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SYNTHESIS AND COMPLEX FORMATION OF SUBSTITUTED AMINO-P-CHLOROPHENYLGLYOXIMES OF UNSYMMETRICAL *vic*-DIOXIMES

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ABSTRACT

In this study, anti-p-chlorophenylchloroglyoxime ($C_8H_6Cl_2N_2O_2$) has been synthesized by chlorination of anti-p-chlorophenylglyoxime. The reaction of $C_8H_6Cl_2N_2O_2$ with p-chloroaniline, o-toluidine, 1-naphthylamine and benzidine in ethanol between -10°C and -15°C gives unsymmetrical vic-dioximes, namely, p-chloroanilino-p-chlorophenylglyoxime($C_{14}H_{11}Cl_2N_3O_2$), o-toluidino-p-chlorophenylglioxime ($C_{15}H_{14}ClN_3O_2$), 1-naphtylamino-p-chlorophenylglioxime ($C_{18}H_{14}ClN_3O_2$), 1,1'-biphenyl-4-amino-4'-amino-p-chlorophenylglioxime ($C_{20}H_{17}ClN_4O_2$). The Ni(II) and Cu(II) complexes of these ligands are square-planer while the Co(II) complexes are octahedral with water molecules as axial ligands. ^{1}H-NMR, AAS, IR spectra and elemental analyses data are given.

INTRODUCTION

Recently, since the increasing use of coordination compounds in analytical, bio, pigment and medicinal chemistry, many investigators have studied these topics, especially, the important role of the complexes of 1,2-dioximes in coordination chemistry. The transition metal complexes of vic-dioximes have been of particular interest as biological model compounds[1]. Most of the work carried out so far has been on symmetrically disubstituted[2-4] glyoximes and partly on mono-substituted ones[5-7]. The substitution pattern of the vic-dioxime moiety affects the structure and the stability of the complexes, e.g. Co(II) complexes of dialkyl- or diaryl-glyoximes, dithioglyoximes 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 of and complex formation by four new substitued amino-p-chlorophenylchloroglyoximes as examples of unsymmetrically substituted vic-dioximes. The unsymmetry of the ligands is also expected to enhance the solubility of planer complexes derived from them.

RESULTS AND DISCUSSION

In this study, starting with p-chlorophenylketone, anti-p-chlorophenylglioxime was obtained first by oxidation of $-CH_3$ to the isonitroso group and subsequently conversion of C=O to the oxime by condensation with hydroxylammonium chloride as given in the literature[9]. Chlorination of this compound in chloroform afforded anti-p-chlorophenylchloroglyoxime ($C_8H_6Cl_2N_2O_2$), a suitable starting material to obtain various unsymmetrically substituted p-chlorophenyl-glyoximes (Fig.1).

The reaction of $C_8H_6Cl_2N_2O_2$ with four different aryl-amines in ethanol at -15°C gave four new substituted amino-p-chlorophenylglioximes (Fig.2.).

The structures of the ligands have been verified by elemental analyses, ^{1}H-NMR, AAS and IR spectral data (Tables I, II and III).

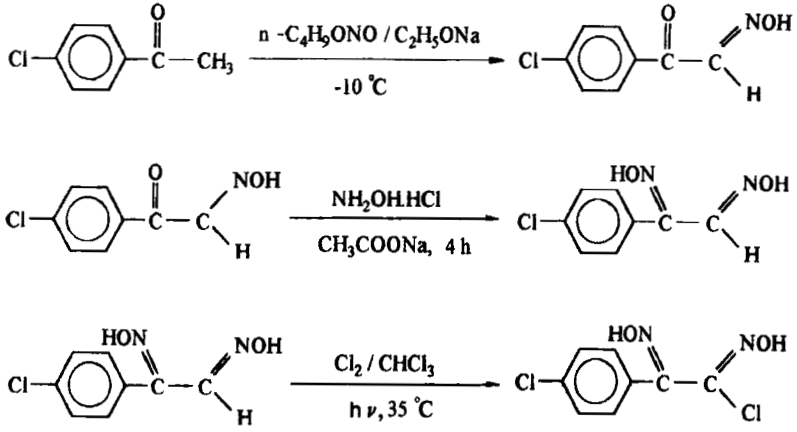
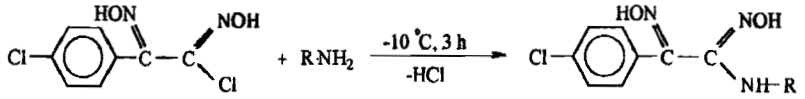


