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Molecular Modeling of 4-Ethyl-1-(pyridin-2-yl)thiosemicarbazide and its Cu(II) Complex Utilized for Separation of Cu(II) from Water Samples

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Molecular modeling and spectroscopic characterization of 4-ethyl-1-(pyridin-2-yl) thiosemicarbazide (HEPTS) and its complex $[Cu_4(EPTS)_3(H_2O)(EtOH)(OH)Cl_4]_2H_2O$ are investigated. Structural, electronic, and vibrational features are discussed, and assignments were proposed on the basis of semiempirical quantum mechanics calculations (ZINDO/S and PM3). The simulated IR and UV−vis spectra are in reasonable accordance with the experimental data. Moreover, a rapid and selective procedure for extraction of Cu(II) at trace levels using silica gel immobilized with 4-ethyl-1-(pyridin-2-yl)thiosemicarbazide is proposed. The Cu(II)−EPTS complex was easily adsorbed on silica gel and eluted with 5.0 M HNO_3. The pH, amount of HEPTS, sample volume, and detection limit were evaluated in synthetic, spiked, and tap water samples. The interfering effect of some cations and anions on the recovery of Cu(II) was studied. Under optimum conditions, the recovery of Cu(II) ions was (97 ± 1) % at the 95 % confidence level. The adsorption isotherm was studied, and the binding equilibrium constant and the adsorption capacity were 3.585 $L \cdot mg^{-1}$ and 520.8 $\mu g \cdot g^{-1}$, respectively. The detection limit and relative standard deviation were 4 $ng \cdot L^{-1}$ and 1.5 %, respectively. The proposed method was applied for the separation of Cu(II) ions from water samples.

Introduction

Thiosemicarbazides are interesting because they form highly stable and intensely colored complexes that are used for the spectrophotometric determination of metal ions in different media[1−5] and show catalytic activity.[6,7] Also, they possess antibacterial and anticancer activity.[8,9] 4-Ethyl-1-(pyridin-2-yl)thiosemicarbazide and its Cu(II) complexes with different anions have been synthesized and characterized[10] and used as a chelating agent for separation, preconcentration, and determination of Cu(II) ions in saturated saline solutions by a cloud point extraction technique.[11]

The high activity of many thiosemicarbazides to form stable complexes in solid and solution prompted us to use 4-ethyl-1-(pyridin-2-yl)thiosemicarbazide (HEPTS) as a chelating agent and silica gel as solid support for the separation, preconcentration, and determination of Cu(II) from water samples.

Silica gel immobilized with various organic compounds has received great attention.[12−24] Solid phase extraction (SPE) is considered to be a powerful tool for the separation and enrichment of various inorganic and organic analytes.[25] The basic principle of SPE is to transfer the analyte from the aqueous mobile phase to bind to the active sites of the adjacent solid phase. SPE has several advantages such as high preconcentration factor, easiness of separation, enrichment under dynamic conditions, no need for organic solvents, and low consumption of reagents. Selective solid-phase extractors have been prepared by either physical loading or chemical binding of selected chelating reagents to different supports such as cellulose, fibers, activated carbon, sand, clay, zeolites, polymers, metal oxides, and highly dispersed silica.[25]

Table 1. Calculated Frequencies (cm^{-1}) of HEPTS and its Cu(II) Complex in the Gaseous State and Their Observed IR Spectra in KBr as well as Their Vibrational Assignment

HEPTS	HEPTS PM3	Cu(II) complex	Cu(II) complex PM3	
cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	assignment
		3443, 3365	3631	$\nu(OH)_{solv}$
3250	3350	3257	3353	$\nu(N^4H)$
3153	3255	3163	3175	$\nu(N^1H)$
		1640	1641	$\nu(C{=}N^2)$
1604	1745	1611	1746	$\nu(C{=}N)_{Py}$
1518, 1446	1525, 1496	1530, 1455	1512, 1484	thio I, III
800	842			$\nu(C{=}S)$
772	772	778	781	$\rho(NH)$

1,5-Bis(di-2-pyridyl)methylene thiocarbohydrazide immobilized on silica gel was used for the determination of Pd(II) and Pt(IV) by a flow injection technique with a detection limit of 0.4 $ng \cdot mL^{-1}$ for Pd(II)[26] and 0.8 $ng \cdot mL^{-1}$ for Pt(IV).[27] The method has been applied for the determination of platinum in catalysts, vegetation, soils, and water samples[27] and Pt(IV) in spiked foods and beverages.[28]

