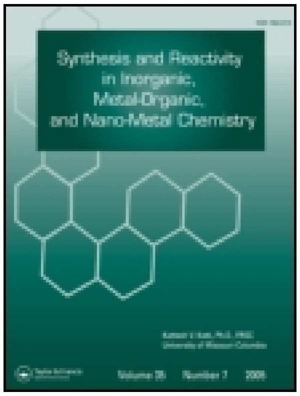

Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt19

2-Hydroxy-1-naphthaldehyde S-(Alkyl)-N^4-phenylthiosemicarbazone Complexes with Fe(III), Co(III), Ni(II), and Cu(II) Ions

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Version of record first published: 15 Feb 2007.

To cite this article: İrfan Kızılcıklı & Yılmaz Mesut (2003): 2-Hydroxy-1-naphthaldehyde S-(Alkyl)-N^4-phenylthiosemicarbazone Complexes with Fe(III), Co(III), Ni(II), and Cu(II) Ions, Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 33:6, 949-963

To link to this article: http://dx.doi.org/10.1081/SIM-120021929

SYNTHESIS AND REACTIVITY IN INORGANIC AND METAL-ORGANIC CHEMISTRY
Vol. 33, No. 6, pp. 949–963, 2003

2-Hydroxy-1-naphthaldehyde S-(Alkyl)-N^4-phenylthiosemicarbazone Complexes with Fe(III), Co(III), Ni(II), and Cu(II) Ions

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ABSTRACT

2-Hydroxy-1-naphthaldehyde S-(alkyl)-N^4-phenyl-thiosemicarbazones (alkyl = CH_3, C_2H_5, n-C_3H_7 and $C_6H_5CH_2$) were synthesized according to common procedures. The 1:1 and 1:2 metal to ligand complexes with Fe(III), Co(III), Ni(II), and Cu(II) salts were synthesized and characterized by analytical data, IR, ^{1}H NMR spectroscopy, magnetic susceptibility, molar conductivity and TGA analysis. It was determined that the tridentate behavior of the ligands is accomplished *via* the phenolic hydroxy group, the azomethine and thioamide nitrogens.

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DOI: 10.1081/SIM-120021929 0094-5714 (Print); 1532-2440 (Online)

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INTRODUCTION

2-Hydroxy-1-naphthaldehyde thiosemicarbazone and its S-alkyl derivatives belong to multidentate thiosemicarbazone compounds having wide biological activities, and thus, they are used widely in pharmacology.[1–9] It is found that they function as antimicrobial, antimalarial, antitumor and antileukemic agents in compounds with transition metals and other metal ions.[10–13] It should be noted that 2-hydroxy-1-naphthaldehyde thiosemicarbazone and its derivatives are used as selective reactants with glucose, cholesterol, uric acid and amino acid in fluorometric determinations, as well as of Fe(III) and Cu(II) in spectrophotometric methods.[14–19] The molecular geometries of S-alkyl derivatives, which are obtained by alkylation of the sulfur atom in thiosemicarbazones, and the bonding mode to the metal ion are changed on coordination, and, consequently, the terminal nitrogen (N^4) is involved in coordination instead of the sulfur atom, the donor property of which is very diminished.[20]

This study consists in the preparation and identification of 2-hydroxy-1-naphthaldehyde S-alkyl-N^4-phenylthiosemicarbazones (Figure 1) and their Fe(III), Co(III), Ni(II), and Cu(II) complexes. The coordination behavior of the ligands are discussed and structures for the metal complexes are suggested.

RESULTS AND DISCUSSION

Synthesis and Some Properties of the Compounds

The interaction of metal salts with the ligands in 1:1 and 1:2 molar ratio in ethanol yielded stable solid complexes corresponding to the general

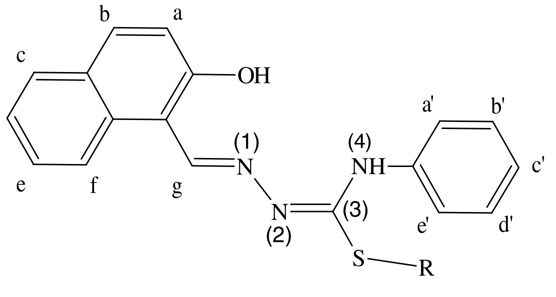

Figure 1. The ligands (R = CH_3: H_2L^1; C_2H_5: H_2L^2; n-C_3H_7: H_2L^3; $C_6H_5CH_2$: H_2L^4).