Fig.1. anti-p-chlorophenylchloroglioxime ($C_8H_6Cl_2N_2O_2$)



R = p-Cl –C_6H_5–($C_{14}H_{11}Cl_2N_3O_2$)
R = o-CH_3–C_6H_4–($C_{15}H_{14}ClN_3O_2$)
R = 1-$C_{10}H_7$–($C_{18}H_{14}ClN_3O_2$)
R = p-H_2N–C_6H_4–C_6H_4–($C_{20}H_{17}ClN_4O_2$)

Fig.2. Substituted Amino-p-Chlorophenylglioxímes

^{1}H-NMR Spectra of Ligands and Complex

In the ^{1}H-NMR spectra, two peaks are present for the -OH protons of the oxime groups (Table II). 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[2,4-7](Fig.2.). When the chemical shift values of the two -OH groups are compared in the four different ligands, the ones at lower field quite closely resemble each other (12.06-11.43 ppm) while a considerable difference is observed for the ones at

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

Compounds	Color	Yield (%)	m.p. (d.p) °C	Calcd. (Found) % of C	H	N	M
$C_{14}H_{11}N_3O_2Cl_2$	Dark Brown	85	83-85	51.87 (50.43)	3.42 (3.57)	12.96 (12.81)	–
$[C_{14}H_{10}N_3O_2Cl_2]_2Ni$	Red	84	267	47.70 (48.01)	2.86 (2.90)	11.92 (12.06)	8.33 (8.30)
$[C_{14}H_{10}N_3O_2Cl_2]_2Cu$	Dark Brown	78	168	47.37 (47.34)	2.84 (2.78)	11.84 (11.86)	8.95 (8.85)
$[C_{14}H_{10}N_3O_2Cl_2]_2Co.2H_2O$	Dark Brown	87	279	45.37 (45.12)	3.26 (3.04)	11.33 (11.37)	7.95 (7.92)
$C_{15}H_{14}N_3O_2Cl$	Creem	94	109-111	59.31 (59.45)	4.64 (4.25)	13.83 (13.65)	–
$[C_{15}H_{13}N_3O_2Cl]_2Ni$	Red	80	256	54.25 (54.14)	3.94 (3.31)	12.65 (12.40)	8.84 (8.71)
$[C_{15}H_{13}N_3O_2Cl]_2Cu$	Dark Brown	70	195	53.86 (53.36)	3.92 (3.37)	12.56 (12.51)	9.50 (9.44)
$[C_{15}H_{13}N_3O_2Cl]_2Co.2H_2O$	Dark Brown	78	184	51.44 (51.23)	4.32 (4.25)	12.00 (12.22)	8.41 (8.48)
$C_{18}H_{14}N_3O_2Cl$	Brown	86	108-109	63.63 (63.06)	4.15 (4.10)	12.36 (12.30)	–
$[C_{18}H_{13}N_3O_2Cl]_2Ni$	Red	88	227	58.89 (58.51)	3.57 (3.20)	11.44 (11.40)	8.00 (7.93)
$[C_{18}H_{13}N_3O_2Cl]_2Cu$	Dark Brown	80	187	58.50 (58.79)	3.54 (3.43)	11.37 (11.21)	8.60 (8.58)
$[C_{18}H_{13}N_3O_2Cl]_2Co.2H_2O$	Dark Brown	91	214	56.12 (55.73)	3.42 (3.48)	10.91 (10.58)	7.65 (7.60)
$C_{20}H_{17}N_4O_2Cl$	Brown	69	111-113	63.08 (63.36)	4.50 (4.66)	14.71 (14.42)	–
$[C_{20}H_{17}N_4O_2Cl]_2Ni$	Red	88	182	58.70 (58.02)	3.94 (3.74)	13.69 (13.60)	7.17 (7.00)
$[C_{20}H_{17}N_4O_2Cl]_2Cu$	Dark Brown	75	191	58.36 (58.02)	3.92 (3.98)	13.61 (13.44)	7.72 (7.81)
$[C_{20}H_{16}N_4O_2Cl]_2Co.2H_2O$	Dark Brown	87	198	56.21 (55.83)	4.24 (4.01)	13.11 (12.84)	6.89 (6.69)