Separation, preconcentration, and determination of trace amounts of Cu(II) ions in aqueous solutions quantitatively during the passage of its solution through tetradecyldimethylbenzyl ammonium chloride (TDMBAC) treated with analcime pyrocatechol-immobilized zeolite were developed. The retained Cu(II) ions were desorbed with 5.0 mL of 4.0 M nitric acid and determined by flame atomic absorption spectrometry (FAAS) with a correlation coefficient of 0.9987. The detection limit was 0.05 $ng \cdot mL^{-1}$. Copper was determined in alloys with a recovery of 97 %.[29]

In a continuation of our pervious work, the molecular modeling of 4-ethyl-1-(pyridin-2-yl)thiosemicarbazide and its Cu(II) complex as well as the vibrational and electronic spectra simulated using semiempirical theoretical methods are described.

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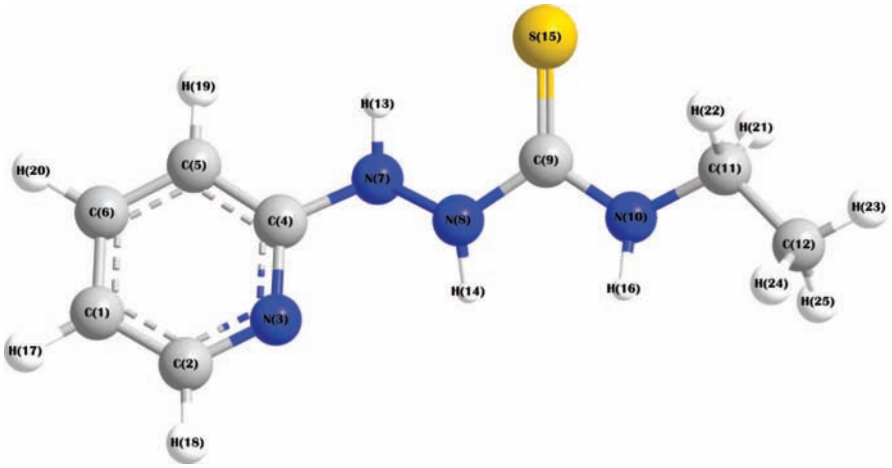

Figure 1. PM3-optimized structure of HEPTS.

Table 2. Electronic Spectral Bands of HEPTS and its Cu(II) Complex in the Gas State (ZINDO/S Calculations) and Those Observed in DMF

compound	obsd (nm)	calcd (nm)	assignment
HEPTS	278	275	$(\pi \rightarrow \pi^*)_{Py}$
	313	310	$(\pi \rightarrow \pi^*)_{C=S}$
	370	378	$(n \rightarrow \pi^*)_{Py}$
	400	389	$(n \rightarrow \pi^*)_{C=S}$
$[Cu_4(EPTS)_3(H_2O)(EtOH)(OH)Cl_4]_2H_2O$	275	274	$(\pi-\pi^*)$py
	330	346	$(\pi-\pi^*)CN^2$
	395	405	$(n-\pi^*)$
	605	610	(d−d)

Experimental Section

Apparatus. A Perkin-Elmer 2380 FAAS (Vernon Hills) with a conventional 10 cm slit burner head for air acetylene flame and Pye Unicam (England) hollow cathode lamps for the investigated elements were used as spectral radiation sources. The IR absorption spectra were recorded with a Mattson 5000 FTIR spectrophotometer at Mansoura University, Egypt. ^1H NMR spectra, in DMSO-d_6, were recorded on an EM-390 (200 MHz) spectrometer at Cairo University, Cairo, Egypt. The electronic spectra were recorded on a Unicam UV−vis spectrophotometer UV2 at Mansoura University, Egypt. The pH of the solution was measured using a Hanna instruments model 8519 digital pH meter.

Computational Details. All theoretical calculations of the quantum chemistry were performed on a Pentium 4 (3 GHz) computer using the HyperChem 7.5 program system (HyperChem 7.51 version, Hypercube Inc., FL, 2003). Initially, molecular geometries of the ligand and its Cu(II) complex were optimized using molecular mechanics (MM+). Second, the geometry with minimum energy obtained from MM+ was optimized with the Semi-Empirical Parametrization Model 3 (PM3) using the Polak−Ribiere algorithm in RHF-SCF set to terminate at an rms gradient of 0.0419 $kJ\cdot Å^{-1}\cdot mol^{-1}$, and the convergence limit was fixed to $4.187\cdot 10^{-8}$ $kJ\cdot mol^{-1}$. Afterward, vibrational analysis and electronic spectra were performed by PM3 and RHF-SCF ZINDO/S calculations, respectively. The configuration interaction was limited to ten occupied and ten unoccupied orbitals.

