes 13 and 15 in DMF solution, which has weak acceptor properties (AN = 16.0) further supports this suggestion. The obtained values: 163 and 65 S cm² mol⁻¹ corresponding to 1:2 and 1:1 electrolyte, respectively [18].

The magnetic moments data of the current complexes are found in the range 1.57–2.20 B.M (Table 1). These values are in consistent with those obtained in the cases of four- and five-coordinated Cu(II)-complexes [4,5,10,11].

2.5. Mass spectra

Mass spectroscopy was performed for the selected representative complexes to determine their molecular weights and fragmentation patterns. The mass spectra of the investigated compounds are relatively complex and exhibit a large number of peaks that extend to m/e value above 700 a.m.u. (Scheme 2a-d). The most significant features in the spectra of all investigated complexes is the most abundant small molecular ion peak due to the loss of the diamine ligand fragment

| 1 | |
|----|--|
| S | |
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| 9 | |

| Table 1 | |
|---|---|
| Colors, analytical data, molar conductance in aqueous solution, and magnetic mo | pments (per one Cu^{2+}) of $Cu_n(RMal)(diam)_n X_m$ complexes |

| No. | Complex/empirical formula | Formula Color weight | | Yield, | Anal, found | (Calc) | $\Lambda/$ S cm ² mol ⁻¹ | $\mu_{\rm eff}$ (B M) | |
|------|---|-------------------------|---------------------|--------|---------------|----------------|---|--------------------------------|-------|
| | | weight | | 70 | C% | H% | N% | 5 cm mor | (B.W) |
| (1) | $[Cu_2(Mal)(en)_2](ClO_4)_2C_7H_{18}N_4O_{12}Cl_2Cu_2$ | 548.0 | Reddish-vio- let | 46.4 | 14.96(15.33) | 3.08 (3.29) | 9.89 (10.22) | 269.9 | 1.68 |
| (2) | $[Cu_2(Mal)(1,3\text{-}pn)_2](ClO_4)_2C_9H_{22}N_4O_{12}Cl_2Cu_2$ | 576.18 | Reddish-vio- let | 37.3 | 19.04 (18.74) | 3.79 (3.85) | 9.65 (9.72) | 247.3 | 1.73 |
| (3) | $[Cu_2(Mal)(Et_3en)_2](ClO_4)_2C_{19}H_{42}N_4O_{12}C_{12}Cu_2$ | 716.34 | Reddish-vio- let | 43.4 | 32.14 (31.83) | 5.67 (5.91) | 8.07 (7.82) | 223.4 | 1.81 |
| (4) | $[Cu_2(Mal)(Me_4pn)_2](ClO_4)_2C_{17}H_{38}N_4O_{12}Cl_2Cu_2$ | 688.30 | Bluish | 54.2 | 29.38 (29.64) | 5.81 (5.56) | 8.21 (8.14) | 193.2 | 1.66 |
| (5) | $[Cu_2(Mal)(Me_4en)_2](ClO_4)_2C_{15}H_{34}N_4O_{12}Cl_2Cu_2$ | 660.27 | Reddish-vio- let | 63.5 | 26.92 (27.26) | 5.06 (5.19) | 8.65 (8.48) | 187.9 | 1.62 |
| (6) | $[Cu(DEtEMal)(Me_4en)](ClO_4)_2C_{16}H_{32}N_2O_{13}Cl_2Cu$ | 594.73 | Dark-violet | 74.1 | 32.49 (32.28) | 5.53 (5.42) | 5.03 (4.71) | 190.4 | 1.57 |
| (7) | $[Cu(DEtEMal)(Me_4pn)](ClO_4)_2C_{17}H_{34}N_2O_{13}Cl_2Cu$ | 608.73 | Bluish | 63.2 | 33.29 (33.51) | 5.35 (5.63) | 4.85 (4.60) | 178.5 | 1.67 |
| (8) | $[Cu(DEtMal)(Me_4en)]ClO_4C_{13}H_{27}N_2O_8ClCu$ | 438.0 | Reddish-vio- let | 57.8 | 35.26 (35.62) | 5.98 (6.21) | 6.17 (6.39) | 107.5 | 2.03 |
| (9) | $[Cu(DEtMal)(Me_3en)]ClO_4C_{12}H_{25}N_2O_8ClCu$ | 423.0 | Reddish-vio- let | 44.5 | 33.83 (34.04) | 5.79 (5.96) | 6.47 (6.62) | 90.4 | 1.72 |
| (10) | $[Cu(DEtMal)(Et_3en)]ClO_4C_{15}H_{31}N_2O_8ClCu$ | 465.0 | Reddish-vio- let | 59.6 | 39.05 (38.71) | 6.56 (6.72) | 6.23 (6.02) | 87.6 | 1.68 |
| (11) | $[Cu(DEtMal)(medach)]ClO_4C_{13}H_{25}N_2O_8ClCu$ | 435.0 | Violet | 67.4 | 36.21 (35.86) | 5.58 | 6.27 (6.44) | 103.2 | 2.14 |
| (12) | $[Cu_2(Mal)(Me_4en)_2Cl_2]C_{15}H_{34}N_4O_{12}Cl_2Cu_2$ | 532.27 | Green | 58.5 | 33.56 (33.82) | 6.50 (6.44) | 10.68 (10.52) | 123.9 | 2.06 |
| (13) | $[Cu_{2}(DEtEMal)(Me_{4}en)_{2}Cl_{2}]Cl_{2}C_{22}H_{48}N_{4}O_{5}Cl_{4}Cu_{2}$ | 717.23 | Green | 62.5 | 37.21 (36.81) | 6.92 (6.69) | 7.67 (7.81) | 243.1 (163.3) ^a | 1.98 |
| (14) | $[Cu_2(DEtEMal)(Me_4pn)_{22}Cl_2]Cl_2C_{24}H_{52}N_4O_5Cl_4Cu_2$ | 745.23 | Green | 54.8 | 38.29 (38.65) | 6.81 (7.03) | 7.23 (7.52) | 248.7 | 1.98 |
| (15) | $Cu_2(DEtMal)(Me_4en)_2Cl_2]ClC_{19}H_{43}N_4O_4Cl_3Cu_2$ | 624.84 | Green | 63.7 | 36.14 (36.49) | 6.78 (6.94) | 9.17 (8.96) | 311.2 (65.3) ^a | 2.12 |