Table II. ^{1}H-NMR Spectra of the Ligands and $(C_{14}H_{10}Cl_2N_3O_2)_2Ni$ in DMSO-d_6(ppm)Compounds.

Compunds	O-H···O[a]	O-H[a]	O-H[a]	H_{Arom}	N-H[a]	Other
$C_{14}H_{11}N_3O_2Cl_2$	–	12.06 $(1H)^s$	10.42 $(1H)^s$	8.01-6.77 $(8H)^m$	8.24 $(1H)^s$	–
$C_{15}H_{14}N_3O_2Cl$	–	11.95 $(1H)^s$	10.85 $(1H)^s$	7.91-6.78 $(8H)^m$	8.45 $(1H)^s$	2.05(-CH_3) $(3H)^s$
$C_{18}H_{14}N_3O_2Cl$	–	11.97 $(1H)^s$	10.88 $(1H)^s$	8.09-6.93 $(11H)^m$	8.46 $(1H)^s$	–
$C_{20}H_{17}N_4O_2Cl$	–	11.43 $(1H)^s$	10.70 $(1H)^s$	7.77-6.70 $(12H)^m$	8.72 $(1H)^s$	3.80(-NH_2) $(2H)^s$
$[C_{14}H_{10}N_3O_2Cl]_2Ni$	15.30 $(2H)^s$	–	–	7.84-7.05 $(16H)^m$	8.00 $(2H)^s$	–

[a]Disappears on D_2O exchange s: singlet m: multiplet

Table III. Characteristic IR Bands of the Ligands and their Complexesas KBr Pellets (cm^{-1}).

Compunds	N-H ν	O-H ν	C-HArom ν	O-H..O ν	C=N ν	N-O ν	C-Cl ν
$C_{14}H_{11}N_3O_2Cl_2$	3300	3380	3140	–	1630	940	680
$[C_{14}H_{10}N_3O_2Cl_2]_2Ni$	3400	–	3100	1660	1630	940	710
$[C_{14}H_{10}N_3O_2Cl_2]_2Cu$	3440	–	3140	1660	1610	920	710
$[C_{14}H_{10}N_3O_2Cl_2]_2Co.2H_2O$	–	3280 3540	3120	1680	1610	910	710
$C_{15}H_{14}N_3O_2Cl$	3380	3200	2900	–	1630	990	670
$[C_{15}H_{13}N_3O_2Cl]_2Ni$	3360	–	3080	1700	1590	960	690
$[C_{15}H_{13}N_3O_2Cl]_2Cu$	3400	–	3100	1720	1630	930	700
$[C_{15}H_{13}N_3O_2Cl]_2Co.2H_2O$	–	3310 3500	3080	1700	1625	970	690
$C_{18}H_{14}N_3O_2Cl$	3440	3360	2900	–	1610	960	705
$[C_{18}H_{13}N_3O_2Cl]_2Ni$	3460	–	3080	1730	1590	970	700
$[C_{18}H_{13}N_3O_2Cl]_2Cu$	3410	–	3100	1730	1620	950	700
$[C_{18}H_{13}N_3O_2Cl]_2Co.2H_2O$	–	3310 3440	3090	1720	1640	980	705
$C_{20}H_{17}N_4O_2Cl$	3460	3280	2980	–	1630	960	690
$[C_{20}H_{17}N_4O_2Cl]_2Ni$	3460	–	3040	1730	1610	970	720
$[C_{20}H_{17}N_4O_2Cl]_2Cu$	3400	–	3040	1700	1630	960	700
$[C_{20}H_{16}N_4O_2Cl]_2Co.2H_2O$	–	3380 3500	3140	1740	1625	980	680

