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H. Cahit Sevindir

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SYNTHESIS AND COMPLEX FORMATION OF UNSYMMETRICALLY SUBSTITUTED ARYLTHIO-*p*-CHLOROPHENYL *vic*-DIOXIMES

H. Cahit Sevindir

Department of Environmental Engineering,
Faculty of Engineering, Süleyman Demirel University,
32260 Isparta, Turkey
E-mail: sevindir@mmf.sdu.edu.tr

ABSTRACT

anti-Chlorophenylchloroglyoxime, 4-$ClC_6H_4C(=NOH)CCl(=NOH)$, has been synthesized by chlorination of *anti*-*p*-cholorophenylglyoxime. The reaction of 4-$ClC_6H_4C(=NOH)CCl(=NOH)$ with thiophenol, 4-methylthiophenol and 4-methoxythiophenol in ethanol between −5 and −10 °C gives the unsymmetrical *vic*-dioximes, designated as thiophenolo-*p*-chlorophenylglyoxime, 4-$ClC_6H_4C(=NOH)C(SC_6H_5)(=NOH)$, 4-methylthiophenolo-*p*-chlorophenylglyoxime, 4-$ClC_6H_4C(=NOH)C(SC_6H_4\text{-}CH_3\text{-}p)(=NOH)$, and 4-methoxythiophenolo-*p*-chlorophenylglyoxime, 4-$ClC_6H_4C(=NOH)C(SC_6H_4\text{-}OCH_3\text{-}p)(=NOH)$. The Cu(II) and Ni(II) complexes of these ligands were prepared and are proposed to be square-planar, while the corresponding Co(II) complexes are proposed to be octahedral with water molecules as axial ligands. The

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structural assiguments are supported by ^1H NMR, IR and elemental analyses.

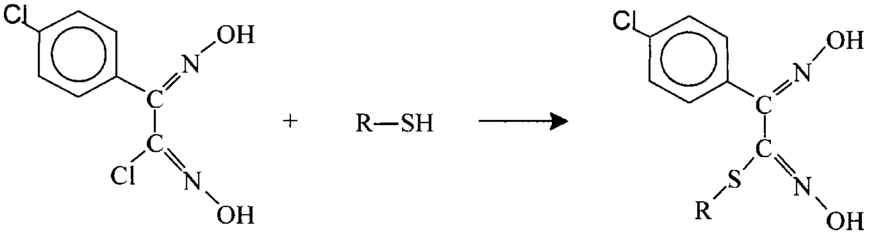
INTRODUCTION

The transition metal complexes of *vic*-dioximes have been of particular interest as biological model compounds.[1] The substitution pattern of the *vic*-dioxime moiety affects the structure and stability of the complexes, *e.g.*, Co(II) complexes of dialkyl- or diarylglyoxime and dithioglyoxime derivatives can be obtained by the reduction of octahedral Co(III) compounds,[4,8] but the complexes are decomposed in the case of diaminoglyoxime derivatives.[2]

In the present paper, we report the synthesis and complex formation of three new substituted arylthioglyoximes as examples of unsymmetrically substituted *vic*-dioximes. The asymmetry of the ligands is expected to enhance the solubility of planar complexes derived from them. A general formula for the ligands is shown in Fig. 1.

RESULTS AND DISCUSSION

The number of *vic*-thiodioximes and thiooximes in the literature[3,5,6] is rather small. The structures of the ligands have been verified by elemental analyses, ^1H NMR and IR spectral data. The elemental analysis results are given in Table I.



HL^1: R = C_6H_5

HL^2: R = C_6H_4-CH_3-*p*

HL^3: R = C_6H_4-OCH_3-*p*

Figure 1. General formulas of ligands.