^a Molar conductance measured in DMF solution.



Scheme 2. (a) Proposed structures of the $Cu_2(Mal)(diam)_2(ClO_4)_2$ complexes 1–5, and mass spectral fragmentation pattern of complex, 5. (b) Proposed structures of $Cu(DEtMal)(diam)ClO_4$ complexes 8–11, and mass spectral fragmentation pattern of $Cu(DEtMal)(Me_4en)ClO_4$ complex, 8. (c) Proposed structures of $[Cu_2(DEtEMal)(Me_4en)_2Cl_2]Cl_2$ complex, 13, and its mass spectral fragmentation pattern. (d) Proposed structures of $[Cu_2(DEtMal)(Me_4en)_2Cl_2]Cl_2$ complex, 15, and its mass spectral fragmentation pattern.

 $(CH_3)_2NC_2H_4N(CH_3)CH_2^+$ (*m*/*e* = 115 a.m.u) in all Me4en complexes, and the other more abundant peak due to $Cu(Me_4en)^+$ (m/e = 179 a.m.u). A less abundance peak at different m/e positions depending on the type of RMal ligand and the anions employed were observed. The extent of fragmentation of the molecular ions is inversely proportional to the relative stability of the complex, which depends on the basicity of RMal ligand. Consequently, Mal-complexes show less fragmentation than the corresponding DEtEMalcomplexes. This is due to the fact that Mal is dibasic but DEtEMal ligand is neutral. According to the highest mass peak in the spectrum a bridged binuclear structure could be suggested for Malcomplexes, 1-5, and 12 as well as for chloride complexes, 13-15. However; a mononuclear is proposed for the rest of complexes, 6-11, as shown in Scheme 2a-d.

2.6. Infrared spectra

Selected IR absorption frequencies for the investigated complexes are shown in Table 2. The observed bands are assigned based on comparison with related Cu(II)-complexes [4,5,10,11,25,26]. The main characteristic IR absorption bands for the current complexes are observed in the finger print region. The broad band observed in the range 3225-3320 cm⁻¹ are assigned to $v_{\rm NH}$ of the unsymmetrical alkylated and non-alkylated diamine complexes [25].

The coordination modes of perchlorate and chloride anions have been inferred from the IR data. Two intense stretching vibrational bands at 1100 and 630 cm⁻¹ are observed for the perchlorate complexes, 1-11 [25,26]. While, chloride complexes 12–15, show the following bands: at about 340, 290, 250 and 170 cm⁻¹ which might correspond to the stretching frequencies of Cu–Cl [14].

The partial splitting observed for the broad band at 1100 cm^{-1} 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 [27]. Complex 12, shows a stretching vibration band at 343, 296 and 234 cm⁻¹, attributed to a terminal $v_{\text{Cu-Cl}}$ vibrations, which is confirmed by the reported bands for [(Me₄N)₂CuCl₄] [28–30]. However, complexes **13** and **15**, show bands at 332, 287, 256 and 198, 165 cm⁻¹; 310, 291, 255 and 198, 173 cm⁻¹; respectively, indicating a terminal $v_{\text{Cu-Cl}}$. The vibration bands observed at 165 and 173 cm⁻¹ for complexes **13** and **15**; respectively could be assigned as a bridging $v_{\text{Cu-Cl}}$ vibration [25,31]. The formation of five coordinate Cu(II)-complexes containing terminal and/or bridging chloride anion(s) is supported by the X-ray crystallography for similar complexes, such as [Cu(bipy)₂Cl]⁺ and Cu₂(µ-Cl)(L₁)₂](ClO₄)₃; $L_1 =$ 1,4-bis(pyridin-2-ylmethyl)-1,4-diazacycloheptane [32–34].

