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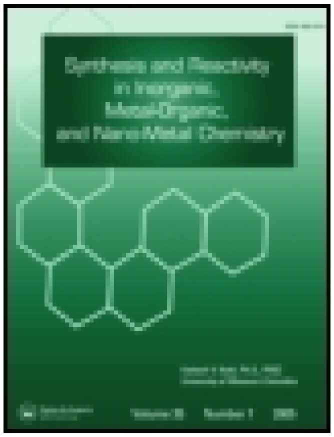

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

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Synthesis, Characterization and Extraction Properties of Four Unsymmetricall vic-Dioximes and their Complexes with Nickel (II), Cobalt (II) and Copper (II)

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Synthesis, Characterization and Extraction Properties of Four Unsymmetricall *vic*-Dioximes and their Complexes with Nickel (II), Cobalt (II) and Copper (II)

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Four new unsymmetrical *vic*-dioximes: [L^1H_2] *N*-(4-acetanilidyl)amino-*amphi*-glyoxime, [L^2H_2] *N*-(4-acetanilidyl)amino-*anti*-glyoxime, [L^3H_2] *N*-(2-thiazolyl)amino-*amphi*-glyoxime and [L^4H_2] *N*-(2-thiazolyl)amino-*anti*-glyoxime were prepared by the reaction of *amphi*-chloroglyoxime and *anti*-chloroglyoxime with 4-aminoacetanilide and 2-aminothiazol in absolute ethanol. The preparation Ni(II), Co(II), and Cu(II) complexes of the *amphi*- and *anti*-isomers of these ligands are described.The ligands and their complexes were characterized by elemental analyses, IR, mass, H^1 and ^{13}C NMR spectra and magnetic susceptibility measurements. Ligands complexing properties were studied by the liquid-liquid extraction of selected alkali (Li^+, Na^+, K^+, Cs^+) and transition metals (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}). It has been observed that all ligands show a high affinity to Cu^{2+} and Hg^{2+} ions, where as almost no affinity to alkali metals. The extraction equilibrium constants (K_{ex}) for complexes of ligands with Cu^{2+} and Hg^{2+} metal picrates between dichloromethane and water have been determined at 25°C.

Keywords liquid-liquid extractions, *vic*-dioximes, transition metal complexes, alkali cations

INTRODUCTION

One of the major interests in coordination chemistry is to study the interaction of a central atom with surrounding atoms, ions or molecules. Coordination compounds containing *vic*-dioxime ligands have been known and studied from the beginning of this century.[1,2] The numerous dioximes and their transition metal complexes have been investigated.[3,4] Since the increasing use of coordination compounds in analytical, pigment, medicinal and biochemistry, many investigators have studied these topics, especially the important role of the complexes of 1,2-dioximes in coordination chemistry. *vic*-dioximes have received considerable attention as model compounds that mimic biofunctions such as the reduction of B_{12}[3,5] Oxime metal chelates are biologically active[6] and are reported to possess semiconducting properties.[7,8] Derivatives of monoaminoglyoxime, heterocyclic and macrocyclic *vic*-dioximes, tetraoximes and their complexes with transition metals have been described.[2,9–21]

Amines or mercaptans react with (E,E)-dichloroglyoxime or cyanogen-di-*N*-oxide to yield various heterocyclic and macrocyclic *vic*-dioximes.[13,16,22–24] The (E,E)- and (E,Z)-stereoisomers of *vic*-dioximes coordinate through their N,N or N,O sites and, in a few cases, interconversion of (E,E)- and (E,Z)-complexes[10,25–27] is possible. Tschugaef[28] was the first to identify the bidentate nature of *vic*-dioximes in his significant work on the reaction between nickel (II) salts and dimethylglyoximes. Transition metal complexes of these *vic*-dioximes are essentially N,N-coordinated square-planar structures, but the uranyl complexes form μ-hydroxo-bridged dimers with N,O-coordination as shown by infrared and ^1H NMR spectroscopy.[18,29]

Although numerous investigations have been recently reported regarding the extraction of alkali metals and transition

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metals from aqueous phase into an organic phase by crown ether and calixarene.[30–35] As yet, reports on solvent extraction with the complexes of oxime compounds are scarce.[36–43] Therefore, we have investigated the solvent extraction of metal cations through oxime compounds. In this work, we have investigated the effectiveness of four glyoxime derivatives in transferring the alkaline metal cations (Li^+, Na^+, K^+, Cs^+) and transition metals (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}) and Pb^{2+} cation from the aqueous phase into the organic phase.

In this paper, we report the synthesis and complex formation of four new substituted aminoglyoximes of unsymmetrically substituted *vic*-dioximes.

