

## Supramolecular Copper(II) Complexes with Tetradentate Ketoenamine Ligands

by H.A. El-Boraey and A.S. El-Tabl\*

Chemistry Department, Faculty of Science, Menoufia University, Shebin El-Kom, Egypt

(Received May 8th, 2003; revised manuscript August 18th, 2003)

A new series of symmetric and unsymmetric supramolecular copper(II) complexes derived from  $\beta$ -diketones and aniline derivatives have been synthesized and characterized by elemental analyses, IR, UV-VIS spectra, magnetic moments, conductances, thermal analyses (DTA and TGA) and ESR measurements. The IR data show that the ligands behave as monobasic bidentate type towards copper(II) ion. The supramolecular structure is achieved through the dimerization of complexes (1), (3), (5) and (6) or polymerization of complexes (2), (4) and (7) via intermolecular hydrogen bonding of the –OH and C=O of carboxylic groups. Molar conductances in DMF solution indicate that the complexes are non-electrolytes. ESR spectra of the solid complexes (1) and (3) at room temperature show axial-type with a  $d_{xz}$  ground state, however, the complexes (2), (4), (5) and (6) show axial-type spectra with  $g_{\parallel} > g_{\perp} > 2.00$ , indicating a  $d_{x^2-y^2}$  ground state with significant covalent bond character. Electronic and ESR spectra show that the complexes represent square planar or tetragonally distorted octahedral geometry. The catalytic properties of the complexes (1) and (5) were investigated by decomposition of hydrogen peroxide.

**Key words:** complexes, spectroscopic studies, conductivity, thermal analyses, syntheses, magnetism

Studies on structural, spectral and magnetic properties of polynuclear transition metal complexes, aimed the understanding of the structural and chemical factors, governing electronic exchange coupling mediated by multiatom bridging ligands, are of continuing interest for bioinorganic chemists, investigating the structure and the role of polymetallic active sites in biological processes, and inorganic chemists, seeking to design new molecular materials exhibiting unusual magnetic, optical and electrical properties, that are bound to their molecular nature [1–3].

Among multiatom bridging ligands, carboxylate has been extensively studied. It is well known that the carboxylic group can exhibit different types of bridging conformations. Numerous examples exist of well structurally characterized copper(II) complexes involving the last triatomic bridging mode, but only a few of them so far have been studied magnetically [3]. Thus, earlier reports have included acetylacetonate-carboxylate [4,5], oxinate-carboxylate [5,6], and the oximate-carboxylate complexes [7]. Transition metal complexes with potential catalytic activities are being investigated more frequently now than ever before. A large number of symmetrical

---

\*Author to whom all correspondence should be directed.

tetradentate ligands have been reported. Relatively little is known, however, of the related unsymmetrical compounds, which may be useful as models for metal binding sites in various metal-proteins. Mononuclear copper(II) complexes of N-(2-pyridinyl)-acetylacetamide ligand have been prepared and spectroscopically characterized. The complexes show various interesting properties [8,9]. Other points of interest deal with the investigation of the tendency of copper(II) complexes to exhibit supramolecular structures. Using the ligand substituents, as a suitable binding unit, the studies are carried out for developing the inorganic metallosupramolecular systems [10]. In this paper, we report the syntheses, structures, spectroscopic, magnetic and catalytic properties of new supramolecular copper(II) complexes.

## EXPERIMENTAL

All chemicals and solvents used were of reagent grade and used as received. Elemental analyses for C, H, N and Cu were determined at the Analytical Unit of Cairo University, Egypt. All the complexes were dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>. IR spectra were measured as nujol mulls with KBr and CsBr prisms, using a Perkin-Elmer 681 spectrophotometer (4000–200 cm<sup>-1</sup>). Electronic spectra (nujol mull and DMF solution) in the 900–200 nm region were recorded on a Perkin-Elmer 550 spectrophotometer. Magnetic susceptibilities were measured at 25°C by the Gouy method, using mercuric tetrathiocyanatocobaltate(II) as the magnetic susceptibility standard. Diamagnetic corrections were estimated from Pascal's constant [11]. The magnetic moments were calculated from:  $\mu_{\text{eff}} = 2.84\sqrt{\chi_M^{\text{corr}}}$  T. Molar conductances were measured on a Tacussel type CD<sub>6</sub>NG conductivity bridge, using 10<sup>-3</sup> M of DMF solutions. Thermal analyses (DTA and TGA) were carried out in air (20–800°C) using a Shimadzu DT-30 thermal analyser. ESR spectra of solid complexes at room temperature were recorded using a Varian E-109 spectrophotometer. DPPH was used as a standard material. The catalytic activities of the complexes (1) and (5) towards the decomposition of hydrogen peroxide (as a model reaction) were determined from the rates of oxygen evolution at room temperature [12]. A 0.5 mL of H<sub>2</sub>O<sub>2</sub> (30%) was mixed with 20 mL distilled water in a thermostated glass vessel and 50 mg of the complex was introduced. The reaction was followed by measuring the volume of the oxygen gas released. The TLC of the all complexes confirmed their purity.

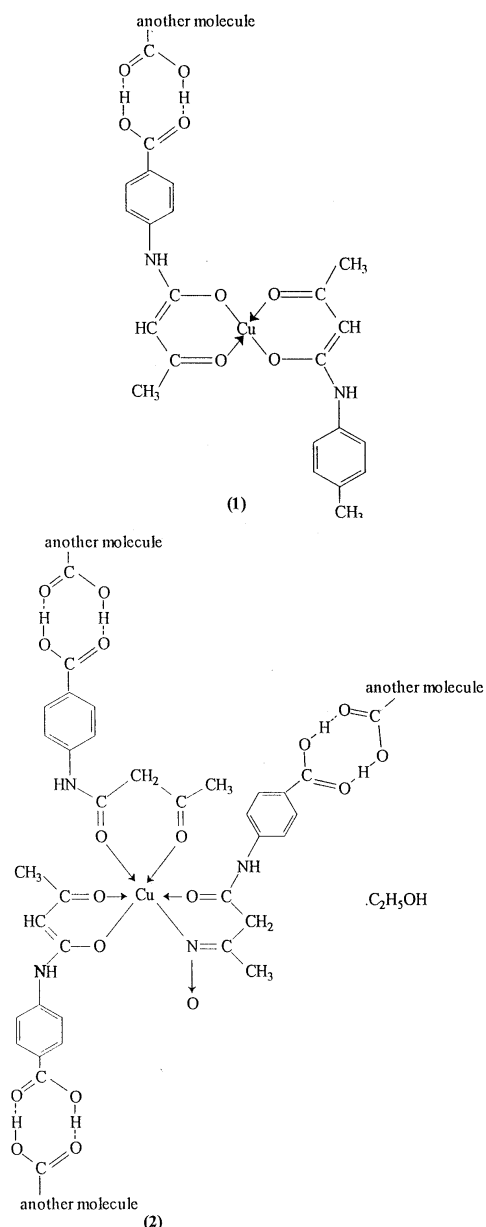
**Preparation of complexes (1), (3), (4) and (5):** Solution of 1-(4-carboxyphenylamino)-buta-1,3-dione (5.0 g, 0.02 mol) in ethanol (30 cm<sup>3</sup>) was added dropwise to a warm solution of ethanol (30 cm<sup>3</sup>) of 1-(4-methylphenylamino)-buta-1,3-dione (4.3 g, 0.02 mol), complex (1), (4.1 g, 0.02 mol) of 1-(pyridylamino)-buta-1,3-dione, complex (3), (5.0 g, 0.02 mol) of 1-(4-carboxyphenyl-amino)-buta-1,3-dione, complex (4), and (2.26 g, 0.02 mol) of acetyl acetone, complex (5). A hot ethanolic solution (50 cm<sup>3</sup>) of copper(II) acetate monohydrate (4.5 g, 0.02 mol) was added to the mixture. The mixture was refluxed with stirring for 3 hours, then, concentrated under reduced pressure until a solid complex was precipitated. It was filtered off, washed with ethanol and dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>. The analytical data for C, H, N, and Cu agree in the limits of 2–3% with formulae given in Table 1.

