# Articles

## Synthesis and Characterization of Cobalt(II)/(III), Nickel(II) and Copper(II) Complexes of New 14, 15 and 16-Membered Macrocyclic Ligands

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A new series of nickel(II), cobalt(II)/(III) and copper(II) complexes of 14, 15 and 16-membered of macrocyclic ligands have been prepared and characterized by elemental analyses, IR, UV-VIS and ${}^1$H-NMR spectra, magnetic susceptibilities, conductivities, DTA and ESR measurements. Molar conductances in DMF solution indicate that, the complexes are nonelectrolytes except (9-12) complexes. The electronic spectra show that, all complexes are square planar or distorted octahedral geometry. The ESR spectra of solid complexes (4), (8) and (11) show square planar of axial type symmetry ($d_{x^2-y^2}$) with considerable covalent bond character. However, complex (12) shows a spectrum of octahedral geometry with $d_{z^2}$ ground state. Complex (12) shows exploitation in reducing the amount of electron adducts formed in DNA during irradiation with low radiation products.

**Key Words :** Complexes, Syntheses, Spectral studies, Conductivity, Magnetism

## Introduction

There has been considerable interest in the synthesis of transition metal complexes of macrocyclic ligand systems because they play vital roles in biological systems.[1] Also, interest in these species stems largely from the enhanced kinetic and thermodynamic stability of their complexes relative to those of related open chain ligands. Generally macrocyclic complexes are also of interest because of the synthetic flexibility involved in their preparation which allows for systematic variation in parameters such as ring size, the nature of the donor atoms, and the steric and electronic effects associated with the groups located on the periphery of the macrocyclic ring.[2] Increasing interest in the macrocyclic metal complexes as model compounds for active sites in enzymes comprising corrin or porphyrin moieties has resulted in various preparative routes to such compounds. Earlier work had demonstrated that use of a difunctional macrocycle in such reactions resulted in the production of polymers that were highly cross-linked and hence insoluble.[3] The aim of this work was the production of symmetric and asymmetric macrocyclic complexes containing a single reactive functional site. New cobalt(II)/(III), nickel(II) and copper(II) have been prepared and characterized and also, to study the effect of $\gamma$-radiation on DNA molecules in the presence of cobalt(III) complex (12).

## Experimental Section

All chemicals and solvents were reagent grade and used as received. C, H, N and M analyses were determined at the

Analytical Unit of Cairo University, Egypt. The complexes were dried in air or in vacuo over $P_2O_5$. IR spectra (as KBr pellets) and (as Nujol mull between CsBr prisms) were recorded on a Perkin-Elmer 681 spectrophotometer. Electronic spectra in the 200-900 nm region were recorded on a Perkin-Elmer 550 spectrophotometer. ${}^1$H-NMR spectra were obtained with a Perkin-Elmer R32-90 MHz spectrometer using TMS as internal standard. Magnetic susceptibilities were measured at 25 °C by the Gouy method using mercuric tetrathiocyanato-cobaltate(II) as the magnetic standard. Diamagnetic corrections were estimated from Pascal's constant. The magnetic susceptibilities were calculated from the equation $\mu_{eff} = 2.84 \sqrt{\chi_M^{cor} \cdot T}$. Molar conductances were measured on a Tacussel type CD$_6$NG conductivity bridge using $10^{-3}$ M DMF. DTA analysis was carried out in air (20-700 °C) using a Schimadzu DT-30 thermal analyzer. The ESR spectra of solid complexes (4, 8 and 11) at room temperature and (12) in the $CD_3OD$ + $D_2O$ (10%) in the form of small beads at 77 K were measured using a Varian E-109 spectrometer. The complex (12) and DNA molecules were exposed to ${}^{60}Co$ $\gamma$-rays at 77 K using a 0.22 M radh$^{-1}$ dose for 5 h (Leicester University, England). DPPH was used as the marker. The TLC of the all complexes confirmed their purity.

**Preparation of the ligands.**

$H_2L^1$, **Compound (1).** To a solution of 4-nitro-1,2-diaminobenzene (5.0 gm, 0.033 mol) in DMF (100 cm$^3$) was added to 3-ethoxyvinylidene-2,4-pentanedione (5.1 gm, 0.033 mol) in (20 cm$^3$) DMF. A few drops of conc. HCl was added and the mixture was refluxed for 4 h, then the solvent was reduced to a small volume *in vacuo* and methanol was added to precipitate the yellow product. The solid was collected by filtration, washed with methanol, and then dried

over $P_4O_4$. The analytical data are given in Table 1.