Table I. Melting Points, Yields, and Elemental Analytical Results of the Ligands and Their Complexes

				Analysis Found (Calcd.)					
Chemical Formula	Formula Wt.	Yield %	M. p. °C (d.p.)	%C	%H	%N	%S	%Cl	%M
$C_{14}H_{11}ClN_2O_2S$				54.81	3.58	9.13	10.44	11.58	–
HL^1	306.5	83	144	(54.80)	(3.60)	(9.10)	(10.47)	(11.57)	
$C_{28}H_{20}Cl_2NiN_4O_4S_2$				50.17	2.98	8.36	9.55	10.60	8.76
$Ni(L^1)_2$	669.7	86	(180)	(50.20)	(3.00)	(8.36)	(9.54)	(10.59)	(8.79)
$C_{28}H_{20}Cl_2CuN_4O_4S_2$				49.81	2.96	8.30	9.48	10.52	9.41
$Cu(L^1)_2$	674.5	70	(195)	(49.79)	(2.96)	(8.31)	(9.50)	(10.52)	(9.43)
$C_{28}H_{24}Cl_2CoN_4O_6S_2$				47.59	3.39	7.93	9.06	10.05	8.34
$Co(L^1)_2(H_2O)_2$	705.9	75	(170)	(47.61)	(3.41)	(7.90)	(9.06)	(10.07)	(8.35)
$C_{15}H_{13}ClN_2O_2S$				56.16	4.05	8.73	9.98	11.07	–
HL^2	320.5	80	152	(56.18)	(4.07)	(8.72)	(10.00)	(11.06)	
$C_{30}H_{24}Cl_2NiN_4O_4S_2$				51.59	3.43	8.02	9.17	10.17	8.41
$Ni(L^2)_2$	697.7	85	(175)	(51.60)	(3.43)	(8.01)	(9.16)	(10.19)	(8.40)
$C_{30}H_{24}Cl_2CuN_4O_4S_2$				51.24	3.41	7.97	9.11	10.10	9.03
$Cu(L^2)_2$	702.5	65	(199)	(51.24)	(3.40)	(8.00)	(9.10)	(1012)	(9.00)
$C_{30}H_{28}Cl_2CoN_4O_6S_2$				49.05	3.81	7.63	8.72	9.67	8.02
$Co(L^2)_2(H_2O)_2$	733.9	88	(210)	(49.06)	(3.80)	(7.63)	(8.75)	(9.70)	(8.00)
$C_{15}H_{13}ClN_2O_3S$				53.49	3.86	8.32	9.50	10.54	–
HL^3	336.5	80	160	(53.50)	(3.88)	(8.33)	(9.51)	(10.54)	
$C_{30}H_{24}Cl_2NiN_4O_6S_2$				49.33	3.28	7.67	8.77	9.73	8.04
$Ni(L^3)_2$	729.7	90	(180)	(49.35)	(3.29)	(7.70)	(8.79)	(9.72)	(8.05)
$C_{30}H_{24}Cl_2CuN_4O_6S_2$				49.01	3.26	7.62	8.71	9.66	8.64
$Cu(L^3)_2$	734.5	70	(166)	(49.00)	(3.29)	(7.60)	(8.74)	(9.68)	(8.63)
$C_{30}H_{28}Cl_2CoN_4O_8S_2$				47.00	3.65	7.31	8.35	9.27	7.69
$Co(L^3)_2(H_2O)_2$	765.9	82	(203)	(46.99)	(3.65)	(7.32)	(8.32)	(9.30)	(7.80)

^{1}H NMR Spectra of Ligands and Complexes

In the ^{1}H NMR spectra of the ligands two deuterium-exchangeable singlets were observed, corresponding to two non-equivalent OH protons, which also indicate the *anti*-configuration of the OH groups relative to each other.[7] When the chemical shift values of the two OH groups in the three ligands are compared, the peaks at lower field vary little (12.00–11.90 ppm, $\Delta = 0.1$ ppm), while a considerable difference is observed for those at higher field (10.50–10.30 ppm, $\Delta = 0.2$ ppm) (Table II). The former is assigned to the OH proton adjacent to the phenyl groups, and the latter to the OH proton of the arylthio-oxime group, since the effect of various substituents is expected to be higher on the arylthio-oxime group. The methyl protons are seen at 2.15 ppm as singlets.