EXPERIMENTAL

Materials and Measurement

All remaining reagents were purchased from Merck or Fluka or Sigma Company and were used without further purification. Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. Elemental analyses (C, H, and N) were determined using a Leco, CHNS-932 model analyzer. ^1H, ^{13}C NMR spectra were recorded on a Bruker DPX-400 400 MHz High Performance Digital FT-NMR and i.r spectra on a Perkin Elmer 1605 FT-IR spectrometer in KBr pellets. The pH was measured on a Orion Expondoble Ion Analyzer EA 940. Mass spectra were recorded on a MS 12 Mass spectrometer, Kratos at 70 eV and 220°C ion source temperature, electron impact ionization. The u.v.-vis. spectra were recorded on a Shimadzu 160A spectrometer. Magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility balance (Model MK1) at room temperature using $Hg[Co(SCN)_4]$ as a calibrate; diamagnetic corrections were calculated from Pascal's contants. The metal analyses were determined using a Unicam 929 AAS spectrometer.

Synthesis

amphi- and *anti*-chloroglyoxime were prepared according to published methods.[44,45] Experimental procedures are given below.

Synthesis of Substituted Aminoglyoximes [$L^{1-4}H_2$]

To *amphi*-chloroglyoxime or *anti*-chloroglyoxime (1.225 g, 10 mmol) dissolved in Et_2O (30 cm^3), a solution of 4-aminoacetanilide (1.50 g, 10 mmol) and 2-aminothiazol (1.00 g, 10 mmol) in absolute EtOH (30 cm^3) was added dropwise at room temperature with constant stirrring. The reaction mixture was stirred continuously for 1 h. at room temperature. The pH of the solution, which decreased to ca. 4.0, was adjusted to 5.5–6.0 with 1% KOH solution in EtOH. Ligands were precipitated by addition of CH_2Cl_2 with continuous stirring. The precipitated ligand was filtered off, washed with cold EtOH. The ligand was recrystallied from to 1:1 H_2O-EtOH solution and dried at 105°C.

amphi-$C_{10}H_{12}N_4O_3$ [$\mathbf{L^1H_2}$]; Yield; 1.17 g (%49). The product is soluble in H_2O and DMSO, and slightly soluble in DMF. It is insoluble in Et_2O, $CHCl_3$ and CCl_4. Characterictic ^{13}C NMR bands (DMSO-d_6, δ ppm): 145.16 (C_1), 141.54 (C_2), 133.11 (C_3), 120.82 (C_4), 123.06 (C_5), 130.73 (C_6), 160.44 (C_7), 26.89 (C_8).

anti-$C_{10}H_{12}N_4O_3$ [$\mathbf{L^2H_2}$]; Yield; 0.97 g (%43). The product is soluble in H_2O and DMSO, and slightly soluble in $CHCl_3$. It is insoluble in Et_2O and CCl_4. Characterictic ^{13}C NMR bands (DMSO-d_6, δ ppm): 144.86 (C_1), 142.11 (C_2), 134.58 (C_3), 121.35 (C_4), 124.46 (C_5), 131.27 (C_6), 161.01 (C_7), 26.36 (C_8).

amphi-$C_5H_6N_4SO_2$ [$\mathbf{L^3H_2}$]; Yield; 0.84 g (%45). The product is soluble in EtOH and DMSO, and slightly soluble in $CHCl_3$. It is insoluble in Et_2O and CCl_4. Characterictic ^{13}C NMR bands (DMSO-d_6, δ ppm): 140.23 (C_1), 150.94 (C_2), 149.67 (C_3), 132.78 (C_4), 113.14 (C_5).

anti-$C_5H_6N_4SO_2$ [$\mathbf{L^4H_2}$]; Yield; 0.76 g (%41). The product is soluble in EtOH and DMSO, and slightly soluble in $CHCl_3$. It is insoluble in Et_2O and CCl_4. Characterictic ^{13}C NMR bands (DMSO-d_6, δ ppm): 139.58 (C_1), 148.85 (C_2), 148.06 (C_3), 131.98 (C_4), 113.42 (C_5).

Table 1 gives the ^1H NMR data for the above four ligands. The colors, yields, melting points and elemental analyses, IR and mass spectra data of the ligands are given Tables 2, 3 and 4, respectively.