**$H_2L^2$, Compound (5).** To a solution of 4-nitro-1,2-diaminobenzene (2.5 gm, 0.0165 mol) in DMF (50 cm$^3$) was added to 3-ethoxyvinylidene-2,4-pentanedione (5.1 gm, 0.033 mol) in (30 cm$^3$) DMF. Using a method described above, the solid (I) was collected and then dried in air. To (5.0 gm, 0.013 mol) of a solid (I) in DMF (50 cm$^3$) was added to 1,3-diaminopropane (1.1 cm$^3$, 0.013 mol) in the presence of a few drops of conc. HCl. The reaction mixture was refluxed for 3 h, then the solvent volume was reduced *in vacuo* and methanol was added to precipitate the yellowish brown product which was collected by filtration, washed with methanol and then dried over $P_4O_{10}$. The analytical data are given in Table 1.



(I)
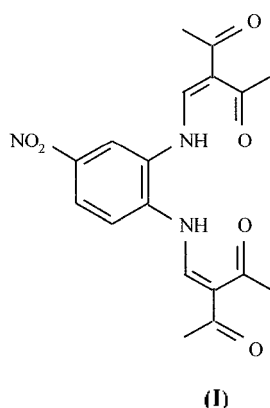
**Preparation of metal complexes.** Neutral dichloro-$\beta$-diketone and 3-(benzylidene)-$\beta$-diketone cobalt(II) complexes were prepared by literature procedure.[4]

**Complexes (2-4) using $H_2L^1$:** To a rapidly stirred suspension of $H_2L^1$ (5.0 gm, 0.01 mol) in methanol (70 cm$^3$) was added sodium hydroxide (0.8 gm, 0.02 mol) in (15 cm$^3$) $H_2O$ followed by metal(II) acetate, [Ni(OAc)$_2$·4H$_2$O, complex (2), Co(OAc)$_2$·4H$_2$O, complex (3), (2.5 gm, 0.01mol) and Cu(OAc)$_2$H$_2$O, complex (4), (2.0 gm, 0.01 mol)]. The reaction mixture was refluxed with stirring for 2 h. A solid complex appeared was collected by filtration and then washed with warm methanol and dried. The analytical data are given in Table 1.
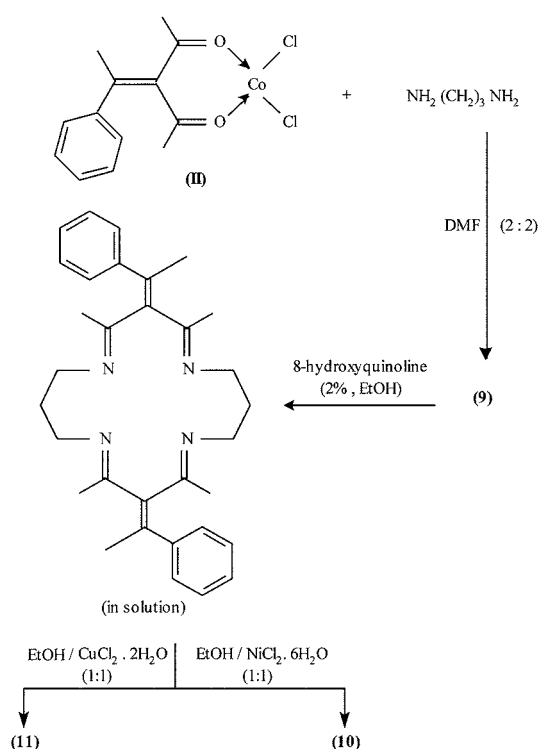
**Complexes (6-8) using $H_2L^2$:** To a rapidly stirred suspension of $H_2L^2$ (5.0 gm, 0.01 mol) in methanol (50 cm$^3$) was added sodium hydroxide (0.89 gm, 0.02 mol) in (15 cm$^3$), $H_2O$ followed by Ni(OAc)$_2$·4H$_2$O, complex (6), Co(OAc)$_2$·4H$_2$O, complex (7), (2.5 gm, 0.01 mol) and Cu(OAc)$_2$·H$_2$O, complex (8), (2.2 gm, 0.01 mol)]. Using a method described above, the product was removed by filtration, washed with warm methanol and then dried. The analytical data are given in Table 1.

**Complexes (9):** This complex (9) was prepared as follows:- A mixture of 3-(benzylidene)-$\beta$-diketone cobalt(II), (Scheme 1) (5.0 gm, 0.016 mol) and piperidine in DMF (100 cm$^3$) was gradually added to a 1,3-diaminopropane (1.2 gm, 0.016 mol) in DMF (25 cm$^3$) in a round bottom flask. The mixture was refluxed for 3 h. Upon concentration to one-