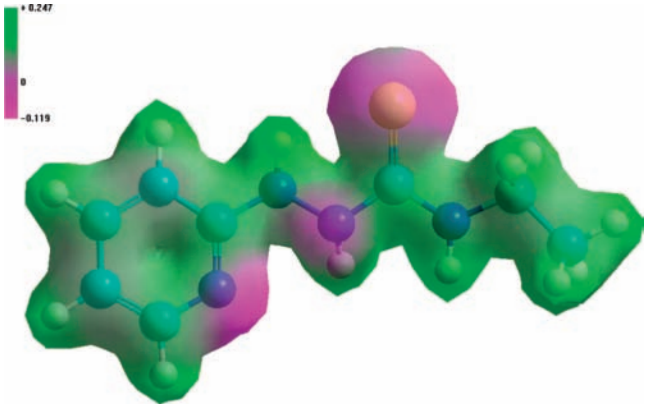

Figure 2. Electrostatic potential diagram of PM3-optimized HEPTS.

Reagents. All reagents used were of analytical grade (A.R. from Fluka, Aldrich, or Merck). All solutions were prepared using double-distilled water. Standard solutions (1000 $mg\cdot L^{-1}$) of Cu(II) were used. We prepared HEPTS solution (10^{-2} M) by dissolving 0.001 mol (0.1963 g) in 100 mL of absolute EtOH. Hexamine buffer solution was used to adjust the pH of the solutions in the range of 3 to 11. We prepared the buffer solutions by mixing different volumes of 0.5 M hexamine with 0.1 M HNO_3 or 0.2 M NaOH to obtain 50 mL at the desired pH. The mixture was left overnight in a refrigerator, and the pH was readjusted.[30] Silica gel ((63 to 88) μm) was homogenized by milling in a ball mill for 2 h to a pore size of < 0.09 mm. Its surface area is a mesoporous type VI, imonolayer volume (V_m) = 93.85 $m^3\cdot g^{-1}$, surface area (BET) = 410.1 $m^2\cdot g^{-1}$, pore volume = 0.685 $mL\cdot g^{-1}$, and r = 33.4 nm.

Solid Phase Extraction and Preconcentration. To study the effect of pH, 1.0 mL of hexamine buffers was used to adjust the pH of 50 mL solutions containing 10 $\mu g\cdot mL^{-1}$ Cu(II) ions and $4\cdot 10^{-4}$ M HEPTS (2.0 mL of 0.01 M) in the pH range of 3 to 11; then, 0.1 g of silica gel was added, and the solution was shaken for 10 min and then left to settle for 30 min.

To study the adsorption kinetics, 0.1 g silica gel was shaken with 50 mL solution containing 10 $\mu g\cdot mL^{-1}$ Cu(II) ions in the presence of $4\cdot 10^{-4}$ M HEPTS (2.0 mL of 0.01 M) at pH 6 for interval times ((2 to 15) min).

To investigate the effect of HEPTS on the recovery of Cu(II) ions, 0.1 g silica gel was shaken with 50 mL of solution

