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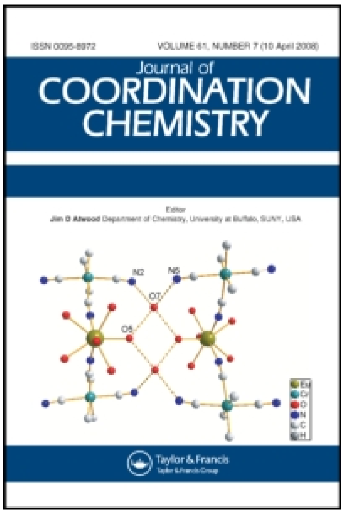

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Spectroscopic, magnetic and thermal studies on complexes of Cu(II) and VO^{2+} with diacetylmonoxime derivatives: new method for extraction of Cu(II)

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Spectroscopic, magnetic and thermal studies on complexes of Cu(II) and VO^{2+} with diacetylmonoxime derivatives: new method for extraction of Cu(II)

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The coordination behavior of Cu(II) and VO^{2+} towards some oximes has been investigated. The isolated complexes were characterized by elemental analysis, molar conductance, magnetic moment, spectra (electronic, IR, ESR and mass) and thermal measurements. The IR spectra showed most ligands are deprotonated during complex formation acting as mononegative bi- or tridentate, binegative tetradentate and neutral tridentate. The magnetic moments and electronic spectra showed octahedral, square pyramidal and square-planar structures for the Cu(II) and VO^{2+} complexes. The ESR spectra of the complexes are quite similar and exhibit axial symmetric g-tensor parameters with $g_{\|} > g_{\perp} > 2.0023$ and confirmed the structures. The TG curves showed decomposition steps and indicate stability of the complexes. The ligands can remove Cu(II) ions from water by flotation technology using oleic acid surfactant with high efficiency.

Keywords: Complexes; Thiosemicarbazone; Spectra; Thermal analysis; Flotation

1. Introduction

Oximes have insecticidal activities and are employed as antidotes against organophosphorous poisoning; their biochemical activity increases by chelation. Oximes are also used as reagents for estimation of trace metal ions in solution, coordinating in different modes to metals. Diacetylmonoxime thiosemicarbazone was effective against vaccinia infections in mice [1], probably by removing essential metal ions from vaccinia virus by chelation [2, 3]. Thiosemicarbazones are of interest due to their anticarcinogenic and antimicrobial activities [4, 5]. The fungicidal activity of these compounds is due to their ability to form stable chelates with essential metal ions [6]. Mono- and polynuclear Cu(II) complexes of thiosemicarbazones serve as models for galactose oxidase and are used as redox catalysts. The redox behavior of Cu(II) has special interest in biological systems [7, 8].

Vanadium is an essential element in plants and animals [9] and is the active site of haloperoxidase and nitrogenase. Its complexes inhibit several enzymes including

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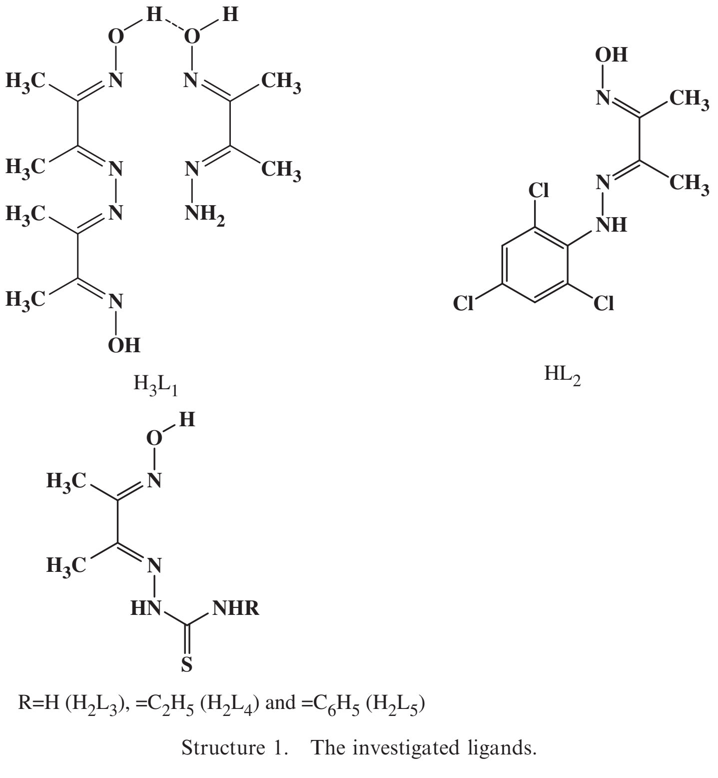
phosphotases, nucleases and kinases [10]. Several *in vivo* and *in vitro* studies on antidiabetic vanadium complexes have been reported [11].

