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Synthesis of four new *vic*-dioximes and their nickel(II), cobalt(II), copper(II) and cadmium(II) complexes

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Abstract

Four unsymmetrical *vic*-dioximes: [L^1H_2] *N*-(4-butylphenyl)amino-*amphi*-glyoxime, [L^2H_2] *N*-(4-butylphenyl)amino-*anti*-glyoxime, [L^3H_2] *N*-(4-phenylazophenyl)amino-*amphi*-glyoxime and [L^4H_2] *N*-(4-phenylazophenyl)amino-*anti*-glyoxime have been prepared from *amphi*-chloroglyoxime, *anti*-chloroglyoxime, 4-butylaniline and 4-(phenylazo)aniline respectively. The complexes of these *vic*-dioximes with Ni^{II}, Co^{II}, Cu^{II} and Cd^{II} ions have been investigated. All are insoluble in common solvents. Their i.r. spectra and elemental analyses are given, together with mass and ^{1}H-n.m.r. spectra of the ligands.

Introduction

Vic-dioximes have received considerable attention as model compounds which mimic biofunctions such as the reduction of B_{12} [1, 2]. Oxime metal chelates are biologically active [3] and are reported to possess semiconducting properties [4, 5]. Derivatives of monoaminoglyoxime, heterocyclic and macrocyclic *vic*-dioximes, tetraoximes and their transition metal complexes have been described [2, 6–21].

Vic-dioximes have a high tendency to form isomers. When the molecule is formally symmetrical, three forms are possible: *syn*-, *anti*- and *amphi*-. The *amphi*-isomers are known to react with nickel(II), but their complexes have not been well characterized until recently, metal–ligand ratios of 1:1 as well as 1:2 have been reported [9, 18–20]. The dioxime *anti*-isomers are responsible for the formation of brightly colored chelate derivatives with nickel and the other transition metal ions [14, 17, 21]. Especially, the *anti*-form of these gives blood-red complexes with nickel ions. The *anti-bis*(dioximato)nickel(II) complex seems to be more stable than the *amphi-bis*(dioximato)nickel(II) complexes. The conversion can be accomplished by boiling with dilute ethanoic acid, followed by treatment with hydrogen chloride [21], however this change has not been investigated thoroughly. The substitution pattern of the *vic*-dioxime moiety affects the structure and the stability of the complexes, *e.g.*, cobalt(II) complexes of dialkyl- or diaryl-glyoximes and dithioglyoximes can be obtained by reducing octahedral cobalt(III) compounds [6, 16, 22], but the complexes decompose in the case of diaminoglyoxime derivatives [17].

In this paper, we report the synthesis and complex formation of four new substituted aminoglyoximes of unsymmetrically substituted *vic*-dioximes. The asymmetry of the ligands is also expected to enhance the solubility of planar complexes derived from them.

Experimental

Amphi- and *anti*-chloroglyoxime were prepared according to published methods [23, 24]. All reagents were purchased from Merck (Germany) or Fluka (Switzerland), and were used without further purification. M.p.s were measured on an Electrothermal IA 9100 digital melting point apparatus and are uncorrected. Elemental analyses (C, H, and N) were determined using a Carlo-Erba 1106 model analyzer. ^{1}H-n.m.r. and i.r. spectra were recorded on a Bruker 200 MHz spectrometer and Jasco FT/IR-300e instrument, respectively. The pH values were measured on a WTW pH.537 pH meter. Mass spectra were obtained in the research laboratories of TUBITAK (Center of Sciences and Technology Research of Turkey).

N-(4-butylphenyl)amino-amphi-*glyoxime,*
amphi-$C_{12}H_{17}N_3O_2[L^1H_2]$

To a stirred solution of *amphi*-chloroglyoxime (1.225 g, 0.010 mol) dissolved in Et_2O (15 cm^3) kept at −10 °C,

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was added dropwise a solution of freshly distilled 4-butylaniline (1.49 g, 0.010 mol) in absolute Et_2O (15 cm^3) during 15 min. The pH of the solution increased from 4.0 to 5.0–5.5 upon addition of a solution of 0.1 M KOH in EtOH. The reaction mixture was stirred continuously for 15 min at −10 °C. The resulting dark-yellow precipitate was filtered, washed with petroleum ether and dried in vacuum. Yield: 0.92 g (39%). The product is soluble in EtOH, $CHCl_3$ and DMSO, and slightly soluble in DMF. It is insoluble in H_2O, Et_2O and CCl_4.

