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Synthesis and Characterization of Transition **Metal Complexes Derived from** (E)-N-(1-(Pyridine-2-yl)ethylidiene)benzohydrazide (PEBH)

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Three metal complexes derived from (E)-N-(1-(pyridine-2yl)ethylidene)benzohydrazide (PEBH) with Cu(II), Co(II), and Ni(II) have been synthesized and characterized using elemental analyses, spectral analyses (infrared [IR], ultraviolet [UV], mass spectroscopy [MS], nuclear magnetic resonance [¹H-NMR]), thermal analyses, conductance, and magnetic measurements. The results showed that 1:1 (M:L) chelates with the general formula [M L Ac]*n*H₂O have been formed. IR and ¹H-NMR spectra of the ligand (E)-N-(1-(pyridine-2-yl)ethylidene)benzohydrazide (PEBH) showed that the free ligand exists in the keto form, while it binds to the metal ions in the enol form. The difference between v_{as} and v_{s} stretching vibrations of the acetate group suggests the monodentate nature of this group. Some semiempirical calculations of the vibrational spectra have been done using AM1, PM3, and ZINDO/1 methods to assist in the assignments of the experimental results. The optical band gap (Eg) values of Co, Ni, and Cu were found to be 3.4, 1.45, and 1.20 eV, respectively, arising from direct transitions. These values indicate the semiconductivity nature of these complexes.

Keywords metal complexes, spectral characterization, (E)-N-(1-(pyridine-2-yl)ethylidene)benzohydrazide

INTRODUCTION

Interest in the study of hydrazones has been growing because of their anti- tuberculosis, anti-oxidant and anti-tumor activity.^[1-4] Hydrazones derived from condensation of isonicotinic acid hydrazide with pyridinealdehydes have been found to show better anti-tubercular activity than INH.^[5] A novel class of anti-cancer compounds derived from quinoxaline hydrazides has been reported.^[6] The remarkable biological activity of acid hydrazides R-CO-NH-NH2 and their corresponding aroylhydrazones R-CO-NH-N=CH-R' comes from their ability to bind with the transition metal ions present in the living system.^[7,8] Aroylhydrazones are highly effective in terms of their ability to bind Fe, and have been used for the treatment of Fe

overload disease and cancer.^[9] Two series of ligands based on the very active 2-pyridylcarboxaldehyde isonicotinoyl hydrazone were synthesized and tested as potent antitumor agents.^[10] The increasing applications in medicine, analytical chemistry, syntheses of novel heterogeneous catalysts of oxido-reduction processes, and molecular semiconductors, as well as in numerous fields of science and technology,^[11] make these compounds of special interest.

In view of the versatile importance of hydrazones, we herein describe the synthesis and identification of (E)-N-(1-(pyridine-2-yl)ethylidene)benzohydrazide (PEBH) and its metal complexes with Cu(II), Co(II), and Ni(II). The ligand and its metal complexes have been characterized by different spectral techniques. The optical band gap of the isolated complexes has been calculated to shed light on the conductivity of these complexes.

EXPERIMENTAL

Reagents

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

Analysis and Equipment

Carbon and hydrogen contents were determined at the Microanalytical Unit of Mansoura University. The metal analyses were carried out by standard methods.^[12] Molar conductance measurements of the complexes (10^{-3} M) in dimethyl sulfoxide (DMSO) were carried out with a conductivity bridge YSI model 32. Infrared spectra were measured using KBr discs on a Mattson 5000 Fourier-transform infrared (FTIR) spectrometer. Calibration with the frequency reading was made with polystyrene film. Electronic spectra were recorded on the UV2 Unicam ultraviolet/visible (UV/Vis) spectrometer using 1-cm stoppered silica cells. Magnetic measurements were carried out on a Sherwood magnetic balance at Mansoura University. Thermal analyses measurements (TGA and DTG) were recorded on a Schimadzu model 50 instrument using 20-mg samples. The nitrogen flow rate and heating were 20 cm³/min and 10 °C/min, respectively. The nuclear magnetic resonance (¹H-NMR) spectrum of the ligand was recorded in d_6 -DMSO on a Gemini-200 spectrometer

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at Cairo University. Mass spectra of the ligand were recorded on a Shimadzu GC-MS-QP 1000 Ex mass spectrometer at 70 eV at Cairo University.

