

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

The Synthesis of New *bis*(Amino-p-nitro-phenylglyoximes) and Their Polymeric Complexes with Cu(II), Ni(II), and Co(II)

H. Cahit Sevndr^a

^a Department of Environmental Engineering Faculty of Engineering, Süleyman Demirel University, Isparta, Turkey

To cite this Article Sevndr, H. Cahit(1995) 'The Synthesis of New *bis*(Amino-p-nitro-phenylglyoximes) and Their Polymeric Complexes with Cu(II), Ni(II), and Co(II)', *Journal of Macromolecular Science, Part A*, 32: 1, 1227 — 1235

To link to this Article: DOI: 10.1080/10601329508020344

URL: <http://dx.doi.org/10.1080/10601329508020344>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

THE SYNTHESIS OF NEW *BIS*(AMINO-*p*-NITRO-PHENYLGLYOXIMES) AND THEIR POLYMERIC COMPLEXES WITH Cu(II), Ni(II), AND Co(II)

H. Cahit SEVİNDİR

Department of Environmental Engineering, Faculty of Engineering
Süleyman Demirel University, Isparta, TURKEY

ABSTRACT

In this study, five new bis(amino-*p*-nitrophenylglyoximes), 1,4-phenylene bis(amino-*p*-nitrophenylglyoxime), 1,1'-biphenyl-4,4'-bis(amino-*p*-nitrophenylglyoxime), 1,1'-diphenyloxy-4,4'-bis(amino-*p*-nitrophenylglyoxime), 1,1'-diphenylmethene-4,4'-bis(amino-*p*-nitrophenylglyoxime) and 1,1'-diphenylethylene-4,4'-bis(amino-*p*-nitrophenylglyoxime) have been synthesized from anti-*p*-nitrochlorophenylglyoxime and the corresponding aromatic diamines. Their polymeric complexes with Cu(II), Ni(II) and Co(II) have been obtained. The Cu(II) and Ni(II) complexes of these ligands are square-planar while the Co(II) complexes are octahedral with water molecules as axial ligands. ¹H-NMR, IR and elemental analyses data of the complexes and ligands are given

INTRODUCTION

The transition metal complexes of 1,2-dioximes have been of particular interest as biological model compound¹⁻³. The synthesis of substituted aminoglyoximes from anti-chloroglyoxime or anti-*p*-tolylchloroglyoxime and the corresponding amines was also reported¹⁻⁶. In these compounds, the two oxime groups are no longer equivalent.

Additional substituents on the aromatic group bound to the N-atom of aminoglyoxime are expected to enhance the difference between the two oxime groups.

In the present paper, we report the synthesis of polymeric complex from five new bis(amino-p-nitrophenylglyoximes) as examples of unsymmetrically substituted 1,2-dioximes.

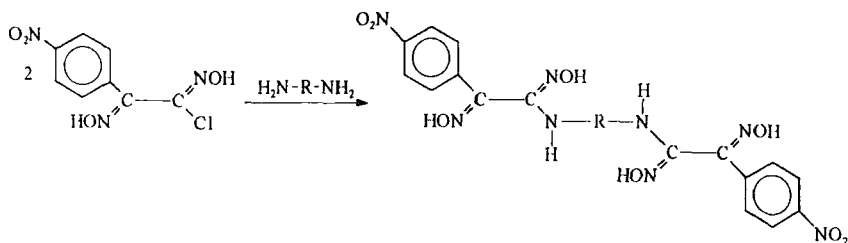
RESULTS AND DISCUSSION

In this study, five new bis(amino-p-nitrophenylglyoximes) were synthesized from the reaction of anti-p-nitrochlorophenylglyoxime and the corresponding aromatic diamines in ethanol at -15°C . General formulas of these are as shown in (Fig. 1). The structures of the new ligands have been verified by elemental analyses, and by $^1\text{H-NMR}$, IR spectral data as shown in Tables I, II and III.