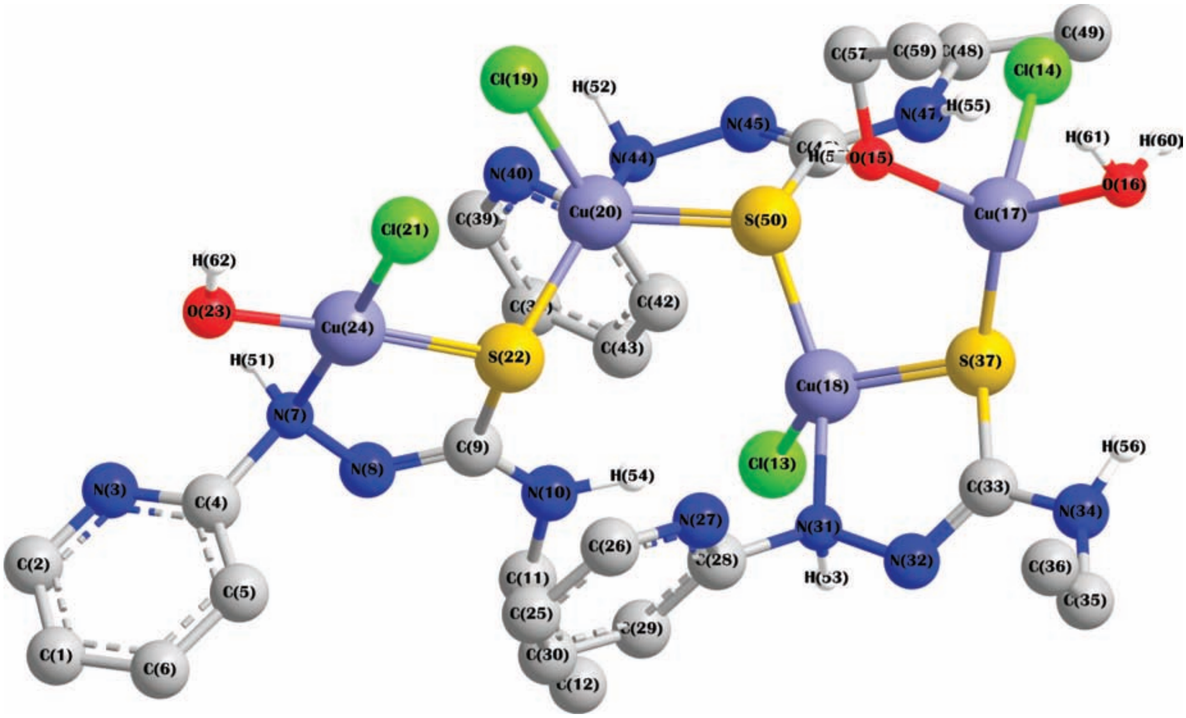

Figure 3. Optimized structure of Cu(II) complex. The hydrogen atoms were omitted for clarity.

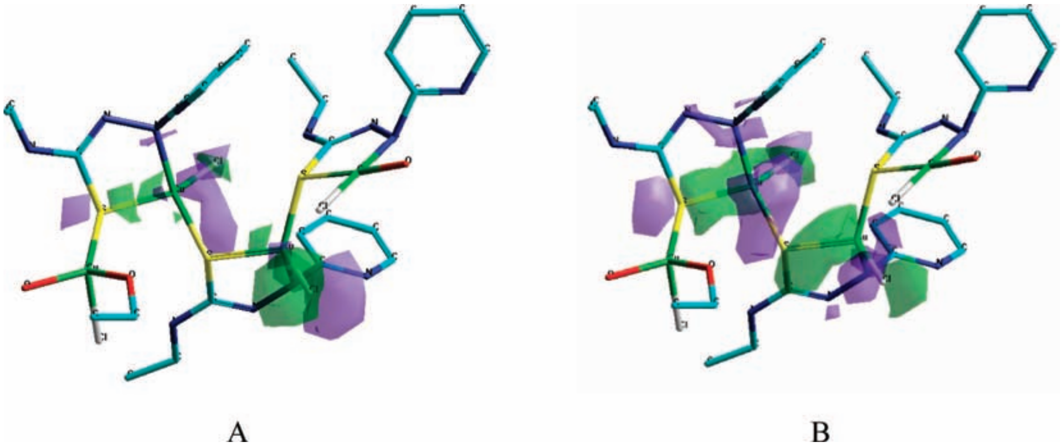

Figure 4. Representation of the (A) HOMO and (B) LUMO orbitals of the Cu(II) complex.

Table 3. Some Properties of HEPTS and Its Cu(II) Complex Calculated by PM3 Method

property	HEPTS	Cu(II) complex
total energy (kJ·mol^{-1})	−189 835	−1 267 889
binding energy (kJ·mol^{-1})	−10 188	−38 700
electronic energy (kJ·mol^{-1})	−1 084 334	−13 341 077
heat of formation (kJ·mol^{-1})	323	−1 839
dipole moment (D)	3.931	8.067
HOMO (eV)	−8.691	−6.722
LUMO (eV)	−0.749	−3.052

containing 10 μg·mL^{-1} Cu(II) with different volumes ((0.1 to 2.0) mL) of 0.01 M HEPTS at pH 6 for 10 min.

To choose the eluent, 0.1 g of silica gel was shaken with 50 mL of a solution containing 10 μg·mL^{-1} Cu(II) ions in the presence of 2·10^{-4} M HEPTS (1.0 mL of 0.01 M) at pH 6 for 10 min and filtered off after settling for 30 min. HCl, H_2SO_4, and HNO_3 (10 mL) with different concentration were used as eluents ((0.5 to 10) M). The effect of volume of 5.0 M HNO_3 was studied.