Furthermore, perchlorate and chloride of Malcomplexes exhibited two partially resolved bands at 1650 and 1575 cm⁻¹, which assigned to v_{as} (COO) and a single band at about 1470 cm^{-1} for $v_{\rm s}$ (COO) [25]. However, the rest of perchlorate complexes showed only single intense bands in the regions 1700-1600 and 1470 cm⁻¹. The strong splitting observed for the Mal-complexes, 1-5 and 12 with $\Delta v (v_{as} - v_s)$ values in the range of 102–185 cm^{-1} , indicates that, the carboxylate group acts as a bidentate ligand, which is due to the difference in the binding strength with the metal ion. Therefore a bridged binuclear structure is proposed for Cu(II)-Mal complexes [27]. Similar conclusions were elucidated from the crystal structures of resembling complexes [35,36]. The presence of $v_{\text{CIO}_{4}}$ vibrations in the IR spectra of the Mal complexes 1-5, which have a diprotic ligand (Mal^{2-}) , suggest that malonato act as a tetradentate ligand, because the other possibility (bidentate) should lead to a neutral complex with Cu(II) ion. This agrees with the molar conductance data of 1:2 electrolyte as discussed above.

The perchlorate of DEtEMal-complexes 6–7, display $\Delta v (v_{as}-v_s)$ values in the range 205–228 cm⁻¹, suggesting that COOEt group behaves as mono-dentate, while the splitting values for the perchlorate of DEtMal-complexes, 8–11 are in the range 135–186 cm⁻¹. This may seem at first, to be due to a bidentate behavior for COOEt group [37,38], but it is clearly due to the conjugation of $v_{C=O}$ with $v_{C=C}$ upon chelation, which leads to lower $v_{C=O}$ and $\Delta v (v_{as}-v_s)$ values [25]. This

| No. | Complex | <i>v</i> (NH) | v(COO | D) | | $\Delta v (v_{as} - v_s)$ | v(ClO | <u>4</u>) | | | v(Cu–O) | v(Cu–N) |
|------|--|---------------|-------|------------|------|---------------------------|-------|------------|------|-----|---------|---------|
| (1) | $[Cu_2(Mal)(en)_2](ClO_4)_2$ | 3308 | 1640 | 1582 | 1455 | 127, 185 | 1144 | 1090 | 1046 | 627 | 525 | 478 |
| (2) | [Cu ₂ (Mal)(1,3-pn) ₂](ClO ₄) ₂ | 3250 | 1636 | 1590 | 1470 | 120, 166 | 1146 | 1090 | 1026 | 627 | 494 | _ |
| (3) | $[Cu_2(Mal)(Et_3en)_2](ClO_4)_2$ | 3315 | 1645 | 1580 | 1474 | 106, 171 | 1145 | 1090 | 1020 | 629 | 507 | 455 |
| (4) | $[Cu_2(Mal)(Me_4pn)_2](ClO_4)_2$ | - | 1653 | 1577 | 1472 | 105, 181 | 1146 | 1090 | 999 | 627 | 500 | 472 |
| (5) | $[Cu_2(Mal)(Me_4en)_2](ClO_4)_2$ | - | 1620 | 1576 | 1474 | 102, 146 | 1146 | 1090 | 1054 | 625 | 517 | 482 |
| (6) | [Cu(DEtEMal)(Me ₄ en)](ClO ₄) ₂ | _ | 1673 | | 1468 | 205 | 1142 | 1090 | 1045 | 625 | 513 | 480 |
| (7) | [Cu(DEtEMal)(Me4pn)](ClO4)2 | _ | 1698 | | 1470 | 228 | 1142 | 1089 | 1024 | 629 | 475 | _ |
| (8) | [Cu(DEtMal)(Me ₄ en)]ClO ₄ | _ | 1655 | | 1474 | 181 | 1146 | 1090 | 1043 | 629 | 521 | 482 |
| (9) | [Cu(DEtMal)(Me ₃ en)]ClO ₄ | 3225 | 1605 | | 1470 | 135 | 1145 | 1090 | 1028 | 623 | _ | 475 |
| (10) | [Cu(DEtMal)(Et ₃ en)]ClO ₄ | 3320 | 1620 | | 1477 | 143 | 1146 | 1089 | 1053 | 626 | 520 | 481 |
| (11) | [Cu(DEtMal)(medach)]ClO ₄ | 3290 | 1637 | | 1475 | 162 | 1149 | 1090 | 1073 | 625 | 570 | 453 |
| (12) | $[Cu_2(Mal)(Me_4en)_2Cl_2]$ | - | 1647 | 1601 | 1472 | 129, 175 | _ | | _ | _ | 512 | 474 |
| (13) | [Cu ₂ (DEtEMal)(Me ₄ en) ₂ Cl ₂]Cl ₂ | | 1673 | 1607 | 1468 | 139, 205 | - | - | - | _ | 511 | 489 |
| (14) | [Cu ₂ (DEtEMal)(Me ₄ pn) ₂ Cl ₂]Cl ₂ | | 1694 | 1611 | 1472 | 139, 222 | - | | - | - | 513 | 475 |
| (15) | [Cu ₂ (DEtMal)(Me ₄ en) ₂ Cl ₂]Cl | _ | 1653 | 1559 | 1470 | 89, 183 | - | | - | - | 506 | 484 |