**Table 1.** Analytical, physical and thermal properties of the ligands and their metal complexes

| Comp. No./Formula | Colour | Yield (%) | M.p. (C°) | $\mu_{eff}$ (B.M.) | $\Lambda_m$ ($\Omega^{-1}$cm$^2$mol$^{-1}$) | Found (Calcd.) % | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | C | H | N | M | Cl |
| (1) $H_2L^1$ | yellow | 85 | 168 | – | – | 58.7 | 4.5 | 17.2 | – | – |
| [C$_{24}$H$_{22}$N$_6$O$_6$] | | | | | | (58.8) | (4.5) | (17.1) | – | – |
| (2) | red | 78 | 195 | diamag. | 13.2 | 49.6 | 4.0 | 14.2 | 9.9 | – |
| [C$_{24}$H$_{20}$N$_6$O$_6$Ni]·2H$_2$O | | | | | | (49.4) | (4.1) | (14.4) | (10.1) | – |
| (3) | brown | 82 | 200 | 4.91 | 10.8 | 49.5 | 4.1 | 14.5 | 10.3 | – |
| [C$_{24}$H$_{20}$N$_6$O$_6$Co]·2H$_2$O | | | | | | (49.4) | (4.1) | (14.4) | (10.1) | – |
| (4) | brown | 75 | 195 | 1.95 | 11.8 | 50.4 | 4.0 | 15.0 | 11.3 | – |
| [C$_{24}$H$_{20}$N$_6$O$_6$Cu]·H$_2$O | | | | | | (50.6) | (3.9) | (14.8) | (11.1) | – |
| (5) $H_2L^2$ | yellowish brown | 83 | 165 | – | – | 56.1 | 6.5 | 15.4 | – | – |
| [C$_{21}$H$_{25}$N$_5$O$_4$]·2H$_2$O | | | | | | (56.3) | (6.5) | (15.6) | – | – |
| (6) | red | 82 | 200 | diamag | 12.3 | 50.1 | 5.4 | 14.0 | 11.8 | – |
| [C$_{21}$H$_{23}$N$_5$O$_4$Ni]·2H$_2$O | | | | | | (50.0) | (5.4) | (13.9) | (11.6) | – |
| (7) | deep brown | 76 | 205 | 4.75 | 13.1 | 50.1 | 5.4 | 14.0 | 11.8 | – |
| [C$_{21}$H$_{23}$N$_5$O$_4$Co]·2H$_2$O | | | | | | (50.0) | (5.4) | (13.9) | (11.7) | – |
| (8) | brown | 80 | 198 | 1.87 | 13.8 | 49.6 | 5.3 | 13.8 | 12.5 | – |
| [C$_{21}$H$_{23}$N$_5$O$_4$Cu]·2H$_2$O | | | | | | (49.5) | (5.3) | (13.7) | (12.4) | – |
| (9) | dull red | 75 | 212 | 4.8 | 115 | 60.0 | 6.1 | 9.1 | 9.0 | 12.0 |
| [C$_{30}$H$_{36}$N$_4$Co]Cl$_2$·H$_2$O | | | | | | (60.2) | (6.3) | (9.3) | (8.8) | (11.8) |
| (10) | red | 78 | 208 | diamag | 118 | 58.4 | 6.3 | 9.1 | 9.7 | 11.2 |
| [C$_{30}$H$_{36}$N$_4$Ni]Cl$_2$·2H$_2$O | | | | | | (58.5) | (6.4) | (9.0) | (9.5) | (11.4) |
| (11) | violet | 75 | 210 | 2.0 | 123 | 57.9 | 6.2 | 8.7 | 9.9 | 11.5 |
| [C$_{30}$H$_{36}$N$_4$Cu]Cl$_2$·2H$_2$O | | | | | | (58.1) | (6.4) | (8.9) | (10.1) | (11.4) |
| (12) | Orange | 81 | 192 | diamag | 168 | 34.0 | 6.5 | 18.2 | 9.6 | 18.0 |
| [C$_1$·H$_{36}$N$_8$O$_4$Co]Cl$_3$·H$_2$O | | | | | | (34.2) | (6.3) | (18.6) | (9.8) | (17.8) |

(in solution)

EtOH / CuCl₂ . 2H₂O          EtOH / NiCl₂. 6H₂O
(1:1)                                    (1:1)

(11)                                        (10)

**Scheme 1**

third volume followed by the addition of petroleum ether (3 volume) and subsequent cooling at 0 °C (2 h). Dull red

crystalline solid product precipitated. This product was removed by filtration, washed with 50% (v/v) MeOH-Me₂CO and dried. The analytical data are given in Table 1.

**Complexes (10) and (11):** Complexes (10) and (11) were prepared as follows:- In a two-necked 250 cm³ round-bottomed flask equipped with a condenser and a stirrer. Complex (9) (5.0 gm, 0.008 mol) was dissolved in DMF (50 cm³). An aqueous solution of NaOH (0.66 gm, 0.016 mol) was added for neutralization. 8-hydroxyquinoline (EtOH solution, 2%) was added, then the mixture was heated to 60-80 °C until the light brown amorphous cobalt oxinate became crystalline. The latter was allowed to settle at room temperature and was removed by filtration. The filtrate was concentrated and NiCl₂·6H₂O (7.5 gm, 0.016 mol) (10) or CuCl₂·2H₂O (2.8 gm, 0.016 mol) in ethanol (50 cm³), (11) was added. The formed complexes were filtred off, washed with warm EtOH and dried. The analytical data are given in Table 1.

