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Spectral, thermal, optical and biological studies on (*E*)-4-[(2-hydroxyphenyl)imino]pentan-2-one and its complexes

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Abstract: Metal complexes derived from the reaction of Cu(II), Co(II), Ni(II) and Zn(II) acetates and (*E*)-4-[(2-hydroxyphenyl)imino]pentan-2-one (H_2L) were synthesized and characterized by elemental analyses, MS, IR, UV–Vis and ^{1}H-NMR spectroscopy, thermogravimetry (TG) and differential TG (DTG), and magnetic measurements. In all complexes except for the Zn(II) complex, the Schiff base ligand acts as a mono-negative tridentate (NOO) donor, through the azomethine nitrogen, the hydroxyl oxygen and the enolic carbonyl oxygen. The structure of the Cu(II) complex is square planar, the Co(II) is octahedral while, the Ni(II) and Zn(II) are tetrahedral. Optical band gap measurements indicated the semi-conducting nature of these complexes. The biological activities were screened against two bacteria and two fungi. Some of the studied complexes showed activity against bacteria and fungi.

Keywords: Schiff bases; band gap; anti-fungal and anti-bacterial agents.

INTRODUCTION

Complexes of Schiff bases represent an important class of compounds. The enol form of Schiff bases of mono- and diamines have attracted much attention because of their advantages, such as ease of synthesis and the presence of variety of coordination sites that make them invaluable in coordination chemistry.[1,2] Schiff base complexes have many applications, *e.g.*, they are used as catalyst in oxygenation, decomposition, electro-reduction and hydrolysis reactions.[3,4] Schiff bases of β-diketones stabilize different metals in various oxidation states in many useful catalytic transformations.[5] Moreover, Schiff base complexes showed optical[6] and magnetic properties[7] that enabled them to be used as good candidates in modern technologies. Furthermore, Schiff-base complexes have found biological applications as antibacterial,[8–11] anti-HIV[12] and anti-inflammatory

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agents.[13] The biological activity of Schiff bases comes from their ability to bind with transition metal ions in living systems.[14,15]

This work describes the synthesis and spectral, thermal, optical and biological activities of Cu(II), Co(II), Ni(II) and Zn(II) complexes with (*E*)-4-[(2-hydroxyphenyl)imino]pentan-2-one with the aim of shedding more light on their structures and biological application.

RESULTS AND DISCUSSION

All the isolated complexes were colored and soluble in coordinating solvents such as dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) but insoluble in H_2O.

The ligand can exist either in the keto (Fig. 1, A) or in the enol form (Fig. 1, B).

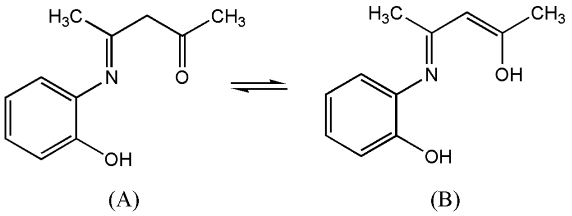

Fig. 1. The keto (A) and enol (B) tautomeric forms of the ligand.

IR spectra of the complexes

The most important IR bands of the ligand and its complexes are given in the Supplementary material to this paper.

The bands at 3435 and 3380 cm^{-1} in the spectrum of the ligand are attributed to phenolic and enolic ν(OH), respectively, while the bands due to ν(C=N), ν(CH=C), δ(OH), ν(C–O) and ν(C–N) appear at 1598, 1546, 1033, 1315 and 1238 cm^{-1} respectively.[16] The absence of the band assigned to ν(C=O) of pentanedione and the appearance of a new band at 1546 cm^{-1} due to ν(HC=C) confirmed that the free ligand exists in the enol form. The IR spectra of the metal complexes showed the disappearance of the enolic OH band, indicating the participation of this group in bonding after deprotonation. The shift of ν(C=N) to 1586–1615 cm^{-1} confirmed that the azomethine group coordinated to the metal ion. The spectra of Cu(II), Co(II) and Ni(II) complexes exhibited bands in the region 3440–3469 cm^{-1}, assigned to the phenolic OH. Furthermore, these complexes showed two new bands assigned to $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ at 1534 and 1333 cm^{-1} in the Co(II) complex and at 1565 and 1375–1345 cm^{-1} in the Cu(II) and Ni(II) complexes, respectively. These bands did not appear in the spectrum of the Zn(II) complex. The difference between $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ bands indicates the bidentate nature in the Co(II) complex and monodentate in the

Cu(II) and Ni(II) complexes.[17–20] The shift of the bands at 1315 and 1284 cm^{-1}, due to the phenolic and enolic C–O, supports the participation of the phenolic and enolic oxygens in the bonding. The spectra showed new bands in the regions 530–540 and 426–435 cm^{-1}, assigned to ν(M–O) and ν(M–N), respectively.[21]

These findings suggest the involvement of C=N, C–O and the phenolic hydroxyl groups in the coordination (Figs. 2–4).