The solubility of the complexes prepared from the three new unsymmetrical ligands is not sufficient to obtain ^{1}H NMR spectra in solution on our 100 MHz instrument except for $Ni(L^1)_2$. The proton NMR spectrum of this diamagnetic complex indicates $O{-}H\cdots O$ bridge formation by the strong shift of the OH protons to lower field (15.20 ppm) compared to the ligand.[2,7,10]

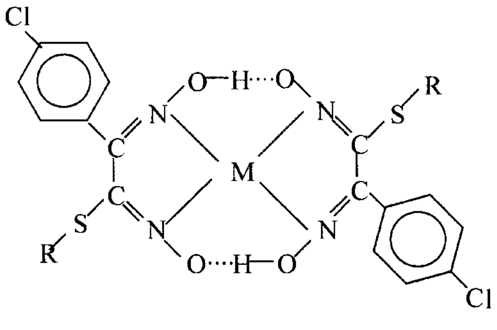
As a consequence of the asymmetry in the ligands, the complexes are expected to form two isomers (Fig. 2). TLC (silicagel-G) was employed with different solvent mixtures and varying polarities, but only one spot appears in each case. This result implies the formation of only one isomer under these reaction conditions. The geometric isomerism of $Ni(L^1)_2$ can be inferred from the ^{1}H NMR spectrum, since

Table II. ^{1}H NMR Data[a] (in ppm) for the Ligands (in DMSO-d_6) and Ni(II) Complex (in CF_3COOH)

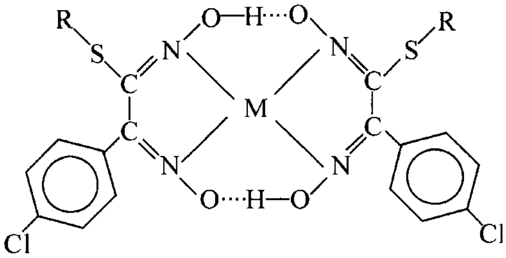
Compound	O-H[b]	O-H[a]	$O{-}H\cdots O$	OCH_3	H(arom).	CH_3
HL^1	11.98 (s, 1H)	10.33 (s, 1H)	–	–	7.64–6.61 (m, 9H)	–
$Ni(L^1)_2$	–	–	15.20 (s, 2H)	–	7.54–7.88 (m, 18H)	–
HL^2	11.90 (s, 1H)	10.50 (s, 1H)	–	–	7.86–6.75 (m, 8H)	2.15 (s, 3H)
HL^3	12.00 (s, 1H)	10.30 (s, 1H)	–	3.63 (s, 3H)	7.77–6.81 (m, 8H)	–

[a] s: singlet; m: multiple.

[b] Disappears on D_2O exchange.



H_2O
|
Trans-Form: M = Ni(II), Cu(II), or Co(II)
|
H_2O



H_2O
|
Cis-Form: M = Ni(II), Cu(II), or Co(II)
|
H_2O

Figure 2. Square-planar and octahedral metal complexes of the unsymmetrical ligands HL^1, HL^2, and HL^3. All complexes are suggested to exist in the *trans*-form.

the alternative chemical environments will show two O—H···O bridge protons in the *cis*-form, but only one in the *trans*-structure. The observed spectrum has only one resonance at 15.20 ppm implying the *trans*-form of the complex.

IR Spectra of Ligands and Complexes

In the IR spectra of the ligands, C-S (680–660 cm^{-1}), OH (3230–3260 cm^{-1}), C=N (1650–1610 cm^{-1}), and NO (980–950 cm^{-1}) stretches appear at frequencies expected for substituted glyoximes[9–12] (Table III). The characteristic IR absorptions of the complexes are given in Table III. The metal-ligand ratio in all of the complexes is 1:2, but the Co(II) complexes have coordinated two additional water molecules for each Co ion. Thus, it is reasonable to propose an octahedral structure for the Co(II) and square-planar coordination for the Ni(II) and Cu(II) compounds (Fig. 2).

The IR spectra of the complexes support these structures by the weak bending vibration of the O—H···O bridges around 1660–1690 cm^{-1} and the shift of the C=N vibration to lower frequencies at 1620–1660 cm^{-1} due to N,N-metal coordination.[7,10] In the case of the Co(II) complexes, the coordinated H_2O molecules were identified by a broad OH absorption around 3040–3060 cm^{-1} which retains its intensity even after heating at 100 °C for 24 h under vacuum.