**Complex (12):** Complex (12) was prepared as a method used for preparaing [Co(NO₂)₂-sar)]Cl₃.[5]

## Results and Discussion

The reaction of 3-ethoxyvinylidene-2,4-pentanedione with 4-nitro-1,2-diaminobenzene (2 : 2) or (2 : 1) in DMF, *via* a Michael addition followed by elimination, give the 2 : 2 substitution product H₂L¹(1) and (2 : 1) product (I) which is reacted directly with 1,3-diaminopropane to give H₂L²(5)
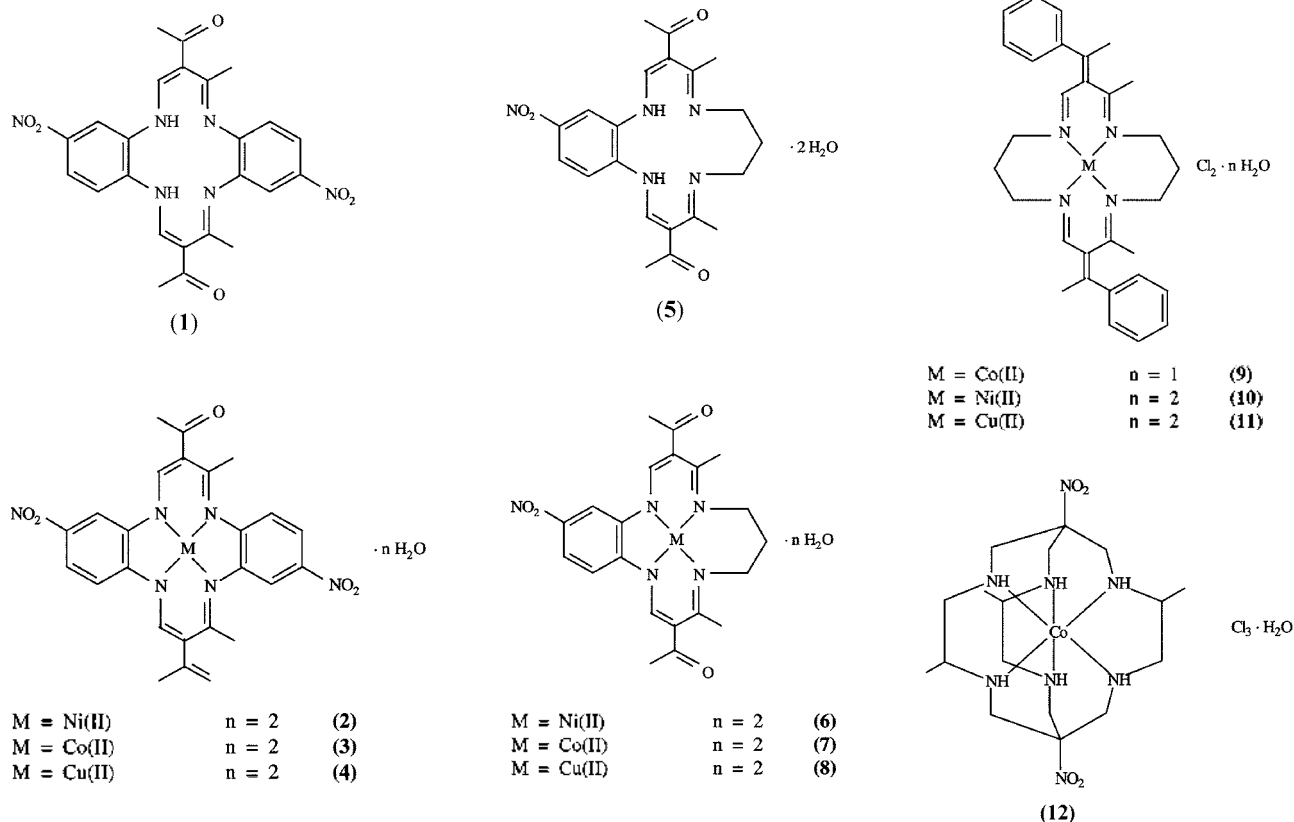


(1)

(5)

M = Co(II)          n = 1          (9)
M = Ni(II)          n = 2          (10)
M = Cu(II)          n = 2          (11)

M = Ni(II)          n = 2          (2)
M = Co(II)          n = 2          (3)
M = Cu(II)          n = 2          (4)

M = Ni(II)          n = 2          (6)
M = Co(II)          n = 2          (7)
M = Cu(II)          n = 2          (8)

(12)