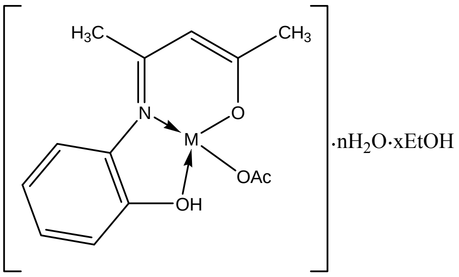

Fig. 2. Suggested structure of the Cu(II) and Ni(II) complexes, *n* = 1.5 and *x* = 0 for the Cu(II), and *n* = 1, *x* = 1/2 for the Ni(II) complex.

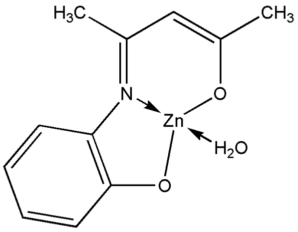

Fig. 3. Suggested structure for the Zn(II) complex.

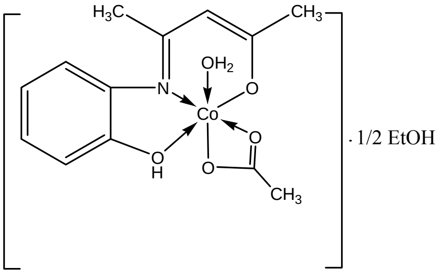

Fig. 4. Suggested structure for the Co(II) complex.

^{1}H-NMR spectra

The ^{1}H-NMR spectrum of the ligand in DMSO-d_6 showed two singlet signals at 2.34 and 2.50 ppm downfield from TMS, assigned to the protons of the two CH_3 groups. In addition, another singlet signal at 5.20 ppm corresponded to the proton of the HC=C group.[22] The multiplet signal in the region 6.75–7.18 ppm was assigned to the phenyl protons. The two singlet signals at 9.93 and 12.15 ppm were attributed to the phenolic and enolic OH protons, respectively.[23] The presence of the enolic proton together with HC=C confirmed that the ligand exists in the enol form.

The ^{1}H-NMR spectrum of the Zn(II) complex in DMSO-d_6 showed two singlet signals at 2.23 and 2.43 ppm due to the protons of the two CH_3 groups. The multiplet signal in the region 6.96–7.11 ppm corresponded to the phenyl protons. The spectrum showed another singlet signal at 7.6 ppm, assigned to the proton of the HC=C group. The shift of the latter signal in comparison with its position in the free ligand indicates the participation of the enolic group in the bonding. The disappearance of the enolic and phenolic OH protons confirmed the participation of these groups in the bonding.

Mass spectra of the complexes

The mass spectral fragmentation mode of H_2L was investigated. It showed an intense molecular ion peak at *m*/*z* 191, corresponding to the formula $C_{11}H_{13}NO_2$. A stable peak at 176 was due to the loss of CH_3. The loss of hydroxyl group gives a peak at *m*/*z* 160. The latter peak loses C_2H_2 with rearrangement to give the base peak at *m*/*z* 134. The base peak undergoes loss of CH_3 to give a peak at *m*/*z* 120, which undergoes loss of CH, OH, OH and CH_4 to give peaks at *m*/*z* 109, 93, 80 and 63, respectively, as indicated in Scheme S-1 of the Supplementary material to this paper.

The MS of the Cu(II) complex exhibited the molecular ion peak at *m*/*z* 340, in good agreement with the formula $[Cu(HL)(OAc)]\cdot 1.5H_2O$. Its fragmentation pattern is shown in Scheme S-2 of the Supplementary material.

The mass spectrum of the Co(II) complex showed the molecular ion peak at *m*/*z* 350, corresponding to the formula $[Co(HL)(OAc)(H_2O)]\cdot 0.5EtOH$. Its fragmentation pattern is indicated in Scheme S-3 of the Supplementary material.

The Ni(II) complex has a mass spectrum with the molecular ion peak at *m*/*z* 350, corresponding to $[Ni(HL)(OAc)(H_2O)]\cdot 0.5EtOH$. The fragmentation pattern of this formula is illustrated in Scheme S-4 of the Supplementary material.