N-(4-butylphenyl)amino-anti-*glyoxime,* anti-$C_{12}H_{17}N_3O_2$ $[L^2H_2]$

To a stirred solution of *anti*-chloroglyoxime (1.225 g, 0.010 mol) dissolved in 1:1 Et_2O–CH_2Cl_2 (30 cm^3) kept at −10 °C was added dropwise a solution of freshly distilled 4-butylaniline (1.49 g, 0.010 mol) in CH_2Cl_2 (30 cm^3) during 15 min. The pH of the resulting solution was increased from 3.0–3.5 to 4.5–5.0 by adding an EtOH solution of Et_3N (0.1 M). The reaction mixture was stirred continuously for 30 min at −10 °C. The resulting light-yellow precipitate was filtered, washed with CH_2Cl_2 and dried *in vacuum*. Yield: 1.22 g, (51%). The product is soluble in H_2O, EtOH, $CHCl_3$, DMSO and DMF, but insoluble in Et_2O and dioxan.

Amphi- *and* anti-*isomers of N-(4-phenylazophenyl)-amino glyoxime (*amphi-$C_{14}H_{13}N_5O_2$ $[L^3H_2]$ *and* anti-$C_{14}H_{13}N_5O_2$ $[L^4H_2]$*)*

To *amphi*-chloroglyoxime or *anti*-chloroglyoxime (1.225 g, 10 mmol), dissolved in Et_2O (30 cm^3), a solution of 4-(phenylazo)aniline (2.83 g, 10 mmol) in Et_2O (30 cm^3) was added dropwise at room temperature with constant stirring. The reaction mixture was stirred continuously for 1 h at room temperature. The pH of the solution, which decreased to *ca.* 3.0, was adjusted to 5.0–5.5 with 1% NaOH solution. The ligand started to precipitate and the mixture was left in the waterbath at 50–55 °C for 15–20 min until precipitation was complete. The precipitated ligand was filtered off, washed with Et_2O and dried in vacuo. *Amphi*-L^1H_2; yield: 1.27 g (45%), m.p. 183 °C. This compound is soluble in EtOH, DMSO, DMF and dioxan, slightly soluble in H_2O, $CHCl_3$ and CCl_4. *Anti*-L^2H_2; yield: 0.85 g (30%), m.p. 128 °C. This compound is soluble in DMSO, DMF and dioxan, and slightly soluble in H_2O and $CHCl_3$. It is insoluble in CCl_4.

Table 1 gives the ^{1}H-n.m.r. data for the above four ligands. The colors, yields, melting points and elemental analyses, i.r., and mass spectra data of the ligands are given Tables 2, 3 and 4, respectively.

Ni^{II}, Cu^{II} and Cd^{II} complexes of amphi-$C_{12}H_{17}N_3O_2$ $[L^1H_2]$

A solution of 0.005 mol metal salt [$NiCl_2 \cdot 6H_2O$ (1.189 g), $CuCl_2 \cdot 2H_2O$ (0.852 g), $CdCl_2 \cdot H_2O$ (1.007 g)] dissolved in H_2O (30 cm^3), was added to a stirred solution of the ligand (1.177 g, 0.005 mol) dissolved in EtOH (30 cm^3). On addition of the metal salt, the pH dropped to 3.5–4.0 from 5.0–5.5 at the onset of the reaction. After addition of an EtOH solution of Et_3N (0.1 M) to raise the pH to 4.5 (nickel complex), 5.0 (copper complex) and 9.0 (cadmium complex), the mixture was stirred on a waterbath at 50–55 °C for 15 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-$C_{12}H_{17}N_3O_2$ $[L^2H_2]$

A solution of the metal salt (0.005 mol) [$NiCl_2 \cdot 6H_2O$ (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 (2.35 g, 0.01 mol) dissolved in EtOH (30 cm^3). On addition of the metal salt, the pH dropped to 3.0–3.5 from 4.0–4.5 at the beginning of the reaction. After addition of a 1% NaOH solution in H_2O to raise the pH to 5.5–6.0 (nickel and cobalt complexes) and 7.0 (copper complex), the mixture was stirred on a waterbath at 50–55 °C for 15 min. The precipitated complexes were filtered off, washed with H_2O and dried at 100 °C.