Ni(II), Co(II), and Cu(II) Complexes of Amphi-$C_{10}H_{12}N_4O_3$ [L^1H_2]

A solution of 5 mmol metal salt [$NiCl_2 \cdot 6H_2O$ (1.189 g), $CoCl_2 \cdot 6H_2O$ (1.190 g), $CuCl_2 \cdot 2H_2O$ (0.852 g)] dissolved in H_2O (30 cm^3), was added to a stirred solution of the ligand (1.18 g, 5 mmol) dissolved in EtOH (30 cm^3). On addition of the metal salt, the pH dropped to 3.5–4.0 from 5.0 at the onset of the reaction. After addition of a 1% NaOH solution in H_2O to raise the pH the mixture was stirred on a water bath at 55–60°C for 30 min. The precipitated complexes were filtered off, washed with H_2O and dried at 60°C.

Ni(II), Co(II), and Cu(II) Complexes of Anti-$C_{10}H_{12}N_4O_3$ [L^2H_2], Amphi-$C_5H_6N_4SO_2$ [L^3H_2] and, Anti-$C_5H_6N_4SO_2$ [L^4H_2]

A solution of the metal salt (5 mmol) [$NiCl_6{\cdot}6H_2O$ (1.189 g), $CoCl_2 \cdot 6H_2O$ (1.190 g), $CuCl_2 \cdot 2H_2O$ (0.852 g)] in H_2O (30 cm^3) was added dropwise to a solution of the ligand [$\mathbf{L^2H_2}$ (2.36 g, 10 mmol) and $\mathbf{L^3H_2}$, $\mathbf{L^4H_2}$ (1.86 g, 10 mmol)] dissolved in 1:1 EtOH-H_2O (30 cm^3) mixture. Upon adding metal salt, the pH of the mixtures dropped to 3.5–4.0. After addition of a 1% NaOH solution in H_2O to raise the pH to 5.0–5.5 the mixture was stirred on a water bath at 50–55°C for 30 min. The precipitated complexes were filtered off, washed with H_2O and dried at 100°C.

TABLE 1
^1H NMR spectra of the ligands in DMSO-d_6 δ (p.p.m.)

Compound	O-H^a	O-H^a	H_{Arom}	^{a}HN-C=	=CH	-CH_3	other
L^1H_2 *amphi*- $C_{10}H_{12}N_4O_3$	11.16 s (1H)	10.17 s (1H)	6.41–7.21 dd (4H)	7.69 s (1H) *J*(6.35)	8.19 s (1H)	2.01 s (3H)	O=CNH-Ar 9,51 S (1H)
L^2H_2 *anti*- $C_{10}H_{12}N_4O_3$	11.37 s (1H	10.72 s (1H	6.50–7.45 dd (4H) *J*(6.84)	7.77 s (1H)	8.25 s (1H)	2.00 s (3H)	O=CNH-Ar 9,81 s (1H)
L^3H_2 *amphi*- $C_5H_6N_4SO_2$	11.01 s (1H)	10.10 s (1H)	6.93–6.53 d (1H) *J*(3.70)	8.19 s (1H)	7.94 s (1H)		
L^4H_2 *anti*- $C_5H_6N_4SO_2$	11.30 s (1H)	10.70 s (1H)	6.85–6.50 d (1H) *J*(3.68)	8.27 s (1H)	7.80 s (1H)		

^{a}Disappears on D_2O exchange, s: singlet, d: doublet, dd: doublet of doublet; all *J* values are averages.

The colors, yields, melting points, elemental analyses and IR spectral data of the compounds are given in Tables 2 and 3.

Solvent Extraction

Picrate extraction experiments were performed following Pedersen's procedure.[46] 10 cm^3 of a 2.10^{-5} M aqueous picrate solution and 10 cm^3 1.10^{-3} M solution of ligand in CH_2Cl_2 were vigorously agitated in a stoppered glass tube with a mechanical shaker for 2 min, then magnetically stirred in a thermostated water bath at 25°C for 1 h, and finally left standing for an additional 30 min. The concentration of the picrate ion remaining in the aqueous phase was then determined spectrophotometrically, as previously described.[43,47] Blank experiments showed that no picrate extraction occurred in the absence of ligand. The alkali picrates were prepared as described elsewhere[43,47,48] by stepwise addition of a 2.10^{-2} M aqueous picric acid solution to a 0.14 M aqueous solution of alkali metal hydroxide until neutralization, which was checked by pH control with a glass electrode. They were then rapidly washed with ethanol and ether before being dried in vacuo for 24 h. Transition metal picrates were prepared by successive addition of a 1.10^{-2} M metal nitrate solution to 2.10^{-5} M aqueous picric acid solution and shaken at 25°C for 1 h. This metal picrates (Li^+, Na^+, K^+, Cs^+, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}) were measure by u.v.-vis. using does maximum wavelength 352 nm). The extractability of the metal cations is expressed by means of the following equation (1):

$$\text{Extractability}(\%) = [(A_0 - A)/A_0] \times 100 \qquad (1)$$

where A_0 and A are the absorbencies in the absence and presence of ligands, respectively.