Wavenumbers (cm⁻¹) of the main absorption bands in the infrared spectra of $Cu_n(RMal)(diam)_n X_m$ complexes

Table 2

suggest a mono-dentate behavior for the ester group of HDEtMal ligand, yielding a mononuclear chelate, whereas, the splitting observed in the case of chloride complexes of DEtEMal and DEtMal ligands is due to a bidentate behavior for the ester group (Table 2). This, conclusion agrees with the elemental analyses and mass spectral data.

2.7. Electronic spectra

Fig. 1 shows the visible absorption spectra of the $Cu_2(Mal)(Me_4en)_2(ClO_4)_2$ complex, **5** in different organic solvents. There is only one broad band that could be observed in the visible region, which is due to the promotion of an electron to the hole in $d_{x^2-y^2}$ orbital of the Cu(II) ion (d⁹) [7]. The position of the d–d transition band exhibits a red shift as the Lewis basicity of solvent increases [22], which indicates that these complexes are positively solvatochromic [1,3,7]. This red shift could be attributed to the strong repulsion of the electrons in d_{x^2} orbital by the lone pair of solvent that is axially coordinated to the central copper ion, therefore a less energy will be required to transfer the electrons to $d_{x^2-y^2}$.

The d-d visible absorption spectral data of the present complexes in various solvents are given in Table 3. The position of the d-d band, of the perchlorate complexes in the region of 19000-

 $17\,500~{\rm cm^{-1}}$ (except, at about 16500 and 15150 cm^{-1} for 4 and 7; respectively), in non- or very weak-coordinating solvent (MeNO₂), suggests square planar geometry for these complexes. The exceptions might be explained by the presence of steric 1,3-diamine ligand (Me₄pn) in these complexes, that forms also a less favored six-members chelate ring. This leads to a highly distorted square planar expected for these complexes. So, when the ligand field strength of the equatorial ligands is weak, the positive charge on Cu²⁺ cannot be efficiently obscured by their coordinating electrons [7]. Consequently, the Cu(II) ion will strongly attract the perchlorate anion to compensate the electron deficiency around it. This explanation is further supported by the splitting observed for the broad band of the perchlorate anion at 1100 cm^{-1} , indicating a bidentate chelation of perchlorate anion toward the central Cu(II) ion. This leads to a highly distorted octahedral structure that has a bluish color in solid state [25].

A number of significant points can be extracted from the data in Table 3 are with discussing. (a) Non-alkylated diamine complexes, 1 and 2, exhibit a less pronounced color change in comparison with those of alkylated diamine, 3-5. (b) Solutions of complexes 2, 4 and 7 in different solvents display higher λ_{max} values than the corresponding 1, 5 and 6. This can be explained by the fact that the former type has 1,3-diamine ligands (1,3-pn



Fig. 1. Electronic absorption spectra of 4.0×10^{-3} mol 1^{-1} Cu₂(Mal)(Me₄en)₂(ClO₄)₂ complex, **5** solutions in MeNO₂, MeCN, Me₂CO, DMF and DMSO solvents at 25 °C.

Table 3

Absorption maxima bands, λ_{max} (nm) (molar extinction coefficients are in the range 100–120 l mol⁻¹ cm⁻¹) for the Cu_n(RMal)(diam)_n X_m complexes solutions in various organic solvents at 25 °C