**Figure 1**

**Table 2.** IR spectral (cm$^{-1}$) of the ligands and their metal complexes

| Comp. No. | v(N-H/O-H) | v(C=O) | v(C=N) | v(C=C)$_{Al,Ar}$ | v(NO$_2$) | v(M-N) |
|---|---|---|---|---|---|---|
| (1) | 3230, 3150 | 1650 | 1612 | 1570, 1595 | 1330, 1525 | – |
| (2) | 3630-3100 | 1638 | 1605 | 1568, 1590 | 1320, 1523 | 570 |
| (3) | 3640-3120 | 1640 | 1608 | 1567, 1592 | 1325, 1530 | 565 |
| (4) | 3600-3130 | 1640 | 1605 | 1565, 1590 | 1320, 1515 | 570 |
| (5) | 3430, 3350 3560-3150 | 1650 | 1610 | 1580, 1598 | 1320, 1512 | – |
| (6) | 3630-3050 | 1640 | 1605 | 1575, 1595 | 1317, 1520 | 571 |
| (7) | 3640-3120 | 1640 | 1605 | 1571, 1595 | 1316, 1518 | 565 |
| (8) | 3630-3130 | 1638 | 1606 | 1578, 1596 | 1315, 1515 | 570 |
| (9) | 3360-3100 | – | 1608 | 1585, 1618 | – | 550 |
| (10) | 3420-3150 | – | 1610 | 1582, 1615 | – | 545 |
| (11) | 3400-3120 | – | 1607 | 1580, 1616 | – | 560 |
| (12) | 3480-3395 3350-3120 | – | – | – | 1350, 1560 | 575 |

(Figure 1).

A suspension of ligands **(1)** and **(5)** in methanol at reflux in the presence of sodium hydroxide reacts with metal(II) acetate to generate the corresponding complexes (Figure 1) in high yield (75-82%). The same complexes were obtained using the template reaction. Complexes **(9-11)** were prepared according to Scheme 1.

Analytical and physical data (Table 1). and spectral data (Tables 2 and 3) are compatible with the proposed structures (Figure 1). The complexes are coloured. stable in air and partialy soluble in common solvents except DMF and DMSO. The $^1$H-NMR spectra of the compounds **(1)** and **(5)** exhibit signals in the 8.2-8.7 ppm range corresponding to aromatic and methine protons and in the 2.4-2.6 ppm range due to the four acetyl group protons. Resonances at 11.3-11.8 ppm range were assigned to the NH group. This downfield phenomenon is attributed to hydrogen bonding.[6] Compound **(5)** shows signals at 2.0-3.8 ppm range. assigned to methylene groups.[7] Complex **(12)** shows resonances at 2.72. 2.85 and 2.96 ppm. ascribed to the propylenediamine methylene protons. another two peaks appear at 3.41 and 3.55 ppm corresponding to the methylene groups of the caps. another peak at 2.48 ppm. assigned to the protons of methyl group of the propylenediamine. A single symmetrical resonance appears at 7.9 ppm assigned to the NH group.[8]

**IR spectra.** Important spectral bands for the ligands and their metal complexes are presented in Table 2. The IR spectra of the ligands. **(1)** and **(5)** show two bands in the 3430-3150 cm$^{-1}$ range. assigned to $v$ (NH). Another band appears at 1650 cm$^{-1}$ due to $v$ (C=O) of acetyl group. The $v$ (C=N) appears at 1612 and 1610 cm$^{-1}$ respectively.[9] Two bands appear in the 1598-1570 cm$^{-1}$ range. assigned to $v$ (C=C)$_{Al}$ and $v$ (C=C)$_{Ar}$ groups respectively and two bands at 1525-1320 cm$^{-1}$ range. ascribed to $v$ (NO$_2$) group.[6] The IR spectra of the complexes exhibit new bands and shifts of characteristic bands. The $v$(C=O) of acetyl group was observed at a lower frequency (1640 and 1638 cm$^{-1}$). indicating minor change in symmetry of this group due to

metal coordination. The absence of $v$(NH) in the complexes **(2-4. 6-8)** indicates the aza proton is lost upon metal ion complexion. However. complex **(12)** shows a broad band in the 3480-3395 cm$^{-1}$ range. assignable to the NH group. In each spectrum of metal complexes a medium intensity band is observed at 575-545 cm$^{-1}$ range. assigned to the metal-nitrogen stretching vibration.[10] Bands at 3640-3100 cm$^{-1}$ range due to $v$(OH) of water molecules associated with the compounds.[11,12] The $v$(C=N) is shifted towards a lower wave number by 4-7 cm$^{-1}$ range **(2-4. 6-8)** indicating a decrease in the C=N bond order as a result of M-N bond formation.[10] however. complexes **(9-11)** show $v$(C=N) band at 1610-1608 cm$^{-1}$ range. The bands at 1585-1565 and 1618-1590 cm$^{-1}$ ranges assigned to $v$(C=C)$_{Al}$ and $v$(C=C)$_{Ar}$ respectively. The complexes **(2-4. 6-8** and **12)** show two bands at 1350-1315 and 1560-1512 cm$^{-1}$ ranges. assigned to $v$(NO$_2$) group. Catalytic reduction of a suspension complex **(2)** in ethyl acetate solution by hydrogen readily produced the corresponding primary amine substituted macrocycle. This complex was confirmed by microanalyses data and IR spectrum which gives a characteristic bands at 3320 and 3250 cm$^{-1}$. assigned to $v$(NH$_2$) group.[7]