Log Log Plot Analyses

To characterize the extraction ability, the dependence of the disribution coefficient D of the cation between the two phases upon the ligand concentration was examined. If the general extraction equilibrium to be given by Eq. (2).

$$M^{n+}_{(aq)} + nPic^-_{(aq)} + x[L]_{(org)} \longrightarrow [M(Pic)_n(L)_x]_{(org)} \qquad (2)$$

the overall extraction equilibrium constant is

$$K_{ex} = \frac{[M(Pic)_n(L)_x]}{[M^{n+}][Pic^-]^n[L]^x} \qquad (3)$$

and the distribution ratio D is defined by

$$D = \frac{[M(Pic)_n(L)_x]}{[(M^{n+})]} \qquad (4)$$

By introducing D into Eq. (4) and taking logarithm of both sides, Eq. (5) is obtained.

$$\log D = \log(K_{ex}[Pic]^n) + x\log[L] \qquad (5)$$

Under these assumptions, a plot of log D versus log [L] should be linear and its slope should be equal to the number of ligand molecules per metal cation in the extracted species.

RESULTS AND DISCUSSION

Four new aminoglyoxime derivatives were prepared by reacting aromatic amines with *amphi*-chloroglyoxime[44,45] or *anti*-chloroglyoxime,[44,45] respectively. The structure of these

TABLE 2
Colors, m.p., yields and elemental analytical results of the ligands and their complexes

Compounds	Formulas	Color	Yield (%)	μ_{eff} (B.M.)	Mp°C (dec)	Calculated (found) % C	H	N
L^1H_2	*amphi*-$C_{10}H_{12}N_4O_3$	Reddish-brown	49	—	>300	50,8 (58.9)	5,1 (5,0)	23,7(23,7)
$[(L^1H)(H_2O)ClNi]$	$C_{10}H_{13}N_4O_4ClNi$	Green	36	2.96	>300	34,6 (34,5)	3,8 (3,7)	16,1 (16,0)
$[(L^1H)(H_2O)ClCo]$	$C_{10}H_{13}N_4O_4ClCo$	Brown	58	4.21	(286)	34,6 (34.4)	3,8 (3.5)	16,1 (16.1)
$[(L^1H)(H_2O)ClCu]$	$C_{10}H_{13}N_4O_4ClCu$	Dark brown	79	1.79	(248)	34,1 (34,1)	3,7 (3,7)	15,9 (15,8)
L^2H_2	*anti*-$C_{10}H_{12}N_4O_3$	Light brown	43	—	>300	50,8 (50.9)	5,1 (5,0)	23,7 (23.6)
$[(L^2H)_2Ni]$	$C_{20}H_{22}N_8O_6Ni$	Dark reddish	45	Dia.	>300	45,4 (45,3)	4,2 (4.2)	21,2 (21,3)
$[(L^2H)_2Co]$	$C_{20}H_{22}N_8O_6Co$	Light brown	70	1.92	(206)	45,4 (45,4)	4,2 (4.1)	21,2 (21,1)
$[(L^2H)_2Cu]$	$C_{20}H_{22}N_8O_6Cu$	black	49	1.67	(192)	45,0 (44.9)	4,2 (4.1)	20,5 (20.5)
L^3H_2	*amphi*-$C_5H_6N_4SO_2$	Dark yellow	45	—	132	32.3 (32.0)	3.3 (3.1)	30.1 (30.2)
$[(L^3H)_2Ni]$	$C_{10}H_{10}N_8O_4S_2Ni$	Greenish-brown	62	2.93	(144)	28.0 (28.2)	2.4 (2.3)	26.1 (25.9)
$[(L^3H)_2Co]$	$C_{10}H_{10}N_8O_4S_2Co$	Dark brown	74	4.24	(175)	28.0 (27.6)	2.4 (2.2)	26.1 (26.0)
$[(L^3H)_2Cu]$	$C_{10}H_{10}N_8O_4S_2Cu$	Green	63	1.72	(170)	27.7 (27.7)	2.3 (2.3)	25.8 (25.8)
L^4H_2	*anti*-$C_5H_6N_4SO_2$	Light yellow	41	—	(154)	32.3 (32.1)	3.3 (3.2)	30.1 (29.9)
$[(L^4H)_2Ni]$	$C_{10}H_{10}N_8O_4S_2Ni$	Brick red	78	Dia.	(230)	28.0(27.8)	2.4 (2.3)	26.1 (26.0)
$[(L^4H)_2Co]$	$C_{10}H_{10}N_8O_4S_2Co$	Light brown	71	1.91	(245)	28.0 (28.1)	2.4 (2.2)	26.1 (26.1)
$[(L^4H)_2Cu]$	$C_{10}H_{10}N_8O_4S_2Cu$	Black	80	1.69	(249)	27.7 (27.5)	2.3 (2.2)	25.8 (25.7)

ligands were identified by employing elemental analyses, ^{13}C and ^1H NMR, IR and mass spectroscopy (text-Tables 1–4, respectively). The metal complexes were identified by elemental analyses and IR spectroscopy (Tables 2 and 3, respectively). The general formulas of the ligands are shown in Figure 1.