To show the effect of sample volume, 0.1 g of silica gel was shaken with different volumes of a solution containing 10

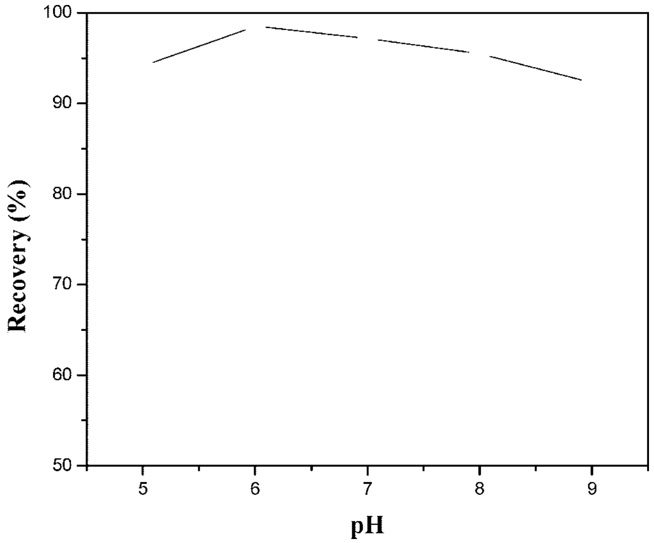

Figure 5. Recovery of a 50 mL of solution containing 10 μg·mL^{-1} Cu(II) and 4·10^{-4} M HEPTS (2 mL of 0.01 M) in the pH range of 3 to 11 on 0.1 g silica gel.

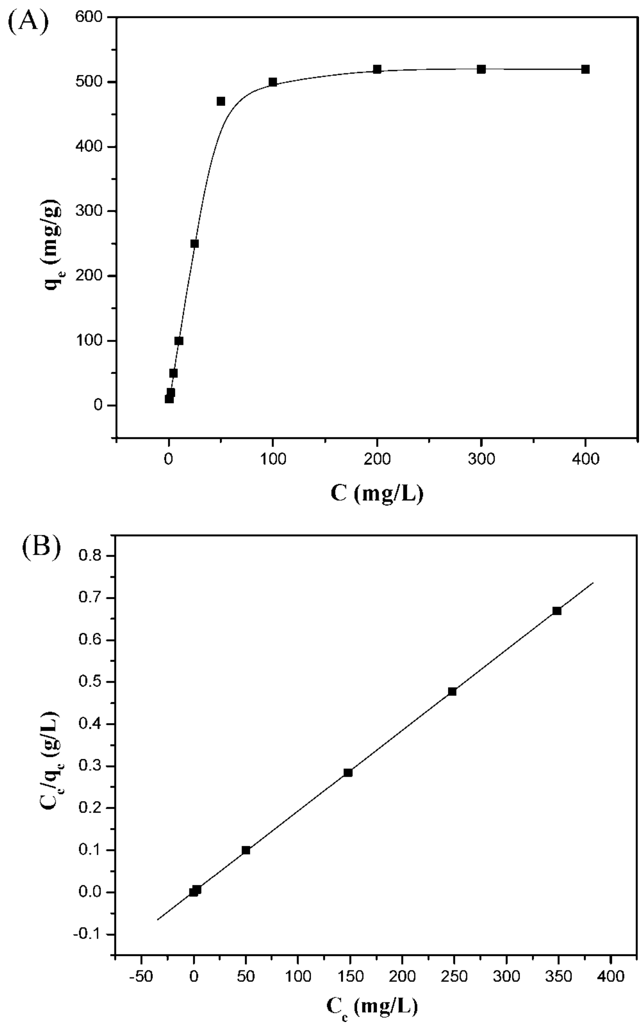

Figure 6. Adsorption isotherm of the Cu(II)−HEPTS complex on silica gel.

Table 4. Determination of the Separation Factor (R_1) from the Langmuir Isotherm

C mg·L^{-1}	R_1 value	C mg·L^{-1}	R_1 value
1	0.876	50	0.125
2	0.780	100	0.067
5	0.588	200	0.034
10	0.417	300	0.023
25	0.222	400	0.018

Table 5. Recovery of Cu(II) Ions Spiked in 1 Liter Water Samples with Preconcentration Factor of 200

water samples	Cu(II) content ng·mL^{-1}	added ng·mL^{-1}	total^a μg·mL^{-1}	recovery %
distilled water	0	10	1.96	98.00
tap water	6	10	3.14	98.13
river water	30	10	7.76	97.00
lack water	90	10	19.50	97.50

[a] Main value of three determinations.