Copper is an essential constituent of about thirty enzymes and glycol-proteins and is required for the synthesis of hemoglobin and for some biological processes [12, 13]. When levels of copper exceed certain values, defense mechanisms are overcome and toxicity results, thus an effective process for removing copper from wastewater is necessary. Flotation has received considerable interest owing to its simplicity, rapidity, economy and good separation yields (10^{-6}–10^{-2} mol L^{-1}) [14]. It is believed that this process will be incorporated as technology to treat water and wastewater [15].

The work reported herein is focused on the synthesis and characterization of Cu(II) and VO^{2+} complexes of oxime derivatives (structure 1). In addition, a new method to preconcentrate Cu(II) from water samples is described.

2. Experimental

All chemicals used were of analytical reagent grade (BDH) and used as supplied. Oleic acid (HOL) was used as received. Its stock solution (3.36×10^{-2} mol L^{-1}) was prepared from food grade with specific gravity 0.895 (J.T. Baker Chemical Co.) by dispersing 20 mL in 1L of kerosene.



H_3L_1

HL_2

R=H (H_2L_3), =C_2H_5 (H_2L_4) and =C_6H_5 (H_2L_5)

Structure 1. The investigated ligands.

2.1. *Synthesis of ligands*

Oxime derivatives were prepared as reported earlier [16] by reaction of diacetylmonoxime with hydrazine, trichlorophenylhydrazine, thiosemicarbazide, 4-ethyl and 4-phenylthiosemicarbazides. Ethanolic solutions were heated under reflux on a water bath for 2–3 h in 3 ml glacial acetic acid. The formed precipitate was separated by filtration, recrystallized from ethanol and dried. The formulas of the ligands are proposed from their elemental analyses, mass spectra, IR and ^{1}H NMR spectra. A mixture of diacetylmonoxime hydrazone and bis(diacetylmonoxime hydrazone) is formed from reaction of diacetylmonoxime with hydrazine; its mass spectrum (Supplemental Material) supported the proposed formula. The color, melting points, elemental analyses and formula weights of the ligands are presented in table 1.

IR spectral bands at 3269–3412, 1516–1624, 1485–1580, 1355–1365, 1007–1138 and *ca* 970 cm^{-1} are assigned to υ(OH), υ(C=N$_{hy}$), υ(C=N$_{ox}$), δ(OH), υ(N–N) [17] and υ(NOH) [18] vibrations, respectively. ^{1}H NMR peaks of H_3L_1, HL_2, H_2L_4 and H_2L_5: $\delta = 11.66-10.85$ (s, 1H), 10.11–10, $9.89-8.27$, $7.2-7.6$ and 3.37 (s, 3H) due to the OH, N^{2}H, N^{4}H, aromatic ring and CH_3, protons. Mass spectra (table 1) gave confirmation of the molecular weights of the ligands.

2.2. *Synthesis of complexes*

The complexes were prepared by mixing 1 : 1 molar ratio of the ligand (3 mmol) and copper acetate or vanadyl sulfate (3 mmol) and the mixture was heated under reflux on a water bath for 4–6 h. The precipitate was filtered, washed with hot water, hot ethanol and diethylether and finally dried in a vacuum desiccator.

2.3. *Physical measurements*

C and H content of the compounds were determined at the Microanalytical Unit of Cairo University. Copper and vanadyl analyses were carried out according to the standard methods [19]. The IR (KBr discs), electronic (Nujol mulls and DMSO solutions), ^{1}HNMR (d$_6$-DMSO, 200 MHz) and mass spectra were recorded on a Mattson 5000 FTIR spectrophotometer, UV$_2$ Unicam UV/Vis, Varian Gemini and Varian MAT 311 spectrometers, respectively. The magnetic moment values were evaluated at room temperature (25 ± 1°C) using a Johnson Matthey magnetic susceptibility balance. ESR spectra were obtained on a Bruker EMX spectrometer in

Table 1. Color, melting point, elemental analysis and formula weight of the ligands.

			% Found (Calcd)			F.W.	
Ligand (formula)	Color	M.P.,(°C)	C	H	N	Found	Calcd
H_3L_1 ($C_{12}H_{23}N_7O_3$)	White	141	45.9 (45.5)	7.1 (7.5)	31.2 (31.3)	313	314.4
HL_2 ($C_{10}H_{10}Cl_3N_3O$)	Yellowish white	175	40.8 (40.8)	3.4 (4.1)	14.3 (13.9)	293	294.6
H_2L_3 ($C_5H_{10}N_4OS$)	Yellow	220	34.5 (34.2)	5.8 (5.6)	32.2 (32.9)	–	174.2
H_2L_4 ($C_7H_{14}N_4OS$)	White	203	41.6 (41.5)	7.0 (7.2)	27.7 (26.9)	202	202.3
H_2L_5 ($C_{11}H_{14}N_4OS$)	White	204	52.8 (52.7)	5.6 (5.4)	22.4 (23.0)	268	250.3

the X-band (9.78 GHz) with 100 kHz modulation frequency. The microwave power and the modulation amplitude were set at 1 mW and 4 Gauss, respectively. The low field signal was obtained after 4 scans with a ten-fold increase in receiver gain. Powder ESR spectra were obtained in 2 mm quartz capillaries at room temperature (25 ± 1°C). Thermal studies were carried out on a Shimadzu thermogravimetric analyzer at a heating rate of $10^{\circ}\mathrm{C\,min^{-1}}$ under nitrogen using platinum holders. The flotation cell (a cylindrical tube of 29 cm length and 1.5 inner diameter, provided with a stopcock at the bottom) used was the same as described earlier [20].