^1H NMR Spectra of the Ligands

In the ^1H NMR spectra of the ligands, two peaks are present for the -OH protons of the oxime groups. These two deuterium-exchangeable singlets correspond to two non-equivalent -OH protons which also indicate the configuration of the -OH groups relative to each other[9,11,21] (Figure 1). When the chemical shifts of the two -OH groups in the four different ligands are compared, the ones at lower field quite closely resemble each other (11.16, 11.37, 11.01, 11.30 p.p.m.) whereas a considerable difference is observed for the shift at the higher field (10.17, 10.72, 10.10, 10.70 p.p.m.). Consequently, the first one is assigned to the -OH proton on the aromatic side and the latter to the -OH proton of the amidoxime group, since the effect of various substituents is expected to be greater on the amidoxime group. The D_2O exchangeable -NH-protons of the aminoglyoximes measured at 7.69, 7.77, 8.19, 8.27 p.p.m., N=CH protons at 7.80–8.25 p.p.m. as singlets. Addition of D_2O causes the disappearance of the -NH-and -OH peak. These values are in good agreement with the similar *vic*-dioximes.[9–27]

In the ^{13}C NMR spectrum of LH_2 carbon resonances of the dioxime groups were observed around 139.58–150.94 ppm. Observation of *vic*-dioxime and -OH protons in the ^1H NMR and of dioxime carbons in the ^{13}C NMR spectra at two different frequencies in each case, indicates that the *vic*-dioxime has a structure.[50–53] All the signals in the 149.67–113.14 ppm range are assigned to the carbon atoms of the aromatic rings.

IR Spectra of Ligands and Complexes

The ligands, -NH (3392–3442 cm^{-1}), -OH (3200–3240 cm^{-1}), C=N-(1645–1605 cm^{-1}) and NO (955–

TABLE 3
Characteristic IR bands of the ligands and their complexes[a] (KBr pellets)

Compounds	$\nu_{(N\text{-}H)}$	$\nu_{(O\text{-}H)}$	$\nu_{(C\text{-}H)}$ (aliph)	$\nu_{(C\text{-}H)}$ (arom)	$\nu_{(O\ldots H\ldots O)}$	$\nu_{(C{=}N)}$	$\nu_{(N\text{-}O)}$
amphi-L^1H_2	3396 w	3240 m	2920 s	3030 s	—	1640 m	970 w
$[(L^1H)(H_2O)ClNi]$	3362 w	3202 m	2926 s	3035 s	—	1607 w	972 w
$[(L^1H)(H_2O)ClCo]$	3373 w	3221 w	2923 s	3032 s	—	1601 w	976 w
$[(L^1H)(H_2O)ClCu]$	3343 w	3220 w	2927 s	3024 s	—	1605 w	973 w
anti-L^2H_2	3400 w	3200 w	2921 s	3028 s	—	1645 m	965 w
$[(L^2H)_2Ni]$	3398 w	—	2924 s	3036 s	1810 w	1611 w	962 w
$[(L^2H)_2Co]$	3396 w	—	2926 s	3035 s	1810 w	1602 w	960 w
$[(L^2H)_2Cu]$	3395 w	—	2923 s	3022 s	1800 w	1612 w	960 w
amphi-L^3H_2	3440 m	3210 w	2922 s	3028 s	—	1605 m	955 w
$[(L^3H)_2Ni]$	3407 w	3210 w	2929 s	3023 s	1780 w	1618 m	968 w
$[(L^3H)_2Co]$	3405 w	3240 w	2926 s	3030 s	1785 w	1614 w	966 w
$[(L^3H)_2Cu]$	3446 w	3200 w	2926 s	3031 s	1800 w	1598 w	961 w
anti-L^4H_2	3442 m	3208 w	2921 s	3035 s	—	1605 m	960 w
$[(L^4H)_2Ni]$	3420 w	—	2923 s	3035 s	1750 w	1600 w	955 w
$[(L^4H)_2Co]$	3446 w	—	2921 s	3024 s	1800 w	1595 w	953 w
$[(L^4H)_2Cu]$	3419 w	—	2925 s	3026 s	1790 w	1595 m	958 m

[a] cm^{-1}.