In the $^1\text{H-NMR}$ spectra, two peaks are present for the OH protons of the oxime groups. When the chemical shift values of the two OH protons are compared in the five different ligands, the ones at lower field quite closely resemble each other (11.78-11.62 ppm) while a considerable difference is observed for the one at the higher field (10.60-10.40 ppm) (Table II). The chemical shift for OH protons have a characteristic value for these types of oximes^{7,8}. The 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^{4,9}. The deuterium-exchangeable NH protons, neighbouring the oxime groups, and the C-H protons are observed at 8.20-7.88 ppm and 7.55-6.55 ppm respectively⁷⁻¹⁰. The chemical shift values of the $-\text{CH}_2$ protons appear at 2.68-2.51 ppm.

In the IR spectra of the ligands (Table III), NH ($3420\text{-}3375\text{ cm}^{-1}$), OH ($3270\text{-}3150\text{ cm}^{-1}$), C=N ($1670\text{-}1640\text{ cm}^{-1}$) and NO ($970\text{-}950\text{ cm}^{-1}$) stretches appear at frequencies expected for substituted bis(amino-p-nitrophenylglyoximes)^{4,11-13}.

The Cu(II), Ni(II) and Co(II) complexes of the five new ligands were prepared in ethanol by the addition of the 1 % NaOH solution to raise the pH 4.5-5.0. The complexes were characterized by IR and elemental analyses and the data in shown Tables IV and V. Since the solubilities of the complexes in the organic solvents are very low, $^1\text{H-NMR}$ spectra could not be taken. The metal-ligand ratios in all these polymeric complexes are 1:1, but Co(II) complexes also have, two coordinated water molecules for each complex. Consequently, an octahedral structure for Co(II) and square-planar coordination for Ni(II) and Cu(II) compounds are proposed⁴ (Fig. 2).



$$\text{R: } 1,4\text{-C}_6\text{H}_4\text{-}, 4,4'\text{-C}_6\text{H}_4\text{-C}_6\text{H}_4\text{-}, 4,4'\text{-C}_6\text{H}_4\text{-O-C}_6\text{H}_4\text{-}$$

$$4,4'\text{-C}_6\text{H}_4\text{-CH}_2\text{-C}_6\text{H}_4\text{-}, 4,4'\text{-C}_6\text{H}_4\text{-CH}_2\text{CH}_2\text{-C}_6\text{H}_4\text{-}$$

Fig. 1. General formulas of ligands

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

Compounds	Color	Yield (%)	m.p°C (d.p)	Calcd.(found) %		
				C	H	N
$\text{C}_{22}\text{H}_{18}\text{N}_8\text{O}_8$	pale yellow	75	(177)	50.58 (50.60)	3.47 (3.49)	21.45 (21.41)
$\text{C}_{28}\text{H}_{22}\text{N}_8\text{O}_8$	white	80	(185)	56.19 (56.23)	3.70 (3.71)	18.72 (18.70)
$\text{C}_{28}\text{H}_{22}\text{N}_8\text{O}_9$	pale yellow	79	(165)	54.73 (54.74)	3.61 (3.60)	18.23 (18.25)
$\text{C}_{29}\text{H}_{24}\text{N}_8\text{O}_8$	pale yellow	84	(170)	56.86 (56.86)	3.95 (3.96)	18.29 (18.29)
$\text{C}_{30}\text{H}_{26}\text{N}_8\text{O}_8$	pale yellow	80	(180)	57.51 (57.52)	4.18 (4.20)	17.88 (17.88)

Table II. ¹H-NMR Data for the Ligands in DMSO-d₆ δ (ppm)

Compounds	O-H ^a	O-H ^a	N-H ^a	H(arom.)	-CH ₂ -
C ₂₂ H ₁₈ N ₈ O ₈	11.78 (2H,s)	10.60 (2H,s)	7.88 (2H,s)	7.50-6.75 (12H,m)	-
C ₂₈ H ₂₂ N ₈ O ₈	11.65 (2H,s)	10.55 (2H,s)	8.20 (2H,s)	7.55-6.90 (16H,m)	-
C ₂₈ H ₂₂ N ₈ O ₉	11.75 (2H,s)	10.40 (2H,s)	8.23 (2H,s)	7.50-6.55 (16H,m)	-
C ₂₉ H ₂₄ N ₈ O ₈	11.62 (2H,s)	10.50 (2H,s)	8.10 (2H,s)	7.50-6.75 (16H,m)	2.53 (2H,s)
C ₃₀ H ₂₆ N ₈ O ₈	11.65 (2H,s)	10.45 (2H,s)	8.14 (2H,s)	7.53-6.77 (16H,m)	2.68-2.51 (4H,m)