μg·mL^{-1} Cu(II) ions in the presence of $2\cdot10^{-4}$ M HEPTS (1.0 mL of 0.01 M) at pH 6 for 10 min and was then filtered off after settling for 30 min.

To determine the adsorption isotherm and adsorption capacity, 0.1 g of silica gel was shaken with 50 mL of a solution containing different concentrations of Cu(II) ions ((1 to 400) μg·mL^{-1}) in the presence of $2\cdot10^{-4}$ M HEPTS (1.0 mL of 0.01 M) at pH 6 for 10 min, was then filtered off after settling for 30 min, and was finally eluted with 5.0 mL of HNO_3 (5.0 M).

To investigate the effect of matrix elements, 0.1 g of silica gel was shaken with 50 mL of a solution containing 10.0 μg·mL^{-1} Cu(II) ions and 1.0 mL HEPTS (0.01 M) at pH 6 for 10 min in the presence of Pd(II), Au(III), Ag(II), Pt(IV), K^+, Na^+, Mg^{2+}, Ca^{2+}, Cl^-, Br^-, I^-, SO_4^{2-}, IO_3^-, NO_3^-, SCN^-, PO_4^{3-}, acetate, oxalate ions, and EDTA with different concentrations, was then filtered off after settling for 30 min, and was finally eluted with 5.0 mL of HNO_3 (5 M).

Procedure for Separation of Cu(II) Ions in Water. All samples were filtered using a sintered glass G4, acidified with concentrated nitric acid to pH ~2, and then preserved in polyethylene vessels for further use. The organic matter was digested before the separation process using (0.5 to 1.0) g of $K_2S_2O_8$ added to 1000 mL of the selected water sample and was heated for 30 min to 95 °C. After cooling to room temperature, the samples were spiked with Cu(II) ions, the pH was adjusted to 6, 0.1 g of silica gel and 1 mL of HEPTS (0.01 M) were added, and the solution was shaken for 10 min and then filtered off after settling for 30 min.

Results and Discussion

Molecular Modeling and Spectral Analysis Data. The main features of the IR spectrum of HEPTS recorded in KBr are the bands at (3250, 3153, 1604, 1518, 1446, and 772) cm^{-1}. The theoretical spectrum carried out using the PM3 method of HyperChem supports the following assignments, $\nu(N^4H)$, $[\nu(N^1H) + \nu(N^2H)]$, $\nu(C{=}N)_{Py}$, and thioamide (I, II, and IV) for the above bands, respectively (Table 1).[10]

A comparison between the spectrum of HEPTS and that of $[Cu_4(EPTS)_3(H_2O)(EtOH)(OH)Cl_4]_2H_2O$ indicates that HEPTS reacts in its thioenol form where a new band due to $\nu(C{=}N^2)$ is observed with the absence of $\nu(C{=}S)$. The ligand coordinates with Cu(II) in a mononegative bidentate manner where the $\nu(N^1H)$ band is shifted from (3153 to 3163) cm^{-1} with the absence of any bands due to $\nu(S-H)$. The existence of coordinated water and hydrated ethanol is strongly supported by the existence of (3365 and 3443) cm^{-1} bands, respectively. The simulated spectrum carried out using the PM3 method of HyperChem supports these assignments. Considering the fact that the calculations apply to molecules in the gas phase, the coherence of the frequencies with the experimental data is significant (Table 1).

The electronic spectrum of HEPTS in DMF showed bands at (282, 313, 324, and 401) nm attributed to $(\pi \rightarrow \pi^*)_{Py}$, $(\pi \rightarrow \pi^*)_{C=S}$, $(n \rightarrow \pi^*)_{Py}$, and $(n \rightarrow \pi^*)_{C=S}$, transitions, respectively. The electronic spectrum of $[Cu_4(EPTS)_3(H_2O)(EtOH)(OH)Cl_4]_2H_2O$ in DMF shows bands at (275, 329, and 605) nm attributed to $(\pi \rightarrow \pi^*)_{Py}$, $(n \rightarrow \pi^*)_{Py}$, and d−d transition in a tetrahedral structure.[10] A spectral simulation based on RHF-SCF ZINDO/S calculations was performed. The data are in good agreement with those obtained experimentally in DMF for the ligand and its complex (Table 2).

The selected bond lengths, bond angles, and dihedral angles (Tables 1S−3S in the Supporting Information) were calculated from PM3 geometry optimizations. A nonplanar structure (Figure 1) was concluded for HEPTS. It is clear that S(15) is in the opposite direction to pyridine nitrogen, N(3). The electrostatic potential calculation shows that the nitrogen and sulfur atoms have negative potentials, supporting its involvement in coordination to Cu(II) (Figure 2).