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formulae $[M(HL)_2]Cl_x \cdot nH_2O$ (M = Fe, Co, Ni; x = 0,1; n = 0–2), $[Fe(HL)Cl_2]$ and $[Cu(HL)H_2O]NO_3$. The metal/ligand stoichiometry of the Fe(III) complexes is 1:1 for $H_2L^1$and H_2L^2, and 1:2 for H_2L^3 and H_2L^4, and 1:1 for Cu(II) and 1:2 for Ni(II) complexes with H_2L^1, H_2L^2, H_2L^3 and H_2L^4 (see Table 1).

Typical complexation reactions are given below.

$$FeCl_3 \cdot 6H_2O + 2H_2L \rightarrow [Fe(HL)_2]Cl \cdot H_2O + 2HCl + 5H_2O$$

$$FeCl_3 \cdot 6H_2O + H_2L \rightarrow [Fe(HL)Cl_2] + HCl + 6H_2O$$

$$2CoCl_2 \cdot 6H_2O + 4H_2L + 1/2O_2 \rightarrow 2[Co(HL)_2]Cl + 2HCl + 13H_2O$$

$$NiCl_2 \cdot 6H_2O + 2H_2L \rightarrow [Ni(HL)_2] + 2HCl + 6H_2O$$

$$Cu(NO_3)_2 \cdot 3H_2O + H_2L \rightarrow [Cu(HL)H_2O]NO_3 + HNO_3 + 2H_2O$$

The ligands H_2L^1, H_2L^2, H_2L^3 and $H_2L^4$are insoluble in alcohols, but soluble in polar organic solvents such as DMF and MeCN. The metal complexes are easily soluble in DMSO and DMF, sparingly soluble in ethanol and methanol, whereas they are insoluble in chlorinated hydrocarbons.

The metal complexes generally have 70–100 °C higher melting points than the corresponding ligands. The Fe(III) complexes are black, Co(III) complexes are brown, Ni(II) complexes are deep yellow and Cu(II) complexes are green.

Molar Conductivity and Magnetic Susceptibility

Conductivity measurements were made in acetonitrile for the Cu(II) complexes, while methanol was used for the other complexes. (Λ: Ω^{-1} cm^2mol^{-1}, at 25 ± 1 °C).

$[Fe(HL^4)_2]Cl \cdot H_2O$ and $[Fe(HL^3)_2]Cl \cdot H_2O$ have conductivity values of 112 and 108, respectively, indicating their electrolytic nature. The conductivity of all other complexes are between 40 and 80 $\Omega^{-1}cm^2mol^{-1}$, indicating that these complexes are non-electrolytic.

The 1:1 Fe(III) complexes with H_2L^1 and H_2L^2 and 1:2 complexes with H_2L^3 and H_2L^4 are paramagnetic and high-spin, the μ_{eff} values are 5.58, 5.60, 5.80, 5.66 B.M., respectively. The Co(III) complexes are low-spin and diamagnetic, and the probable distorted octahedral structure is $[Co(HL)_2]Cl \cdot nH_2O$ (for $H_2L = H_2L^1$, H_2L^2 and H_2L^3, n = 0; for $H_2L = H_2L^4$, n = 2). It is determined that the stoichiometric ratio for Ni(II) complexes is

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Table 1. Analytical data and physical properties of the ligands and their complexes.