^aDisappears on D₂O exchange
s: singlet m: multiplet

Table III. Characteristic IR Bands of the Ligands as KBr Pellets (cm⁻¹)

Compounds	N-H ν	O-H ν	C-H (arom.)	C-H (aliph.)	C=N	N-O
C ₂₂ H ₁₈ N ₈ O ₈	3375	3150	3040	-	1650	950
C ₂₈ H ₂₂ N ₈ O ₈	3390	3250	3060	-	1640	960
C ₂₈ H ₂₂ N ₈ O ₉	3400	3270	3040	-	1660	960
C ₂₉ H ₂₄ N ₈ O ₈	3420	3210	3000	2980	1670	970
C ₃₀ H ₂₆ N ₈ O ₈	3410	3200	3030	2970	1660	970

In the IR spectra of the complexes, the shifts of C=N stretching frequency to lower frequency and vibration corresponding to the N-O band to higher frequency indicate to formation of the coordination bond between metal and the nitrogen the coordinated H₂O groups are identified by broad OH absorptions around 3580-3310 cm⁻¹ which keep their intensities even after heating at 110°C for 24 h.

EXPERIMENTAL

Solvents and reagents were purified by drying over suitable dehydrating agents followed by distillation. IR spectra were obtained using apye-Unicam SP 1025

Table IV. The Colors, Melting Points, Yields, and Elemental Analytical Results of the Complexes.

Compounds	Color	Yield %	Calcd. (Found) %		
			C	H	N
$(C_{22}H_{18}N_8O_8Ni)_n$	maroon	90	45.47 (45.49)	3.12 (3.15)	19.28 (19.27)
$(C_{22}H_{18}N_8O_8Cu)_n$	dark brown	85	45.09 (45.12)	3.10 (3.10)	19.12 (19.13)
$(C_{22}H_{18}N_8O_8Co2H_2O)_n$	brown	90	42.80 (42.84)	3.59 (3.61)	18.15 (18.14)
$(C_{28}H_{22}N_8O_8Ni)_n$	maroon	95	51.17 (51.20)	3.37 (3.41)	17.05 (17.05)
$(C_{28}H_{22}N_8O_8Cu)_n$	dark brown	90	50.80 (50.82)	3.35 (3.37)	16.92 (16.90)
$(C_{28}H_{22}N_8O_8Co2H_2O)_n$	brown	85	48.49 (48.50)	3.78 (3.81)	16.16 (16.17)
$(C_{28}H_{22}N_8O_9Ni)_n$	maroon	75	49.96 (49.99)	3.29 (3.82)	16.64 (16.65)
$(C_{28}H_{22}N_8O_9Cu)_n$	dark brown	80	49.60 (49.60)	3.27 (3.29)	16.53 (16.54)
$(C_{28}H_{22}N_8O_9Co2H_2O)_n$	brown	85	47.40 (47.42)	3.69 (3.70)	15.79 (15.81)
$(C_{29}H_{24}N_8O_8Ni)_n$	maroon	90	51.89 (51.90)	3.60 (3.60)	16.69 (16.71)
$(C_{29}H_{24}N_8O_8Cu)_n$	dark brown	90	51.52 (51.54)	3.58 (3.61)	16.57 (16.57)
$(C_{29}H_{24}N_8O_8Co2H_2O)_n$	brown	86	49.23 (49.22)	3.99 (3.40)	15.84 (16.58)
$(C_{30}H_{26}N_8O_8Ni)_n$	maroon	82	52.58 (52.60)	3.82 (3.91)	16.35 (16.37)
$(C_{30}H_{26}N_8O_8Cu)_n$	dark brown	90	52.21 (52.22)	3.80 (3.80)	16.24 (16.25)
$(C_{30}H_{26}N_8O_8Co2H_2O)_n$	brown	94	49.62 (49.62)	4.16 (4.18)	15.43 (15.42)