TABLE 4
Mass spectral data of the ligands, (70 eV): m/e (rel. intensity)

L^1H_2	235,2 (28,8) (M^+-1); 219,2 (42,3); 217,2 (100); 173,2 (6.3); 162,2 (6,3); 161,2 (55,0); 159,1 (8.8); 139,1 (14,4); 93,1 (11,3); 79,1 (34,4).
L^2H_2	235,2 (23,7) (M^+-1); 219,2 43,8; 217,2 (100); 173,2 (8,2); 162,2 (5,6); 159,1 (8.8); 93,1 (5,9); 78,9 (70,6).
L^3H_2	186.2 (36.4) (M^+); 169.3 (25.2); 155.2 (100); 124.2 (40.1); 111.3 (28.1); 84.2 (72.9); 72.2 (16.0).
L^4H_2	186.2 (19.6) (M^+); 169.2 (27.8); 155.2 (100); 124.3 (54.2); 111.2 (30.5); 84.2 (70.0); 72.2 (15.7).

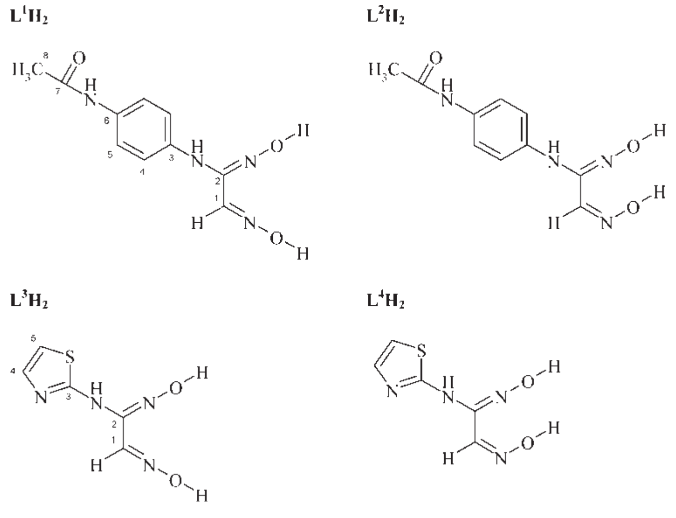

FIG. 1. General formulas of ligands.

970 cm^{-1}) exhibit stretching frequencies as for substituted aminoglyoximes[9–22, 49] (Table 3).

The complexes of **L^2H_2** and **L^4H_2** support the structures shown in Figure 2 by the weak bending vibration of the O-H. . .O bridges et.*ca*. 1750–1810 cm^{-1} and shift of the C=N vibration to lower frequencies (1595–1618 cm^{-1}) due to *N,N*-metal coordination.[9,11,21,54] Meanwhile, the band observed at 955–976 cm^{-1} in the free *anti*-ligands, assigned to the υ(N-O) is shifted to lower frequency after complexation (Table 3).

The metal complexes of **L^2H_2**, **L^3H_2**, and **L^4H_2** were prepared under similar conditions from the ligands and the corresponding metal salts by addition of a strong base. In all of these complexes, the metal/ligand ratio was found to be 1:2 as found for most of the *vic*-dioximes.[9,11,21,54,55]

L^1H_2 reacts with metal salts to give 1:1 metal-ligand ratio complexes with two of the four coordination sites on the metal occupied by the N atom of one of the oxime group and the O atom of the other, respectively. For **L^1H_2**, a

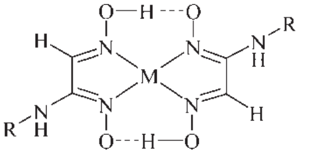

FIG. 2. Square-planar metal complexes of *anti*-L^{2}H$_2$ and *anti*-L^{4}H$_2$, R^1: Me-CONH-C$_6$H$_4$-, R^2: C$_3$H$_2$NS-.

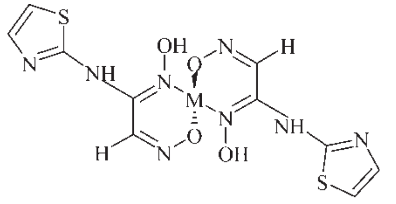

FIG. 4. Tetrahedral *N,O*-coordinated complexes of *amphi*-L^{3}H$_2$.

chloride ion and a water molecule are also coordinated to the metal ion in [(L^{1}H)Cl(H$_2$O)M] (Figure 3). The elemental analyses results and IR spectra are consistent with such a structure.[9,11]

The distinctive colors of the *amphi*-and *anti*-**LH$_2$** complexes with nickel (II) (greenish-brown and brick red, respectively) make the identification of these complexes straightforward[1]. As with most *vic*-dioximes,[9,11,21,54,55] the nickel(II) complex of *anti*-**L^{2}H$_2$** is planar *N,N′*-coordination is verified by the diamagnetism of this compound, since it is known that a d^8 metal complex does not have unpaired electrons in a square planar field.