2.4. *Recommended flotation procedure*

A known amount of Cu(II) was mixed with the ligand followed by addition of 3 ml of twice distilled water. After adjusting the pH with HCl and/or NaOH to the required value, the solution was transferred to the flotation cell and the total volume was completed to 10 ml with twice distilled water. The cell was shaken for a few seconds to ensure complexation, then 2 mL of HOL was added (with known concentration). The cell was then inverted twenty times by hand. The concentration of Cu(II) in the mother liquor was determined after 5 min and the floatability (F) was determined from: $F = (C_i - C_f)/C_i \times 100\%$; C_i and C_f denote the initial and final concentration of Cu(II) in the mother liquor, respectively.

3. Results and discussion

Cu(II) and VO^{2+} ions form complexes with the investigated oximes (table 2) that have high melting points, are insoluble in most common organic solvents, partially soluble in DMF and some are completely soluble in DMSO. The values of molar conductance measured for the soluble complexes indicate non-electrolytes [21].

3.1. *IR spectra*

The ligands coordinate as:

(i) Mononegative tridentate in $[Cu(HL_4)(OH))EtOH)(H_2O)]_2$, $[Cu(HL_5)(OH)]H_2O$ and $[(VO)_2(HL_5)(OH)_3(EtOH)_2]$ through $C{=}N_{hy}$, $C{=}N_{ox}$ and C–S. The shifts of $\upsilon(C{=}N_{ox})$, $\upsilon(C{=}N_{hy})$, υ(N–N) and υ(NOH) are attributed to participation of C=N in bonding. The disappearance of υ(C=S) is followed by the appearance of two bands at *ca* 615 and *ca* 1590 $\mathrm{cm^{-1}}$, attributed to υ(C–S) [22] and υ(C=N*). The υ(OH) became strong with a new absorption due to EtOH; δ(OH) at 1366 $\mathrm{cm^{-1}}$ is split into bands at 1377 and 1334 $\mathrm{cm^{-1}}$ due to oxime OH and the new OH. The 3347, 841 and 528 $\mathrm{cm^{-1}}$ bands are assigned to υ(OH), $\rho_r(H_2O)$ and $\rho_w(H_2O)$ of water coordination [23]. The 3448 and 1317 $\mathrm{cm^{-1}}$ bands attributed to υ(OH) and δ(OH) confirm OH coordination [24]; new bands at 1216 and 985 $\mathrm{cm^{-1}}$ are assigned to Cu–OH [25] and υ(Cu–OH–Cu) [26].

(ii) Mononegative bidentate in $[Cu(L_2)(H_2O)_2(OAc)]$ and $[(VO)_2(L_2)(SO_4)(OH)(H_2O)]$ confirmed by the shift of azomethine bands to lower wavenumbers (table 3) and

Table 2. Formula weight, color, melting point and elemental analysis of the complexes.

Complex	Formula weight		Color	M.p., (°C)	% Found (Calcd)		
	Calcd	Found			C	H	M
$[Cu(HL_1)]H_2O$	393.9	–	Brown	>300	37.4 (36.6)	5.5 (5.9)	16.2 (16.1)
$[(VO)_2(HL_1^-)_2(H_2O)_2(SO_4)]$	662.5	663	Faint green	>300	29.5 (29.0)	5.2 (4.6)	16.0 (15.7)
$[Cu(L_2)(H_2O)_2(OAc)]$	452.2	451	Green	>300	32.5 (31.9)	3.2 (3.6)	14.6 (14.1)
$[(VO)_2(L_2)(OH)(H_2O)(SO_4)]$	560.6	553	Green	>300	21.1 (21.5)	2.8 (2.2)	18.6 (18.5)
$[Cu(H_2L_3)_2(OH)_2]$	445.9	450	Olive green	245	26.7 (26.9)	4.9 (5.0)	14.1 (14.2)
$[(VO)(H_2L_3)(H_2O)(SO_4)]$	356.3	355	Reddish brown	>300	19.5 (19.1)	3.8 (3.7)	14.2 (13.7)
$[Cu(HL_4)(OH))EtOH)(H_2O)]_2$	691.7	692	Dark green	221	31.3 (30.7)	5.6 (5.4)	18.3 (18.0)
$[Cu(HL_5)(OH)]H_2O$	347.8	–	Brown	>300	38.3 (38.0)	4.7 (4.6)	18.2 (18.3)
$[(VO)_2(HL_5)(OH)_3(EtOH)_2]$	529.4	526	Green	>300	34.5 (34.0)	5.0 (5.5)	19.0 (19.6)

$H_2L_1^-$ is *bis*(diacetylmonoxime hydrazone).