Computational Details

Molecular geometries of the ligand and its metal complexes were optimized using molecular mechanics and the semiempirical ZINDO/1, PM3, and AM1 methods (Polak-Ribiere), RMS 0.01 kcal, using the hyperchem series of programs.^[13] Results of a recent literature study indicate that frequencies computed using semiempirical PM3, and AM1 methods compare well to values obtained at the *ab initio* level using medium-size basis sets. Of these methods, PM3 showed the closest correspondence to experimental values, which is generally about 10% too high in value from stretches.^[14]

Preparation of the Ligand

The ligand was prepared by refluxing solution of benzoylhydrazide (6.75 g; 0.05 M) with 2-acetylpyridine (6.05 mL; 0.05 M) in absolute EtOH. The reaction mixture was refluxed on water bath for 3 h and then left to cool. Yellowish brown crystals were separated. The product was filtered off, washed several times with ethanol, and then kept to dry in a desiccator over CaCl₂; yield, 7.5 g (63.0%).

Preparation of the Metal Complexes

The metal complexes were prepared by adding stoichiometric quantities of (1 mmol) of the metal(II) acetate in 20 mL absolute EtOH to a hot solution of the ligand (1 mmol, 0.24 gm) in 20 mL absolute EtOH. A direct change in color was observed. The mixture was refluxed on a water bath for 3 h. The precipitate is formed on reflux. To ensure the isolation of pure complexes the resulting solid complexes were filtered immediately, washed several times with hot EtOH, and kept in a vacuum desiccator over CaCl₂.

RESULTS AND DISCUSSION

In this study, one type of metal complexes has been isolated from the reaction of (E)-N-(1-(pyridine-2-yl)ethylidene)benzohydrazide (PEBH) with Cu, Co, and Ni acetates. The ligand is chelated to all the metal ions in the enol form with replacement of one hydrogen atom. Ethanol was used as a solvent in the preparation of all the metal complexes.

A



FIG. 1. Suggested structure of the metal complexes, with M=Cu(II), Co(II), or Ni(II), and n = 1 or 4.

The formation of metal chelate may be represented by the following equation:

$$\begin{array}{l} \text{PEBH} + \text{M}(\text{CH}_{3}\text{COO})_{2} \xrightarrow[6 \text{ hours reflux}]{} \text{EtOH} \\ + \text{CH}_{3}\text{COOH}, \end{array} [M(\text{PEBH})\text{OAc}]n\text{H}_{2}\text{O}$$

where M=Cu(II), Co(II), or Ni(II), $OAc=CH_3COO^-$ and n = 1 or 4.

The elemental analyses measurements of the ligand and its metal complexes confirm the 1:1 (M:L) composition for the synthesized complexes (Figure 1). Data of the elemental analyses and some physical properties for the ligand and its metal complexes are illustrated in Table 1.

All the metal complexes are colored and stable in air, insoluble in most common organic solvents, but soluble in coordinating solvents as dimethylformamide (DMF) and DMSO. The molar conductivity values (\sim 3.0 ohm⁻¹ cm² mol⁻¹) in 1 × 10⁻³ M DMF at 25°C show that all the complexes are nonconducting.^[15]

Mass Spectra

The mass spectrum (Figure 2) of the ligand (PEBH) gives the molecular ion peak $[M^+]$ at m/z = 240. The fragmentation pattern of the ligand is represented in Scheme 1.