In the IR spectrum of the paramagnetic *amphi*-**L^{3}H$_2$** metal complexes, the -OH strecthing band appears at *ca.* 3202–3240 cm^{-1} indicating that free -OH groups are present in the molecule. Consequently, a *N,O*-chelated tetrahedral structure can be proposed for these complexes (Figure 4).[11]

Mass Spectra of Ligands

The mass spectra of the ligands also support their structures (Table 4). The molecular ion peak is 235.2 indicates the formula weight of a **L^{1}H$_2$** and **L^{2}H$_2$** ligands. Also, the molecular ion peak of **L^{3}H$_2$** and **L^{4}H$_2$** is 186.2. Four ligands give similar mass spectra. For example, the first fragment ion is -OH.[9,11]

Magnetic Susceptibility of Complexes

Magnetic susceptibility measurement provide sufficient data to characterize the structure of the complexes (Table 1). The mononuclear complexes of Ni(II) are diamagnetic as expected for d^8 metal ion in a square-planer field,[2] and paramagnetic as expected for d^8 metal ion in a tetrahedral field whereas the Co(II) and Cu(II) complexes are paramagnetic.[52,53] For these complexes additional pysical and analytical data are given Table 3. According to these results, the Cu(II) and Co(II) complexes of **L^{2}H$_2$** and **L^{4}H$_2$** ligands have a square-planer geometry[21,52,53] and the metal complexes of **L^{1}H$_2$** and **L^{3}H$_2$** ligands have a tetrahedral geometry.[9,11]

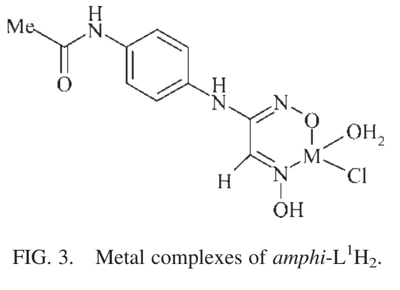

FIG. 3. Metal complexes of *amphi*-L^{1}H$_2$.

Solvent Extraction

Up to now, studies related with solvent extraction with complexes of oxime compounds are very limited. Therefore, this work focused on elaboration of strategic requirements for the two-phase extraction measurements. For this purpose, solvent extraction experiments were performed to estimate the effectiveness of ligands in transfering alkali metals (Li$^+$, Na$^+$, K$^+$, Cs$^+$) and transition metals (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}) and Pb^{2+} from the aqueous into organic phase. The results are summarized in Table 5. These data were obtained using dichloromethane solutions of ligands to extract metal picrates from aqueous solution according to Pedersen's procedure.[46] The equilibrium concentration of picrate in aqueous phase was then determined spectrophotometrically.[43]

As it can be interpreted from Table 5, the alkali metal cations were not significantly extracted by ligands. However, all the compounds extracted transition metals, in particular Cu^{2+} and Hg^{2+}. The effectiveness in transferring transition metals rather than the other metal cations by the synthesized compounds indicates that a cation-π electron interaction is operative since the metal is bounded by the opposite N, N or N, O sites of these compounds. In this study, the extraction data of ligands show a pronounced increased for the extraction ability of Cu^{2+} and Hg^{2+}. The reason of high affinity of transition metals due to the soft donar nitrogen groups exist in ligands causes the icrease in the extraction ability of these ligands.[36–43]

Despite the great affinity of nickel to aminoglyoximes, surprisingly, after a contact time of 1 h. The extraction percentage of nickel is very low, but that of copper is very high. Dioxime compounds usually form stable N, N- or N,O- chelated complexes containing a conjugated -N=C-C=N- or -N=C-C=O- system, respectively.[43]

The high extraction percentage of Hg^{2+} is another surprising phenomenon in this work. The ionic radius of Hg^{2+}, which is 1.1 A°, cannot explain alone this phenomenon because Pb^{2+}, which has a similar ionic radius to Hg^{2+}, could not be extracted as much as Hg^{2+} by all ligands. The type of the donar atoms, polarizability effect, steric hindrance and cavity size are probably important factors here.[43]

Figure 5a and b show the extraction of Cu^{2+} and Hg^{2+} into dichloromethane at different concentrations of ligands, recpectively. The observed metal-ligand ratios of Hg^{2+} and Cu^{2+} with ligands are 1:2. For the systems the following logarithmic extraction constants corresponding to Eq. (5) were determined (Figure 5).

