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THE SYNTHESIS AND CHARACTERIZATION OF SOME NEW vic-DIOXIME LIGANDS AND THEIR Ni(II), Cu(II) AND Co(II) COMPLEXES

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ABSTRACT

In this study, N-(3,4-dimethylphenyl)aminoglyoxime ($DMPGH_2$), N-(3,4-dichlorophenyl)aminoglyoxime ($DCPGH_2$), N,N'-bis(3,4-dimethylphenyl)diaminoglyoxime ($BDMPGH_2$) and N,N'-bis(3,4-dichorophenyl)diaminoglyoxime ($BDCPGH_2$) have been synthesised from anti-chloroglyoxime or anti-dichloroglyoxime and the corresponding substituted aromatic amines in ethanol. Their complexes with Ni(II), Cu(II) and Co(II) have been obtained. Structures of the ligands and complexes are proposed based on IR, ^1H NMR spectra, magnetic measurements and elemental analyses. The Ni(II), Cu(II) complexes are square-planar while the Co(II) complexes are octahedral.

INTRODUCTION

vic-Dioximes have great importance in coordination chemistry since they are used as analytical reagents in the extraction of metals, in potentiometric titrations and as models for

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biological systems, such as vitamin B_{12}[1,2]. In the literature, several symmetrical and unsymmetrical aminoglyoximes have been described as having been synthesized from anti-chloroglyoxime and anti-dichloroglyoxime with amines and their metal complexes have been prepared[1-12]. It is reported that the two oxime groups in the unsymmetrical aminoglyoximes are no longer equivalent[6,10]. Additional substituents on the aromatic group bound to the N-atom of aminoglyoxime are expected to further enhance the difference between the two oxime groups[6-9].

vic-Dioximes may exist in three isomers which are the syn, anti and amphi forms, depending on the position of the OH groups in the molecule[2-6]. The anti and amphi forms of these ligands give two differently coloured complexes with the same metal. Generally, the anti-forms of the Ni(II) and Cu(II) complexes are square-planar while the Co(II) complexes are octahedral [3-12].

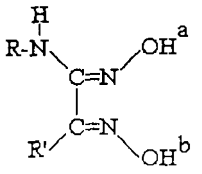
In this study, we report the synthesis of some new symmetrically and unsymmetrically substituted vic dioximes from anti-chloro or anti-dichloroglyoxime and substituted aromatic amines and their complexes with Ni(II), Cu(II) and Co(II) ions.

RESULTS AND DISCUSSION

In this study, four new ligands have been synthesized to investigate the structure and formation of their metal complexes. The ligands have been obtained from the reaction of substituted aromatic amines with anti-chloroglyoximes or anti-dichloroglyoximes in ethanol at -10° C. The molecular structures, names of ligands and their complexes are given in Figs. 1 and 2, respectively. The structures of the ligands were confirmed by ^{1}H NMR, IR spectral data, elemental analyses and magnetic measurements are shown in Tables I, II and III.

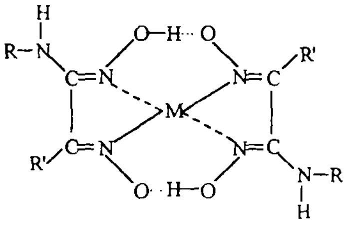
^{1}H NMR Spectra of Ligands and Ni(II) Complexes

In the ^{1}H NMR spectra of $DMPGH_2$ and $DCPGH_2$, two peaks are present for the OH protons of the oxime groups (Table I). These two singlets correspond to two non-equivalent OH protons which also indicate the anti-configuration of the OH groups (a and b in Fig.1) relative to each other. When the ^{1}H NMR signals of the two OH groups are compared in the two different ligands, the ones at lower field quite closely resemble each other (11.5-11.4 ppm) while a considerable difference is observed for the ones at higher



R = 3,4-dimethylphenyl, R' = H ($DMPGH_2$)
R = 3,4-dichlorophenyl, R' = H ($DCPGH_2$)
R = 3,4-dimethylphenyl, R' = 3,4-dimethylphenylamino ($BDMPGH_2$)
R = 3,4-dichlorophenyl, R' = 3,4-dichlorophenylamino ($BDCPGH_2$)

Fig. 1. The Structure of the Ligands



M = Ni(II), Cu(II) and Co(II).$2H_2O$

Fig. 2. The Structure of Square-Planar and Octahedral Metal Complexes.