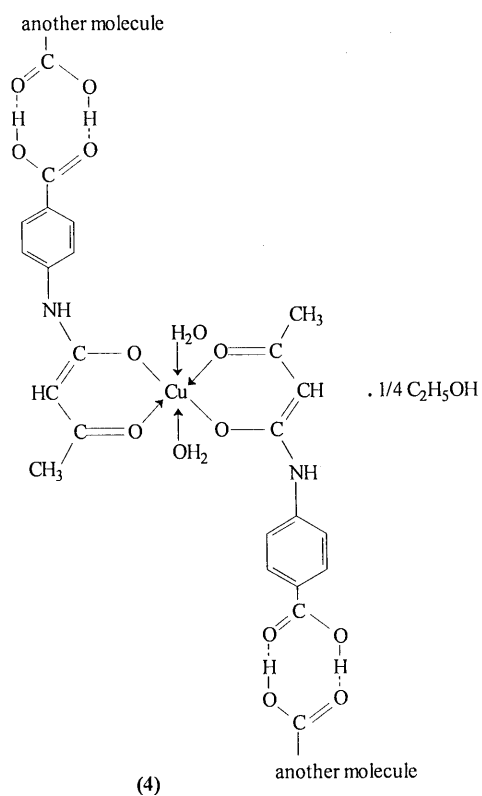
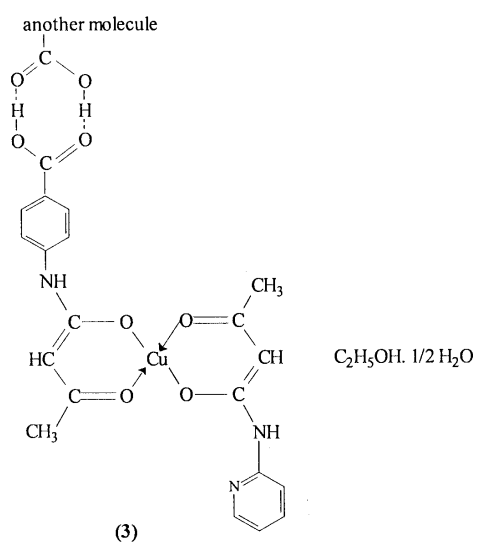
**Preparation of complexes (2), (6) and (7):** These complexes were prepared by mixing 1-(4-carboxyphenylamino)-buta-1,3-dione (10.0 g, 0.04 mol) in ethanol (50 cm<sup>3</sup>), (4.5 g, 0.02 mol) of Cu(OAc)<sub>2</sub> · H<sub>2</sub>O and (5.3 g, 0.02 mol) of 1-(4-carboxyphenylamino)-3-oxime-butanone, (2:1:1, molar ratio), complex (2), (5.0 g, 0.02 mol) of 1-(4-carboxyphenylamino)-buta-1,3-dione, 4.5 g, (0.02 mol) of Cu(OAc)<sub>2</sub> · H<sub>2</sub>O and (6.8 g, 0.04 mol) of 1-phenylamino-keto-butane-3-imine-benzene, (1:1:2, molar ratio), complex (6), and 10.0 g, (0.04 mol) of 1-(4-carboxyphenylamine)-buta-1,3-dione, 4.5 g, (0.02 mol), of Cu(OAc)<sub>2</sub> · H<sub>2</sub>O and 2.8 g, (0.02 mol) of oxalic acid, (2:1:1 molar ratio), complex (7), in the same solvent (50 cm<sup>3</sup>), using the above procedure. The product was removed by filtration, washed with ethanol and dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>. The analytical data for C, H, N, and Cu agree in the limits of 2–3% with formulae given in Table 1.

## RESULTS AND DISCUSSION

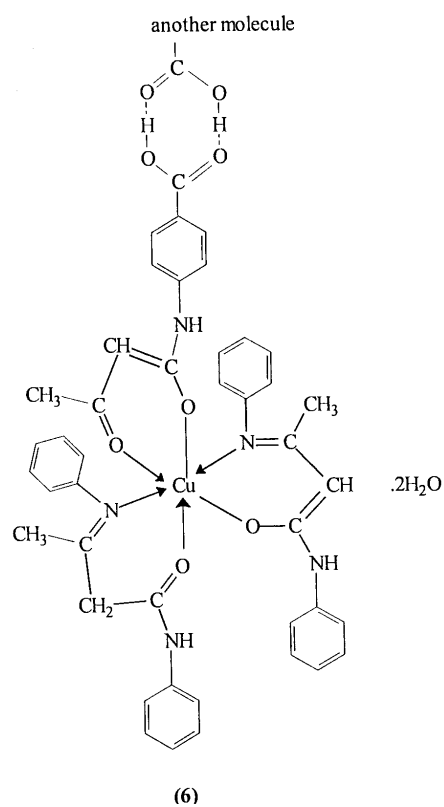
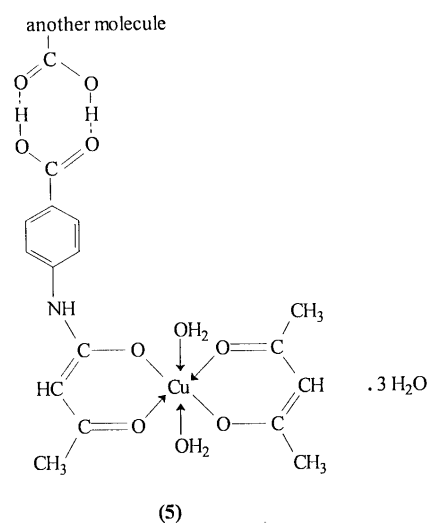
All the complexes are intensely coloured, air stable and partially soluble in common organic solvents except DMF and DMSO. The physical and spectral data (Tables 1, 2 and 3) are compatible with the proposed structures (Scheme 1). The low molar conductances in DMF solutions ( $\leq 36.3 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ; Table 1) of the metal complexes imply that they are non-ionic in nature [13].