Thermal gravimetric analysis

Thermal gravimetric analysis gives useful data about the thermal stability of the metal complexes. The TG and DTG curves were recorded within the temperature range 25–800 °C. The TG curves for the complexes are given in Figs. S-1–S-4 and the results are tabulated in Table S-I of the Supplementary material to this paper.

The results indicated that $[Cu(HL)(OAc)]\cdot 1.5H_2O$ decomposed in several steps. The first occurred in the range 26–133 °C, corresponding to the loss of 1.5 H_2O (calcd. 7.9 %; found 8.0 %). The final step leaves CuO as a residue (calcd. residue 23.4 %; found 22.6 %).

The TG curve of the Co(II) complex showed a decomposition step at 22–104 °C, assigned to the loss of $0.5C_2H_5OH$ (calcd. 6.5 %; found 5.7 %). The last step could leave Co_2O_3 as the residue (calcd. residue 47.4 %; found 46.5 %).

The TG curve of the Ni(II) complex showed a decomposition step at 54–130 °C due to the loss of $0.5C_2H_5OH$ (calcd. 6.5 %; found 6.0 %). The last step can generate NiO as the residue (calcd. residue 19.8 %; found 20.0 %).

The TG curve of the Zn(II) complex showed a decomposition step at 26–200 °C, assigned to the loss of coordinated water (calcd. 6.5 %; found 5.6 %). The third step could leave ZnO as the residue (calcd. residue 29.6 %; found 28.7 %).

The intermediate steps for all four complexes appear to represent the decomposition of the ligand to different organic moieties.[2,10]

Electronic spectra and magnetic moments

The electronic spectrum of the Cu(II) complex in DMF showed a broad band centered at 14005 cm^{-1}, attributed to $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions in a square-planar geometry.[24] The band recorded at 26775 cm^{-1} was assigned to ligand to metal charge transfer (LMCT) (Table S-II of the Supplementary material). The magnetic moment (2.1 μ_B) of the complex was in the range expected for monomeric Cu(II) complexes. The high value of the square–planar complex compared with those reported for the octahedral may be taken as supporting evidence for the presence of a square-planar geometry.[25]

The electronic spectrum of the Co(II) complex in DMSO showed three bands at 22222, 19379 and 15948 cm^{-1} due to L→M charge-transfer, $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ transitions, respectively. The ligand field parameters (B = 878 cm^{-1}, β = 0.90 and $10Dq$ = 8340 cm^{-1}) correspond with those reported for Co(II) complexes with octahedral geometry.[25,26] The value of the magnetic moment (5.2 μ_B) supports the presence of octahedral geometry around the Co(II) ion (Table S-II).

The spectrum of the Ni(II) complex, in DMSO, exhibits three bands at 15128, 23201 and 25000 cm^{-1} assigned to $^3T_1 \rightarrow {}^3T_1(P)$, $^3T_1 \rightarrow {}^1T_2$ and LMCT transitions, respectively, in a tetrahedral geometry around Ni(II) ion.[25] The value of magnetic moment (3.9 μ_B) falls in the range reported for tetrahedral geometry around a Ni(II) ion.[26]

Optimized modeled structures of the complexes were proposed based on the previous analytical and spectral data. The experimental and theoretical electronic spectra of the optimized structures are collected in Table S-III.

Selected bond lengths and angles are presented in Table S-IV of the Supplementary material. In case of Co(II) complex, the (N–M–O enolic) angle was 93.67°, which is slightly greater than is normal for an octahedral structure. The corresponding values for the Ni(II), Cu(II) and Zn(II) complexes were 102.59, 102.40 and 99.4°, respectively, deviate from the angle of normal tetrahedral structures. The optimization was performed for single molecules and the interactions between neighboring molecules were not taken into consideration; this may be the cause of the deviations.