Compound	FW (yield %)	M.p. (°C)	Elemental analysis % found (calculated)				
			C	H	N	M	Cl
H_2L^1 ($C_{19}H_{17}N_3OS$)	335.4 (58)	149–150	67.48 (68.03)	4.96 (5.11)	11.94 (12.53)	–	–
$Fe(HL^1)Cl_2$ ($C_{19}H_{16}Cl_2FeN_3OS$)	461.2 (34)	252	49.28 (49.48)	3.36 (3.50)	8.90 (9.11)	11.86 (12.11)	15.04 (15.38)
$[Co(HL^1)_2]Cl$ ($C_{38}H_{32}ClCoN_6O_2S_2$)	763.2 (62)	267	59.78 (59.80)	4.08 (4.23)	10.76 (11.01)	7.34 (7.72)	4.19 (4.65)
$[Ni(HL^1)_2]\cdot H_2O$ ($C_{38}H_{34}N_6NiO_3S_2$)	745.5 (71)	260.5	60.16 (61.22)	4.17 (4.60)	10.38 (11.27)	7.20 (7.87)	–
$[Cu(HL^1)H_2O]NO_3$ ($C_{19}H_{18}CuN_4O_5S$)	478.0 (32)	283.5 dec.	47.75 (47.74)	3.93 (3.80)	11.19 (11.72)	13.10 (13.29)	–
H_2L^2 ($C_{20}H_{19}N_3OS$)	349.5 (46)	157–158	68.09 (68.74)	5.91 (5.48)	12.42 (12.02)	–	–
$Fe(HL^2)Cl_2$ ($C_{20}H_{18}Cl_2FeN_3OS$)	475.2 (30)	246	50.85 (50.55)	3.80 (3.82)	8.60 (8.84)	11.40 (11.75)	14.45 (14.92)
$[Co(HL^2)_2]Cl$ ($C_{40}H_{36}ClCoN_6O_2S_2$)	791.3 (64)	268.5	61.20 (60.72)	4.62 (4.59)	10.21 (10.62)	7.44 (7.45)	3.91 (4.48)
$[Ni(HL^2)_2]\cdot H_2O$ ($C_{40}H_{38}N_6NiO_3S_2$)	773.6 (58)	250.5	61.39 (62.10)	4.88 (4.95)	10.04 (10.86)	7.05 (7.59)	–

$[Cu(HL^2)H_2O]NO_3$ ($C_{20}H_{20}CuN_4O_5S$)	492.0 (32)	263.5 dec.	49.13 (48.82)	4.14 (4.10)	11.25 (11.39)	13.02 (12.92)	–
H_2L^3 ($C_{21}H_{21}N_3OS$)	363.5 (44)	144–145	68.92 (69.39)	5.71 (5.82)	10.74 (11.56)	–	–
$[Fe(HL^3)_2]Cl{\cdot}H_2O$ ($C_{42}H_{42}ClFeN_6O_3S_2$)	834.3 (51)	251	61.35 (60.47)	4.78 (5.07)	9.75 (10.07)	6.44 (6.69)	3.86 (4.25)
$[Co(HL^3)_2]Cl$ ($C_{42}H_{40}ClCoN_6O_2S_2$)	819.3 (67)	248.5	61.39 (61.57)	4.91 (4.92)	9.41 (10.26)	7.10 (7.19)	3.98 (4.33)
$[Ni(HL^3)_2]{\cdot}H_2O$ ($C_{42}H_{42}N_6NiO_3S_2$)	801.6 (73)	244	61.97 (62.93)	5.62 (5.28)	9.57 (10.48)	6.95 (7.32)	–
$[Cu(HL^3)H_2O]NO_3$ ($C_{21}H_{22}CuN_4O_5S$)	506.0 (42)	243.5 dec.	49.74 (49.84)	4.15 (4.38)	10.94 (11.07)	12.25 (12.56)	–
H_2L^4 ($C_{25}H_{21}N_3OS$)	411.5 (56)	112–113	73.31 (72.97)	5.19 (5.14)	9.69 (10.21)	–	–
$[Fe(HL^4)_2]Cl{\cdot}H_2O$ ($C_{50}H_{42}ClFeN_6O_3S_2$)	930.3 (65)	244	64.55 (64.55)	4.32 (4.55)	8.48 (9.03)	5.60 (6.00)	3.24 (3.81)
$[Co(HL^4)_2]Cl{\cdot}2H_2O$ ($C_{50}H_{42}ClCoN_6O_3S_2$)	951.4 (69)	240.5	64.65 (63.12)	4.70 (4.66)	8.48 (8.83)	5.60 (6.19)	3.31 (3.73)
$[Ni(HL^4)_2]{\cdot}H_2O$ ($C_{50}H_{42}N_6NiO_3S_2$)	897.7 (59)	229.5	66.09 (66.89)	4.49 (4.72)	8.56 (9.36)	6.15 (6.54)	–
$[Cu(HL^4)H_2O]NO_3$ ($C_{25}H_{22}CuN_4O_5S$)	554.1 (37)	221.5 dec.	54.04 (54.19)	4.23 (4.00)	9.90 (10.11)	11.00 (11.47)	–

1:2. These complexes are paramagnetic and high-spin ($\mu_{eff} = 2.84-3.1$ BM). The 1:1 Cu(II) complexes are paramagnetic ($\mu_{eff} = 1.65-1.80$ B.M.).