Melting points of all the compounds are above 360°C

Table V. Characteristic IR Band of the Complexes as KBr pellets (cm⁻¹)

Compounds	N-H γ	O-H γ	CH (arom)	CH (aliph)	O- H.O	C=N	N-O
(C ₂₂ H ₁₈ N ₈ O ₈ Ni) _n	3370	-	3030	-	1710	1620	1000
(C ₂₂ H ₁₈ N ₈ O ₈ Cu) _n	3380	-	3010	-	1720	1620	1010
(C ₂₂ H ₁₈ N ₈ O ₈ Co2H ₂ O) _n	-	3480 3320	3070	-	1710	1610	960
(C ₂₈ H ₂₂ N ₈ O ₈ Ni) _n	3370	-	3020	-	1720	1630	960
(C ₂₈ H ₂₂ N ₈ O ₈ Cu) _n	3370	-	3000	-	1715	1620	980
(C ₂₈ H ₂₂ N ₈ O ₈ Co2H ₂ O) _n	-	3500 3310	3040	-	1710	1620	960
(C ₂₈ H ₂₂ N ₈ O ₉ Ni) _n	3340	-	3080	-	1715	1650	990
(C ₂₈ H ₂₂ N ₈ O ₉ Cu) _n	3350	-	3060	-	1710	1630	1000
(C ₂₈ H ₂₂ N ₈ O ₉ Co2H ₂ O) _n	-	3510 3350	3030	-	1720	1640	960
(C ₂₉ H ₂₄ N ₈ O ₈ Ni) _n	3370	-	3070	2960	1715	1650	970
(C ₂₉ H ₂₄ N ₈ O ₈ Cu) _n	3380	-	3010	2980	1720	1640	960
(C ₂₉ H ₂₄ N ₈ O ₈ Co2H ₂ O) _n	-	3500 3340	3020	2940	1720	1630	870
(C ₃₀ H ₂₆ N ₈ O ₈ Ni) _n	3360	-	3040	2970	1710	1620	990
(C ₃₀ H ₂₆ N ₈ O ₈ Cu) _n	3400	-	3040	2950	1710	1620	960
(C ₃₀ H ₂₆ N ₈ O ₈ Co2H ₂ O) _n	-	3580 3340	3020	2950	1715	1610	970

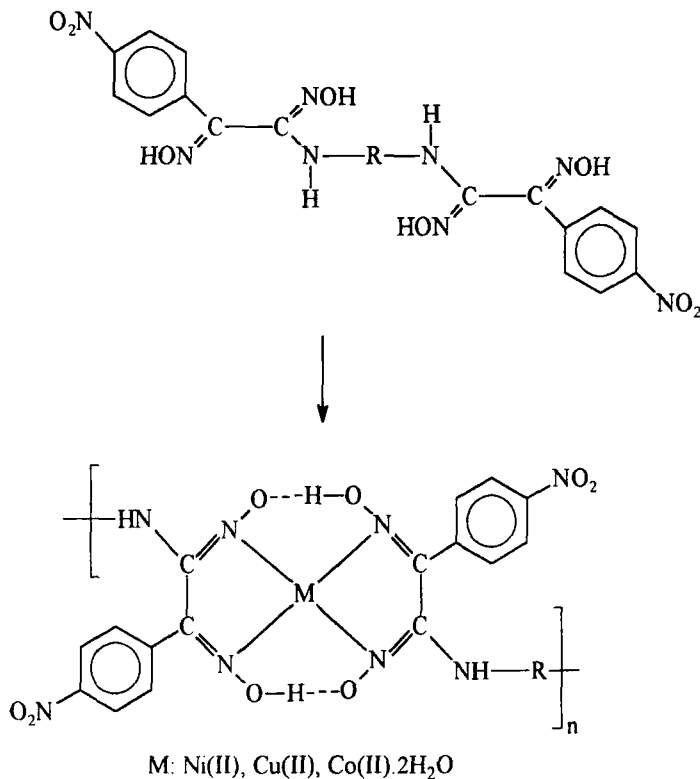


Fig. 2. Octahedral and square-planar polymeric metal complexes of the bis(amino-p-nitrophenylglyoximes).

spectrophotometer with KBr pellets. ¹H-NMR spectra were recorded on a Varian T 100-A spectrometer with deuterium dimethyl sulphoxide as solvent and TMS as internal reference. Elemental analyses (C, H and N) were determined using a Carlo-Ebra 1106 model.