(See Fig.1 for the definitions of R and R')

Table I. ^1H NMR Spectra of the Ligands and Ni(II) Complexes in DMSO-d_6 δ (ppm)

Compounds	O-H^a	O-H^b	$H_{arom.}$	N-H	C-H	CH_3	O-H···O
$DMPGH_2$	11.4	10.7	7.5-6.6	8.3	7.7	2.1	-
$(DMPGH)_2Ni$	-	-	7.3-6.9	8.3	7.2	2.2	14.6
$DCPGH_2$	11.5	11.2	7.3-6.9	8.3	7.6	-	-
$BDMPGH_2$	10.3	-	6.9-6.6	7.9	-	2.1	-
$(BDMPGH)_2Ni$	-	-	6.8-6.3	8.4	-	2.3	15.2
$BDCPGH_2$	10.8	-	7.4-6.7	8.6	-	-	-
$(BDCPGH)_2Ni$	-	-	6.9-6.5	8.6	-	-	14.9

a and b refer to the two OH groups in Fig.1.

Table II. Magnetic Moments of the Complexes and Characteristic IR Bands of the Ligands and Their Complexes as KBr Pellets (cm^{-1})^{a}

Compounds	**μ_{eff} (BM)**	**N-H**	**O-H**	**O-H---O**	**C=N**	**N-O**
DMPGH$_2$	-	3420 s	3300 s	-	1654 s	980 s
(DMPGH)$_2$Ni	Dia	3420 s	-	1710 w	1620 s	990 w
(DMPGH)$_2$Cu	1.79	3450 m	-	1710 w	1655 s	990 w
(DMPGH)$_2$Co.2H$_2$O	3.56	-	3250 3550 s	1710 w	1610 s	990 w
DCPGH$_2$	-	3420 s	3320 s	-	1670 s	990 s
(DCPGH)$_2$Ni	Dia	3420 m	-	1716 w	1670 m	1000 w
(DCPGH)$_2$Cu	1.79	3420 m	-	1716 w	1670 s	1000 w
(DCPGH)$_2$Co.2H$_2$O	3.81	-	3250 3550m	1716 w	1620 s	1030 m
BDMPGH$_2$	-	3420 s	3300 s	-	1655 s	980 w
(BDMPGH)$_2$Ni	Dia	3420 m	-	1725 w	1620 m	1020 w
(BDMPGH)$_2$Cu	1.85	3420 m	-	1725 w	1600 s	1020 m
(BDMPGH)$_2$Co.2H$_2$O	3.48	-	3300 3500 m	1640 w	1600 s	1000 m
BDCPGH$_2$	-	3400 s	3370 s	-	1650 s	985 m
(BDCPGH)$_2$Ni	Dia	3350 m	-	1600 w	1580 s	1000 m
(BDCPGH)$_2$Cu	2.04	3370 m	-	1610 w	1590 s	1030 m
(BDCPGH)$_2$Co.2H$_2$O	3.92	-	3250 3500 s	1635 w	1600 m	990 w

$^{a}\mu_{eff}$: Magnetic moment
Dia: Diamagnetic
s: strong
m: medium
w: weak

Table III. Colours, Melting Points, Yields and Elemental Analyses of the Ligands and Complexes

