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Synthesis, characterisation and antimicrobial activity of manganese(II), nickel(II), cobalt(II), copper(II) and zinc(II) complexes of a binucleating tetradentate ligand

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The binucleating, tetradentate Schiff base ligand (H_2L) has been synthesised by condensation of bis-(4-aminophenyl)-methane with salicyladehyde. The resulting metal(II) complexes [metal = Mn^{II}, Ni^{II}, Co^{II}, Cu^{II} and Zn^{II}] have been characterised by elemental analyses, molar conductances, magnetic moment, IR, UV-vis spectra, thermal analyses (DTA and TGA) and ESR spectra. Antimicrobial activities of the ligand and its metal(II) complexes have been tested against different microorganisms. The electrochemical data of complexes (**2**), (**9**) and (**10**) are discussed.

Keywords: antimicrobial activity, bionucleating tertradentate ligand

Synthetic model studies involving magnetically coupled bi-, tri- and polynuclear transition metal systems have attracted much current interest. Although the greatest effort and success have been in the study of binuclear copper(II) complexes, there has been little work on oligomeric copper(II) complexes with more than two copper ions, particularly linear complexes.[1–3] In this work, we have synthesised and characterised new binuclear and polynuclear metal(II) complexes of bis-(4-aminophenyl)-methane salicyladehydeimine ligand.

Results and discussion

The complexes are stable at room temperature, non hygroscopic, insoluble in water and partially soluble in some organic solvents such as $CHCl_3$ but soluble in DMF and DMSO. The analytical and physical data and spectral data are compatible with the suggested structures (Fig. 1). The complexes are non electrolytes and showed biological effects against microorganisms studied.

IR spectra: The IR spectra of the ligand shows two ν(OH) bands commensurate the presence of two types of (intra-and intermolecular) hydrogen-bonded phenolic groups to the basic imino-nitrogen atoms. The ν(C=N) vibrations are located at 1632 and 1613 cm^{-1}, however, the aromatic ν(C=C) frequency appears at 1578 and 1558 cm^{-1}. Two bands at 1538 and 1285 cm^{-1} are assigned to ν(OH) vibrations. Upon complexation, the bands due to OH modes are no longer observed in the spectra of the complexes except (**3**), (**4**) and (**8**), indicating that the hydroxyl protons are displaced by the metal(II) ions leading to covalent M-O bonding with the ligand. The ν(C=N) band (1620–1580 cm^{-1}) (Table 2) is shifted to lower wave number (compared with the ligand), denoting that the nitrogen atom of the azomethine group is coordinated to the metal(II) ion. The bonding of metal(II) ions to the ligand through the nitrogen and oxygen atoms is further supported by the presence of new bands in the 640–610 and 530–510 cm^{-1} ranges, due to ν(M–O) and ν(M–N) respectively.[5] The existence of water molecules is shown by the appearance of the broad band in the 3660–3100 cm^{-1} range, due to (OH) vibrations of the coordinated or lattice water. Complex (**3**) gives a band at 350 cm^{-1} corresponding to (Cu-Cl),[6,7] However, complex (**4**) shows several bands at 1465, 1272, 865, and 770 cm^{-1}, assigned to the monodentate mode of the nitrate group.[8] Two bands (**8–13**) in the 1570–1425 cm^{-1} range, are attributed to the coordinated acetate group.[9]

Magnetic moment: The room temperature magnetic moments for the complexes (**2–4, 9 and 10**) are in the 1.68–1.43 B.M. range (Table 1), indicating spin-exchange interactions between the copper(II) ions.[10] Complexes (**6**) and (**12**) show values 2.1 and 1.96 B.M., indicating low spin cobalt(II) complexes. However, the magnetic moments for the complexes (**5**) and (**11**) show the values 2.85 and 2.72 B.M., indicating square pyramidal and tetrahedral nickel(II) complexes.[5,11,12] The magnetic moment of complex (**7**) is 6.1 B.M. indicates an octahedral structure.[13,14] Complexes (**8**) and (**13**) are diamagnetic zinc(II) complexes.