**Conductivity.** The molar conductances of the complexes (Table 1). indicate their non-electrolytic nature except **(9-12)** which have high values suggesting 1 : 2 or 1 : 3 electrolytes.[9,13,14]

**Magnetic moment.** The magnetic moments for the complexes are shown in Table 1. Complexes **(2)**. **(6)**. **(10)** and **(12)** are diamagnetic and the complexes **(3)**. **(7)** and **(9)** show values 4.91. 4.75 and 4.8 B.M. respectively. indicating high spin. cobalt(II) complexes.[10] However. the complexes **(4)**. **(8)** and **(11)** show values 1.95. 1.87 and 2.0 B.M. respectively. indicating Cu(II) square planar complexes.[4,15,16]

**Electronic spectra.** The electronic spectra of the ligands and their complexes are summarized in Table 3. The ligands **(1)** and **(5)** give bands at 298 nm ($\varepsilon = 0.45 \times 10^{-3}$ mol$^{-1}$cm$^2$). 290 nm ($\varepsilon = 1.8 \times 10^{-3}$ mol$^{-1}$cm$^2$) and 310 nm ($\varepsilon = 0.75 \times 10^{-3}$ mol$^{-1}$cm$^2$). 314 nm ($\varepsilon = 0.32 \times 10^{-3}$ mol$^{-1}$cm$^2$). These bands were assigned to $\pi$-$\pi^*$ transitions within the ligands

**Table 3.** Electronic spectra of the ligands and their metal complexes

| Comp. No. | $\lambda$max (nm) | Medium |
|---|---|---|
| (1) | 298 nm ($\varepsilon$ = 0.45 × $10^{-3}$ mol$^{-1}$ cm$^{2}$) | DMF |
| | 310 nm ($\varepsilon$ = 0.75 × $10^{-3}$ mol$^{-1}$ cm$^{2}$) | – |
| (2) | 540, 490, 350, 280 | N.M. |
| | 510, 475, 330, 268 | DMF |
| (3) | 535, 465, 348, 300 | N.M. |
| | 508, 430, 325, 290 | DMF |
| (4) | 546, 505, 350, 277 | N.M. |
| | 510, 490, 300, 268 | DMF |
| (5) | 290 nm (1.8 × $10^{-3}$ mol$^{-1}$cm$^{2}$) | DMF |
| | 314 nm (0.32 × $10^{-3}$ mol$^{-1}$cm$^{2}$) | – |
| (6) | 540, 438, 350, 306 | N.M. |
| | 515, 430, 337, 290 | DMF |
| (7) | 510, 468, 348, 300 | N.M. |
| | 495, 405, 325, 288 | DMF |
| (8) | 540, 498, 355, 280 | N.M. |
| | 510, 433, 350, 268 | DMF |
| (9) | 520, 480, 335, 290 | N.M. |
| | 505, 465, 328, 265 | DMF |
| (10) | 525, 485, 350, 275 | N.M. |
| | 508, 465, 342, 270 | DMF |
| (11) | 538, 490, 350, 270 | N.M. |
| | 507, 465, 338, 260 | DMF |
| (12) | 515, 495, 365 | N.M. |
| | 490, 465, 352 | DMF |

(*i.e.* within the aromatic ring and C=N group).[17] The complexes (2), (6) and (10) show bands in nujol mull at 525-540 and 438-490 nm ranges, however, in DMF, it appears at 508-515 and 430-475 nm ranges, attributed to $^{1}A_{1g} \rightarrow {}^{2}E_{g}$ and $^{1}A_{1g} \rightarrow {}^{1}A_{2g}$ transitions. The anticipated absorption band due to the $^{1}A_{1g} \rightarrow {}^{3}E_{g}$ transition is probably masked by the intense charge transfer absorption at (N.M = 350 nm and DMF 330, 342 and 337 nm respectively).[18] The complexes (3), (7) and (9) exhibit bands around 535 nm, characteristic of the square planar environment and probably arising from the $^{2}A_{1g}$ transition with configuration e$^{4}$gb$_{2}$$^{2}$a$_{1g}$.[19] Complex (12) in nujol mull shows peaks at 365, 495 and 515 nm, however, in DMF, it appears at 352, 465 and 490 nm. The first one is within the ligand and the other peaks are assigned to $^{4}T_{1g} \rightarrow {}^{4}T_{1g}(P)$ and $^{4}T_{1g} \rightarrow {}^{4}A_{2g}$ transitions respectively, indicating an distorted octahedral structure.[20,21] The electronic