Ni^{II}, Co^{II} and Cu^{II} complexes of amphi-$C_{14}H_{13}N_5O_2$ $[L^3H_2]$ *and* anti-$C_{14}H_{13}N_5O_2$ $[L^4H_2]$

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 [L^1H_2, L^2H_2 (2.83 g, 10 mmol)] dissolved in 1:1 EtOH–H_2O (30 cm^3). Upon adding metal salt, the pH of the mixtures dropped to 3.5–4.0 (L^1H_2 complexes) and 2.0–2.5 (L^2H_2 complexes). After addition of a 1% NaOH solution in H_2O to raise the pH to 5.5–6.0 (L^1H_2) and 5.5–6.0 (L^2H_2), the mixture was stirred on a waterbath at 50–55 °C for 30 min. The precipitated complexes were filtered off, washed with H_2O and dried at 100 °C.

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

Results and discussion

Four new aminoglyoxime derivatives were prepared by reacting aromatic amines with *amphi*-chloroglyoxime [23, 24] or *anti*-chloroglyoxime, [23, 24] respectively. The structure of these ligands were identified by employing elemental analyses, ^{1}H-n.m.r., i.r. and mass spectroscopy (Tables 1–4). The metal complexes were identified by elemental analyses and i.r. spectroscopy (Tables 2 and 3, respectively). The formation and general formulae of the ligands are shown in Figure 1.

Table 1. ^{1}H-n.m.r. spectra of the ligands in DMSO-d_6 δ (p.p.m.)

Compound	O—H[a]	O—H[a]	H_{Arom}	HN—Arom[a]	=CH	$-CH_3$	$-CH_2-$	$-CH_2-$	$-CH_2-Ar$
L^1H_2 *amphi*-$C_{12}H_{17}N_3O_2$	11.57	10.30	6.99–7.47	8.30	7.94	0.89	1.29	1.52	3.05
	s	s	dd	s	s	t	m	m	t
	(1H)	(1H)	(4H)	(1H)	(1H)	(3H)	(2H)	(2H)	(2H)
			J(8.21)			*J*(7.48)			*J*(7.25)
L^2H_2 *anti*-$C_{12}H_{17}N_3O_2$	10.63	10.37	6.73–7.01	8.50	7.80	0.88	1.19	1.38	3.06
	s	s	dd	s	s	t	m	m	t
	(1H)	(1H)	(4H)	(1H)	(1H)	(3H)	(2H)	(2H)	(2H)
			J(8.35)			*J*(7.28)			*J*(7.25)
L^3H_2 *amphi*-$C_{14}H_{13}N_5O_2$	11.25	10.75	7.07–7.54	7.97	7.80	–	–	–	–
	s	s	m	s	s	–	–	–	–
	(1H)	(1H)	(9H)	(1H)	(1H)	–	–	–	–
L^4H_2 *anti*-$C_{14}H_{13}N_5O_2$	11.52	11.27	6.91–7.73	8.52	7.80	–	–	–	–
	s	s	m	s	s	–	–	–	–
	(1H)	(1H)	(9H)	(1H)	(1H)	–	–	–	–

s: Singlet; t: triplet; m: multiplet; dd: doublet of doublet; all *J* values are averages.
[a] Disappears on D_2O exchange.

Table 2. Colors, formula weights, m.p.s, yields and elemental analytical results for the ligands and their complexes