Electronic spectra: H_2L in DMF solution shows two bands at 371 nm ($\in = 9 \times 10^3$ mol^{-1} cm^{-1}) and 319 nm ($\in = 7 \times 10^3$ mol^{-1} cm^{-1}) which may be assigned to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.[15] In nujol mulls, the copper(II) complexes (**2**), (**4**) and (**10**) show three bands in the 535–530, 490–465 and 345–335 nm ranges; due to transitions $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ respectively, suggesting a square planar geometry,[16] however, complexes (**3**) and (**9**) show, in nujol mulls, three bands at 335 and 325 nm, 492 and 495 nm, 610 and 650 nm respectively. The first two peaks are within the ligand and the third transition corresponds to the $^2B_{1g} \rightarrow {}^2E_g$ transition of a copper(II) ion in a tetragonally elongated octahedron.[10] The electronic spectrum of nickel(II) complex (**5**) shows, in nujol mull, peaks at 860, 530 and 480 nm, respectively assigned to $^3B_1 \rightarrow {}^2B_2$, $^3A_2$, $^3B_1 \rightarrow {}^2E$ and $^3B_1 \rightarrow {}^3A_2$, ^2E (P) transitions which are consistent with five-coordinate nickel(II) complex.[11] However, complex (**11**) shows, in nujol mull, peaks at 535 and 490 nm respectively assigned to $^3T_1(F) \rightarrow {}^3T_1(P)$ and $^3T_1 \rightarrow {}^3T_2$ transitions. The positions of the peaks are consistent with a tetrahedral environment around the central nickel(II) ion.[5,12] The cobalt complexes (**6**) and (**12**) in nujol mull, show three peaks at 350 and 340 nm, 510 and 530 nm and 660 and 690 nm, respectively. The first one is within the ligand and the other peaks are assigned to $^4T_{1g} \rightarrow {}^4T_{1g}$ (P) and $^4T_{1g} \rightarrow {}^4A_{2g}$ transitions respectively indicating an distorted octahedral structure.[15] The electronic spectrum of complex (**7**), in nujol mull shows bands at 600, 510 and 420 nm respectively, assignable to $^6A_{1g} \rightarrow {}^4T_{1g}$, $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ and $^6A_{1g} \rightarrow {}^4T_{2g}(D)$ transitions respectively indicating an octahedral structure.[13,14]

Electron spin resonance: The ESR spectra of the solid complexes (**2**), (**4**) and (**10**) at room temperature are characteristic of the d^9 configuration with an axial type of $d_{x^2-y^2}$ ground state. The complexes show G values smaller than 4.0, indicating the presence of spin exchange interactions between the copper(II) ions. The orbital reduction factors (K_{11}, $K_{\perp}$, K) which are a measure of covalency,[17,18] 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 covalent character. The low values of K for the copper(II) complexes are indicative of their covalent nature.[18] The g_{11} values reported here show covalent bonding character.[19] Also, the in-plane σ-covalency parameter α^2(Cu) suggest covalent bonding.[20,21] The complexes show β_1^2 values in the 0.52–0.70 range indicating a moderate degree of