Two fragmentation pathways are followed by the molecular ion of (PEBH). The first includes the cleavage of the azomethine group -C=N-, leading to the formation of the base peak resulting from the fragment PhCONHN at m/z = 134 (100%).

TABLE 1
analytical data and physical properties of the the ligand (PEBH) and its complexes

			Percent found (calculated)				
Compound	Color	m.p. (°C)	С	Н	М		
HL	Yellowish brown	160	71.4(71.2)	4.6(4.2)			
[Cu L Ac]4H ₂ O	Green	>300	44.6(44.4)	5.8(5.3)	15.1(14.7)		
[Co L Ac]H ₂ O	Brown	>300	51.5(51.4)	5.0(4.5)	15.4(15.8)		
[Ni L Ac]4H ₂ O	Brown	>300	45.3(44.9)	5.7(5.3)	14.0(13.7)		



SCH. 1. Fragmentation pattern of the ligand (PEBH).

Then it is cleaved through the amide group –CO–NH– leading to benzoyl fragment at m/z = 105 (97%). The elimination of CO from the benzoyl group leads to the formation of phenyl radical with peak at m/z = 77 (34%). Liberation of acetylene from the phenyl group can be observed at m/z = 51 (37%). The second pathway involves the removal of methyl group and the liberation of acetylene from the phenyl group; as a result of this fragmentation the peak at m/z = 198 (23%) is formed.

¹H-NMR

The ¹H-NMR spectrum (Figure 3) of the ligand (PEBH), in d_6 -DMSO shows a singlet signal at 3.38 ppm, downfield with respect to tetramethylsilane (TMS), and is assigned to the protons of the CH₃. The multiplet signals in the 7.47–8.68 ppm region are assigned to the protons of pyridyl and phenyl rings. The spectrum shows also a singlet signal at 10.92 ppm, due to the NH proton. The presence of this signal indicates that the ligand exists in the keto form.

IR Spectra

The assignments of some of the observed and calculated IR bands are included in Table 2. (PEBH) can be represented by two tautomeric forms, the keto form (Structure I) and enol form (Structure II).





Structure II

The IR spectrum of (PEBH) shows a band at 3179 cm^{-1} assigned to the ν (NH) of the amino group. The bands at 1658, 1630, 1620, 1544, 1373, and 984 cm⁻¹ can be assigned to the amide (1) ν (C=O), amide (2) ν (CONH), ν (NH), ν (C=N), amide (3) ν (C-N) and ν (N–N) modes, respectively.^[16,17] The presence of the bands assigned to ν (C=O), amide (2) ν (CONH) and ν (NH) confirms the presence of the free ligand in the keto form. The bands located at 1578, 1052, 620, and 433 cm^{-1} may be assigned to ν (C=N)_{pv}, ring skeletal, and in and out of plane ring deformation modes, respectively.^[18,19] These bands are of considerable importance in deciding whether the pyridyl nitrogen participates in coordination to the metal ions or not.^[20] The bands observed at 1544 and 984 cm⁻¹ in the spectra of the ligand can be assigned to ν (C=N) and ν (N–N), respectively.^[21] In the spectra of the metal complexes all the amide bands (amide 1 and amide 2) disappear, while new bands appear in the region 1631–1650 and 1417–1428 cm⁻¹ due to ν (C=N)* and ν (C-O), respectively. This indicates the transformation of carbonyl oxygen to the enol form with subsequent coordination of the oxygen upon deprotonation. The band suggested to the azomethine group is shifted to lower frequency in all the metal complexes. Also, the bands assigned to ν (C=N) and ν (C=N)_{py} are shifted to higher wavenumber in the spectra of all complexes, indicating the possibility of back donation and the participation of nitrogen atoms in bonding. The IR spectra of all metal complexes show that (PEBH) behaves as a mononegative tridentate ligand, coordinating to the metal ions through carbonyl oxygen in the enol form after deprotonation, azomethine nitrogen, and pyridyl nitrogen. This suggestion is supported by the positive shift of the band assigned to ν (C=N) from 1544 cm⁻¹ in the free ligand to 1565 and 1580 cm^{-1} in the metal complexes. Also, the shift to