Table 3. Assignments of the IR spectral bands of the ligands and their complexes.

Compound	ν(OH)	$\nu_{as}(NH_2)$, $\nu_s(NH_2)$	$\nu(N^2H)$	ν (C=N_{hy}) + $\delta(NH_2)$	ν(C=N_{ox})	δ(OH)	ν(C=S)	ν(M–O)	ν(M–S)	ν(M–N)
H_3L_1	3342	3202, 3015	–	1624	1580	1365	–	–	–	–
$[Cu(HL_1)]H_2O$	–	3250, 3166	–	1600, 1624	1477	–	–	–	–	352
$[(VO)_2(HL_1^-)_2(H_2O)_2SO_4]$	–	3198	–	1530	1517	–	–	510	–	330
HL_2	3333	–	3237	1499	1448	1365	–	–	–	–
$[Cu(L_2)(H_2O)_2(OAc)]$	–	–	–	1478	1426	–	–	482	–	365
$[(VO)_2(L_2)(OH)(H_2O)(SO_4)]$	–	–	3310	1485	1441	–	–	518	–	324
H_2L_3	3415	3254, 3231	3146	1550, 1615	1485	1385	765	–	–	–
$[Cu(HL_3)_2(OH)_2]$	3412	3281	3149	1499, 1625	1474	1364	767	457	421	327
$[(VO)(H_2L_3)(H_2O)(SO_4)]$	3415	3185, 3175	3133	1500, 1600	1437	1380	754	497	427	327
H_2L_4	3345	–	3224	1528	1502	1366	800	–	–	–
$[Cu(HL_4)(OH))EtOH)(H_2O)]_2$	3347	–	–	1516	1454	1377	–	489	400	372
H_2L_5	3269	–	3104	1548	1492	1355	814	–	–	–
$[Cu(HL_5)(OH)]H_2O$	–	–	–	1484	1433	–	748	483	419	352
$[(VO)_2(HL_5)(OH)_3(EtOH)_2]$	–	–	–	1519	1432	–	771	476	405	376

the appearance of bands at 3443, 1653, 846 and 596 cm^{-1} attributed to υ(OH), δ(H_2O), ρ_r(H_2O) and ρ_w(H_2O) confirming water coordination [23]. The bands at 1544 and 1512 cm^{-1} with difference of 32 cm^{-1} are due to bidentate acetate [27]. The bands in VO^{2+} complex at (1147; 1005), 940, (645; 593; 550) and 440 cm^{-1} are due to υ_3, υ_1, υ_4 and υ_2 for bidentate SO_4 [28].

(iii) Binegative tetradentate in [Cu(HL_1)]H_2O indicated by shifts of υ(C=N_{hy}), and υ(C=N_{ox}) to lower wavenumber and υ(NOH) to higher wavenumber indicating participation of nitrogen in bonding. Two of the oxime OH's are deprotonated and the third is uncoordinated with υ(OH) at 3423 cm^{-1}.

(iv) Neutral tridentate through (C=N_{ox}), (C=N_{hy}) and C=S in [Cu(H_2L_3)$_2$(OH)$_2$] and [VO(H_2L_3)(SO_4)(H_2O)]. The band at 1320 may be due to δ(OH) while bands at 1189, 1128, 1087(υ_3), 1034(υ_1), 693, 597, 546(υ_4) and 455(υ_2) cm^{-1} confirm bidentate SO_4 [28]. The band at 995 cm^{-1} is assigned to υ(V=O). Recently, the ligand formed complexes with Cd(II) and Hg(II) and coordinated as neutral tridentate through OH, C=N and C=S groups [29].

3.2. *Spectral and magnetic studies*

The magnetic moments and the electronic spectral bands of the Cu(II) complexes are given in table 4. The ligands have $\pi \rightarrow \pi^*$ and two $n \rightarrow \pi^*$ bands at 32785–40815, 28570–30960 and 27000–28250 cm^{-1} [30]; little change is shown in their complexes. The band at 22220–26040 cm^{-1} in the spectra of the complexes may be due to LMCT [31].

Electronic spectra of [Cu(L_2)(H_2O)$_2$(OAc)] (Supplemental Material), [Cu(H_2L_3)(H_2O)-(OH)$_2$] and [Cu(HL_4)(OH)(EtOH)(H_2O)]$_2$ in Nujol have bands at 16340–16890 and 18730–19835 cm^{-1} assigned to $^2E_g \leftarrow {}^2T_{2g}$. The broadness of the bands may be due to Jahn-Teller effect in octahedral geometry [32]. The magnetic moment of the first complex (1.8 BM) is normal and the others have subnormal (1.12–1.60 BM) indicating interaction between Cu(II) centers. The spectra of [Cu(HL_1)]H_2O [structure 2] and [Cu(HL_5)(OH)]H_2O showed one band at 18660–18730 cm^{-1}, in Nujol, corresponding to $^2B_{1g} \rightarrow {}^2A_{1g}$ in a square-planar geometry [33].