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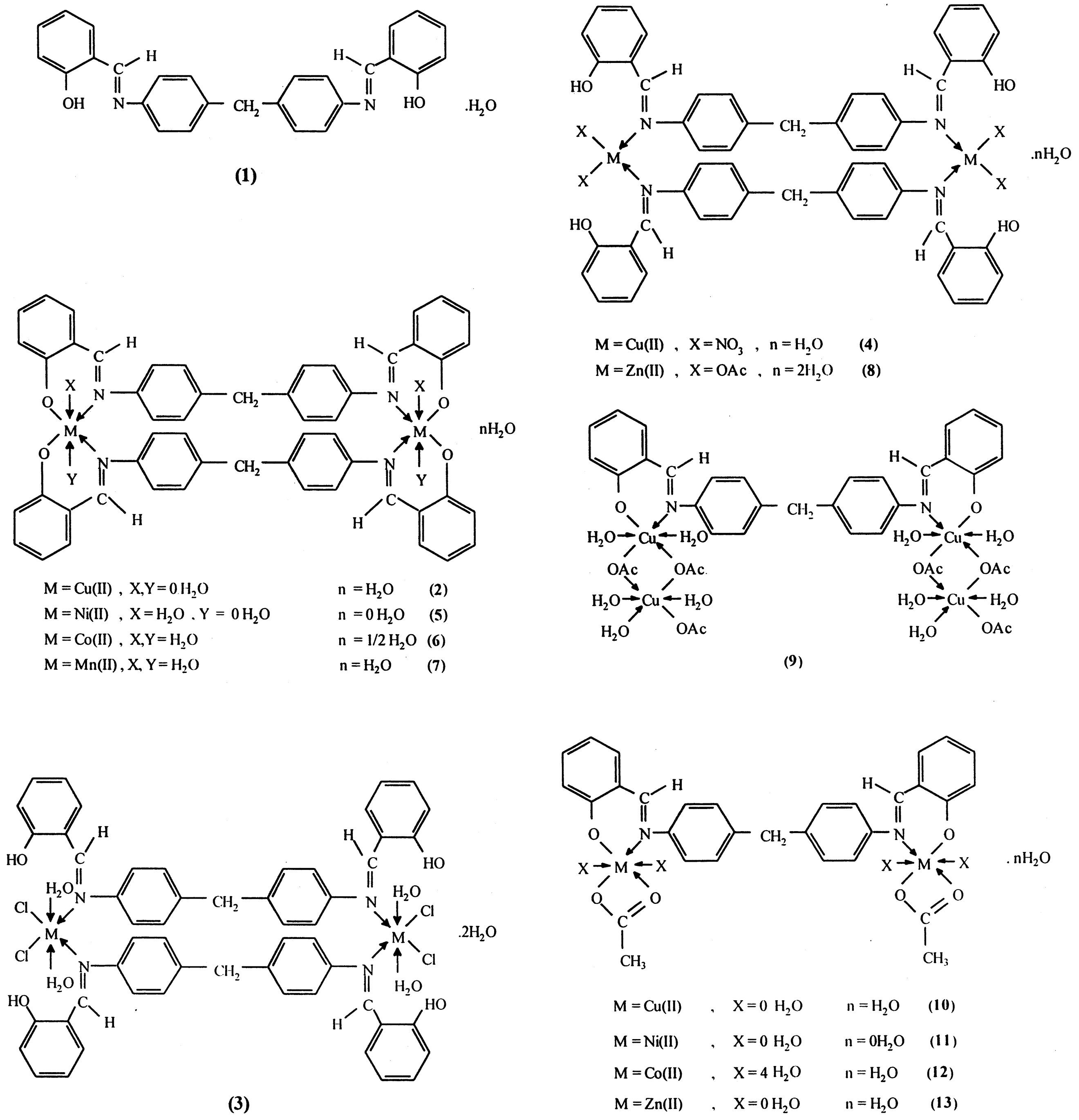

(1)

M = Cu(II), X,Y = 0 H_2O n = H_2O **(2)**

M = Ni(II), X = H_2O, Y = 0 H_2O n = 0 H_2O **(5)**

M = Co(II), X,Y = H_2O n = 1/2 H_2O **(6)**

M = Mn(II), X, Y = H_2O n = H_2O **(7)**

(3)

M = Cu(II), X = NO_3, n = H_2O **(4)**

M = Zn(II), X = OAc, n = $2H_2O$ **(8)**

(9)