| No. | Complex | DMSO | DMF | MeOH | Me ₂ CO | MeCN | MeNO ₂ |
|------|--|------|-----|------|--------------------|------|-------------------|
| (1) | $[Cu_2(Mal)(en)_2](ClO_4)_2$ | 552 | 555 | 544 | 542 | 553 | 532 |
| (2) | [Cu ₂ (Mal)(1,3-pn) ₂](ClO ₄) ₂ | 573 | 575 | 562 | 544 | 566 | 558 |
| (3) | $[Cu_2(Mal)(Et_3en)_2](ClO_4)_2$ | 670 | 657 | 641 | 598 | 616 | 536 |
| (4) | $[Cu_2(Mal)(Me_4pn)_2](ClO_4)_2$ | 694 | 677 | 665 | 641 | 635 | 614 |
| (5) | $[Cu_2(Mal)(Me_4en)_2](ClO_4)_2$ | 669 | 654 | 629 | 597 | 617 | 560 |
| (6) | [Cu(DetEMal)(Me4en)](ClO4)2 | 635 | 629 | 616 | 596 | 609 | 562 |
| (7) | [Cu(DetEMal)(Me ₄ pn)](ClO ₄) ₂ | 733 | 727 | 697 | 677 | 694 | 660 |
| (8) | [Cu(DetMal)(Me4en)]ClO4 | 677 | 661 | 644 | 594 | 626 | 572 |
| (9) | [Cu(DetMal)(Me ₃ en)]ClO ₄ | 645 | 628 | 626 | 592 | 600 | 574 |
| (10) | [Cu(DetMal)(Et ₃ en)]ClO ₄ | 666 | 649 | 625 | 565 | 560 | 541 |
| (11) | [Cu(DetMal)(medach)]ClO ₄ | 666 | 649 | 625 | 565 | 563 | 541 |
| (12) | $[Cu_2(Mal)(Me_4en)_2Cl_2]$ | 696 | 698 | 650 | 667 | 660 | 669 |
| (13) | [Cu2(DetEMal)(Me4en)2Cl2]Cl2 | 705 | 719 | 649 | 723 | 702 | 705 |
| (14) | [Cu ₂ (DetEMal)(Me ₄ pn) ₂ Cl ₂]Cl ₂ | 737 | 788 | _ | 797 | 764 | 774 |
| (15) | [Cu2(DetMal)(Me4en)2Cl2]Cl | 733 | 726 | 684 | 700 | 695 | 694 |
| a | Cu(DEM)(medach)Cl | 755 | 750 | 682 | 717 | 718 | 700 |

^a Chloride complex is formed in MeNO₂ solution by mixing Bu₄NCl with the perchlorate complex, **11** in a ratio (5:1).

and Me_4pn), that form six-members chelate rings and, the later has 1,2-diamines (en and Me₄en) which form five-members chelate rings; respectively. This behavior indicates that the five-members ring is more favorable than the six-members ring. (c) The d-d visible absorption band of complexes 5 and 12 in most solvents show a less noticeable red shift than those of the complexes, 8 and 15. This could be due to the increase in the l.f.s of the equatorial ligand Mal (dibasic) as compared to the monobasic DEtMal ligand. Consequently, a stronger repulsion between the equatorial ligand, Mal with the electron of $d_{x^2-y^2}$ (highest occupied molecular orbital) shift it to a higher energy than the case of DEtMal ligand. Hence, a greater d-d gap and blue shift will be remarkable in the former case than the later. This behavior is converse to that discussed above for the effect of the axially coordinated solvent. (d) Finally, although donor strength (DN) [22], of acetone is higher than that of acetonitrile, the solutions of the present perchlorate complexes in acetone show a slightly lower $\lambda_{\rm max}$ values than in acetonitrile. This discrepancy was recognized to the effect of steric and π -bonding in acetone and acetonitrile, since they are acting in opposite directions [11].

The solvatochromic behavior of the present complexes is conceivably characterized quantitatively using the linear solvation free energy relationship. The correlation's data is summarized in Table 4. $v_{\text{max}}/10^3 \text{ cm}^{-1} = v^0 + a$ (DN); where v_{max} , the measured d-d absorption frequency; v^0 , the extrapolated frequency (measured the relative stability of un-solvated species); and *a*, the slope, represent the sensitivity of the complex toward solvent (solvatochromicity). The linearity of the v_{max} vs. DN, predicts, stabilization of the reactive perchlorate complexes toward Lewis bases (Lewis acid-base interactions) [5].

According to the solvatochromic parameters data, v^0 and *a*-values, for the complexes 1, 5 and 6 in comparison with 2, 4 and 7 (Table 4), one can deduce that, the five-members chelate ring is thermodynamically favored and offers a greater solvatochromic response than six-members ring. Where, the former complexes contain 1,2-diamine, while the later have 1,3-diamine ligands.

Additive rule is holding to deduce the effect of subsituents at both diamine and RMal ligands on the solvatochromic parameters of the perchlorate complexes. Linear relationships of both, v^0 and *a*-values vs. σ -Hammett constants were found as follows: *a*-values = -91.34-161.2 σ -Hammett,

1382

Table 4

Solvatochromic parameters of the perchlorate complexes, $Cu_n(RMal)(diam)_n(ClO_4)_m$ (n = 1 or 2, m = 1 or 2), according to the equation, $v^c/10^3 = v^0 + a$ (DN)