Compound	Color	Yield (%)	M.p. (°C) (dec)	Calcd. (Found) (%)		
				C	H	N
L^1H_2 *amphi*-$C_{12}H_{17}N_3O_2$	dark yellow	39	122	61.3 (61.2)	7.3 (7.2)	17.9 (17.8)
$[(L^1H)(H_2O)ClNi]$ $C_{12}H_{18}N_3O_3ClNi$	yellow green	47	(134)	41.6 (41.6)	5.2 (5.2)	12.1 (12.1)
$[(L^1H)(H_2O)ClCu]$ $C_{12}H_{18}N_3O_3ClCu$	dark brown black	55	(115)	41.0 (41.1)	5.2 (5.1)	12.0 (11.9)
$[(L^1H)(H_2O)ClCd]$ $C_{12}H_{18}N_3O_3ClCd$	light yellow	53	(84)	36.0 (36.0)	4.5 (4.5)	10.5 (10.5)
L^2H_2 *anti*-$C_{12}H_{17}N_3O_2$	light yellow	51	(182)	61.3 (61.3)	7.3 (7.3)	17.9 (17.8)
$[(L^2H)_2Ni]$ $C_{24}H_{32}N_6O_4Ni$	brick red	48	(232)	54.7 (54.7)	6.1 (6.1)	15.9 (15.9)
$[(L^2H)_2Co]$ $C_{24}H_{32}N_6O_4Co$	light brown	61	(145)	54.7 (54.7)	6.1 (6.1)	15.9 (15.9)
$[(L^2H)_2Cu]$ $C_{24}H_{32}N_6O_4Cu$	black	100	(149)	54.2 (54.2)	6.1 (6.0)	15.8 (15.8)
L^3H_2 *amphi*-$C_{14}H_{13}N_5O_2$	red black	45	183	59.3 (59.3)	4.6 (4.6)	24.7 (24.7)
$[(L^3H)_2Ni]$ $C_{28}H_{24}N_{10}O_4Ni$	dark brown	73	(140)	54.0 (54.0)	3.9 (4.0)	22.5 (22.6)
$[(L^3H)_2Co]$ $C_{28}H_{24}N_{10}O_4Co$	dark red	68	(154)	53.9 (53.7)	3.9 (3.9)	22.5 (22.4)
$[(L^3H)_2Cu]$ $C_{28}H_{24}N_{10}O_4Cu$	dark brown	65	(166)	53.6 (53.5)	3.9 (4.1)	22.3 (22.2)
L^4H_2 *anti*-$C_{14}H_{13}N_5O_2$	light brown	30	(128)	59.3 (59.3)	4.6 (4.7)	24.7 (24.7)
$[(L^4H)_2Ni]$ $C_{28}H_{24}N_{10}O_4Ni$	brick red	50	(148)	54.0 (53.0)	3.9 (3.9)	22.5 (22.6)
$[(L^4H)_2Co]$ $C_{28}H_{24}N_{10}O_4Co$	brown	54	(132)	53.9 (53.7)	3.9 (3.9)	22.5 (22.3)
$[(L^4H)_2Cu]$ $C_{28}H_{24}N_{10}O_4Cu$	light brown	63	(147)	53.6 (53.6)	3.9 (3.9)	22.3 (22.2)

Table 3. Characteristic i.r. bands of the ligands and their complexes[a] (KBr pellets)

Compound	$\nu_{(N-H)}$	$\nu_{(O-H)}$	$\nu_{(C-H)}$ (aliph)	$\nu_{(C-H)}$ (arom)	$\nu_{(O\cdots H\cdots O)}$	$\nu_{(C=N)}$	$\nu_{(N-O)}$	$\nu_{(C=C)}$ (arom)	$\nu_{(C-C)}$
Amphi-$[L^1H_2]$	3440w	3200w	2920s	3035w	–	1605m	955w	1495s	1450s
$[(L^1H)(H_2O)ClNi]$	3400w	3210w	2920s	3035w	–	1595m	970w	1495m, sh	1450m
$[(L^1H)(H_2O)ClCu]$	3400w	3240w	2920s	3035w	–	1595w	965w	1490m, sh	1450m
$[(L^1H)(H_2O)ClCd]$	3440w	3200w	2920s	3035w	–	1595w	950w	1480m, sh	1450m
Anti-$[L^2H_2]$	3440w	3200w	2920s	3035w	–	1605m	960w	1495s	1450s
$[(L^2H)_2Ni]$	3420w	–	2920s	3035w	1750w	1600w	965w	1500w	1450w
$[(L^2H)_2Co]$	3440w	–	2920s	3035w	1750w	1595w	970w	1495w	1450w
$[(L^2H)_2Cu]$	3410w	–	2920s	3035w	1750w	1595m	960m	1495w, sh	1450m
Amphi-$[L^3H_2]$	3405w	3190w	2920s	3035m	–	1600w	960w	1490m	1450m
$[(L^3H)_2Ni]$	3400w	3200w	2920s	3035m	–	1595w	970w	1490m	1450m
$[(L^3H)_2Co]$	3400w	3195w	2920s	3035m	–	1580w	960w	1490m	1450m
$[(L^3H)_2Cu]$	3405w	3200w	2920s	3035s	–	1580w	975w	1485m, sh	1440m
Anti-$[L^4H_2]$	3380w	3240w	2920s	3035s	–	1600m	975w	1500m	1450m
$[(L^4H)_2Ni]$	3400w	–	2920s	3035s	1750w	1600m	970w	1495m	1450m
$[(L^4H)_2Co]$	3400w	–	2920s	3035m	1750w	1595w	975w	1495w	1450m
$[(L^4H)_2Cu]$	3400w	–	2920s	3035m	1750w	1610w	960w	1490w, sh	1450s