M = Cu(II), X = 0 H_2O n = H_2O **(10)**

M = Ni(II), X = 0 H_2O n = $0H_2O$ **(11)**

M = Co(II), X = 4 H_2O n = H_2O **(12)**

M = Zn(II), X = 0 H_2O n = H_2O **(13)**

Scheme 1

covalency in the in-plane π-bonding, while $\beta^2 > 1$ indicates the ionic character of the out-of-plane π-bonding.[20,21] The ESR spectrum of the manganese(II) complex (**7**) shows six isotropic lines, with g value 2.0037, the hyperfine coupling constant (A_{iso}) is 92G. However, the spectrum of cobalt(II) complex (**12**) is characteristic of a low spin d^7 configuration. The spectrum exhibits two features, assigned to $g_{||}$ and $g_{\perp}$ which are characteristic of species with octahedral symmetry.

Thermal analyses: The DTA and TGA curves in the temperature range 25–800°C show that all the metal complexes are thermally stable up to 65°C. Dehydration is characterised by endothermic peaks within the temperature range 65–150°C for complexes (**2**), (**6**), (**8**) and (**10**) corresponding to the loss of hydrated water molecules.[22] Another peak was observed at 210°C, corresponding to the loss of coordinated water[23] as demonstrated by t.g.a. weight loss. Endothermic DTA peaks for the complexes (**2**), (**5**), (**6**) and (**10**) at 230, 260 and 210°C, respectively, with no weight loss may be due to a lattice rearrangement of the anhydrous complex. The complexes (**8**), (**9**) and (**10**) show endothermic peak in the range 280–300°C corresponding to loss of acetate groups.[7,24] Another peak is observed in the 370–530°C range, corresponding to a thermal decomposition process with the liberation of salicyladehyde molecules. The decomposition proceeds slowly 650–720°C range with a final residue assigned to metal oxides. These observations are confirmed by TGA weight losses. The thermal decomposition of complex (**9**) can be represented by:

$$[\mathrm{LCu_4(OAc)_6(H_2O)_{10}}]\ \ [\mathrm{LCu_4(OAc)_6}] + 10\mathrm{H_2O}$$

$$[\mathrm{LCu_4(OAc)_6}] \xrightarrow{300°\mathrm{C}} [\mathrm{LCu_4}] + 6\mathrm{OAc}$$

$$[\mathrm{LCu_4}] \xrightarrow{415–650°\mathrm{C}} 4\mathrm{CuO}\ +\ \text{organic residues}$$

Electrochemical studies: Cyclic voltammetric data of the complexes (**2**), (**9**) and (**10**) were recorded in acetonitrile medium containing 0.1M $LiClO_4$ as supporting electrolyte. The Schiff base ligand do not exhibit any redox peaks in the investigated potential range (–0.2 – 1.2V). The C.V. of binuclear complex (**2**) shows an oxidation peak at E_{Pa} = 0.62V corresponding to Cu^{II} Cu^{II} → Cu^{III} Cu^{II}. Complex (**9**) shows oxidation peaks at E_{Pa} = 0.60 V and E_{Pa} = 0.85 V which are assigned to $Cu^{II}\ Cu^{II}\ Cu^{II}\ Cu^{II} \xrightarrow{-2e} Cu^{III}\ Cu^{II}\ Cu^{II}\ Cu^{III}$ and $Cu^{III}\ Cu^{II}\ Cu^{II}\ Cu^{III} \xrightarrow{-2e} Cu^{III}\ Cu^{III}\ Cu^{III}\ Cu^{III}$. We observed that the terminal Cu^{II} ions are oxidised at a lower potential than the internal ions. This can be explained by the σ and π bonding nature of the ligands. However, complex (**10**) shows an oxidation peak at E_{Pa} = 0.55V and a reduction peak at E_{Pc} = 0.30V. This step is only partially reversible. The behaviour of the complex can be interpreted according to the following scheme at high potential, Cu^{II} $Cu^{II}Cu^{II}Cu^{III}$ and at low potential, $Cu^{II}\ Cu^{II} \xrightarrow{-e} Cu^{II}\ Cu^{I}$. Complexes (**2**) and (**10**) exhibit completely irreversible behaviour.[25,26]