| No. | Complex | v^0 | -a | r |
|------|---|-------|--------|------|
| (1) | $[Cu_2(Mal)(en)_2](ClO_4)_2$ | 18.87 | 28.0 | 0.95 |
| (2) | $[Cu_2(Mal)(1,3-pn)_2](ClO_4)_2$ | 17.97 | 19.20 | 0.95 |
| (3) | $[Cu_2(Mal)(Et_3en)_2](ClO_4)_2$ | 19.02 | 140.40 | 0.99 |
| (4) | $[Cu_2(Mal)(Me_4pn)_2](ClO_4)_2$ | 16.49 | 65.4 | 0.98 |
| (5) | $[Cu_2(Mal)(Me_4en)_2](ClO_4)_2$ | 18.02 | 103 | 0.97 |
| (6) | [Cu(DetEMal)(Me ₄ en)](ClO ₄) ₂ | 17.73 | 66.30 | 0.99 |
| (7) | [Cu(DetEMal)(Me ₄ pn)](ClO ₄) ₂ | 15.36 | 57.4 | 0.99 |
| (8) | [Cu(DEtMal)(Me4en)]ClO4 | 17.77 | 98.30 | 0.99 |
| (9) | [Cu(DEtMal)(Me ₃ en)]ClO ₄ | 17.62 | 67.85 | 0.99 |
| (10) | [Cu(DEtMal)(Et ₃ en)]ClO ₄ | 18.01 | 108.00 | 0.99 |
| (11) | [Cu(DEtMal)(medach)]ClO ₄ | 18.84 | 126.50 | 0.99 |
| a | Cu(EtAA)(Me ₄ en)ClO ₄ | 17.70 | 70.58 | 0.98 |
| a | Cu(EtBA)(Me ₄ en)ClO ₄ | 17.74 | 69.87 | 0.99 |

r, Correlation coefficient.

^a Data taken from Ref. [11].

r = 0.98, and $v^0/10^3 = 14.36 - 3.16 \sigma$ -Hammett r = 0.94. The negative slopes in both cases, indicates an increase in the solvatochromicity and relative stability of the square planar species as the electron donating properties of the subsituents at both RMal and diamine ligands increase. Accordingly, increasing the relative stability of square planar species will make the environment of Cu(II) more planar in which the coordinated solvent molecule comfortably attacks the axial position in the same order [11]. Once again, the solvatochromicity of the current perchlorate complexes are mainly attributed to the axial solvation extent at the square planar species, and the l.f.s. of the equatorial ligands.

All phenomena discussed above could be clarified by considering the dissociation of the perchlorate complex solution into the square planar complex cation and ClO_4^- anion. The complex cation then converts into a series of structures with various degrees of elongation (tetragonalities) from a regular octahedron, depending upon the coordination ability of solvent molecules. This enhances the possibility of utilizing these complexes as a color indicator for Lewis basicity [1,11].

The d-d visible absorption maximum bands of the chloride complexes 12-15 in most solvents is extremely shifted to a longer wavelength in comparison with the analogous perchlorate complexes. The position of the d-d absorption bands of these complexes in the region of 14 000 cm⁻¹, suggests a square-based pyramidal distorted trigonal bipyramide (SBRDTBP) geometry [10,39,40]. This indicates that, the chloride anion is strongly coordinated to the central metal ion, since the coordination ability of chloride anion is strong as expected from its anion's donor number (DN_X, $M_{eNO_2} = 34.1$) [13]. The formation of the five-coordinated structure [7,14,30,41-44], explains the terminal coordination of the chloride anion in case of complex, **12** and a mixture of terminal and bridging coordination in complexes, **13–15**, as discussed above in the IR section.

The effect of solvents on the chloride complexes 12–15, is rather complicated as it depends upon both the donor and acceptor properties of the solvent. To provide an independent interpretation of their v_{max} results in different solvents (Table 3), the linear solvation energy relationship method, based on multi-parametric Kamlet-Taft equation [45], has been used to analyze the spectral data, where $v_{\text{max}}/10^3$ cm⁻¹ = aDN+bAN+c. Regression coefficients and constants were determined multi-linear regression bv analysis, using standard software, and the results are listed in Table 5.

| | Complex | v^0 | а | b | r | Relative co | ntribution, % |
|------|--|-------|-------|-------|------|-------------|---------------|
| | | | | | | DN | AN |
| (12) | $[Cu_2(Mal)(Me_4en)_2Cl_2]$ | 14.12 | -18.8 | 43.1 | 0.99 | 30.4 | 69.6 |
| (13) | [Cu ₂ (DEtEMal)(Me ₄ en) ₂ Cl ₂]Cl ₂ | 12.90 | 1.7 | 62.1 | 0.99 | 2.7 | 97.3 |
| 14) | [Cu2(DEtEMal)(Me4pn)2Cl2]Cl2 | 8.20 | 32.5 | 229.0 | 0.97 | 12.4 | 87.6 |
| 15) | [Cu2(DEtMal)(Me4en)2Cl2]Cl | 13.75 | -24.0 | 35.9 | 0.98 | 40.0 | 60.0 |
| L . | [Cu(DEM)(medach)Cl] | 13.26 | -33.4 | 55.0 | 0.99 | 37.8 | 62.2 |

Table 5

Solvatochromicity parameters of the chloride complexes, $Cu_n(RMal)(diam)_n Cl_m$ according to the equation, $v^c/10^3 = v^0 + a(DN) + b(AN)$

r, Correlation coefficient.

^a Prepared in solution by mixing Bu4NCl with MeNO₂ solution of the perchlorate complex, 11 in a ratio 5:1.