EXPERIMENTAL

All chemicals and solvents used were of "Analytical Reagent" (Merck) grade. *anti*-Chlorophenylchloroglyoxime, $4\text{-}ClC_6H_4C(=NOH)$-

Table III. Characteristic IR Bands[a] (cm^{-1}) of the Ligands and Their Complexes in KBr

Compound	OH	$CH_{arom.}$	O—H···O	C=N	N-O	C-S	C-CI
HL^1	3240 s	3070 s	–	1610 s	950 s	670 w	690 s
$Ni(L^1)_2$	–	3030 s	1680 m	1640 s	960 s	680 w	700 s
$Cu(L^1)_2$	–	3020 s	1660 m	1620 s	960 s	670 w	670 s
$Co(L^1)_2(H_2O)_2$	–	3040 s	1675 m	1640 m	970 s	680 w	700 s
HL^2	3230 s	3060 s	–	1630 s	970 s	660 w	680 s
$Ni(L^2)_2$	–	3040 s	1680 m	1650 s	950 s	670 w	705 s
$Cu(L^2)_2$	–	3040 s	1690 m	1620 s	970 s	670 w	680 s
$Co(L^2)_2(H_2O)_2$	–	3050 s	1680 m	1620 m	960 s	675 w	700 s
HL^3	3260 s	3070 s	–	1650 s	980 s	680 w	670 s
$Ni(L^3)_2$	–	3020 s	1680 m	1660 s	960 s	660 w	710 s
$Cu(L^3)_2$	–	3040 s	1690 m	1650 s	990 s	670 w	705 s
$Co(L^3)_2(H_2O)_2$	–	3060 s	1685 m	1630 m	970 s	680 w	690 s

[a] s: strong, m: medium, w: weak.

CCl(=NOH), was prepared by reported procedures.[14,15] ^{1}H NMR spectra were recorded on a Varian T 100-A spectrometer. IR spectra were recorded on a Pye Unicam SP1025 spectrophotometer as KBr pellets. The elemental analyses were determined at the TUBITAK Laboratory (Scientific and Technical Research Council of Turkey).

Synthesis of Substituted Arylthioglyoximes

To a stirred solution of *anti*-4-$ClC_6H_4C(=NOH)CCl(=NOH)$ (2.33 g, 0.01 mol) in absolute ethanol (20 mL) at −10 and −15 °C was added dropwise a solution of 0.01 mol of the thiol compound [thiophenol (0.11 g), 4-methylthiophenol (0.124 g), 4-methoxythiophenol (0.1 mL)] in a mixture of 30 mL of absolute ethanol and 10 mL of diethyl ether in 30 min in a fume hood. After addition of a 1% NaOH solution in ethanol to raise the pH to 4-5, the reaction mixture was further stirred for 2 h, diluted with 120 mL water, and left overnight at 5 °C. The resulting precipitate was filtered and recrystallized from ethanol-water (1:2). The crystalline product was filtered, washed with water and dried at room temperature.

Synthesis of the Ni(II), Cu(II), and Co(II) Complexes

Solutions of 0.5 mmol of the metal salts [$NiCl_2{\cdot}6H_2O$) (0.119 g), $CuCl_2{\cdot}2H_2O$ (0.086 g) and $CoCl_2{\cdot}6H_2O$ (0.119 g)] in 20 mL absolute ethanol were added to a solution of the ligand (1 mmol) [HL^1 (0.306 g), HL^2 (0.320 g), HL^3 (0.25 mL)] dissolved in 30 mL of ethanol. The pH of the mixtures dropped to 3.0–3.5 and the color turned to red-brown. After addition of a 1% NaOH solution in ethanol to raise the pH to 4.5–5, the mixtures were stirred on a water bath at 50–55 °C for 20 min. The precipitated complexes were filtered while hot. They were then washed with water, ethanol and diethyl ether. The complexes were then dried under vacuum at 100 °C. The yields and melting points of the compounds are noted in Table I. The complexes are soluble in CF_3COOH and slightly soluble in hot DMF or DMSO.

Yields: $Ni(L^1)_2$, 0.555 g; $Ni(L^2)_2$, 0.593 g; $Ni(L^3)_2$, 0.656 g; $Cu(L^1)_2$, 0.472 g; $Cu(L^2)_2$, 0.456 g; $Cu(L^3)_2$, 0.514 g; $Co(L^1)_2(H_2O)_2$, 0.529 g; $Co(L^2)_2(H_2O)_2$, 0.645 g; $Co(L^3)_2(H_2O)_2$, 0.628 g.

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Referee I: K. Moedritzer
Referee II: A. T. Odom