Optical band gap (E_g*)*

The aim of measuring the conductive and semi-conductive properties of metal complexes is to reveal the feasibility of their potential use in molecular electronics. According to the conducting properties, metal complexes are applicable in optical devices, organic transistors and sensors.[27,28] To clarify the conductivity of the isolated complexes, the optical band gaps (E_g) of the Co(II), Ni(II), Cu(II) and Zn(II) complexes was determined from the absorption spectra of these complexes. The absorption coefficient (α) was determined from the relation:

$$\alpha = \frac{1}{d}\ln A \qquad (1)$$

where d is the path length of the sample. The optical band gap (E_g) was calculated from the relation:

$$\alpha h\nu = A\left(h\nu - E_g\right)^m \qquad (2)$$

where m is equal to 1/2 and 2 for direct and indirect transition, respectively, and A is an energy independent constant.[29,30] A plot of $(\alpha h\nu)^2$ *vs.* $h\nu$ was used to determine the direct band gap (Fig. 5) by extrapolating the linear portion of the curve to $(\alpha h\nu)^2 = 0$. The curves revealed that the values of the direct band gap (E_g) were equal to 3.37 (calcd. 4.2), 3.38 (calcd. 3.9), 3.74 (calcd. 3.6) and 3.58 (calcd. 6.0) eV for the Co(II), Ni(II), Cu(II) and Zn(II) complexes, respectively. The band gap values suggest that these complexes may behave as semi-conductors. In addition, the values of E_g are in the same range as those of highly

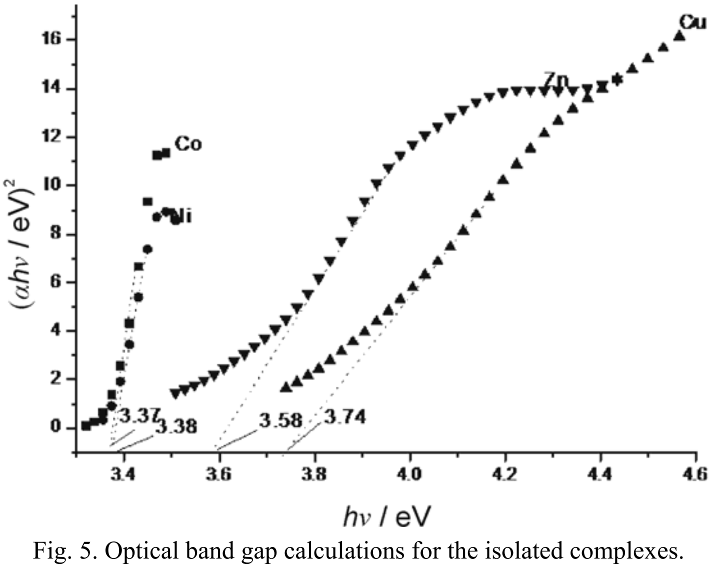

Fig. 5. Optical band gap calculations for the isolated complexes.

efficient photovoltaic materials. The present compounds could be used in harvesting solar radiation.[31]

Biological activity

The biological activities of the isolated complexes were tested against two bacteria (*Staphylococcus aureus* NCMB 6571 and *Vibrio cholerae* TCBS) and two fungi *(Aspergillus niger* and *A. flavus*) by the disc diffusion method. The activities were measured as the diameter of inhibition zone (Table I). It is clear that, the four complexes had anti-bacterial activities. The highest anti-bacterial activity was registered for the Cu(II) complex. Only the Co(II) complex showed both antibacterial and antifungal activity and hence, it could be used as a wide spectrum antibiotic. The Zn(II) complex showed antifungal activity against *A. niger* only and hence, it could be considered as a selective antibiotic for this microorganism. The Cu(II) and Ni(II) complexes did not show any effect against the two fungi.

TABLE I. Anti-microbial activity presented as the diameter of the inhibition zone, cm; –: negative

Metabolite	Complex with:			
	Co	Ni	Cu	Zn
S. aureus	0.7	0.75	0.9	0.85
V. cholerae	1.0	1.0	1.1	0.7
A. niger	2.9	–	–	3.0
A. flavus	1.75	–	–	–

EXPERIMENTAL

Reagents

All the employed chemicals were of analytical grade and were used without further purification.

Equipment and measurements

The carbon and hydrogen contents were determined using a CHN analyzer (Perkin–Elmer model 2400). Infrared spectra were measured as KBr discs on a Mattson 5000 FTIR spectrometer. Electronic spectra were recorded on a UV2 Unicam UV–Vis spectrometer using 1 cm silica cells. Thermogravimetric measurements (TG) were performed on a Shimadzu model 50 H instrument with a nitrogen flow rate and heating rate of 20 cm^3 min^{-1} and 10 °C min^{-1}, respectively. The ^{1}H-NMR spectra were recorded on a Bruker Avance III 400 MHz instrument using TMS as an internal reference and DMSO-d_6 as the solvent.

The physical, analytical and spectral data for the ligand and its complexes are listed in the Supplementary material to this paper.