FIG. 3. ¹H-NMR spectrum of the ligand (PEBH).

higher frequency of the band at 984 cm⁻¹ due to ν (N-N) can be taken as an addition evidence that the azomethine group takes part in bonding. Participation of pyridyl nitrogen in coordination is suggested on the basis of the observed changes in the bands at 1578, 1052, 620, and 433 cm⁻¹ assigned to ν (C=N)_{py}, ring skeletal, and in-plane ring deformation mode and out-of-plane ring deformation mode, respectively.^[22] The new weak bands in the regions 435–480 and 552–565 cm⁻¹ can be assigned to ν (M-N) and ν (M-O), respectively. The spectra of all metal complexes show a band centered at 3440 cm⁻¹ assigned to ν OH of water.

The spectra of the complexes show two bands in the region 1438–1458 cm⁻¹ and 1245–1260 cm⁻¹ assigned to ν_{as} and ν_{s} stretching vibrations of acetate group, respectively. The corre-

lation between the positions of the asymmetric and symmetric stretching vibrations of the acetate group and the type of coordination of this group was earlier studied.^[23] It was concluded from these studies that the frequency difference between the two carboxyl stretching vibrations in the case of ionic acetate groups is usually in the interval ~ 167 cm⁻¹; longer values were found for monodentate and lower values for bidentate groups.^[24] Correspondingly, the split of 178–215 cm⁻¹ in the case of Cu(II), Co(II), and Ni(II) complexes may be evidence for the monodentate nature of the acetate group.

The results showed that AM1 and PM3 methods agree well in the case of the ligand and ZINDO/1 agrees with the Co complex, while ZINDO/1 and PM3 agree to the same extent in the case of Cu and Ni complexes.

Vibration	APBH			Cu complex		Co complex			Ni complex				
	Exp.	AM1	PM3	ZINDO/1	Exp	PM3	ZINDO/1	Exp	PM3	ZINDO/1	Exp	PM3	ZINDO/1
v(NH)	3179	_		_	_		_		_	_		_	_
$\nu(C=N)_{py}$	1578	1593	1600	1581	1607	1618	1600	1596	1462	1591	1631	1639	1634
ν (C=N)	1544	1547	1535	1526	1565	1577	1574	1567	1400	1521	1580	1598	1622
$\nu(C=N)^*$	_	_	_		1635	1631	1658	1632	1682	1625	1650	1681	1664
Py skeletal	1052,	1062,	1102,	1073,	1060,	1063,	1048,	1066,	1071,	1055,	1062,	1073,	1072,
	620,	642,	646,	652,	625,	638,	615,	624,	650,	654,	629,	636,	644,
	433	427	455	431	437	440	437	440	425	410	422	440	434

TABLE 2 Observed and calculated wavenumbers (cm^{-1}) of the ligand (PEBH) and its metal complexes

*Nitrogen of the new azomethine group; py = pyridine nitrogen.



SCH. 2. Thermal decomposition of Ni complex.

Thermal Analyses

Thermal analyses give useful data about the thermal stability of metal complexes and the metal-ligand bonds. The thermal measurements (TGA and DTG) were carried out within a temperature range from 25 up to 800C. The nickel complex is taken as a representative example to clarify the thermal stability of this type of complexes. The decomposition pattern of the nickel complex is represented in Scheme 2. The nickel complex is thermally stable up to 140°C. It decomposes in four steps. The first is endothermic and starts from 54-138°C, corresponding to the liberation of four molecules of water of hydration, the mass loss is 16.1%; calculated 16.7%. The second stage represents the decomposition of acetate group. This step is endothermic and lies in the temperature range $140-270^{\circ}$ C; the loss is 13.4%, which is close to the theoretically calculated 13.7%. The next step is exothermic and lies in the range 270–358°C. It represents the decomposition of a phenyl group, and the loss in weight is 17.3%; calculated 17.9%. The final step corresponds to the loss of the remaining of the organic ligand. This process is endothermic and starts from 358 to 475°C with mass loss 34.0%, which is close to the calculated 33.8%. The remaining residue is 18.6%, calculated 17.5%, and corresponds to NiO.