				Calculated (Found) %		
Compounds Empirical Formula	**Fw (g/mol)**	**Colour[a] Yield (%)**	**M.p. (°C) (Decomp.)**	**C**	**H**	**N**
$DMPGH_2$ **$C_{10}H_{13}N_3O_2$**	207	P. yellow (45)	(167)	57.97 (57.57)	6.28 (5.95)	20.29 (19.85)
$(DMPGH)_2Ni$ **$C_{20}H_{24}N_6O_4Ni$**	470.71	Red (78)	(274)	50.99 (50.61)	5.10 (5.16)	17.85 (17.46)
$(DMPGH)_2Cu$ **$C_{20}H_{24}N_6O_4Cu$**	475.5	Brown (75)	(209)	50.47 (50.61)	5.05 (5.08)	17.66 (17.46)
$(DMPGH)_2Co.2H_2O$ **$C_{20}H_{28}N_6O_6Co$**	506.93	D.brown (65)	>300	47.34 (47.28)	5.52 (5.45)	16.57 (16.52)
$DCPGH_2$ **$C_8H_7N_3O_2Cl_2$**	248	P.yellow (80)	(152)	38.71 (38.55)	2.82 (2.67)	16.94 (16.45)
$(DCPGH)_2Ni$ **$C_{16}H_{12}N_6O_4Cl_4Ni$**	552.71	Red (85)	>300	34.74 (34.94)	2.17 (2.23)	15.20 (15.34)
$(DCPGH)_2Cu$ **$C_{16}H_{12}N_6O_4Cl_4Cu$**	557.5	D. green (75)	(190)	34.44 (34.26)	2.15 (2.17)	15.07 (14.96)
$(DCPGH)_2Co.2H_2O$ **$C_{16}H_{16}N_6O_6Cl_4Co$**	588.93	D. brown (70)	>300	32.60 (32.52)	2.72 (2.65)	14.27 (14.14)
$BDMPGH_2$ **$C_{18}H_{22}N_4O_2$**	326	P.yellow (45)	(161)	66.23 (65.85)	6.75 (6.25)	17.18 (17.35)
$(BDMPGH)_2Ni$ **$C_{36}H_{42}N_8O_4Ni$**	708.71	Red (65)	(244)	60.96 (61.11)	5.943 (5.86)	15.850 (15.76)
$(BDMPGH)_2Cu$ **$C_{36}H_{42}N_8O_4Cu$**	713.5	D.green (65)	>300	60.55 (60.36)	5.89 (6.07)	15.70 (15.82)
$(BDMPGH)_2Co.2H_2O$ **$C_{36}H_{46}N_8O_6Co$**	744.93	D.brown (60)	>300	57.99 (57.72)	6.18 (6.22)	15.03 (14.76)
$BDCPGH_2$ **$C_{14}H_{10}N_4O_2Cl_4$**	408	P.yellow (60)	(193)	41.18 (40.85)	2.45 (2.15)	13.73 (13.25)

(continued)

Table III, continued

(BDCPGH)$_2$Ni **$C_{28}H_{18}N_8O_4Cl_8Ni$**	872.71	Red (80)	(271)	38.50 (38.49)	2.06 (2.11)	12.83 (12.76)
(BDCPGH)$_2$Cu **$C_{28}H_{18}N_8O_4Cl_8Cu$**	877.5	D. green (72)	>300	38.29 (38.28)	2.05 (2.09)	12.77 (12.71)
(BDCPGH)$_2$Co.2H$_2$O **$C_{28}H_{22}N_8O_6Cl_8Co$**	908.93	D. brown (68)	>300	36.97 (36.78)	2.42 (2.36)	12.32 (11.85)

[a]D: Dark
P: Pale

field (11.2-10.7 ppm). Consequently, the former is assigned to the OH proton of the aldoxime and the latter to the OH proton of the amidoxime group since the effect of various substituents is expected to be higher on the amidoxime group. The ^{1}H NMR signals of the OH protons have a characteristic value for these type of oximes[12,13]. The N-H protons which neighbour the oxime groups were observed at 8.6-7.9 ppm, the aromatic C-H protons at 7.5-6.3 ppm, the aldoxime C-H protons at 7.7-7.6 ppm and the CH_3 protons at 2.3-2.1 ppm. As a consequence of the unsymmetry in the ligands, the complexes are expected to form cis and trans isomers[5,11]. The ^{1}H NMR spectrum of (CMPGH)$_2$Ni can be evaluated to determine the isomer formed, since the different chemical environments should show two O-H---O bridge protons for the cis-form, but only one ^{1}H NMR signal is seen at 14.6 ppm, confirming the trans-form of the complex (Fig. 2). In the ^{1}H NMR spectra of BDMPGH$_2$ and BDCPGH$_2$, a singlet at 10.3 and 10.8, respectively, for the OH protons shows that the oxime is in the trans-configuration, as do all known symmetrically substituted vic-dioximes[14].

The ^{1}H NMR spectrum of the Ni(II) complex indicates O-H---O bridge formation by the strong shift of the protons to lower field (15.2-14.6 ppm) compared to the free ligand[7,8].

IR Spectra

In the IR spectra of the ligands, NH (3420-3400 cm^{-1}), OH (3300-3200 cm^{-1}), C=N (1670-1650 cm^{-1}) and N-O (990-980 cm^{-1}) stretches appear at frequencies expected for substituted aminoglyoximes (Table II). The IR spectral values of the complexes are given in Tables II and III. The metal : ligand ratio in all of these complexes is 1:2, but the Co(II) complexes have coordinated two additional water molecules for each metal ion.