Scheme 1

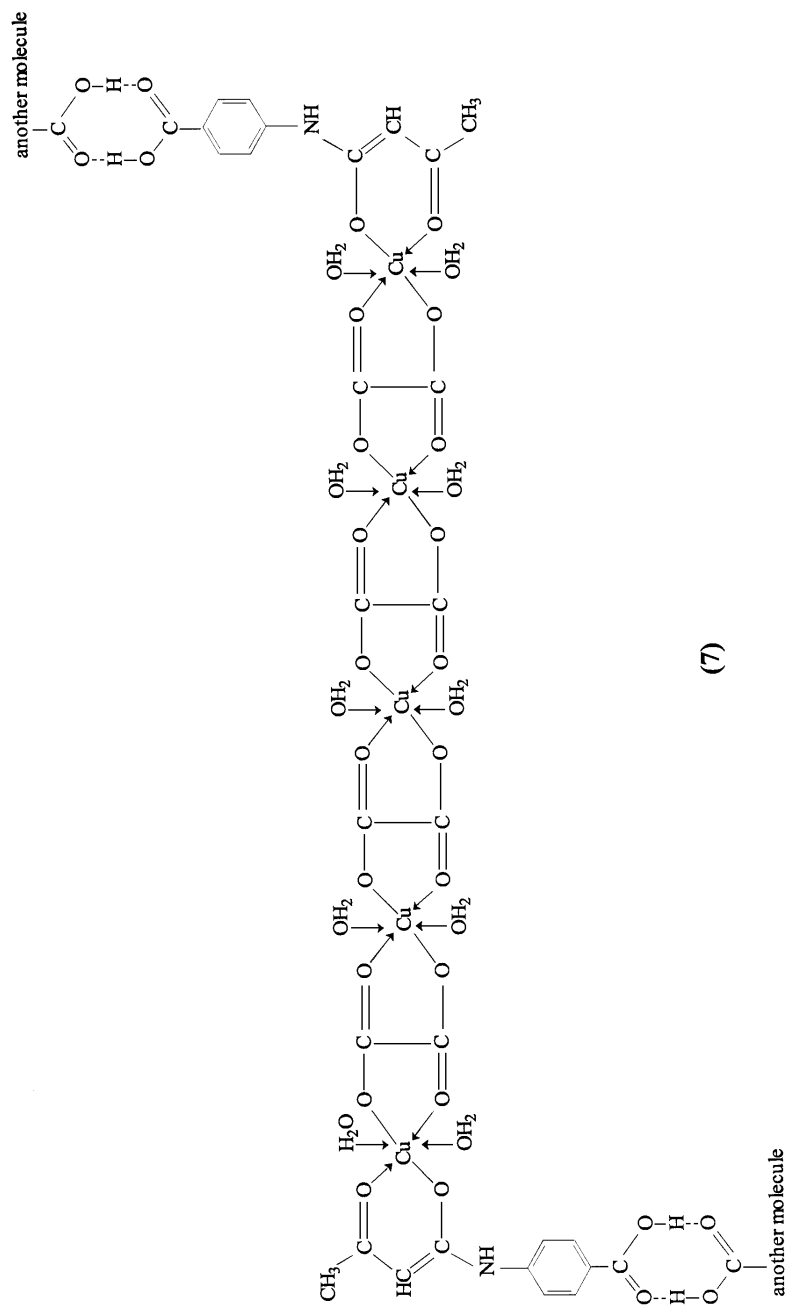




Scheme 1. Continuation



Scheme 1. Continuation



Scheme 1. Continuation

**Table 1.** Physical data of the ligands and their copper(II) complexes.

Compound No.	Colour	Yield (%)	Decomp. Temp. (°C)	Magnetic moment (B.M.)	$\Lambda$ (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )
<b>(1)</b> [C <sub>44</sub> H <sub>44</sub> N <sub>4</sub> O <sub>12</sub> Cu <sub>2</sub> ]	depp green	80	> 300	1.70	19.2
<b>(2)</b> [C <sub>33</sub> H <sub>31</sub> N <sub>4</sub> O <sub>12</sub> Cu] <sub>n</sub> [C <sub>2</sub> H <sub>5</sub> OH] <sub>n</sub>	bluish green	82	270	1.66	17.9
<b>(3)</b> [C <sub>40</sub> H <sub>38</sub> N <sub>6</sub> O <sub>12</sub> Cu <sub>2</sub> ] · 2C <sub>2</sub> H <sub>5</sub> OH · H <sub>2</sub> O	bluish green	85	290	1.69	22.1
<b>(4)</b> [C <sub>22</sub> H <sub>20</sub> N <sub>2</sub> O <sub>8</sub> Cu · 2H <sub>2</sub> O] <sub>n</sub> [ <sup>1</sup> / <sub>4</sub> C <sub>2</sub> H <sub>5</sub> OH] <sub>n</sub> (H <sub>2</sub> O) <sub>2</sub>	deep green	80	260	1.65	23.2
<b>(5)</b> [C <sub>32</sub> H <sub>34</sub> O <sub>16</sub> N <sub>2</sub> Cu <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ] · 6H <sub>2</sub> O	pale green	78	> 300	1.67	36.3
<b>(6)</b> [C <sub>84</sub> H <sub>82</sub> N <sub>6</sub> O <sub>12</sub> Cu <sub>2</sub> ] · 4H <sub>2</sub> O	pale blue	82	290	1.62	14.6
<b>(7)</b> [C <sub>30</sub> H <sub>20</sub> N <sub>2</sub> O <sub>24</sub> Cu <sub>5</sub> · 13H <sub>2</sub> O] <sub>n</sub>	pale blue	80	> 300	0.69	28.7