spectra of the complexes (4), (8) and (11) show bands in nujol mull at 538-546 and 490-505 nm ranges and in DMF it appear at 507-510 and 433-490 nm ranges, assigned to $^{2}B_{1g} \rightarrow {}^{2}B_{2g}$ and $^{2}B_{1g} \rightarrow {}^{2}E_{g}$ transitions, indicating, square planar configuration.[8,9]

**Electron spin resonance.** The ESR spectra of solid complexes (4), (8) and (11) at room temperature are characteristic of a monomer, d$^{9}$, configuration and having an axial type of d$_{x^2-y^2}$ ground state.[13,22] The g-values suggest a square planar geometry.[8,23] The ESR parameters are presented in Table 4. The g-values are related by the expression.[24] 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 values < 4.0, (Table 4), indicating the presence of spin exchange interactions between the copper(II) ions. Also, the g$_{\parallel}$/A$_{\parallel}$ value considered as a diagnostic of stereochemistry,[25] the range reported for square planar complexes, are 105 to 135 cm$^{-1}$ and for tetragonal distorted complexes 150 to 250 cm$^{-1}$. The g$_{\parallel}$/A$_{\parallel}$ values lie just within the range expected for the complexes.

The g-values of the copper(II) complexes with a $^{2}B_{1g}$ ground state (g$_{\parallel}$ > g$_{\perp}$) may be expressed[26,27] by

$$g_{\parallel} = 2.002 - (8 \text{ K}_{\parallel}^{2} \ \lambda^{0}/\Delta E_{xy})$$

$$g_{\perp} = 2.002 - (2 \text{ K}_{\perp}^{2} \ \lambda^{0}/\Delta E_{xz})$$

where K$_{\parallel}$ and K$_{\perp}$ are the parallel and perpendicular components respectively of the orbital reduction factor (K). $\lambda^{0}$ is the spin-orbit coupling constant for the free copper. $\Delta E_{xy}$ and $\Delta E_{xz}$ are the electron transition energies of $^{2}B_{2g} \longleftarrow {}^{2}B_{1g}$ and $^{2}E_{g} \longleftarrow {}^{2}B_{1g}$. From the above relations, the orbital reduction factors (K, K$_{\perp}$, K), which are a measure of covalency,[27] can be calculated. For an ionic environment, K = 1 and for a covalent environment K < 1, the lower value of K, the greater is the covalent.

$$K_{\perp}^{2} = (g_{\perp} - 2.002) \ \Delta E_{xz} / 2\lambda^{0}$$

$$K_{\parallel}^{2} = (g_{\parallel} - 2.002) \ \Delta E_{xy} / 8\lambda^{0}$$

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

K (Table 4) for the copper(II) complexes are indicative of their covalent nature.[28,29] Kivelson and Neiman[30] noted that, for an ionic environment, g$_{\parallel}$ ≥ 2.3 and for a covalent environment, g$_{\parallel}$ < 2.3. Theoretical work by Smith[31] seems to confirm this view. The g$_{\parallel}$-values reported here show considerable covalent bonding character.[32] Also, the in-plane

**Table 4.** ESR parameters of the metal complexes

| Complex No. | g$_{\parallel}$ | g$_{\perp}$ | $^{a}$g$_{iso}$ | A$_{\parallel}$ (G) | A$_{\perp}$ (G) | $^{b}$A$_{iso}$ (G) | $^{c}$G | g$_{\parallel}$/A$_{\parallel}$ (cm) | $\Delta E_{xy}$ (cm$^{-1}$) | $\Delta E_{xz}$ (cm$^{-1}$) | K$_{\perp}^{2}$ | K$^{2}$ | K | $\alpha^{2}_{(Cu)}$ | $\beta^{2}_{1}$ | $\beta^{2}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (4) | 2.27 | 2.07 | 2.14 | 170 | 28 | 75.3 | 3.8 | 126 | 18315 | 19802 | 0.81 | 0.74 | 0.89 | 0.80 | 0.97 | 1.1 |
| (8) | 2.25 | 2.08 | 2.13 | 165 | 25 | 71.7 | 3.1 | 132.3 | 18518 | 20080 | 0.94 | 0.69 | 0.92 | 0.75 | 0.97 | 1.3 |
| (11) | 2.26 | 2.07 | 2.13 | 200 | 20 | 80 | 3.7 | 107.1 | 18587 | 20208 | 0.83 | 0.72 | 0.89 | 0.91 | 0.79 | 0.91 |
| (12) | 2.12 | 2.23 | 2.19 | 42 | 85 | 70.7 | – | – | – | – | – | – | – | – | – | – |