The IR spectra of the complexes indicate a weak bonding vibration of O-H---O bridges around 1700 cm^{-1} and a shift of the C=N vibration to lower frequencies (1670-1580 cm^{-1}) due to N,N'-metal coordination[3-12,15]. In the case of the Co(II) complexes, the coordinated H_2O molecules are identified by broad OH absorption bands around (3550-3250 cm^{-1}) which retain their intensities even after heating at 100° C for 24 h. Consequently, an octahedral structure for the Co(II) and square-planar coordination for the Ni(II) and Cu(II) compounds are proposed (Fig. 2).

Magnetic Measurements

Magnetic susceptibility measurement provide sufficient information to characterize the structure of the complexes (Table III). The mononuclear Ni(II) complexes of these ligands are diamagnetic as expected for a d^8 metal ion in a square planar field[5,16,17]. The Cu(II) and Co(II) complexes at 20° C are paramagnetic, μ_{eff} = 1.79-2.04 BM for the Cu(II) complexes and μ_{eff} = 3.48-3.92 BM for the Co(II) complexes.

EXPERIMENTAL

Anti-chloroglyoxime and anti-dichloroglyoxime were prepared according to the methods reported in the literature[18-19].

All reagents used were purchased from Merck or Carlo Erba and were chemically pure. IR spectra were recorded on a Matson-1000 FT-IR spectrophotometer with the samples in KBr pellets. ^1H NMR spectra were taken on a Bruker 200 MHz FT-NMR spectrometer utilising deuterated dimetylsulphoxide as solvent. The magnetic susceptibilities were measured using a Sherwood Scientific MX1 model Gouy Magnetic susceptibility balance at room temperature. pH measurements were done with a Gresiger Electronic GPHR 1400 pH meter. The elemental analyses were done by the TUBITAK Laboratory (Centre of Science and Technology Research of Turkey, in İzmit).

Synthesis of N-(3,4-Dimethylphenyl)aminoglyoxime ($DMPGH_2$) and N-(3,4-Dichlorophenyl)aminoglyoxime ($DCPGH_2$).

To stirred solutions of 3,4-dimethylaniline (2.38 g, 0.02 mmol) or 3,4-dichloroaniline (3.24 g, 0.02 mmol) in absolute ethanol (40 mL) at -10° C was added dropwise a solution of anti-chloroglyoxime (2.45 g, 0.02 mmol) in absolute ethanol (20 mL). The reaction mixture was stirred further for 3-4 h at -10° C and the pH adjusted to 5-5.5 with aqueous 1% KOH solution. The product precipitated when diluted with water, was filtered and then recrystallized from ethanol-water (1:2). The resulting precipitate was filtered, washed with water and dried in vacuo, at room temperature.

Synthesis of N,N'-Bis-(3,4-dimethylphenyl)diaminoglyoxime ($BDMPGH_2$) and N,N'-Bis-dichlorophenyldiaminoglyoxime ($BDCPGH_2$).

A solution of anti-dichloroglyoxime (1.57 g, 0.01 mmol) in absolute ethanol (20 mL) was added dropwise to a stirred solutions of 3,4-dimethylaniline (2.38 g, 0.02 mmol) or 3,4 dichloroaniline (3.24 g, 0.02 mmol) in absolute ethanol (30 mL) at -10° C. The mixture was stirred further for 3-4 h. After adjusting the pH of the mixture to 5-5.5 with aqueous 1% KOH solution and dilution with 100-120 mL water it was left overnight at 0° C. The resulting precipitate was filtered and then recrystallized from ethanol-water (1:5). The resulting product was then filtered, washed with water and dried in vacuo, at room temperature. The ligands are soluble in ethanol, DMSO, DMF, pyridine and insoluble in water. Some physical properties and spectral data of these compounds are given in Tables I, II and III.

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

A solution of 5 mmol metal salt ($NiCl_2.6H_2O$, $CuCl_2.2H_2O$ or $CoCl_2.6H_2O$) in 10 mL absolute ethanol was added to a solution of 10 mmol of ligand ($DMPGH_2$, $DCPGH_2$, $BDMPGH_2$ or $BDCPGH_2$) dissolved in 30 mL absolute ethanol. The mixture was stirred for 3-4 h at room temperature. The colour of the solution changed and its pH dropped to about 2-2.5, which was then adjusted to about 4-5 with aqueous 1 % KOH solution. The turbid mixture was kept in a water bath at 40-50° C for about 1 h in order to completely precipitate the complex. The precipitated complex was filtered, washed with ethanol and diethyl ether and dried in vacuo, at room temperature.

IR data and magnetic measurements of the complexes are given in Table II. The colours, melting points, elemental analysis results of the compounds are given in Table III.

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