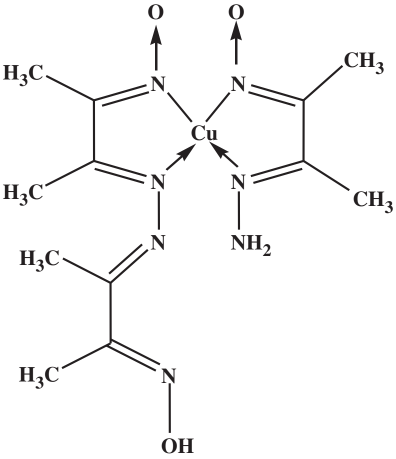
The spectra of [(VO)$_2$(HL_1^-)$_2$ (SO_4)(H_2O)$_2$] (Structure 3), [(VO)$_2$(L_2)(SO_4)(OH)(H_2O)] and [(VO)$_2$(HL_5)(OH)$_3$(EtOH)$_2$] in Nujol or DMSO showed a band at 11520–12225 cm^{-1} as reported for square pyramidal configurations [34]. The bands at 21000 and 19010 cm^{-1} in [(VO)(H_2L_3)(SO_4)]H_2O are assigned to the $^2B_2 \rightarrow {}^2E(n_1)$ and $^2B_2 \rightarrow {}^2B_1(n_2)$ transitions [35] in an octahedral structure. The subnormal magnetic moments for [(VO)$_2$(L_2)(SO_4)(OH)(H_2O)] and [(VO)$_2$(HL_5)(OH)$_3$(EtOH)$_2$] are due to strong interaction between VO ions.

3.3. *ESR spectra*

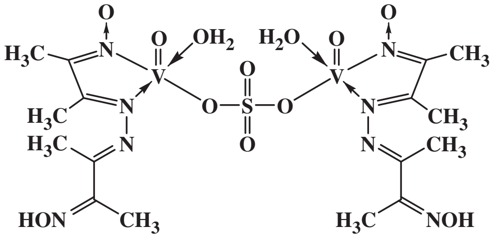
The room temperature solid state ESR spectra (table 5) of the copper complexes exhibit g- parameters with $g_{\parallel} > g_{\perp} > 2.0023$ indicating that $d_{x^2-y^2}$ is the ground state [36], characteristic of square planar, square pyramidal or octahedral stereochemistries [37]. In axial symmetry, $G = (g_{\parallel} - 2)/(g_{\perp} - 2) = 4$, where G is the exchange interaction parameter. The G value of [Cu(L_2)(H_2O)$_2$(OAc)] is 7.5 suggesting no copper–copper

Table 4. Magnetic moments and electronic spectral bands of the complexes.

Complex	μ_{eff} (BM)	State	d–d transition (cm^{-1})	Charge transfer (cm^{-1})	Supposed structure
$[Cu(HL_1)]H_2O$	2.00	Nujol	18660	21370; 24750	Square-planar
$[(VO)_2(HL_1^-)_2(H_2O)_2(SO_4)]$	1.71	DMSO Nujol	11520 13120; 16340; 19010	21835; 21010	Square-pyramidal
$[Cu(L_2)(H_2O)_2(OAc)]$	1.60	Nujol	16340; 19835	21010; 23695	Octahedral
$[(VO)_2(L_2)(OH)(H_2O)(SO_4)]$	1.56	Nujol	12165; 16805; 19420	21835; 23535	Square-pyramidal
$[Cu(H_2L_3)_2(HO)_2]$	1.80	Nujol	16890; 19380	22120; 26180	Octahedral
$[(VO)(H_2L_3)(H_2O)(SO_4)]$	2.00	Nujol	16100; 19010	21000; 24270	Octahedral
$[Cu(HL_5)(OH)]H_2O$	1.92	Nujol	18730	23700	Square-planar
$[(VO)_2(HL_5)(OH)_3(EtOH)_2]$	1.30	DMSO Nujol	12225 12225; 17985	21460; 26315	Square-pyramidal
$[Cu(HL_4)(OH)(EtOH)(H_2O)_2]_2$	1.40	Nujol	16555; 19010	20830; 25150	Octahedral



Structure 2. Structure of [Cu(HL_1)]H_2O.



Structure 3. Structure of [$(VO)_2(HL_1^-)_2(SO_4)(H_2O)_2$].

Table 5. ESR data of Cu(II) and VO^{2+} complexes at room temperature.