**Table 2.** Vibrational features (cm<sup>-1</sup>) of copper(II) complexes.

Compound No.	$\nu$ (OH/H-bonding)	$\nu$ (NH)	$\nu$ (C=O)	$\nu$ (CH=C)	$\nu$ (C–O)	$\nu$ (CuO)
<b>(1)</b>	3520–3340	3225, 3140	1620, 1610	1520	1380	445, 515
<b>(2)</b>	3580–3340	3240, 3140	1620, 1608	1555	1390	440, 515
<b>(3)</b>	3600–3325	3245, 3140	1625, 1607	1530	1380	450, 515
<b>(4)</b>	3600–3350	3245, 3140	1625, 1608	1535	1385	445, 520
<b>(5)</b>	3640–3300	3250, 3140	1625, 1610	1538	1380	460, 505
<b>(6)</b>	3640–3360	3290, 3265	1645, 1632	1538	1390	505
<b>(7)</b>	3680–3320	3260, 3140	1680, 1630, 1608	1535	1365, 1390	400, 505

**Table 3.** Electronic spectra of the copper(II) complexes.

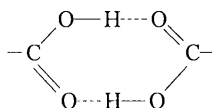
Compound No.	Solvent	$\lambda_{\text{max}}$ (nm)
<b>(1)</b>	N.M. DMF	580, 495, 360 610, 470, 350
<b>(2)</b>	N.M. DMF	675, 570, 450, 300 650, 480, 330
<b>(3)</b>	N.M. DMF	575, 485, 320 605, 455, 340

Table 3 (continuation)

(4)	N.M.	650, 575, 450, 350
	DMF	380, 625, 405, 310
(5)	N.M.	670, 595, 470, 320
	DMF	720, 620, 450, 350
(6)	N.M.	670, 565, 460, 310
	DMF	660, 550, 430, 300
(7)	N.M.	700, 575, 480, 325
	DMF	715, 560, 405, 310

N.M. = Nujol mull.

**IR spectra:** The bonding mode of the ligands in the metal complexes has been deduced from the IR spectroscopy. Important spectral bands of the complexes are presented in Table 2. The spectra show bands in the 3290–3140 and 1680–1608  $\text{cm}^{-1}$  regions attributed to the  $\nu(\text{NH})$  and  $\nu(\text{C}=\text{O})$  vibrations respectively [14–16]. The bands at 1555–1520 and 1390–1365  $\text{cm}^{-1}$  ranges are assigned to  $\nu(\text{CH}=\text{C})$  and  $\nu(\text{C}-\text{O})$  vibrations respectively [14,16]. Also, the spectra show a strong broad band in the 3680–3300  $\text{cm}^{-1}$  range attributed to the vibration of a H-bond of the type O–H---O in the complexes [17–20]. This H-bonding is formed between two carboxylic groups of two different complex molecules giving rise to dimeric ((1), (3), (5) and (6)) or polymeric ((2), (4) and (7)) structures. The dimeric H-bonding is evidenced by the appearance of a medium broad of medium intensity band around 925  $\text{cm}^{-1}$ , due to dimeric  $\delta\text{OH}$  out of plane [17]. The spectra show that, the complexes contain intermolecular hydrogen bonding of the type;



which probably stabilize the structures proposed (Scheme 1). The bands at 520–400  $\text{cm}^{-1}$  range are assigned to  $\nu(\text{CuO})$  vibrations [14,21]. Complex (2) shows bands at 1535 and 1170  $\text{cm}^{-1}$ , assigned to  $\nu(\text{C}=\text{N})$  and  $\nu(\text{N}-\text{O})$  of the oximato group respectively [22,23]. This result is in agreement with N-coordination of oximato group [23]. Complex (6) shows a band at 1605  $\text{cm}^{-1}$  due to  $\nu(\text{C}=\text{N})$  vibration [24].

**Electronic spectra:** The electronic spectra of the copper(II) complexes in nujol mull and DMF solution are summarized in Table 3. Complexes (1) and (3) in nujol mull exhibit three bands located at 360, 320 and 495, 485 and 580, 575 nm, however, in DMF solution, the bands appear at 350, 340 and 470, 455 and 610, 605 nm respectively. The first band is assigned to intraligand transitions. The second band suggests square planar geometry [25] corresponding to  ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$  and  ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$  transitions. The spectra in DMF solution are different than in the solid state, indicating that the geometry is changed to octahedral type. Complexes (2), (4), (5), (6) and (7), in nujol mull, give bands at 350–300, 480–450 and 700–650 nm however, in DMF solution, the bands appear at 350–300, 480–405 and 720–650 nm; the first two bands are within



the ligands and the third band corresponds to the  ${}^2B_{1g} \rightarrow {}^2E_g$  transition of the copper(II) ion in a tetragonally elongated octahedron [14,26].

**Magnetic moment:** The magnetic moments of the complexes are in the 1.70–0.69 B.M. range (Table 1). Complexes **(1)** and **(3)** show values, which confirm the square planar geometry of copper(II) complex and also they show some degree of association [23,24]. However, complexes **(2)**, **(4)**, **(5)** and **(6)** show values, suggesting tetragonal elongated octahedron geometry [14,27,28]. The slight lowering of the magnetic moments of the complexes (Table 1) from the value reported of 1.73 B.M., for  $d^9$ , copper(II) system is in agreement with the intermolecular hydrogen bonding between the carboxylic groups [7,29]. Complex **(7)** shows 0.69 B.M., indicating that antiferromagnetic interactions take place between the copper(II) centers through the oxalate bridge [30].

**Electron spin resonance:** The ESR spectral data for the complexes are presented in Table 4. The spectra of the complexes **(1)** and **(3)** show g-values, indicating a square planar geometry around the copper(II) ion [31,32]. However, complexes **(2)**, **(4)**, **(5)** and **(6)** are characteristic of a system,  $d^9$ , configuration having an axial type a  $d_{x^2-y^2}$  ground state, which is the most common for copper(II) complexes [14,24]. The ESR spectra of solid complexes **(1)**, **(5)** and **(7)** are shown in Fig. 1. The complexes **(2)**, **(4)**, **(5)** and **(6)** show  $g_{\parallel} > g_{\perp} > 2.0023$ , indicating a tetragonal distortion around the copper(II) ion [32], corresponding to elongation along the four fold symmetry z-axis. The spectrum of the complex **(7)** shows a broad signal in the low field region, indicating that spin-exchange interactions take place between the copper(II) ions [24] through the oxalate anion.

The g-values are related by the expression [33],  $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$ . If  $G > 4.0$ , then, local tetragonal axes are aligned parallel or only slightly misaligned, if  $G < 4.0$ , significant exchange coupling is present. The complexes show  $G < 4.0$ , (Table 4), indicating the presence of spin exchange interactions between the copper(II) ions. Also, the  $g_{\parallel}/A_{\parallel}$  values considered as diagnostic of stereochemistry [34], in the range reported for square planar complexes are 105 to 135  $\text{cm}^{-1}$  and for tetragonal distorted complexes 150 to 250  $\text{cm}^{-1}$ . The  $g_{\parallel}/A_{\parallel}$  values lie just within the range expected for the complexes (Table 4).