The term that quantifies the Lewis acidity parameter (AN) of the solvent is relatively important for chloride complexes 12-15, as reflected from the magnitude of the coefficient b and its higher contribution percentage (Table 5). The positive sign of this coefficient indicates blue shift as the solvent's Lewis acidity increases. However; the effect of solvent's Lewis basicity term, DN, is less significant as indicated from the low contribution percentage and/or the negative sign of the coefficient a. This leads to a red shift as the DN of solvent increases. The former case might arises because, when a solvent exhibits strong acceptor properties, it will compete for the coordination of anion (preferentially solvating the anion), i.e. weaken the interaction between the chloride anion and the central copper(II). Consequently, the d-dabsorption exhibits a blue shift as the solvent's acceptor property increases. Whereas, in the later case when the DN of the solvent increased the solvent preferably coordinated to the central metal ion forming an octahedral geometry, resulting in a red shift for the d-d band.

2.8. Electrochemical studies

Electrochemistry of selected complexes 8, 11 and 15, has been investigated, by means of cyclic voltammetry using a platinum microelectrode, for 1.0 mM 1^{-1} of the complex solutions in different solvents and 0.1 M 1^{-1} Bu₄ClO₄ as supporting electrolyte at scanning rate of 100 mV s⁻¹. Ferrocine/ferrocinium (Fc/Fc⁺) and bis(biphenyl)chromium (I)/(0) were used as internal standards for assignment of the potential

values [46–48]. The reduction process of the investigated complexes in all solvents exhibited a quasi-reversible or irreversible, redox associated with a two-electron reduction, and mainly diffusion controlled the process as indicated from the linear dependence of the current peak on the square root of the scan rate [49].

Fig. 2 shows the cyclic voltammogram of $[Cu_2(DEtMal)(Me_4en)_2Cl_2]Cl$ complex, **15** in DMF solution. This voltammogram indicates a quasi-reversible two-electron reduction in a single step for either (a) the dicopper(II) complex, 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:

$$Cu^{II}Cu^{II} \rightleftharpoons Cu^{I}Cu^{I} \tag{1}$$

$$Cu^{II} \rightleftharpoons Cu^0$$
 (2)



Fig. 2. Cyclic voltammogram recorded with a platinum microelectrode for the DMF solution of 1.0×10^{-3} mol l⁻¹ [Cu₂(DEtMal)(Me₄en)₂Cl₂]Cl complex, **15** in presence of 0.1 mol l⁻¹ Bu₄NCO₄ as supporting electrolyte and scan rate of 100 mV s⁻¹

The sequence (Eq. (1)), is quieting unexpected; even if the two-electron process does not proceed stepwise, one electron changes at different potentials due to the different environments around the two Cu(II) ions, the reduction of $Cu-N_2-O-Cl_2$ is more facile than Cu-N₂-O₂-Cl (Scheme 2d) [50,51]. In electrochemical terms this should involve an ECEC, 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 [52]. The other sequence (Eq. (1)) could be excluded according to the molar conductance data of complex 15 which supported the bridged binuclear structure in DMF solution.

The character of the reduction pathway for the investigated mononuclear perchlorate complexes **8** and **11** showed a stepwise two-electron reduction according to the following sequence,

 $Cu^{II} \rightleftharpoons Cu^{I} \rightleftarrows Cu^{0}$

In fact, the voltammetric picture for the present mononuclear complexes corresponds well to that found for similar copper(II) complexes, which has been also explained according to the ECE mechanism [11,51,53–55].

The potential values of the redox peaks (E_{pc} and E_{pa}) of the investigated complexes in different

solvents are shown in Table 6. The $E_{\rm pc}$ potentials for the mononuclear perchlorate and binuclear chloride Cu(II) complexes depend on the solvent's properties. The trend of data also agrees well with the visible absorption spectral results in various solvents where, $E_{\rm pc}/V = 0.175 v_{\rm max}/10^3 - 2.06$, r =0.99, and $E_{\rm pc} = -0.048 v_{\rm max}/10^3 + 1.45$, r = 0.99, for complexes, 8 and 11, respectively.

Once again, the dependence of $E_{\rm pc}$ values of the bridged binuclear chloride complex 15, on the solvent parameters is rather complicated, so the multi-parametric equation has been applied yielding, $E_{\rm pc}/V = 0.048$ AN + 0.02 DN - 0.62, r = 0.99. The relative contribution percentage of the solvent donor properties is only 29.4%, i.e., the reduction process of the chloride complex is extremely controlled by the acceptor properties of the solvent (60.6%). This result agrees with that obtained from the spectral data (Table 5). In conclusion, the combination of the electrochemical and spectroscopic data emphasizes the axial ligation of the perchlorate complexes and well explains the solute-solvent interactions.