TGA Analysis

TGA analyses of the Fe(III), Co(III), Ni(II) and Cu(II) complexes with H_2L^1, H_2L^2, H_2L^3 and H_2L^4 were conducted in air within the range 25–800 °C at 10 °C/min heating rate. The results of the TGA analyses indicated the presence of crystal water molecules in the compounds $[Ni(HL^1)_2]\cdot H_2O$, $[Ni(HL^2)_2]\cdot H_2O$, $[Ni(HL^3)_2]\cdot H_2O$, $[Ni(HL^4)_2]\cdot H_2O$, $[Fe(HL^3)_2]Cl\cdot H_2O$, $[Fe(HL^4)_2]Cl\cdot H_2O$ and $[Co(HL^4)_2]Cl\cdot 2H_2O$. Elimination of the water molecules were observed at 110–140 °C. Table 2 shows representative thermal degradations of the Co(III) complexes. The Co(III) complexes were found to decompose in three main steps like the other complexes. The first step

Table 2. TGA data of Co(III) complexes.

Compounds	Temperature range for each step (°C)	Compound weight (mg)	Actual weight loss %	
			Found	Calculated
$[Co(HL^1)_2]$ Cl	25	11.15		
	1st step 25–279	9.00	19.3	20.2
	2nd step 279–524	5.32	33.0	31.5
	3rd step 524–603	1.27	36.3	38.3
	Residue		11.4	10.0
$[Co(HL^2)_2]$ Cl	25	12.81		
	1st step 25–270	10.41	18.8	19.5
	2nd step 270–514	6.05	34.0	34.1
	3rd step 514–581	1.42	36.1	35.5
	Residue		11.1	10.9
$[Co(HL^3)_2]Cl$	25	10.82		
	1st step 25–270	8.86	18.1	18.8
	2nd step 270–505	4.94	36.2	36.5
	3rd step 505–571	1.24	34.2	33.6
	Residue		11.5	11.1
$[Co(HL^4)_2]Cl\cdot 2H_2O$	25	11.90		
	1st step 25–132[a]	11.30	5.0	4.8
	2nd step 132–246	9.40	16.0	16.1
	3rd step 246–480	4.59	40.4	40.7
	4th step 480–627	1.12	29.2	29.5
	Residue		9.4	8.9

[a] Indicates the presence of crystal water.

ends at 280 °C by the elimination of phenyl rings attached to the terminal N^4 atom. The next step at 525 °C involves chloride loss and a decomposition of the thiosemicarbazone structure, and finally, in the last step at *ca.* 650 °C, decomposition of the naphthaldehyde moiety is observed.[3]

The Co_2O_3 residue is stable beyond this temperature. Only the Co(III) complex with H_2L^4 shows elimination of two molecules of water at 132 °C.

Electronic Spectra

UV-Vis spectra of the ligands and their metal complexes were obtained in $2 \cdot 10^{-5}$ M ethanolic solutions between 200 and 700 nm.

The bands at 232–242 nm, attributed to the $\pi \rightarrow \pi^*$ transitions, did not change in the Co(III) complexes, but underwent a shift to 314–319 nm for the Fe(III) and 276–285 nm for the Cu(II) complexes. The bands of $n \rightarrow \pi^*$ transitions at 378–380 nm showed a bathochromic shift to 427–430 nm for the Co(III) complexes, while hypsochromic shifts were seen to 360–370 nm for the Fe(III), and to 335–345 nm for the Cu(II) complexes. The charge transfer bands of the Fe(III), Co(III) and Cu(II) complexes were observed at 359–372, 443 and 412–417 nm, respectively. The data regarding d–d bonds could not be obtained clearly at the studied concentration