the higher field (10.88-10.42 ppm) (Table II). 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 higher on the amidoxime group. The deuterium exchangeable -NH protons of the arylamino-p-chlorophenyl-glioximes are observed at 8.45-8.72 ppm, and the methylene protons at 2.05 ppm as singlets. Addition of D_2O causes the disappearence of the -NH peak.

The solubility of the complexes isolated from the four new unsymmetrical ligands is not sufficient to obtain ^{1}H-NMR spectra in solution except for $(C_{14}H_{10}Cl_2N_3O_2)_2Ni$. The proton NMR spectrum of this diamagnetic complex indicates O-H··O bridge formation by the strong shift of the -OH protons to lower field (15.30 ppm) than those of the free ligand[2,4,11].

The proton NMR spectrum of $(C_{14}H_{10}Cl_2N_3O_2)_2Ni$ can be evaluated to determine the isomer formed, since the different chemical environments will show two O-H··O bridge protons in cis-form, but only one trans-structure. The observed spectrum has only one peak at 14.81 ppm confirming the trans-form of the complex (Fig.3).

IR Spectra of Ligands and Complex

In the IR spectra of the ligands, -NH (3460-3300 cm^{-1}), -OH (3380-3200 cm-1), -C=N (1630-1610 cm^{-1}) and -NO (990-940 cm^{-1}) stretches appear at frequencies expected for substituted aminoglyoximes[2-7] (Table III).

The Ni(II), Cu(II) and Co(II) complexes of the four new ligands were prepared in ethanol by the addition of 1% NaOH solution to raise the pH to 4.5-5. The elemental analyses results and characterictic IR absorptions are given in Tables I and II. The metal-ligand ratio in all these complexes is 1:2, but Co(II) complexes have coordinated two additional water molecules for each metal ion. Consequently, an octahedral structure for Co(II) and square planer coordination for Ni(II) and Cu(II) compounds are proposed (Fig.3).

The IR spectra of the complexes support these structures by the weak bending vibration of the O-H··O bridges around 1740-1660 cm^{-1} and the shift of the C=N vibration to lower frequencies (1640-1610 cm^{-1}) due to N,N-metal coordination[2,7,9,10]. In the case of Co(II) complexes, the coordinated H_2O molecules are identified by a broad -OH absorptions around 3280-3540 cm^{-1} which keep their intensities constant after heating at 110°C for 24 h.

Cis-Form M= Ni(II), Cu(II), or $\overset{OH_2}{\underset{OH_2}{Co(II)}}$

Fig.3. Octahedral and square-planer metal complexes of the unsymmetrical ligands.

EXPERIMENTAL

Isonitroso-p-chloroacetophenone and anti-p-chloro-phenyloxime were prepared by reported procedures[9,13-16]. ^{1}H-NMR spectra were recorded on a Varian T 100-A spectrometer. IR spectra were recorded on a Pye Unicam SP 1025 spectrophotometer as KBr pellets. The atomic absorption spectra was recorded on a Varian AA-175, and elemental analyses (C, H and N) were determined using a Carlo-Ebra 1106 model.

Synthesis of anti-p-chlorophenylchloroglyoximes ($C_8H_6Cl_2N_2O_2$)

Dry Cl_2 gas was bubbled through a suspension of anti-p-chlorophenylglyoxime (4.96 g, 0.025 mol) in 35 mL of chloroform under sun light for 1/2 h during which time the color of the suspended material changed into grey. After bubbling of Cl_2 gas was continued for further 2 h under UV-irradiation (254 nm), the temperature of the mixture reached 35°C and crystals formed. The mixture was cooled to room temperature, excess Cl_2 was expelled in vacuum and the solution then filtered and the solid washed with chloroform and then water. Recrystallization in ethanol-water (1:2) gave 4.66 g (80%) product, m.p. 134-5°C.