$^{a}$g$_{iso}$ = (g$_{\parallel}$ + 2g$_{\perp}$)/3,   $^{b}$A$_{iso}$ = (A$_{\parallel}$ - 2A$_{\perp}$)/3,   $^{c}$G = $\dfrac{(g_{\parallel} - 2)}{(g_{\perp} - 2)}$

**Table 5.** DTA peaks and their assignments for the metal complexes

| Complex No. | DTA peaks (°C) | | Assignments |
|---|---|---|---|
| | Endo | Exo | |
| (2) | 80 | – | Dehydration process |
| | – | 195 | M.P. of the complex |
| | – | 350 | Decomposition of the complex |
| (3) | 80 | – | Dehydration process |
| | – | 200 | M.P. of the complex |
| | – | 320 | Decomposition of the complex |
| (4) | 80 | – | Dehydration process |
| | – | 195 | M.P. of the complex |
| | – | 360 | Decomposition of the complex |
| (6) | 85 | – | Dehydration process |
| | – | 200 | M.P. of the complex |
| | – | 370 | Decomposition of the complex |
| (7) | 90 | – | Dehydration process |
| | – | 205 | M.P. of the complex |
| | – | 400 | Decomposition of the complex |
| (8) | 85 | – | Dehydration process |
| | – | 198 | M.P. of the complex |
| | – | 385 | Decomposition of the complex |
| (9) | 87 | | Dehydration process |
| | 200 | | Loss of chloride atom |
| | | 212 | M.P. of the complex |
| | | 425 | Decomposition of the complex |
| (10) | 85 | | Dehydration process |
| | 193 | | Loss of chloride atom |
| | | 208 | M.P. of the complex |
| | | 430 | Decomposition of the complex |
| (11) | 90 | | Dehydration process |
| | 202 | | Loss of chloride atom |
| | | 210 | M.P. of the complex |
| | | 420 | Decomposition of the complex |
| (12) | 85 | | Dehydration process |
| | 185 | | Loss of chloride atom |
| | | 192 | M.P. of the complex |
| | | 395 | Decomposition of the complex |

$\sigma$-covalency parameter $\alpha^2$(Cu) was calculated by

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

The calculated values (Table 4) suggest covalent bonding nature[33]

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[33]

$$\alpha^2\beta^2 = (g_\perp - 2.002) \ \Delta E_{xz} / 2\lambda^o$$
$$\alpha^2\beta_1{}^2 = (g_\parallel - 2.002) \ \Delta E_{xy} / 8\lambda^o$$

In this work, the complexes show $\beta_1{}^2$ values 0.97 and 0.79 indicating a moderate degree of covalency in the in-plane $\pi$-bonding, while $\beta^2$ are 1.1, 1.3 and 0.91 indicating ionic and covalent character of the out-of-plane $\pi$-bonding.[34] The complex (12) was studied in $CD_3OD + D_2O$ (10%) at 77 K. The spectrum is a characteristic of a low spin, $d^7$

configuration. Eight lines were observed from the interaction of the unpaired electron spin with $^{59}Co$ (I = 7/2, 100% abundant). The line widths are anisotropic. The ESR parameters (Table 4) show octahedral geometry and the $g_\perp >$ $g_\parallel > 2.0023$, indicating that, the unpaired electron presents in the $d_{z^2}$ orbital with a slight distortion of the symmetry around the z-axis.[35,36]

**DTA analysis.** The DTA data show that, all the complexes are thermally stable up to 80 °C when dehydration begins. This fact is characterized by endothermic peak within 80-90 °C range, corresponding to the loss of hydrated water molecules.[13,37,38] Endothermic peak was observed in the 165-212 °C range, corresponding to the melting[9,39-42] However, complexes (9-12) show exothermic peak in the 230-250 °C range, due to the loss of HCl.[43] The product is stable up to 550 °C when the organic constituents of the complexes start decomposing, finally leaving the decomposition products (550-600 °C).[9,17,43-46] The DTA data for the complexes are shown in Table 1.

**Effect of $\gamma$-radiation on DNA molecules in the presence of complex (12).** Complex (12) has a large positive charge due to the central cobalt ion and the eight nitrogen atoms, this property makes the complex highly reactive to DNA molecules. The suitability for electron-capture in DNA-cobalt(III) complex (12) may be inferred from the results of $\gamma$-radiation on the cobalt complex. This was observed by the reduction of Co(III) to Co(II) species. The efficiency of this reaction my be exploited in reducing the amount of electron adducts formed in DNA during irradiation with low radiation products. With $\gamma$-radiation, DNA molecules can be protected in the presence of Co(III) complex (12) and this could be of help to reduced of aberration in cells.

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