The g-values of the copper(II) complexes with a  ${}^2B_{1g}$  ground state ( $g_{\parallel} > g_{\perp}$ ) may be expressed [35] by

$$g_{\parallel} = 2.002 - (8K_{\parallel}^2 \lambda^{\circ} / \Delta E_{xy}) \quad (1)$$

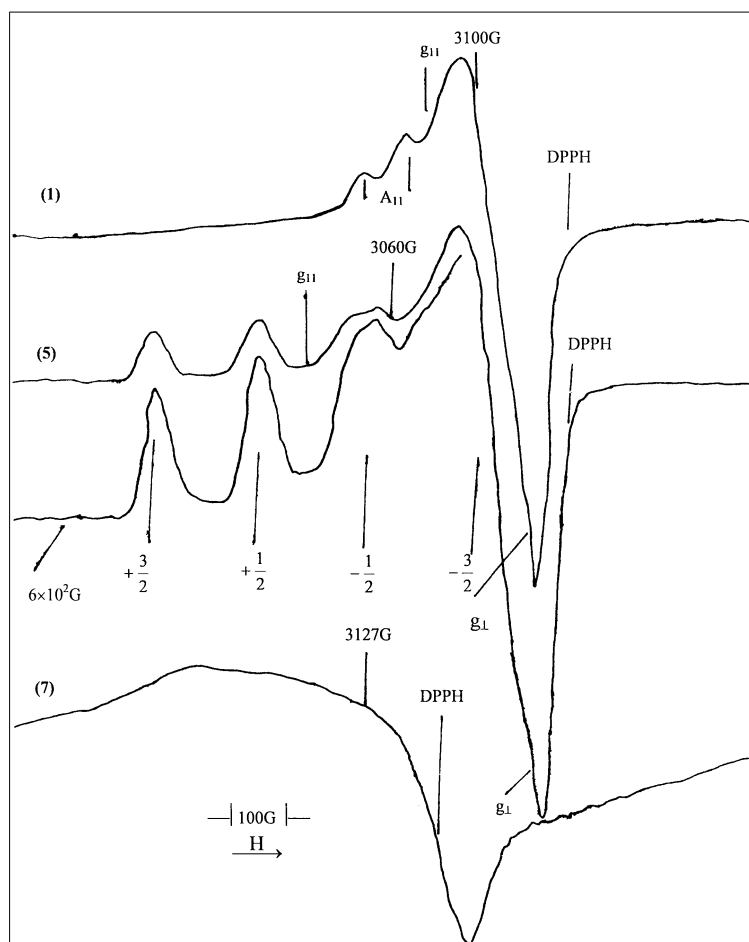
$$g_{\perp} = 2.002 - (2K_{\perp}^2 \lambda^{\circ} / \Delta E_{xz}) \quad (2)$$

where  $K_{\parallel}$  and  $K_{\perp}$  are the parallel and perpendicular components respectively of the orbital reduction factor (K),  $\lambda^{\circ}$  is the spin-orbit coupling constant for the free copper,  $\Delta E_{xy}$  and  $\Delta E_{xz}$  are the electron transition energies of  ${}^2B_{2g} \leftarrow {}^2B_{1g}$  and  ${}^2E_g \leftarrow {}^2B_{1g}$ . From the above relations, the orbital reduction factors ( $K_{\parallel}$ ,  $K_{\perp}$ , K), which are a measure of

**Table 4.** ESR parameters of the copper(II) complexes.

Compound No.	$g_{\parallel}$	$g_{\perp}$	$g_{\text{iso}}^{(a)}$	$A_{\parallel}$ (G)	$A_{\perp}$ (G)	$A_{\text{iso}}$ (G)	$G^b$	$g_{\parallel}/A_{\parallel}$ (cm)	$\Delta E_{xy}$ ( $\text{cm}^{-1}$ )	$\Delta E_{xz}$ ( $\text{cm}^{-1}$ )	$K_{\perp}^2$	$K_{\parallel}^2$	K	$\alpha^2(\text{Cu})$	$\beta^2$	$\beta_1^2$	2B (G)	$a_1^2$ (%)
(1)	2.29	2.08	2.15	168	25	72.7	3.62	128	17241	20202	0.95	0.72	0.93	0.81	1.17	0.89	-228	96.9
(2)	2.24	2.07	2.13	175	25	75.0	3.40	122.4	17391	20618	0.84	0.62	0.87	0.80	1.06	0.78	-177	75.3
(3)	2.16	2.05	2.09	138	27	64.0	3.2	155.4	14815	22222	0.64	0.35	0.73	0.60	1.07	0.58	-139	60
(4)	2.17	2.06	2.10	130	23	59	2.83	164.4	15384	22222	0.78	0.39	0.80	0.59	1.32	0.66	-130	55
(5)	2.15	2.06	2.09	125	25	58	2.50	172	14925	21276	0.74	0.33	0.77	0.46	1.60	0.72	-139	59
(6)	2.19	2.07	2.11	140	26	64	2.70	156.4	14925	21739	0.89	0.42	0.85	0.56	1.59	0.75	-149.2	63

$$g_{\text{iso}}^{(a)} = (2g_{\perp} + g_{\parallel})/3; G^{(b)} = (g_{\parallel} - 2)/(g_{\perp} - 2).$$



**Figure 1.** ESR spectra of solid complexes (1), (5) and (7) at room temperature.

covalency [35], can be calculated. For an ionic environment  $K = 1$  and for a covalent environment  $K < 1$ , the lower the value of  $K$ , the greater is the covalency

$$K_{\perp}^2 = (g_{\perp} - 2.002)\Delta E_{xz}/2\lambda^{\circ} \quad (3) \quad K_{\parallel}^2 = (g_{\parallel} - 2.002)\Delta E_{xy}/8\lambda^{\circ} \quad (4)$$

$$K^2 = (K_{\parallel}^2 + K_{\perp}^2)/3 \quad (5)$$

$K$  (Table 4), for the copper(II) complexes are indicative of their covalent nature [14,36]. Kivelson and Neiman [37] noted that, for an ionic environment,  $g_{\parallel} \geq 2.3$  and for a covalent environment  $g_{\parallel} < 2.3$ . Theoretical work by Smith [38] seems to confirm this view. The  $g$ -values reported here (Table 4) show a covalent bonding character [14]. Also, the in-plane  $\sigma$ -covalency parameters,  $\alpha^2(\text{Cu})$  was calculated by

$$\alpha^2(\text{Cu}) = (A_{\parallel}/0.036) + (g_{\parallel} - 2.002) + 3/7(g_{\perp} - 2.002) + 0.04 \quad (6)$$