Electronic Spectra and Magnetic Moments

The electronic spectrum of the copper(II) complex in Nujol shows a broad band at 14,000 cm⁻¹, which can be assigned to ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$ and ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$ transitions in a square-planar geometry.^[25] The band recorded at 24,630 cm⁻¹ is suggested as LMCT. The magnetic moment (2.1 BM) of copper complex is in the range expected for monomeric copper(II) complexes. The high magnetic moment value of the square-planar complex compared with the observed values for the distorted octahedron may be taken as an additional evidence for the presence of a square-planar geometry.

The electronic spectrum of cobalt complex shows a d–d band at 20,000 cm⁻¹ assigned to ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$ transition, which confirms square-planar geometry.^[26] This is further confirmed by its magnetic moment value (2.85 BM), which indicates a low-spin square-planar cobalt(II) complex^[27] may be arising from one unpaired electron plus an apparently large orbital contribution. The electronic spectrum of Ni complex shows two bands at 17,412 and 10,050 cm⁻¹ assigned to ${}^{3}T_{1} \rightarrow {}^{3}T_{1}$ (P) and ${}^{3}T_{1} \rightarrow {}^{3}A_{2}$ transitions, respectively, in a tetrahedral geometry of Ni(II).^[27] Another band is observed at 20,920 cm⁻¹ and assigned to the forbidden transition ${}^{3}T_{1} \rightarrow {}^{1}T_{2}$. The spectrum shows also a band at 25,906 cm⁻¹ assigned to LMCT. The magnetic moment value (3.80 BM) is taken as an additional evidence of tetrahedral Ni(II). The ligand field parameters (B = 906, $\beta = 0.87$, and 10 Dq = 5431 cm⁻¹) are in agreement with the values reported for tetrahedral Ni(II) complexes.^[26]

Optical Band Gap (Eg)

The conductive and semiconductive properties of molecular materials formed from organometallic or metal-organic species give them potential use in molecular electronics. They have been used in optoelectronic devices, organic transistors, and sensors.^[28]

To clarify the conductivity of the isolated complexes, the optical band gap (Eg) of Cu(II), Co(II), and Ni(II) complexes has been calculated from absorption spectra. The measured absorbance (A) was used to calculate approximately the absorption coefficient (α) by using the relation $\alpha = 1/d \ln A$ (Eq. 1), where, d is the width of the cell. The optical band gap (E_g) is calculated from the relation: $\alpha h\nu = A (h\nu - E_g)^m$ (Eq. 2), where m is equal to $\frac{1}{2}$ and 2 for direct and indirect transition, respectively, and A is an energy-independent constant.^[29,30] The values of α calculated from relation (1) were used to plot $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ versus $h\nu$, from which a direct band gap was found (Figure 4), by extrapolating the linear portion of the curve to $(\alpha \ h\nu)^2 =$ 0. From the curve it is clear that the values of the direct band gap (E_{σ}) equal 3.40, 1.45, and 1.20 eV in the case of Co, Ni, and Cu complexes, respectively. There is a trend between the atomic number of the central atoms and (E_{σ}) values, indicating that (E_{α}) depends on the electronic configuration of the d orbital



FIG. 4. The plots of $(\alpha h\nu)^2$ vs. $h\nu$ of Cu(II), Co(II), and Ni(II) complexes.

of the central ion. The band gap values suggest that these complexes are semiconductors. Also, the values of (E_g) are in the same range of highly efficient photovoltaic materials. Thus, the present compounds could be considered potential materials for harvesting solar radiation in solar cell applications.^[31]

CONCLUSION

The free ligand (E)-N-(1-(pyridine-2-yl)ethylidene) benzohydrazide exists in the keto form, while it coordinates to the investigated metal ions Cu(II), Co(II), and Ni(II) in the enol form. Coordination number four is suggested for all the isolated metal complexes. Both Cu(II) and Co(II) form square-planar complexes, while Ni(II) forms a tetrahedral one. Optical band gap calculations indicate that the transition is direct and the complexes have semiconducting nature.