Complex	$g_\parallel$	$g_\perp$	$A_\parallel \times 10^{-4}$ (cm^{-1})	G	$A_\perp \times 10^{-4}$ (cm^{-1})	$g_\parallel/A_\parallel$	α^2	β^2
[$Cu(HL_5)(OH)]H_2O$	2.17	2.05	110	3.4	–	197	0.77	0.65
[$Cu(HL_4)(OH)(EtOH)(H_2O)]_2$	2.20	–	110	–	–	200	–	–
[$Cu(L_2)(H_2O)_2(OAc)$]	2.15	2.02	150	7.5	–	143	0.61	0.59
[$(VO)_2(HL_1^-)_2$ $(H_2O)_2(SO_4)$]	1.98	1.93	160	–	80	–	0.62	0.43
[$(VO)_2(HL_5)(OH)_3(EtOH)_2$]	1.98	1.94	158	–	80	–	0.73	0.40
[$(VO)(H_2L_3)(SO_4)(H_2O)$]	1.97	1.93	155	–	85	–	0.67	0.57

exchange interaction, while for [$Cu(HL_5)(OH)]H_2O$ it is 3.4, suggesting an exchange coupling between copper(II) centers [38]. The band for a forbidden magnetic dipolar transition is not observed at ca 1600 G, $g = 4.0$ indicating mononuclear complex [39].

Superhyperfine structure is not seen at high field excluding interaction of the nuclear spins of N ($I = 1$) with the unpaired electron density on Cu(II). The tendency of $A_\parallel$ to decrease with increase of $g_\parallel$ indicates tetrahedral distortion of copper [40]. In order to quantify the degree of distortion, $f = g_\parallel/A_\parallel$ is selected from the ESR spectra ($105-135\,cm^{-1}$ is measured for square-planar complexes). In a distorted tetrahedral, this value is much larger. In the present complexes, f is greater than $135\,cm^{-1}$

demonstrating the presence of significant dihedral angle distortion in the *xy*-plane and indicating a distortion from square-planar geometry.

Molecular orbital coefficients, α^2 and β^2, were calculated and their values indicate appreciable covalent bonds. For square-planar geometry, β^2 is lower than α^2 indicating that the in-plane π-bonding is more covalent than the in-plane σ-bonding [41].

ESR spectra of powdered VO^{2+} complexes are similar to other spectra [42], displaying broad lines due to the mutual interaction of neighboring VO^{2+} sites and weak resolved hyperfine structure. The absence of vanadium hyperfine coupling is common in solid state complexes, attributed to simultaneous flipping of neighboring electron spins [43] or strong exchange interactions. The anisotropic ESR spectra of VO^{2+} with $g_{\parallel} < g_{\perp} < 2.0023$ and $A_{\parallel} > A_{\perp}$ is characteristic of square pyramidal complexes with C_{4V} symmetry where V=O is along the z-axis and the other four coordinating atoms are along the *x*- and *y*-axes. The values agree with the *g*-tensor parameters reported for distorted tetragonal vanadium complexes.

The α^2 and β^2 values were calculated using the following equations and their values are presented in table 5.

$$\left.\begin{aligned}
A_{\parallel} &= -PK - \frac{4\beta^2 P}{7} - (g_e - g_{\parallel})\frac{P-3}{7(g_e - g_{\perp})P} \\
A_{\perp} &= -PK + \frac{2\beta^2 P}{7} - \frac{11}{14(g_e - g_{\perp})P} \\
g_0 - g_{\parallel} &= \frac{8\alpha^2\beta^2\lambda}{E}
\end{aligned}\right|$$

where $P = 136\,\mathrm{G}$ (the dipolar interaction constant between magnetic moment of the electron and vanadium nucleus), $\lambda = 170\,\mathrm{cm}^{-1}$, E is the d–d band and k is the Fermi contact term. The values of β^2 are much lower than α^2.

3.4. *Mass spectra*

The mass spectrum of $[Cu(HL_4)(OH))EtOH)(H_2O)]_2$ showed peaks corresponding to successive degradation of the molecule. The peak at m/e = 692 with 12.4% abundance is due to molecular ion peak (M) together with another one at 701 (abundance 11.2%) due to an isotopic species. The stable species (abundance 100%) is due to $Cu_2(CH_6N_6O_5S_2)$. The final species is Cu with abundance 6.7%.

$[Cu(H_2L_3)_2(OH)_2]$ has a molecular ion peak of 450 (445.6). The base peak at 236 corresponds to $Cu(C_2H_2N_6S_2)$ while the last degradable species at 105 is due to CuN_3.

The spectrum of $[(VO)_2(HL_1)_2(H_2O)_2SO_4]$ exhibits a peak at 663 corresponding to the molecular ion peak (659.2) with abundance 10.8%. The base peak at 271 corresponds to $[(VO)_2(N_3SO_4)]$ while the last degradable species at 67 is due to VO.

$[(VO)_2(L_2)(OH)(H_2O)SO_4]$ (Supplemental Material) exhibits a peak at 553 (557.7) with abundance 8.4%. The base peak at 139.00 corresponds to $[(VO)(C_2H_3N_2)(OH)]$ while that at 54.00 is due to vanadium.