The calculated values (Table 4) suggest a covalent bonding [14,39]. The in-plane and out-of-plane  $\pi$ -bonding coefficients  $\beta_1^2$  and  $\beta^2$ , respectively, are dependent upon the values of  $\Delta E_{xy}$  and  $\Delta E_{xz}$  in the following equations [39].

$$\alpha^2\beta^2 = (g_{\perp} - 2.002)\Delta E_{xz}/2\lambda^{\circ} \quad (7)$$

$$\alpha^2\beta_1^2 = (g_{\parallel} - 2.002)\Delta E_{xz}/8\lambda^{\circ} \quad (8)$$

In this work, the copper(II) complexes show  $\beta_1^2$  values in the 0.89–0.58 range (Table 4), indicating a moderate degree of covalency in the in-plane  $\pi$ -bonding, while  $\beta^2 > 1$  (Table 4), indicates the ionic character of the out-of-plane  $\pi$ -bonding [40].

It is possible to calculate approximate orbital populations for s, p or d orbitals [41] by

$$A_{\parallel} = A_{\text{iso}} - 2B[1 \pm (7/4)\Delta g_{\parallel}] \quad (9) \quad A_{\perp} = A_{\text{iso}} + B[1 \pm (7/2)\Delta g_{\perp}] \quad (10)$$

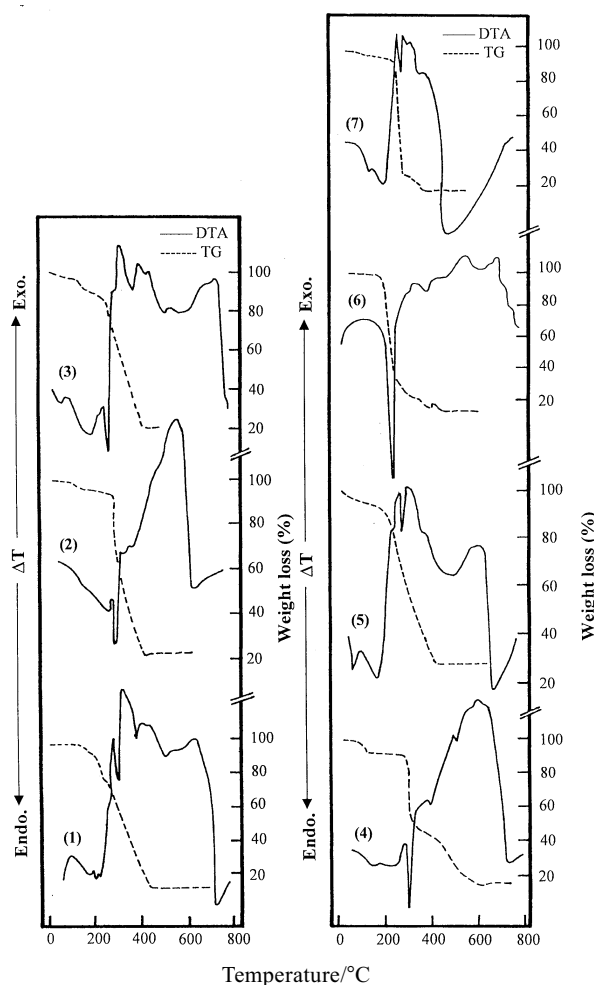
$$a_s^2 = A_{\text{iso}}/A^{\circ}, \quad a_{p,d}^2 = 2B/2B^{\circ} \quad (11)$$

where  $A^{\circ}$  and  $2B^{\circ}$  are the calculated dipolar couplings for unit occupancy of s and d orbitals respectively.

When the data are analysed using the copper hyperfine coupling and considering all the sign combinations, the only physical meaningful results are found when  $A_{\parallel}$  and  $A_{\perp}$  are negative. The resulting isotropic coupling constant ( $A_{\text{iso}}$ ) and the parallel component of the dipolar coupling ( $2B$ ) are also negative. The orbital populations for the copper(II) complexes (Table 4) indicate a  $d_{x^2-y^2}$  ground state [42].

**Thermal studies (DTA and TGA):** DTA and TGA curves of the investigated complexes are shown in Fig. 2. The data of thermal analyses are collected in Table 5. Generally, DTA curves of all complexes except (1) and (6) are characterized by one (splitted) or two endothermic peaks between 31–296°C. These DTA peaks are assigned to desolvation, as indicated from TGA weight loss in that temperature range (Table 5). The low temperature of dehydration for complexes (3) and (5) confirms the presence of water molecules as lattice water [36,43]. The presence of more than one desolvation peak [complexes (3), (4), (5) and (7)] indicates that solvent molecules are not isoenergetically bound and, thus, their elimination takes place in different steps. Complexes (5) and (7) complete their dehydration during decomposition process, whilst complex (6) losses water of crystallization during decomposition.

For complexes (1) and (6), the DTA curves show an exothermic peak between 31–170°C [14]. TGA thermogram shows no weight loss in that temperature range. The DTA peak can be assigned to lattice or chemical rearrangement of the complexes, together with a brake of intermolecular hydrogen bonding. The observed endoeffects between 150–320°C are assigned to loose or partial decomposition of organic ligands (Table 5). It is observed that the decomposition process starts with partial elimination



**Figure 2.** DTA and TGA curves of the complexes (1–7).

or lost of the organic ligand. The observed DTA effects between 320–800°C are assigned to completion of the decomposition processes, leading metallic Cu, for complex (1) or (CuO + C) for the other complexes [44]. The final products of thermal decomposition of the most complexes were investigated by IR spectroscopy, which show no characteristic peaks of the ligands, indicating a complete decomposition of the complexes. The temperature of the decomposition was also confirmed from the heating of the solid complexes on hot stage microscope.

From the above data, it can be concluded that:

1. For the same metal ion, the thermal stability of the investigated mixed ligand complexes depends mainly on the nature of the weakly bonded ligand as well as the decomposition reaction along with the room temperature structure of the complexes.

2. Complex **(2)** is thermally more stable than other complexes. This may be due to the presence of three six-membered chelate rings and also the increase the number of intermolecular hydrogen bondings. The lower thermal stability of the complex **(6)**, compared to complex **(2)**, may be attributed to the steric effect, as well as the presence of  $\text{CuO}_4\text{N}_2$  chromophore, which may be less distorted than  $\text{CuO}_5\text{N}$  chromophore in complex **(2)**.