REFERENCES

- Kamal, A.; Reddy, K. S.; Ahmed S.K.; Naseer, M.; Khan, A.; Sinha, R.K.; Yadav, J.S.; Arora, S.K. Anti-tubercular agents. Part 3. Benzothiadiazine as a novel scaffold for anti-mycobacterium activity. *Bioorg. Med. Chem.* 2006, 14, 650.
- Li, T.R.; Yang, Z.Y.; Wang, B.D.; Qin, D.D. Synthesis, characterization, antioxidant activity and dna-binding studies of two rare earth (III) complexes with naringenin-2- hydroxy benzoyl hydrazone ligand. *Eur. J. Med. Chem.* 2008, 43, 1688.

- Bottari, B., Maccari, R., Monforte, F., Ottan'a, R., Rotondo, E., Vigorita, M.G. Isoniazid- related copper(II) and nickel(II) complexes with antimycobacterial in vitro activity. Part 9. *Bioorg. Med. Chem. Lett.* 2000, 10(7), 657–660.
- Kocyigit K.B.; Rollas S. Synthesis, characterization and evaluation of antituberculosis activity of some hydrazones. *II Farmaco* 2002, 57(7), 595–599.
- Agarwal, R.K.; Sharma, D.; Singh, L.; Agarwal, H. Synthesis, biological, spectral, and thermal investigations of cobalt(II) and nickel(II) complexes of N-isonicotinamido 2',4'- dichlorobenzalaldimine, *Bioinorg. Chem. Appl.* 2006, 29234.
- Grande, F.; Aiello, F.; De Grazia, O.; Brizzi, A.; Garofalo, A.; Neamati, N. Synthesis and antitumor activities of a series of novel quinoxalinhydrazides. *Bioorg. Med. Chem.* 2007, 15, 288.
- Anten, J.A.; Nicholls, D.; Markopoulos, J.M.; Markopoulou, O. Transitionmetal complexes of hydrazones derived from 1,4- diformyl- and 1,4diacetylbenzenes. *Polyhedron* 1987, 6(5), 1075–1080.
- Tossidis, I.A.; Bolos, C.A.; Aslanidis, P.N.; Katsoulos, G.A. Mono halogeno benzoylhydrazones III. Synthesis and structural studies of Pt(II), Pd(II) and Rh(III) complexes of di-(2- pyridyl)ketonechlorobenzoyl hydrazones. *Inorg. Chim. Acta* **1987**, *133*(2), 275–2.
- Baker, E.; Richardson, D.R.; Gross, S. Evaluation of the iron chelation potential of hydrazones of pyridoxal, salicylaldehyde and 2-hydroxy-1naphthylaldehyde using the hepatocyte in culture. *Hepatology* 1992, 15, 492.
- Becker, E.M.; Lovejoy, D.B.; Greer, J.M.; Watts, R.; Richardson, D.R. Identification of the di-pyridyl ketone isonicotinoyl hydrazone (PKIH) analogues as potent iron chelators and anti-tumour agents. *Br. J. Pharmacol.* 2003, *138*, 819.
- Andjelkovic, K.; Sumar, M.; Ivanovic-Burmazovic, I. Thermal analysis in structural characterization of hydrazone ligands and their complexes. *J. Therm. Anal. Calorim.* **2001**, *66*, 759.
- Vogel, I. A Text Book of Quantitative Inorganic Analyses, 2nd ed.; Longman: London, 1961.
- 13. Hyperchem 7, . developed by Hypercube, Inc., 2002.
- Seeger, D.M.; Korzeniewski, C.; Kowalchyk, W. Evaluation of vibrational force fields derived by using semiempirical and *ab initio* methods. *J. Phys. Chem.* 1991, 95, 68.
- Geary, W.J. The use of conductivity measurements in organic solvents for the characterisation of coordination compounds. *Coord. Chem. Rev.* 1971, 7(1), 81–122.
- Nawar, N.; Khattab, M.A.; Hosny, N.M. Some metal (II) complexes of *o*-aminoacetophenone benzoyl hydrazone (AABH): Their preparation, characterization and antimicrobial activity. *Synth. React. Inorg. Met.-Org. Chem.* **1999**, *29*, 1365–1384.
- Rana, V.B.; Sahni, S.K.; Gupta, S.P.; Songal, S.K. Some 5-coordinate nickel(II) complexes of dipicolinic acid hydrazide. *J. Inorg. Nucl. Chem.* 1977, 39, 1098.
- Alpert, N.L.; Keiser, W.E.; Szymonski, H.A. Theory and Practical Infrared Spectroscopy; Plenum: New York, 1970.
- Sakamoto, M. Synthesis and characterization of lanthanoid(III) complexes with a pentadentate ligand derived from 2,6-diacetylpyridine and benzoylhydrazide. *Inorg. Chim. Acta* 1987, 131, 139.
- Bellamy, L.J. Advance in Infrared Group Frequency; Methuen: London, 1969.
- Hosny, N.M.; Shalaby, A.M. Spectroscopic characterization of some metal complexes derived from 4-acetylpyridine nicotinoylhydrazone. *Transition Met. Chem.* 2007, *32*, 1085.
- Hosny, N.M. (*E*)-*N*-(1-Phenylethylidene)nicotinohydrazide (PNH) and some of its metal complexes. *J. Mol. Struct.* 2009, 923, 98–102.
- Cakir, S.; Coskun, E.; Naumov, P.; Bicer, E. Synthesis, spectroscopic and thermal studies of the copper(II) aspartame chloride complex. *J. Mol. Struct.* 2001, 608, 101.
- Nakamoto, K. Infrared Spectra of Inorganic and Coordination Compounds; John Wiley: New York, 1970.