$[(VO)(H_2L_3)(H_2O)(SO_4)]$ exhibits a peak at 357 (Calcd 356.3) with abundance 3.6%. All degradable peaks have low abundances with a base peak of 55 corresponding to vanadium.

The mass spectrum of $[(VO)_2(HL_5)(OH)_3(EtOH)_2]$ shows a peak at 528 (528.7) with low abundance (2.8%). The base peak at 191 is due to $C_3H_8O_4SV$ while the last degradable species at 51.9 is due to V.

3.5. *Thermal analysis*

The TGA of $[Cu(HL_2)(H_2O)_2(OAc)]$ indicates stability until 131°C, then a stage at 222°C [mass loss of 5.0 (4.0%)] for removal of H_2O. The second stage at 310°C [13.8 (13.9%)] corresponds to the removal of H_2O+3CH_3; the third stage ending at 537°C, 22.1 (23.7%) mass loss for $3C+Cl_2$, leaves $[Cu(C_6H_3N_3O_3Cl)]$.

The TG curve of $[Cu(HL_3)_2(OH)_2]$ showed thermal stability to 238°C (Supplemental Material). From 238–682°C mass losses of 37.2 (39.3%) and 24.4 (27.1%) correspond to evolution of $C_8H_{18}N_2O_2$ and $C_2H_4N_2S_2$; CuN_4O_2 is the residual.

$[Cu(HL_4)(OH))EtOH)\text{-}(H_2O)]_2$ showed stability to 206°C indicating that solvents exist in the coordination sphere. The steps at 207−710°C are due to evolution of $2H_2O$ and fragments of ligand leaving 36.0% (35.3) corresponding to CuN_4S_2. The sulfur bridge may give higher stability to the remaining part.

$[Cu(HL_5)(OH)]H_2O$ and $[(VO)(H_2L_3)(H_2O)(SO_4)]$ begin to decompose at 30–146°C with mass loss corresponding to removal of H_2O. The degradation steps at 244 and 246−600°C are assigned to the evolution of C_6H_6N [25% (26.5%)] and $C_5H_7N_2O$ [33.0% (31.9%)]. [CuNOS] and $[VNO_5S]$ are the final fragments.

$[(VO)_2(HL_1^-)_2\ (H_2O)_2(SO_4)]$ and $[(VO)_2(HL_5)(OH)_3(EtOH)_2]$ showed thermal stability to 202 and 240°C. The degradation steps in the first complex at 223 [2.85 (2.72%)], 398 [27.51 (26.10%)] and 515°C [31.50 (32.15%)] correspond to removal of H_2O, $[H_2O+8CH_3+2OH]$ and $C_8N_6O_2$. In the second complex, the steps at 240 °C [C_3H_6; 7.5 (7.6%)], 241–382°C [C_6H_5; 4.0 (14.1%)] and 383–540°C [NOH+EtOH; 15.9 (14.0%)] end with $V_2N_2O_6S$ as residue 38.14 (39.04%).

3.6. *Separation of Cu(II)*

Several experiments were carried out to investigate the floatability of 1×10^{-4} mol L^{-1} Cu(II) using HOL; the floatability does not exceed 40%. Trials were made using the oxime derivatives as coagulants to enhance the results. The data show that ~100% floatability was attained at pH 3–10 for H_2L_3 and H_2L_4 and 4–10 for H_2L_5 and H_3L_1, indicating application of the investigated oxime derivatives for the separation of Cu^{2+} from acidic, neutral and alkaline media. At $pH > 10$, the flotation efficiency decreases, attributed to formation of oleate giving excessive foams distributed through the whole bulk of floating solution [44]. Hence, $pH \sim 7$ is recommended for the following experiments.

Variable concentrations of ligands using HOL at $pH \sim 7$ were investigated. The data show that floatability reaches ~100% at molar ratio of 1 : 1 and sometimes 1 : 2. The use of excess oxime derivative has no effect on the flotation process which facilitates the separation of Cu(II) ions from unknown matrices.

Table 6. Effect of some foreign ions on the flotation of $1 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$ Cu^{2+} using $4 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$ of each ligand in the presence of $1 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ HOL at pH 7.