2.9. Molecular orbital calculations

The structural parameters data of the present ligands as calculated by means of a semi-empirical molecular orbital calculations at the PM3 level provided by the Alchemy 2000 program are shown in Table 7. The calculated energies of the lowest unoccupied and highest occupied molecular orbi-

Table 6

Electrochemical data for the redox processes of Cu(DEtMal)(diam)X complexes in various solvents, potentials E/V vs. bis(biphenyl)-chromium(I)/(0) reference electrode

| Solvent | [Cu(DEtMal)(Me4en)]ClO4 | | | [Cu(DE | tMal)(medac | h)]ClO ₄ | [Cu ₂ (DF | [Cu ₂ (DEtMal)(Me ₄ en) ₂ Cl ₂]Cl | | |
|-------------------|-------------------------|---------------|------------------|--------------|---------------|---------------------|----------------------|--|---------------|--|
| | $E_{\rm pc}$ | $E_{\rm pa1}$ | E _{pa2} | $E_{\rm pc}$ | $E_{\rm pa1}$ | $E_{\rm pa2}$ | $E_{\rm pc}$ | $E_{\rm pa1}$ | $E_{\rm pa2}$ | |
| MeNO ₂ | 0.99 | 0.55 | -0.20 | 0.86 | 0.26 | -0.13 | 0.42 | 0.60 | | |
| MeCN | 0.72 0.12 | 0.07 | -0.94 | 0.60 | 0.38 | 0.19 | 0.48 | 0.66 | -0.11 | |
| FA | 1.02 0.62 | 0.50 | -0.31 | 0.69 0.51 | 0.26 | -0.85 | - | _ | _ | |
| DMF | 0.87 | 0.57 | 0.19 | 0.81 0.70 | 0.11 | - | 0.67 | 0.52 | _ | |
| DMSO | 0.75 0.49 | 0.42 0.18 | -0.29 | 0.89 0.74 | 0.67 0.30 | -0.35 | 0.73 | 0.56 | -0.31 | |

| Ligand | $V, Å^3$ | S, Å ² | $E_{\rm HOMO}$, eV | $E_{\rm LUMO}, {\rm eV}$ | μ , Debye | $-Q_{\rm S}$, e (N) |
|--------------------|----------|-------------------|---------------------|---------------------------|---------------|-----------------------|
| en | 69.2 | 101.8 | -9.43 | 2.97 | 0.16 | -0.382 |
| 1,3pn | 86.2 | 125.0 | -9.36 | 2.88 | 1.70 | -0.383 |
| Me ₄ pn | 154.7 | 204.0 | -8.95 | 2.67 | 1.48 | -0.324 |
| Me ₄ en | 137.23 | 179.1 | -8.82 | 2.63 | 0.75 | -0.323 |
| Me ₃ en | 121.03 | 165.8 | -9.03 | 2.58 | 1.49 | $-0.323 (-0.350)^{a}$ |
| Et ₃ en | 170.82 | 224.9 | -8.97 | 2.44 | 1.57 | $-0.316 (-0.347)^{a}$ |
| medach | 126.65 | 165.6 | -8.97 | 2.41 | 2.06 | $-0.319 (-0.346)^{a}$ |
| H ₂ Mal | 82.76 | 117.19 | -11.67 | 0.47 | 1.72 | _ |
| DetEMal | 203.49 | 272.54 | -10.34 | -0.46 | 4.39 | _ |
| HDEtMal | 150.75 | 204.80 | -11.32 | 0.61 | 4.30 | _ |
| HetAA | 124.77 | 169.47 | -11.13 | 0.32 | 3.63 | _ |
| HetBA | 179.10 | 228.0 | -10.12 | -0.63 | 2.80 | _ |
| Hacac | 100.34 | 140.38 | -10.95 | 0.34 | 0.42 | - |

Atomic charges, Q (e), HOMO (eV), LUMO (eV), volume of the molecule, V (Å³) surface area, S (Å²) and dipole moment, μ (Debye) from the Alchemy 2000 at (PM3) level for the ligands

^a Charge at NH of the unsymmetrical alkylated diamine ligands given in parenthesis.

tals (E_{LUMO} and E_{HOMO}) of the ligands are correlated with the solvatochromic parameters of complexes given in Table 4. The following correlations have been obtained: $E_{HOMO} = -0.0085(a$ r = 0.975; $E_{HOMO} = -0.038(a$ values)-9.64, values) -7.66, r = 0.974, and $E_{LUMO} = -0.032(a - 100)$ values) -2.72, r = 0.97 for $[Cu_2(Mal)(diam)_2]^{2+1}$ (1-5), and $[Cu(O-O)(Me_4en)]^+$ complexes, respectively. The O-O ligand is, Mal, DEtMal, EtAA (ethylacetoacetate), EtBA (ethylbenzolacetate), DEtEMal or acac (acetylacetonate). The linearity indicates a decrease in solvatochromicity (a-value) with the increase of both E_{LUMO} and E_{HOMO} of the diamine and O-O ligands as indicated from the negative slopes of the linear plots. This conclusion is in agreement with the results obtained for related copper(II) and nickel(II) chelates [12,56].

Table 7

Unfortunately, X-ray single crystal structure was not possible due to the lack of facilities. Based on the physicochemical studies discussed above, a general tentative picture of the structures was drawn. A bridged binuclear structure was suggested for the chloride complexes as well as the perchlorate of Mal complexes, while a mononuclear structure was proposed for the rest of perchlorate complexes (Scheme 2a–d).

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