IR Spectra

IR spectra was obtained as KBr disks in the 4000–400 cm^{-1} range. The spectra of the ligands contain the expected $\nu(N^4H)$ and $\nu(OH)$ vibrations are seen as broad, strong bands between 3257–3423 cm^{-1}. The medium-intensity bands at 3048–3122 cm^{-1} and 2868–2998 cm^{-1} are attributed to aromatic $\nu(C{-}H)$ and aliphatic $\nu(C{-}H)$ vibrations, respectively. The $\delta(NH)$ and $\delta(OH)$ bands of the ligands are observed at 1621–1609 cm^{-1}, while the $\nu(C{=}N^1)$ bands are at 1570 ± 7 cm^{-1}. The (N^4H) rocking band at 719 cm^{-1} as well as in-plane aromatic (C–H) bands at 1031–1081 cm^{-1} and out-of-plane aromatic (C–H) bands at 827–646 cm^{-1} have been determined. The $\delta(C{-}OH)$ bands are seen at 1356 ± 2 cm^{-1} in the ligands.[2,9,13,20] The $\delta(OH)$ band at 1356 ± 2 cm^{-1} can also be seen in the spectra of the complexes, by undergoing higher-field shifts of about 7–15 and 2–12 cm^{-1}, respectively.[9]

The $\nu(C{=}N^1)$ band of the ligands is observed to undergo a 5–12 cm^{-1} shift to lower frequency on coordination to the metal ion.[21]

The $(N^4{-}C)$ streching band at 1242 ± 2 cm^{-1} in the ligands undergoes a 20–23 cm^{-1} shift to lower frequency which enhances the possibility of decreasing the electron delocalization on the $N^4{-}C$ system and the change in the electron density in the region.[2,13]

It is seen that the vibration, deformation and out-of-plane bands of the N^4H group at 3240 ± 15, 1620 ± 2 cm^{-1} and 719 cm^{-1} respectively, disappear. This observation indicates that the coordination may occur with deprotonation of the N^4H donor group.[2,13,21]

^1H NMR Spectra

The spectra of the ligands and their Co(III) complexes were recorded in DMSO-d_6 (see Table 3). The methyl protons appear as a singlet at 2.5 ppm in the spectra of H_2L^1, and for H_2L^2 they are seen as a triplet at 1.8–1.2 ppm. The CH_2 groups of H_2L^3 are a triplet at 3.6–3.0 ppm and a quartet at 1.2–0.8 ppm.

The ligands H_2L^3 and H_2L^4 in which no isomerization is seen in their ^1H NMR spectra are relatively more easily coordinated. It is apparent from the yields that these ligands are more effective in the isolation of 1:2 chelates. However, it was not possible to isolate the 1:2 complexes of the ligands $H_2L^1$and H_2L^2, containing lower homologues (CH_3 and C_2H_5) with Fe(III) in even low yields. This is probably caused by isomer mixtures due to the C=N bond with relatively higher solubility.[20]

The azomethine proton ($CH=N^1$) gives a doublet for H_2L^1 showing *cis/trans* isomerism (with an approx. 65/35 ratio) at 9.38 ppm, whereas a doublet is seen at 9.43 ppm, having an isomer ratio of 55/45 for H_2L^2. However, H_2L^3 and H_2L^4 show singlets only at 9.41 and 9.39 ppm, respectively.

The fact that the chemical shifts of the azomethine protons change not in an assessable size is caused by the back-donation of the azomethine system for coordination. Since the π electrons of the azomethine group are not affected, the chemical environment of the proton is not changed. However, the appearance of doublets for the proton g (Figure 1) at 9.38 and 9.43 for $H_2L^1$and H_2L^2, respectively, as singlets at 9.41 and 9.35 in the complexes shows that the complexation occurs with only one isomer.

The disappearance of thioamide (N^4H) resonance peaks in the spectra of the complexes with the ligands definitely proves that the coordination is occurring involving this region with deprotonation. In contrast, the OH groups are involved in the coordination without deprotonation (see Figures 2 and 3). The shifts of the OH group from 8.5–8.9 ppm to 6.0–6.2 ppm support the data obtained from IR spectra.

It is known that the complexation of the thiosemicarbazone-ligands *via* their OH groups affects the conjugated backbone of the ligand and, thus, the π-system of the aromatic ring.[23] Since the coordination is observed without deprotonation, this effect is only seen as small shifts, *i.e.*, the resonance of the proton H_a shifts by 0.25 ppm for H_2L^1 and H_2L^2, and 0.52 ppm for H_2L^3 and H_2L^4 (Figure 1).