The geometry optimization of the Cu(II) complex using PM3 indicates that it has a tetrahedral structure (Figure 3). The bond

Table 6. Sorption Capacity and Preconcentration Factor Data (Previous and Presented Work)

immobilized ligand	support	capacity (μmol$\cdot$g^{-1})	preconc. factor	ref
thiosalicylic acid	Amerlite XAD-2	214	200	34
chromotropic acid	Amerlite XAD-2	133.8	100	35
xylenol orange	Amerlite XAD-7	25.17	50	36
glyoxaldithiosemicarbazone	Amerlite XAD-7	19.7		37
dimethylglyoxal bis(4-phenyl-3-thiosemicarbazone)	Amerlite XAD-7	20.9	100	37
diathiazone	silica gel	95.6		38
salicylaldoxime	silica gel	50.0	40	39
8-hydroxyquinoline	silica gel	65.0		40
acid red 88	silica gel	12.1		41
1-(2-thiazolylazo)-2-naphthol	silica gel	2600		42
4-ethyl-1-(pyridin-2-yl) thiosemicarbazide	silica gel	8183	200	present work

length, bond angle, and dihedral angle calculated from the PM3 method (Tables 4S−6S in the Supporting Information) showed that the HOMO (−6.722 eV) and LUMO (−3.052 eV) were mainly composed of the orbitals of Cu(II) atoms (Figure 4). Some energetic properties of HEPTS and its Cu(II) complex are listed in Table 3.

Solid Phase Extraction, Preconcentration, and Separation. Effect of pH. One of the most important parameters affecting the preconcentration procedure is the pH. The pH of the mixture was adjusted (3 to 11) using hexamine buffer. The number of Cu(II) ions that remain in the aqueous medium was determined by AAS. As shown in Figure 5a, quantitative recovery (≥ 98 %) was obtained at pH 6 to 8; therefore, the work was adjusted to pH 6.

Adsorption Kinetics. Silica gel (0.1 g) was added to 50 mL of solution containing 10 μg$\cdot$mL^{-1} Cu(II) ions and $4\cdot10^{-4}$ M HEPTS at pH 6 and was shaken at interval times ((2.0 to 15) min). The variation of sorption of Cu(II) as a function of time shows that the loading half time, $t_{1/2}$, required to attain 50 % saturation of silica was found to be less than 5.0 min. The reasonable fast kinetic reaction of the Cu(II)−HEPTS complex at the optimum pH reflects a good accessibility of the chelating sites of the organic reagent.

Effect of HEPTS. To investigate the effect of the amount of HEPTS on the recovery of Cu(II), 10 μg$\cdot$mL^{-1} Cu(II) ions and variable volumes ((0.1 to 2.0) mL) of 0.01 M HEPTS solution were added, and the pH was adjusted to 6. After the preconcentration and separation procedure, the recovery of Cu(II) was found to be (0.8 to 2.0) mL of HEPTS. For the subsequent work, 1.0 mL of 0.01 M HEPTS was taken.

Choice of Eluent. The effect of HCl, H_2SO_4, and HNO_3 for the quantitative stripping of the retained Cu(II) ions on the silica gel was studied at different concentrations ((0.5 to 10) M). HCl and HNO_3 were found to be the most suitable for stripping the bound Cu(II). Reproducible results for stripping Cu(II) from the silica surface in the batch mode were obtained at 5.0 M HNO_3 with maximum recovery (≥ 98.5 %). We studied The efficiency of HNO_3 (5.0 M) by taking different volumes ((1.0 to 10) mL). It was found that 5.0 mL was sufficient for complete recovery of Cu(II) to give a 200-fold preconcentration factor.

Effect of Sample Volume. Sample volume is one of the most important parameters affecting the separation and preconcentration process from real water samples. For this reason, the volume of the synthetic solution containing Cu(II), 10 μg$\cdot$mL^{-1}, was varied from (50 to 1000) mL to give maximum separation. The data obtained show that the retention of the Cu(II) complex on silica gel was not altered by increasing the sample volume up to 1000 mL.