$\log K_{ex} = 12.74$ (for Hg^{2+} with $\mathbf{L^1H_2}$) $\log K_{ex} = 9.08$ (for Cu^{2+} with $\mathbf{L^1H_2}$)
$\log K_{ex} = 12.77$ (for Hg^{2+} with $\mathbf{L^1H_2}$) $\log K_{ex} = 12.33$ (for Cu^{2+} with $\mathbf{L^1H_2}$)
$\log K_{ex} = 12.36$ (for Hg^{2+} with $\mathbf{L^1H_2}$) $\log K_{ex} = 10.88$ (for Cu^{2+} with $\mathbf{L^1H_2}$)
$\log K_{ex} = 12.42$ (for Hg^{2+} with $\mathbf{L^1H_2}$) $\log K_{ex} = 10.49$ (for Cu^{2+} with $\mathbf{L^1H_2}$)

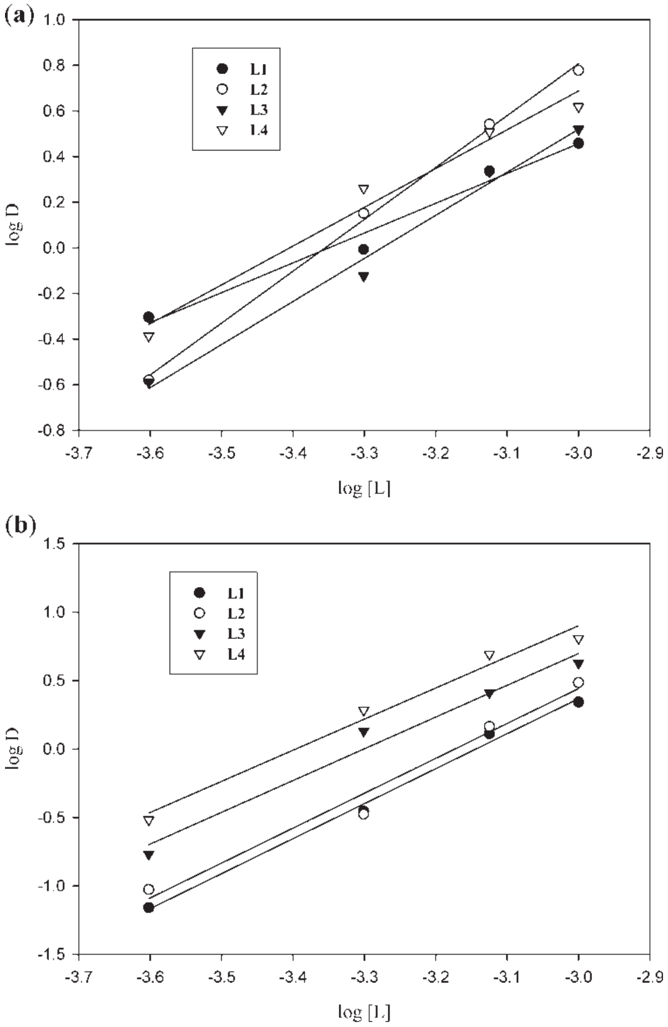

FIG. 5. log D versus log [L] for extraction of Cu picrate (5a) with ligands and Hg picrate (5b) with ligands from an aqueous phase into dichloromethane at 25°C.

TABLE 5
Extraction of metal picrates with ligands[a]

Ligand	Picrate salt extracted (%)										
	Li^+	Na^+	K^+	Cs^+	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Hg^{2+}	Cd^{2+}	Pb^{2+}
L1	<1.0	1.53	3,52	2,54	33.84	31.16	74.20	3.17	68.83	4.86	7.96
L2	<1.0	1.44	4.02	2.47	30.43	24.24	85.72	4.69	75.33	4.01	9.46
L3	<1.0	1.62	4.17	2.86	38.12	30.68	76.84	5.15	80.95	5.95	10.74
L4	<1.0	1.65	3.84	2.97	33.58	32.73	80,59	4.72	86.52	5.13	11.69

[a] $H_2O/CH_2Cl_2 = 10/10(v/v)$:[picric acid] $= 2 \times 10^{-5}$ M, [ligand] $= 1 \times 10^{-3}$ M, [metal hydroxide] $= 1 \times 10^{-2}$ M, 298 K, 1 h contact time. Averages and standard deviations calculated for data obtained from three independent extraction experiments.

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