[a] cm^{-1}.

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

L^1H_2	235.3 (30.4) (M^+); 220.3 (21.3); 176.3 (6.9); 131.2 (40.0); 117.2 (6.6); 105.2 (6.5); 91.2 (12.2); 77.2 (21.3).
L^2H_2	235.3 (36.3) (M^+); 220.3 (10.0); 203.3 (8.8); 176.3 (5.0); 162.3 (10.7); 145.2 (13.1); 131.2 (100.0); 117.3 (9.4); 105.3 (5.9); 91.2 (33.1); 77.2 (80.0).
L^3H_2	283.3 (18.3) (M^+); 265.3 (15.5); 188.2 (14.7); 160.2 (30.9); 145.3 (17.8); 133.3 (19.6); 117.3 (79.0); 105.3 (74.1); 90.2 (100); 76.2 (15.9).
L^4H_2	283.3 (19.6) (M^+); 265.3 (17.2); 188.2 (14.7); 160.2 (31.3); 145.3 (31.3); 133.3 (19.0); 117.3 (69.9); 105.3 (77.9); 90.2 (100); 76.2 (14.7).

^1H-n.m.r. spectra of the ligands

Two peaks are present in the ligands for the —OH protons of the oxime groups. These two deuterium-exchangeable singlets correspond to two non-equivalent —OH protons which also indicate the *anti*-configuration of the —OH groups relative to each other [6, 17, 25, 26] (Figure 1). When the chemical shifts of the two —OH groups in the two different ligands are compared, the ones at lower field quite closely resemble each other (10.63–11.57, 11.52–11.25 p.p.m.) whereas a considerable difference is observed for the shift at the higher field (11.37–10.30, 11.27–10.75 p.p.m.). Consequently, the first one is assigned to the —OH proton on the phenyl 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 8.30–8.50, 7.97–8.52 p.p.m., N=CH protons at 7.80–7.94 p.p.m. as singlets. Addition of D_2O causes the disappearance of the —NH— and —OH peak.

I.r. spectra of ligands and complexes

The ligands, —NH (3380–3440 cm^{-1}), —OH (3190–3240 cm^{-1}), C=N— (1600–1605 cm^{-1}) and NO (955–975 cm^{-1}) exhibit stretching frequencies as for substituted aminoglyoximes [6, 17, 22] (Table 3).

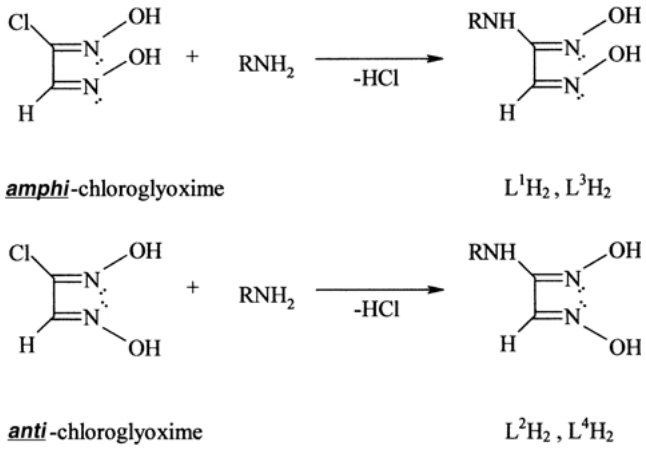

Fig. 1. Ligand formulae: R^1 = *n*-BuC_6H_4—, R^2 = $PhN{=}NC_6H_4$—.