Experimental

Preparation of bis-(4-aminophenyl)-methane salicylaldehy-deimine (H_2L): Bis-(4-aminophenyl)-methane (0.025 mol, 10.0 g) was dissolved in ethanol (50 cm^3) and to this salicylaldehyde (0.05 mol, 12.4 g) in ethanol (25 cm^3) was added dropwise. The solution was refluxed with stirring for 3h. Excess ethanol was distilled out and the yellow solid obtained was washed thoroughly with ethanol and recrystallised from ethanol. Yield; (80%), (m.p. = 230°C)

Synthesis of binuclear complexes (**2–8**): A ligand (0.011 mol, 5.0 g) was dissolved in ethanol (30 cm^3) and to this was added $Cu(OAc)_2.H_2O$ (0.011 mol, 2.35 g) (complex **2**), $CuCl_2.2H_2O$ (0.011 mol, 2.0 g) (complex **3**), $Cu(NO_3)_2.3H_2O$ (0.011 mol, 3.0 g) (complex **4**), $Ni(OAc)_2.4H_2O$ (0.011 mol, 2.9 g) (complex **5**), $Co(OAc)_2.4H_2O$ (0.011 mol, 2.9 g) (complex **6**) $Mn(OAc)_2.4H_2O$ (0.011 mol, 2.8 g) (complex **7**) or $Zn(OAc)_2.2H_2O$ (0.011 mol, 2.6 g) (complex **8**). The mixture was boiled under reflux with stirring for 2h. The mixture was then allowed to cool at room temperature and the precipitates thus obtained were removed by filtration, washed several times with ethanol and dried *in vacuo*. Yield; (80–68%).

Synthesis of complex (9): A ligand (0.011 mol, 5.0 g) was dissolved in ethanol (30 cm^3) and to this was added $Cu(OAc)_2.H_2O$ (0.055 mol, 11.75 g) in ethanol (50 cm^3). The mixture was boiled under reflux with stirring for 2h. The resulting complex was filtered off and washed with ethanol and dried *in vacuo*. Yield; (78%).

Synthesis of complexes (**10–13**): A ligand (0.011 mol, 5.0 g) was dissolved in ethanol (30 cm^3) and to this was added $Cu(OAc)_2.H_2O$ (0.022 mol, 4.7 g) (complex **10**), $Ni(OAc)_2.4H_2O$ (0.022 mol, 5.8 g) (complex **11**), $Co(OAc)_2.4H_2O$ (0.022 mol, 5.8 g) (complex **12**) or $Zn(OAc)_2.2H_2O$ (0.022 mol, 5.2 g) (complex **13**) respectively and then using the same method as described above, the solid obtained was filtered off and washed with ethanol and dried *in vacuo*. Yield; (82–75%).

Physical measurements: C,H,N,Cl and M analyses were determined by the Analytical Unit of Cairo University, Egypt. The IR spectra were measured as KBr and CeBr pellets using a Perkin-Elmer 683 spectrophotometer (4000–200 cm^{-1}). Electronic spectra were recorded on a Perkin-Elmer 550 spectrophotometer. The conductances of 10^{-3}M solutions in DMF were measured at 25°C with a Bibby conductimeter type MC1. Magnetic moments were measured at 25°C on a Gouy balance with $Hg[Co(NCS)_4]$ as a calibrant,[4] using equation: $\mu_{eff} = 2.84 \sqrt{\chi_M\ \mathit{coor}\ T}$. ESR measurement for the solid complexes at room temperature was made using a Varian E-109 spectrophotometer. Thermal analyses (DTA and TGA) were carried out using a Shimadzn DT-50 thermal analyzer. Current-voltage curves were recorded on a Hewlett-Pakard model 7440AX-Y recorded.

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