	H_2L_3		H_2L_5		H_2L_4		H_3L_1	
Foreign ion added	Foreign ion $/Cu^{2+} \times 10^4$	F%	Foreign ion$/Cu^{2+} \times 10^4$	F%	Foreign ion$/Cu^{2+} \times 10^4$	F%	Foreign ion$/Cu^{2+} \times 10^4$	F%
Ca^{2+}	6.0	100.0	1.0	100.0	1.0	99.9	1.0	99.9
K^+	3.0	99.9	1.0	100.0	1.0	99.9	1.0	99.8
Na^+	3.0	99.5	1.0	99.9	1.0	99.9	1.0	99.8
Mg^{2+}	3.0	99.6	1.0	99.9	1.0	99.8	1.0	99.7
NH_4^+	1.70	10.0	2.0	99.9	2.0	99.7	2.0	99.9
Co^{2+}	1.0	99.8	1.0	99.9	1.0	100.0	1.0	99.8
Ni^{2+}	1.0	99.9	1.0	99.7	1.0	100.0	1.0	99.7
Cd^{2+}	1.0	99.9	1.0	99.7	1.0	100.0	1.0	100.0
Al^{3+}	0.50	100.0	1.0	100.0	1.0	100.0	1.0	100.0
Mn^{2+}	1.0	100.0	1.0	100.0	1.0	99.9	1.0	100.0
Zn^{2+}	1.0	100.0	1.0	99.7	1.0	99.9	1.0	99.6
Ba^{2+}	1.0	99.7	1.0	100.0	1.0	99.8	1.0	99.6
Br^-	1.0	99.7	1.0	99.7	1.0	99.9	1.0	100.0
$C_2O_4^{2-}$	0.10	9.6	0.10	99.9	0.10	99.7	0.10	99.7
Cl^-	3.0	100.0	2.0	99.9	2.0	99.9	2.0	99.9
SO_4^{2-}	3.0	100.0	1.0	99.9	1.0	99.7	1.0	100.0
CH_3COO^-	1.0	100.0	1.0	100.0	1.0	99.9	1.0	99.9

Attempts to float different concentrations of Cu(II) using 4×10^{-4} mol L^{-1} of each oxime derivative and 1×10^{-3} mol L^{-1} HOL at pH ~ 7 show that the efficiency ($\sim$100) of Cu(II) remains constant for all the investigated oximes whenever the ratio of (Cu:L) is 1 : 1 or 1 : 2. The floatation begins to decrease in ratios larger than 1 : 1, i.e. the amount of ligand is insufficient for chelation.

Another series of experiments were performed in different concentrations of HOL. The results showed that in the concentration range 1×10^{-5}–$1 \times 10^{-2}\,\mathrm{mol\,L^{-1}}$, complete floatation of Cu(II) is achieved. Below $1 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$, floatation decreases, attributed to the presence of insufficient amounts of surfactant for complete flotation. At higher surfactant concentration the incomplete separation of Cu(II) may be due to surfactant changing particles from coagulation precipitation through coagulation floatation to re-dispersion. Moreover, poor flotation at high surfactant concentration is caused by formation of hydrated micelle coating on the solid surface [45]. As a result, the hydrophobicity of this surface was not satisfactory for flotation. Therefore, a concentration of $1.0 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ of HOL was fixed throughout.

The effect of temperature on a solution containing $1 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$ Cu^{2+} and 4×10^{-4} mol L^{-1} of each oxime at pH 7 was investigated. Temperature (5–80°C) has no appreciable effect on flotation. Since most industrial effluents are hot, the proposed procedure may find application in the removal of Cu(II) directly from industrial wastewater. Subsequent measurements were carried out at room temperature, ca 25 ± 1°C.

The effect of foreign ions on the floatability of $1 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$ Cu(II) and 4×10^{-4} mol L^{-1} of each oxime at pH 7 was investigated. The tolerable amounts of each ion, giving a maximum error of ±2% in the recovery, are summarized in table 6. All investigated foreign ions with a relatively high concentration have no effect on the flotation. Therefore, the recommended procedure may find its applications on natural water samples.

Table 7. Floatability of Cu(II) added to some water samples at pH ~ 7 using $3 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$ ligand and $10^{-3}\,\mathrm{mol\,L^{-1}}$ HOL.

Water sample (Location)	Cu(II) added ($\mathrm{mg\,L^{-1}}$)	*F* (%) H_2L_3	 H_2L_5	 H_2L_4	 H_3L_1
Distilled water	6.3	99.8	100.0	100.0	99.8
	9.5	100.0	99.7	99.8	100.0
Tap water (our laboratory)	6.3	99.7	99.8	100.0	100.0
	9.5	100.0	100.0	99.8	99.9
Nile water (Sherbine)	6.3	99.8	100.0	100.0	100.0
	9.5	100.0	99.8	99.9	99.7
Sea water (Gamasah)	6.3	99.7	99.8	99.8	99.7
	9.5	100.0	100.0	100.0	100.0
Under ground water (Salaka)	6.3	100.0	99.8	99.9	100.0
	9.5	99.7	99.0	99.9	99.7

In order to evaluate the applicability of the flotation method for the recovery of Cu(II) from aqueous solution, various types of water samples were studied. The selection of these samples was done in a way to provide a wide variety of sample matrices characterized by different types of interferences. Solutions of pre-filtered water samples (10 mL) containing Cu(II) with a concentration of 6.3 or $9.5\,\mathrm{mg\,L^{-1}}$ were floated. The data listed in table 7 show that a satisfactory recovery of Cu(II) was obtained from natural water samples under the conditions.

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