- Hamada, M.M.; Shallaby, A.M.; El-Shafai, O.; El-Asmy, A.A. Spectroscopic characterization and catalytic activity of some Cu(II) thiosemicarbazide complexes. *Transition Met. Chem.* 2006, *31*, 522–529.
- 26. Lever, A.B.P. *Inorganic Electronic Spectroscopy*; Elsevier: Amsterdam, 1986.
- Figgis, B.N.; Nyholm, R.S. A convenient solid for calibration of the Gouy susceptibilitity apparatus. *Journal of Chemical Society* 1958, 4190– 4191.
- Mott, N.F.; Davis, E.A. *Electrochemical Process in Non-Crystalline Materials*; Calendron Press: Oxford, 1979.
- Karipcin, F.; Dede, B.; Caglar, Y.; Hur, D.; Ilican, S.; Caglar, M.; Sahin, Y. A new dioxime ligand and its trinuclear copper(II) complex: Synthesis, characterization and optical properties. *Opt. Commun.* 2007, 272, 131.
- Yakuphanoglu, F.; Cukurovali, A.; Yilmaz, I. Refractive index and optical absorption properties of the complexes of a cyclobutane containing thiazolyl hydrazone ligand. *Opt. Mater.* 2005, *27*, 1363.
- Fu, M.L.; Guo, G.C.; Liu, X.; Cai, L.Z.; Huang, J.S. Syntheses, structures and properties of three selenoarsenates templated by transition metal complexes. *Inorg. Chem. Commun.* 2005, *8*, 18.