**Table 5.** Thermal data of the copper(II) complexes.

Com- pound	Temperature range /°C		Weight loss/%		Reaction
	DTA	TGA	Calc. (F)		
<b>(1)</b>	31–150*	–	–	–	Lattice or chemical rearrangement + broken H-bonding
	150–249*	150–249	22.4 (22.1)	–	–( $\text{CH}_3\text{.Ph.NH-}$ ) moiety
	249–444*	249–444	(64.5)	–	Completion of decomposition reaction
	440–800*	–	–	–	–
		at 444	13.4 (13.4) <sup>Δ</sup>	–	$\equiv\text{Cu}$
<b>(2)</b>	50–296*	50–296	5.9 (5.9)	–	$-\text{C}_2\text{H}_5\text{OH}$ + broken H-bonding
	296–320*	296–320	35.2 (35.5)	–	$-(\text{HOOC.Ph.NH.CO.CH}_2\text{-CO-CH}_3)$
	320–645*	320–462	(32.2)	–	Completion of decomposition reaction
		at 462	20.7 (21.4) <sup>Δ</sup>	–	$\equiv\text{CuO} + 7\text{C}$
<b>(3)</b>	31–100*	31–100	1.70 (1.7)	–	$-\frac{1}{2}\text{H}_2\text{O}$
	100–230	100–230	8.6 (8.9)	–	$-\text{C}_2\text{H}_5\text{OH}$ + broken H-bonding
	230–310*	230–310	30.7 (30.7)	–	$-(\text{HOOC-Ph-NH-CO})$
	310–800*	310–450	(38.4)	–	Completion of decomposition reaction
	at 450	19.0 (20.3) <sup>Δ</sup>	–	$\equiv\text{CuO} + 3\text{C}$	
<b>(4)</b>	90–170*	90–170	6.5 (6.5)	–	$-2\text{H}_2\text{O}$ + broken H-bonding
	170–275*	170–275	2.0 (2.0)	–	$-\frac{1}{4}\text{C}_2\text{H}_5\text{OH}$
	275–320*	275–320	40.0 (40.1)	–	$-(\text{HOOC-Ph-NH.CO=CH-CO-CH}_3)$
	320–750*	320–650	(33.1)	–	Completion of decomposition reaction
	at 650	18.7 (18.3) <sup>Δ</sup>	–	$\equiv\text{CuO} + 2\text{C}$	
<b>(5)</b>	31–100	31–100	3.8 (3.8)	–	$-\text{H}_2\text{O}$
	100–220*	100–220	7.6 (7.6)	–	$-2\text{H}_2\text{O}$ + broken H-bonding
	220–750*	212–425	(60.1)	–	$-(2\text{H}_2\text{O}+\text{CO}+\text{HOOC-PhNH-O-C=CH-C-CH}_3)$
		at 425	29.5 (29.4) <sup>Δ</sup>	–	$\equiv\text{CuO} + 5\text{C}$

Table 5 (continuation)

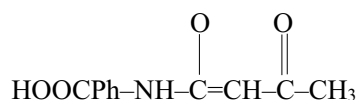
(6)	31–170*	–	–	Lattice or chemical rearrangement + broken H-bonding
	170–259*	170–259	64.9 (64.6)	$-(2\text{H}_2\text{O} + \text{HOOC-Ph.NH-CO=CH-CO-CH}_3) + \text{Ph.NH-CO-CH=C(CH}_3\text{)-N-Ph}$
	259–750*	259–501	(18.0)	Completion of decomposition reaction
		at 501	15.7 (15.4) <sup>Δ</sup>	$\equiv\text{CuO} + 3\text{C}$
(7)	31–165*	31–165	2.8 (2.8)	$-2\text{H}_2\text{O} + \text{broken H-bonding}$
	165–252*	165–252	2.8 (2.9)	$-2\text{H}_2\text{O}$
	252–310*	252–310	44.8 (43.9)	$-(9\text{H}_2\text{O} + 2\text{HOOCPhNH-CO=CH-CO-CH}_3)$
	310–395*	310–395	6.5 (6.5)	$-2\text{CO}_2$ (completion of decomposition reaction)
	395–750*	at 395	42.9 (43.9) <sup>Δ</sup>	$5\text{CuO} + 15\text{C}$

\* Endo

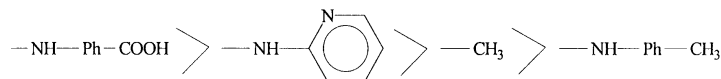
• Splitted

Δ Final product percent

3. For the same metal ion, and fixing one of the two mixed ligand namely,



the thermal stability decreases in the order



This sequence results from the temperature of the first decomposition process.

4. The higher thermal stability of the complex (7) may be due to the strong ability of five-ring forming of oxalato (eight rings), in addition to the presence of two six-membered chelate rings and intermolecular hydrogen bonding.

**Catalytic activity:** The decomposition of  $\text{H}_2\text{O}_2$  was used as a model for the oxidation-reduction reaction to measure the catalytic activity of the complexes obtained. The decomposition reaction was found to follow a first-order kinetics. The results of decomposition of  $\text{H}_2\text{O}_2$  over the complexes (1) and (5) are presented in Fig. 3. The data are plotted as  $\ln a/(a-x)$  versus time, where “a” is the initial concentration of  $\text{H}_2\text{O}_2$  and “x” the concentration after time t; the rate constant values for the complexes (1) and (5) are 0.02 and 0.04 respectively.

As seen in Fig. 3, the rate of catalytic activity of an octahedral complex (5) is larger than a square planar complex (1). Previous researchers reported that the  $\text{Cu}^{2+}/\text{Cu}^+$  system forms catalytic active sites, which are responsible for the decomposition of  $\text{H}_2\text{O}_2$  [45,46]. The  $\text{Cu}^+$  was identified as the species, which control the cata-

lytic activity of the complexes. The decomposition of  $\text{H}_2\text{O}_2$  in the presence of complex (5) may be represented as follows:

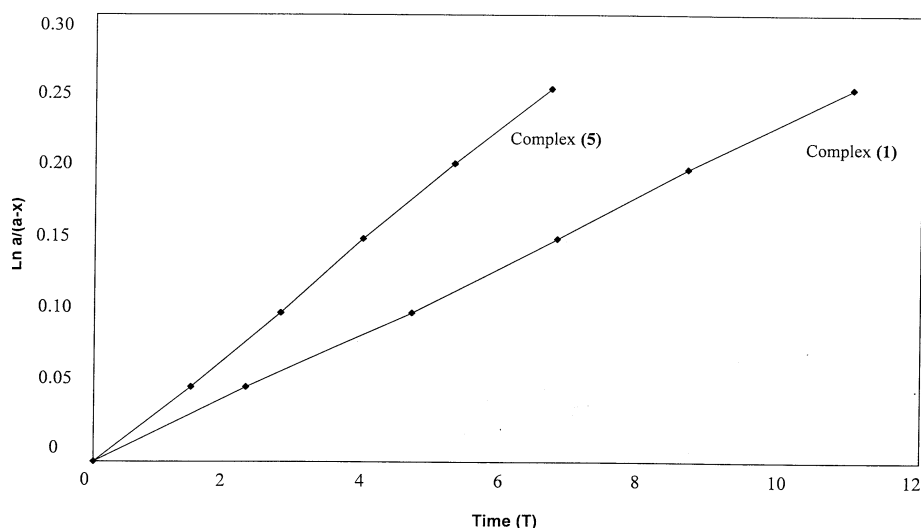
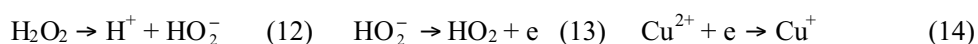


Figure 3. Decomposition of  $\text{H}_2\text{O}_2$  on complexes (1) and (5) at room temperature.

## REFERENCES

1. Kahn O., *Angew. Chem., Int. Ed. Engl.*, **24**, 834 (1985).
2. Kahn O., *Struct. Bonding (Berlin)*, **68**, 89 (1987).
3. Colacio E., Dominguez-Vera J.M., Kivekas R., Moreno J.M., Romerosa A. and Ruiz J., *Inorg. Chim. Acta*, **212**, 115 (1993).
4. Aly M.M. and El-Awad A.M., *J. Inorg. Nucl. Chem.*, **42**, 567 (1980).
5. Aly M.M. and El-Awad A.M., *J. Inorg. Nucl. Chem.*, **42**, 1295 (1980).
6. Aly M.M., *Inorg. Nucl. Chem. Lett.*, **15**, 17 (1979).
7. Aly M.M. and Al-Shatti N.I., *Trans. Met. Chem.*, **23**, 361 (1998).
8. Chan S.C., Koh L.L., Leung P.H., Ranford J.D. and Sim K.Y., *Inorg. Chim. Acta*, **236**, 101 (1995).
9. Iliopoulos P., Fallon G.D. and Murray K.S., *J. Chem. Soc., Dalton Trans.*, 437 (1986).
10. Hanan G.S., Arana G.R., Lehn L.M., Baum G. and Fenske D., *Chem. Eur. J.*, **2**, 1292 (1996).
11. Lewis L. and Wilkins R.G., "Modern Coordination Chemistry", Interscience, NY; p. 403 (1960).
12. Kanungo S.B., Parida K.M. and Sant B.R., *Electrochim. Acta*, **26**, 1157 (1981).
13. Geary W.J., *Coord. Chem. Rev.*, **7**, 81 (1971).
14. El-Tabl A.S., Kashar T.I., El-Bahnasawy R.M. and El-Monsef Ibrahim A., *Polish J. Chem.*, **73**, 245 (1999).
15. El-Sonbati A.Z., *Trans. Met. Chem.*, **16**, 45 (1991).
16. Singh K., Singh R.V. and Tandon J.P., *Polyhedron*, **7**, 151 (1988).
17. Goher M.A.S. and Hafez A.K., *Acta Chim. Hung.*, **121**, 363 (1986).
18. Alyaviya M.K., Rysopaeva R.S. and Kats A.L., *Zh. Neorg. Khim.*, **17**, 957 (1972).
19. Evans R.E. and Kynaston W., *J. Chem. Soc.*, 1005 (1962).



20. Zarembowitch J., Claude R. and Kahn O., *Inorg. Chem.*, **24**, 1576 (1985).
21. Diab M.A., El-Sonbati A.Z., El-Sanabari A.A. and Taha F.I., *Polymer Deg. and Stab.*, **24**, 51 (1989).
22. Aly M.M. and Imam S.M., *Polyhedron*, **13**, 1907 (1994).
23. Aly M.M. and Imam S.M., *Monatsh. Chem.*, **126**, 173 (1995).
24. El-Tabl A.S., Ph.D. Thesis, Menoufia University, Egypt (1993).
25. Aravindakshan K.K., *Indian J. Chem.*, **26**, 241 (1987).
26. Abu-El-Wafa S.M., Salib K.A.R., El-Inany G. and Ismail T.M., *Synth. React. Inorg. Met-Org. Chem.*, **20**, 1343 (1990).
27. Tan S.F., Ang K.P. and Jayachandran H.L., *Trans. Met. Chem.*, **9**, 390 (1984).
28. El-Tabl A.S., *Trans. Met. Chem.*, **22**, 259 (1997).
29. Aly M.M. and Al-Shatti N.I., *Trans. Met. Chem.*, **23**, 361 (1998).
30. Sureshan C.A. and Bhattacharya P.K., *Polyhedron*, **16**, 489 (1997).
31. Bain G.A., West D.X., Krejci J., Martinez J.V., Ortega S.H. and Toscano R.A., *Polyhedron*, **16**, 855 (1997).
32. El-Tabl A.S., *Trans. Met. Chem.*, **23**, 63 (1998).
33. Procter I.M., Hathaway B.J. and Nicholls P.N., *J. Chem. Soc. (A)*, 1678 (1969).
34. Nickless D.E., Power M.J. and Urbach F.L., *Inorg. Chem.*, **22**, 3210 (1983).
35. Ray R.K., *Inorg. Chim. Acta*, **174**, 257 (1990).
36. El-Tabl A.S., *Trans. Met. Chem.*, **27**, 166 (2002).
37. Kivelson D. and Neiman R., *J. Chem. Phys.*, **35**, 149 (1961).
38. Smith D.W., *J. Chem. Soc. A*, 3108 (1970).
39. Kuska H.A. and Rogers M.T., *Coordination Chemistry*, (Ed. by A.E. Martel), Van Nostrand Reinhold Co. N.Y. (1971).
40. Bhadbhade M.M. and Srinivas D., *Inorg. Chem.*, **32**, 2458 (1993).
41. Symons M.C.R., "Chemical and Biochemical Aspects of Electron Spin Resonance, Van Nostrand Reinhold, Wokingham, (1979).
42. El-Tabl A.S., *J. Chem. Res-S*, 529 (2002).
43. Yasodhai S. and Govindarajan S., *J. Thermal Anal.*, **62**, 737 (2000).
44. Din S.U. and Umar M., *J. Thermal Anal.*, **58**, 61 (1999).
45. Schraml-Marth M., Wokavn A., Curry-Hyde H.E. and Baiker A., *J. Catal.*, **133**, 415 (1992).
46. Atia A.A., Radwan N.R. and Donia A.M., *Afinidad*, **496**, 431 (2001).