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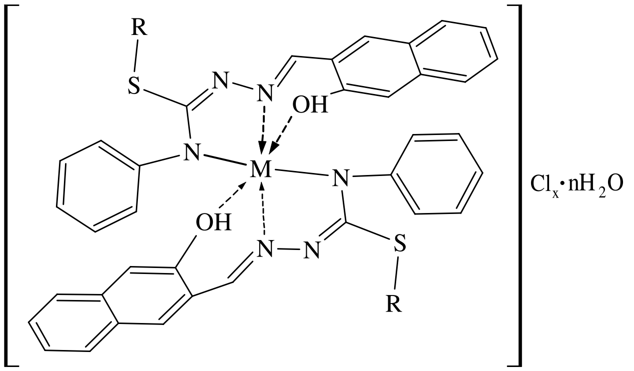
Table 3. ^{1}H NMR chemical shifts (δ, ppm) and coupling constants (J, Hz)[a] of the ligands and their Co(III) complexes (in DMSO-d_6, TMS standard).

Compound	OH	CH_3	CH_2	$CH{=}N^1$	Ar–H	N^4H
H_2L^1	8.56	2.5	–	9.38 d (J = 6.1)	7.0–8.4 (11H) H_a (8.38 d) (J = 8.4)	13.16
H_2L^2	8.34	1.2–1.8 (J = 7.8)	3.0–3.4 (J = 7.4)	9.43 d (J = 5.3)	7.0–8.4 (11H) H_a (8.14 d) (J = 8.1)	13.36
H_2L^3	8.82	0.8–1.2 t (J = 7.3)	3.0–3.6 t 1.2–1.8 q (J = 7.2)	9.41	7.0–8.4 (11H) H_a (8.37 d) (J = 8.42)	13.38
H_2L^4	8.89	–	4.52	9.39	7.0–8.38 (16H) H_a (8.36 d) (J = 8.48)	13.23
$[Co(HL^1)_2]$ Cl	6.21	2.0–3.0	–	9.41	6.8–8.0[22] H_a (8.15 d) (J = 8.54)	–
$[Co(HL^2)_2]$ Cl	6.17	1.0–1.6 (J = 7.3)	3.0–3.8 (J = 7.9)	9.35	6.8–8.0[22] H_a (7.85 d) (J = 8.49)	–
$[Co(HL^3)_2]Cl$	6.16	0.8–1.2 (J = 7.3)	3.0–4.0 1.4–1.8 (J = 7.3)	9.31	6.6–8.0[22] H_a (7.85 d) (J = 8.53)	–
$[Co(HL^4)_2]Cl{\cdot}2H_2O$	6.03	–	4.2–4.8	9.37	6.6–8.0[22] H_a (7.84 d) (J = 8.59)	–

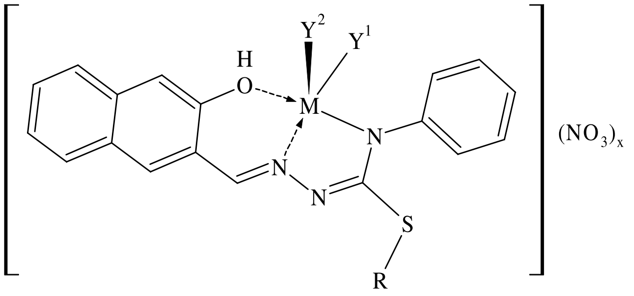
[a] s: singlet, d: doublet, t: triplet, q: quartet.



$[Me(HL)_2]Cl_x \cdot nH_2O$

M	L	x	n
Fe(III)	H_2L^3, H_2L^4	1	1
Co(III)	H_2L^1, H_2L^2, H_2L^3	1	0
Co(III)	H_2L^4	1	2
Ni(II)	H_2L^1, H_2L^2, H_2L^3, H_2L^4	0	1

Figure 2. 1:2 complexes (R = CH_3, C_2H_5, *n*-C_3H_7 and $C_6H_5CH_2$).



$[M(HL)(Y^1)(Y^2)](NO_3)_x$

M	L	Y^1	Y^2	x
Fe(III)	H_2L^1, H_2L^2	Cl	Cl	0
Cu(II)	H_2L^1, H_2L^2, H_2L^3, H_2L^4	H_2O	-	1

Figure 3. 1:1 complexes (R = CH_3, C_2H_5, *n*-C_3H_7 and $C_6H_5CH_2$).