Adsorption Isotherm and Capacity. To examine the adsorption behavior of silica gel, (1 to 400) μg$\cdot$mL^{-1} of Cu(II) ions was added to the synthetic solution after the addition of 1.0 mL of 0.01 M ligand at pH 6. The prepared solutions were shaken for 30 min after the addition of 0.1 g silica gel, filtered off, and eluted with 5.0 mL of 5.0 M HNO_3 acid. The eluted Cu(II) was determined by AAS. The concentration of Cu(II) adsorbed (q_e in mg$\cdot$g^{-1}) was studied as a function of initial Cu(II) concentration (C in mg$\cdot$L^{-1}). The Langmuir treatment is based on the following assumptions: (i) a maximum adsorption corresponds to the saturated monolayer of adsorbate molecules on the surface, (ii) the energy of adsorption is constant, and (iii) there is no transmigration of adsorbate in the plane of the surface. The Langmuir equation (eq 1) was applied to determine the adsorption capacity (q_o) of silica gel and the binding equilibrium constant (K)[31] (Figure 6A). It is seen in the Figure that the linear range for copper is (1 to 50) μg$\cdot$mL^{-1}.

$$\frac{C_e}{q_e} = \frac{1}{q_oK} + \frac{C_e}{q_o} \tag{1}$$

where C_e is the equilibrium concentration of the metal ion in the solution phase (mg$\cdot$L^{-1}) and q_e is the amount adsorbed at equilibrium as expressed as concentration in the solid phase (mg$\cdot$g^{-1}). The linear plot of C_e/q_e versus C_e shows that the adsorption obeys the Langmuir model with a correlation coefficient of 0.99999, probability (uncertainty) < 0.0001, q_o = 520.83 mg$\cdot$g^{-1} (8.196 mmol$\cdot$g^{-1}), and K = 3.585 L$\cdot$mg^{-1} (Figure 6B).

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor, R_1, which is defined by $1/(1 + KC)$, where C is the initial concentration of the Cu(II) ions.[32] The values of R_1 observed between 0 and 1 indicate favorable adsorption of the Cu(II) complex on silica gel (Table 4).

Effect of Matrix Elements. We studied the effect of foreign ions to apply the method for the separation and preconcentration of Cu(II) in water samples. Cu(II) (1 μg$\cdot$mL^{-1}) in 10 mL of solution was tested, and the relative measurement error was no more than 3 %. The tolerance limits of foreign ions under the proposed analytical conditions were found to be 10 fold for Pd(II), 30 fold for Au(III) and Ag(I), and 300 fold for Pt(IV). Large amounts (0.1 % w/v) of K^+, Na^+, Mg^{2+}, Ca^{2+}, Cl^-, Br^-, I^-, SO_4^{2-}, IO_3^-, NO_3^-, SCN^-, acetate, and oxalate ions showed no interference in the separation of Cu(II). In the case of PO_4^{3-} and EDTA, tolerance limits of foreign ions were found to be 40 fold and 1 fold, respectively. Therefore, the method provides a relatively high accuracy and precision for the separation and preconcentration of Cu(II) ions.

Analytical Parameters (Effect of Merits). The reproducibility of the proposed method was tested in a batch mode procedure. The relative standard deviation (R) was 1.5 % for 10 replicate measurements, each containing 0.635 μg$\cdot$mL^{-1} Cu(II). The SD of the blank for calculating the lower detection limit (blank +

3σ, where σ is SD) was 4 ng·L^{-1}. The D.L. of the proposed method is similar to those obtained by different techniques.[33] The accuracy and precision of the method were tested on water samples spiked with Cu(II) ions. The data are collected in Table 5.

Comparison with Other Sorbing Solids. The sorption capacity and preconcentration factor of HEPTS−Cu(II) immobilized on silica gel were compared with some important matrices (Table 6). The proposed method exhibits better capacity and preconcentration factor with respect to a large number of the metal matrix combinations.

Conclusions

4-Ethyl-1-(pyridin-2-yl) thiosemicarbazide (HEPTS) forms a solid Cu(II) complex in high yield. The molecular modeling of the ligand and its Cu(II) complex shows that the ligand has a tetrahedral structure around Cu(II). The simulation of IR and UV−vis spectra by the semiempirical PM3 method is in agreement with the experimental data. The ligand showed high reactivity toward Cu(II) ions; therefore, the formed complex was used for solid phase extraction on silica gel with a high preconcentration factor (200 fold), high capacity ($q_o = 520.83$ mg·g^{-1}), and high binding energy constant ($K = 3.585$ L·mg^{-1}). Common organic chelating agents do not interfere, reflecting high stability for the investigated complex. The proposed procedure was applied successfully for separation and preconcentration of Cu(II) ions in water samples.

Supporting Information Available:

Selected bond lengths, bond angles, and dihedral angles of HEPTS and the Cu(II) complex in the gaseous state (PM3 calculations). This material is available free of charge via the Internet at http://pubs.acs.org.

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