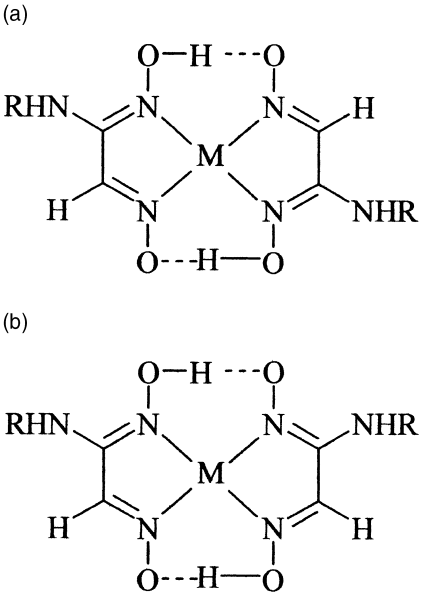

Fig. 2. Square-planar metal complexes of *anti*-L^2H_2 and *anti*-L^4H_2. (a) *trans*, (b) *cis*. R^1 = *n*-BuC_6H_4—, R^2 = $PhN{=}NC_6H_4$—.

The complexes of L^2H_2 and L^4H_2 support the structures shown in Figure 2(a) and (b) by the weak bending vibration of the O—H···O bridges at *ca.* 1750 cm^{-1} and shift of the C=N vibration to lower frequencies (1595–1610 cm^{-1}) due to *N,N*-metal coordination [6, 17, 22, 27, 28].

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 [2, 17, 20, 22, 29].

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 groups and the O atom of the other, respectively. A chloride ion and a water molecule are also coordinated to the metal ion in $[(C_{12}H_{16}N_3O_2)Cl(H_2O)M]$ (Figure 3). The elemental analyses results and i.r. spectra are consistent with such a structure [6, 19].

The distinctive colors of the *amphi-* and *anti*-LH_2 complexes with nickel(II) (yellow-green and brick-red, respectively) make the identification of these complexes straightforward [1]. As with most *vic*-dioximes [2, 17, 20,

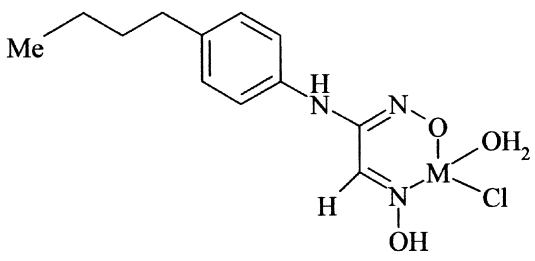

Fig. 3. Metal *amphi*-L^1H_2 complexes.

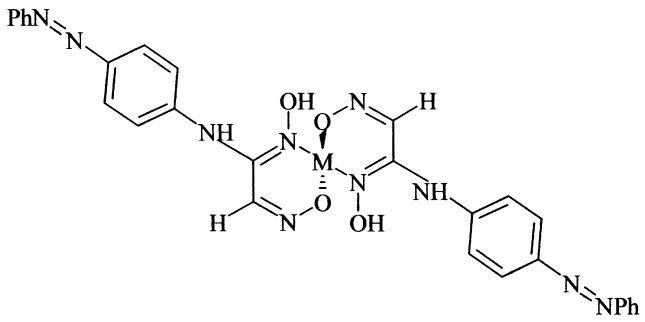

Fig. 4. Tetrahedral N,O-coordinated complexes of *amphi*-L^3H_2.

22, 29], the nickel(II) complex of *anti*-L^2H_2 as 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 i.r. spectrum of the paramagnetic *amphi*-L^3H_2 metal complexes, the —OH stretching band appears at *ca.* 3195–3200 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) [20, 30].

Mass spectra of the ligands

The mass spectra of the ligands also support their structures (Table 4). The molecular ion peak is 235.3 indicates the formula weight of a L^1H_2 and L^2H_2 ligands. Also, the molecular ion peak of L^3H_2 and L^4H_2 is 283.3. Four ligands give similar mass spectra. For example, the first fragment ion is —OH and last is phenyl.

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