It can be accepted that the appearance of new bands at 1008 and 810 cm^{-1} in the IR spectra of the Cu(II) complexes is indicative of ionic bonding of NO_3^- to Cu(II), moreover, X-ray diffraction studies of the Cu(II) complex of salicylaldehyde-S-methyl-N^4-phenylthiosemicarbazone confirm the structure as $[Cu(HL)H_2O]\cdot NO_3$.[21,24]

The analytical and especially spectral data indicate that the ligands have an ONN donor set. All of the ligands function as tridentate (ON^1N^4) for Fe(III), Co(III), Ni(II), and Cu(II) ions. That the proton of the N^4H group rather than OH is dissociated makes 5- and 6-membered chelate structures possible. The structures proposed and based on these approaches are presented in Figures 2 and 3.

EXPERIMENTAL

Chemicals and Apparatus

The chemical used were reagent grade. ^1H NMR spectra were recorded in DMSO-d_6 solutions on a Bruker AC-200 MHz FT-NMR spectrometer (TUBITAK, Turkey) and chemical shifts were referenced relative to Me_4Si. IR spectra were recorded in KBr discs on a Mattson 1000 FT-IR spectrometer. Elemental analyses were obtained with a Carlo-Erba 1106 analyser (TUBITAK, Turkey) and a Hitachi 180/80 model atomic absorption spectrometer. The molar conductances of the compounds were measured in methanol and acetonitrile on a 712 Metrohm conductometer. Chloride ions were determined by a Jenway 3040 ion analyser multimeter. Magnetic measurements were carried out on a Sherwood Scientific apparatus at room temperature by Gouy's method using $CuSO_4\cdot 5H_2O$ as calibrant. Water contents and TGA analyses of the compounds were determined on a Shimadzu 50 Model TGA. pH measurements and melting points were carried out on a Jenway 3040 ion analyser and a Büchi melting point B-545 instrument, respectively.

Synthesis of 2-Hydroxy-1-naphthaldehyde S-Methyl-N^4-phenylthiosemicarbazone (H_2L^1)

To the suspension of N^4-phenylthiosemicarbazide (1 g, 6 mmols) in 10 mL ethyl alcohol, 0.8 mL (12 mmols) of MeI was added dropwise and the mixture was refluxed on an 80 °C water bath for 3–4 hours. The cooled reaction mixture was treated dropwise with 8 mL of a warm ethanolic solution of 2-hydroxy-1-naphthaldehyde (0.86 g, 5 mmols). The yellow product separated was washed with small portions of cold ethanol and diethyl ether. The free ligand was obtained by adding a sufficient amount of aqueous $NaHCO_3$ solution (10%, w/w) before it was recrystallized from ethanol. The final product was dried in a vacuum dessicator over $CaCl_2$.

The other ligands, H_2L^2 , H_2L^3 and H_2L^4, were prepared in a similar manner by using the corresponding alkyl halides[25,26] (see Figure 1).

Synthesis of 2-Hydroxynaphthaldehyde S-Methyl-N^4-phenylthiosemicarbazonatoiron(III) Complex

A quantity of 335 mg (1 mmole) 2-hydroxy-1-naphthaldehyde-S-methyl-N^4-phenyl thiosemicarbazone (H_2L^1) was dissolved in a mixture of acetone (10 mL) and ethanol (20 mL) by means of an ultrasonic water bath. This solution was treated drop-wise with 8 mL of an ethanolic solution of $FeCl_3{\cdot}6H_2O$ (324 mg, 1,2 mmols). The reaction was continued for at least one hour at ambient temperature, and the flask was placed in a refrigerator and kept overnight. The formed black crystalline product was filtered, washed two times with ethanol and one time with diethyl ether, and was dried over $CaCl_2$ in a vacuum dessicator.

The other complexes were prepared similarly using the appropriate ligands and metal salts.[27]

ACKNOWLEDGMENTS

The authors thank Dr. Bahri Ülküseven for his kind remarks on the interpretation of the experimental data, and Mr. Barbaros Akkurt for obtaining analytical and spectral data.

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Received June 22, 2002 Referee I: D. X. West
Accepted February 20, 2003 Referee II: N. V. Duffy