*Synthesis of (*E*)-4-[(2-hydroxyphenyl)imino]pentan-2-one (H_2L)*

2,4-Pentanedione (0.01 mol, 1.4 mL) was added dropwise to 0.01 mol (1.19 g) of a hot ethanolic solution of 2-hydroxyaniline. The reaction mixture was heated under reflux for 6 h.

A brown crystalline precipitate formed on cooling. The precipitate was filtered off and washed with ethanol and diethyl ether.

Synthesis of metal complexes

A general procedure was followed for the synthesis of all complexes. An aqueous solution of 0.01 mol of metal acetates was added to a hot ethanolic solution of 0.01 mol of (*E*)-4-[(2-hydroxyphenyl)imino]pentan-2-one (H_2L) and refluxed for 8 h. The precipitated metal complexes were filtered off, washed with ethanol, and preserved over anhydrous calcium chloride.

Computational details

Molecular mechanics and the semi-empirical methods in the Hyperchem series of programs were used to investigate the geometries of the complexes.[32] AM1 and PM3 methods were used to optimize the molecular geometries of complexes. The low lying conformers obtained by the molecular mechanics technique (MM+ force field) were then optimized at AM1, PM3 (Polak–Ribiere) RMS 0.01 kcal.[33]

Antimicrobial assay

The microbial strains were selected based on their clinical importance in causing disease in humans. Two bacteria (*S. aureus* NCMB 6571 and *V. cholerae*) and two fungi *(A. niger and A. flavus),* ear pathogens isolated from a clinical culture and a laboratory culture of Suez Canal University Center for Environmental Studies and Consultations were used for the evaluation of the antimicrobial activity of the synthesized compounds. The bacteria were subcultured at 37 °C for 6 h on nutrient agar, whereas the fungi were subcultured on Sabouraud dextrose agar (subcultured at 28 °C for 4–7 days on malt agar). Samples (20 μL) of the tested compound at a concentration of 50 mg 10 mL^{-1} in 0.7 cm holes were incubated against the strains at 37 °C for 48 h using the "disc diffusion method".[34]

CONCLUSIONS

New biologically active metal complexes of Cu(II), Co(II), Ni(II) and Zn(II) with (*E*)-4-[(2-hydroxyphenyl)imino]pentan-2-one (H_2L) were synthesized and characterized by different physicochemical techniques. Optical band gap measurements indicated that the isolated complexes are semi-conductors. The optical band gap values showed that the compounds could be used as harvesting materials of the sun radiation in the UV and visible regions. The anti-fungal and anti-bacterial tests showed that the synthesized complexes are biologically active against both bacteria and fungi. One of the investigated compounds could be used as a broad-spectrum antibiotic.

SUPPLEMENTARY MATERIAL

Physical, analytical and spectral data for the ligand and its complexes, MS fragmentation patterns, thermogravimetry results, magnetic moments, electronic bands and ligand field parameters, experimental and calculated electronic spectra and selected bond lengths and angles for the optimized ligand and its metal complexes are available electronically from http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

ИЗВОД

СПЕКТРАЛНА, ТЕРМАЛНА, ОПТИЧКА И БИОЛОШКА ИСПИТИВАЊА (*E*)-4-[(2-ХИДРОКСИФЕНИЛ)ИМИНО]ПЕНТАН-2-ОНА И ЊЕГОВИХ КОМПЛЕКСА СА НЕКИМ ЈОНИМА ПРЕЛАЗНИХ МЕТАЛА

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Комплекси прелазних метала, синтетисани у реакцији између Cu(II)-, Co(II)-, Ni(II)- и Zn(II)-ацетата и (*E*)-4-[(2-хидроксифенил)имино]пентан-2-она (H_2L) као лиганда, окарактерисани су помоћу елементалне микроанализе, MS, IR, UV–Vis и ^{1}H-NMR спектроскопије, термалне анализе (TG и DTG) и магнетних мерења. У испитиваним комплексима, осим у случају Zn(II) јона, наведена Шифова база се тридентатно (NOO) координује преко азометинског атома азота, хидроксилног атома кисеоника и енолног атома кисеоника из карбонилне групе. Нађено је да Cu(II) комплекс има квадратно-планарну геометрију, док је геометрија Co(II) комплекса октаедарска. За испитиване комплексе Ni(II) и Zn(II) нађено је да имају тетраедарску геометрију. Испитивана је биолошка активност комплекса на две врсте бактерија и гљивица. Нађено је да неки од испитиваних комплекса имају одређену активност према бактеријама и гљивицама.

(Примљено 1. фебруара, ревидирано 24. априла, прихваћено 7. јула 2015)

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