This compound is soluble in ethanol, DMSO, DMF and diethyl ether and insoluble in water.

Synthesis of Substituted Amino-p-chlorophenylglyoximes

To a stirred solution of anti-$C_8H_6Cl_2N_2O_2$ (2.330 g, 0.01 mol) in absolute ethanol (35 mL) between -10°C and-15°C was added dropwise the solution of 0.01mol freshly distilled amine compound [p-chloroaniline (1.275 g), o-toluidine (1.1 mL), 1-naphthylamine (1.43 g), benzidine (1.84 g)] in absolute ethanol (30 mL) in 30 min. The reaction

mixture was further stirred for 2 h and then diluted with 120 mL water and left overnight at 5°C. The precipitate was filtred and then 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

When a solution of 0.5 mmol metal salt [$NiCl_2.6H_2O$ (0.119 g), $CuCl_2.2H_2O$ (0.086 g) and $CoCl_2.6H_2O$ (0.119 g)] in 20 mL absolute ethanol was added into a solution of the ligand (1 mmol) [$C_{14}H_{11}Cl_2N_3O_2$ (0.324 g), $C_{15}H_{14}ClN_3O_2$ (0.303 g, $C_{18}H_{14}ClN_3O_2$ (0.340 g), $C_{20}H_{17}ClN_4O_2$ (0.380 g)] dissolved in 20 mL of ethanol, the pH of the mixture dropped to 3.0-3.5 and its color turned to red-brown. After addition of a 1% NaOH solution in ethanol to raise the pH to 4.5, the mixture was stirred on a water bath at 50-55°C for 15 min. The precipitated complexes were filtered while hot, washed with water, ethanol and diethyl ether and dried at 100°C. The colors, yields and melting point of the compounds are given in Table I.

REFERENCES

1. A.Chakravorty, Coord. Chem. Rev.,13, 1 (1974).
2. A.Gül and Ö.Bekaroğlu, J.Chem.Soc. Dalton Trans., 2537 (1983).
3. Y.Gök and Ö. Bekaroğlu, Synth. React. Inorg. Met.-Org. Chem., 11, 621 (1981).
4. V.Ahsen, F. Gökçeli, and Ö Bekaroğlu, J. Chem. Soc. Dalton Trans., 1827 (1987).
5. E. Özcan and R. Mirzaoğlu, Synth. React. Inorg. Met.-Org. Chem., 18, 559 (1988).
6. G. İrez and Ö. Bekaroğlu, Synth. React. Inorg. Met.-Org. Chem., 13, 781 (1983).
7. M. Koçak and Ö. Bekaroğlu, Synth. React. Inorg. Met.-Org. Chem.,15, 479 (1985).
8. G. N. Schrauzer and J. Kohnle, Chem. Ber., 97, 3056 (1964).
9. J.V. Buracevich, A.M. Lore and G.P. Volpp, J. Org. Chem., 36, 1 (1971).
10. A. Gül and Ö. Bekaroğlu, Synth. React. Inorg. Met.-Org. Chem., 12, 889 (1982).
11. A. Nakamura, A. Konishi and S. Otsuka, J. Chem. Soc. Dalton Trans., 488 (1979).
12. M.S., M.A., and R.J. Angeici, Inorg. Chem., 19, 363 (1980).
13. J.J. Norman, R.M. Heggie and J.B. Larose, Can. J. Chem., 40, 1547 (1962).

14. H.İ. Uçan and R. Mirzaoğlu, Synth. React. Inorg. Met-Org. Chem., 20, 437 (1990).

15. H.C. Sevindir and R. Mirzaoğlu, Synth. React. Inorg. Met-Org. Chem., 22, 851 (1992).

16. A.İ. Pekacar and E. Özcan, Macromolecular Reports, A31(suppl.5), 651-661 (1994).