A. Synthesis of Substituted bis(amino-p-nitrophenylglyoximes)

In this study, 1,4-phenylene bis(amino-p-nitrophenylglyoxime), 1,1'-biphenyl-4,4'-bis(amino-p-nitrophenylglyoxime), 1,1'-diphenyloxy-4,4'-bis(amino-p-nitrophenyl-glyoxime), 1,1'-diphenylmethene-4,4'-bis(amino-p-nitrophenylglyoxime)

and 1,1'-diphenylethylene-4,4'-bis(amino-p-nitrophenylglyoxime) have been synthesized from anti-p-nitrochlorophenylglyoxime and the corresponding aromatic diamines. anti-p-nitrochlorophenylglyoxime has been prepared according to the literature¹⁻⁶.

To a stirred solution of 4.16g (0.02 mol) of anti-p-nitrochlorophenylglyoxime in 75 mL absolute ethanol at -15°C was added dropwise over a 30 minute period a solution of 0.01 mol of the appropriate aromatic diamine compound [1,4-phenylenediamine (1.08 g), benzidine (1.84 g), 4,4'-diaminodiphenylether (2.00 g), 4,4'-diaminophenylmethane (1.98 g) or 4,4'-diaminobibenzyl (2.12 g)] in 40 mL absolute ethanol. The reaction mixture was further stirred for 2-3 h, left overnight at 0°C and then diluted with 100-120 mL water. The precipitate which formed was filtered then recrystallized from ethanol-water (1:1). The crystalline product was filtered, washed with water and dried in a vacuum oven.

The ligands are soluble in ethanol, DMF, DMSO and slightly soluble in acetone and insoluble in water.

The color, yield, melting point, elemental analyses, ¹H-NMR and IR data of these ligands are given in Tables I, II and III.

B. Synthesis of Cu(II), Ni(II) and Co(II) Complexes

When a solution of 1 mmol metal salt [$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.238 g), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.172 g) or $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.238 g)] in 30 mL of water-ethanol (2:1) was added to a solution of 1 mmol of the ligand [$\text{C}_{22}\text{H}_{18}\text{N}_8\text{O}_8$ (0.522 g), $\text{C}_{28}\text{H}_{22}\text{N}_8\text{O}_8$ (0.598 g), $\text{C}_{28}\text{H}_{22}\text{N}_8\text{O}_9$ (0.614 g), $\text{C}_{29}\text{H}_{24}\text{N}_8\text{O}_8$ (0.612 g) or $\text{C}_{30}\text{H}_{26}\text{N}_8\text{O}_8$ (0.626 g)] dissolved in 50 mL absolute ethanol, the pH of the mixture dropped to 3-3,5 and its color turned to red-brown or dark-brown. After addition of 1 % NaOH solution in ethanol-water(1.1) to raise the pH to for min. The precipitated complex was filtered while hot, washed with water, ethanol and the diethyl ether and dried in vacuum oven. The colors, yields, melting points, elemental analytical results and IR data of the compounds are given in tables IV and V.

REFERENCES

1. G. N. Schrauzer and J. Kohnle, *Chem. Ber.*, **97**, 3016 (1964).
2. G. N. Schrauzer and R. J. Windgassen, *J. Am. Chem. Soc.*, **89**, 143 (1967).
3. A. Chakravorty, *Coord. Chem. Rev.*, **13**, 1 (1974).

4. H. Cahit Sevindir, E. Özcan and R. Mirzaoğlu, *Synth. React. Inorg. Met.-Org. Chem.*, **22**, 1581 (1992).
5. Emine Özcan and R. Mirzaoğlu, *Synth. React. Inorg. Met.-Org. Chem.*, **18**, 559 (1988).
6. J. V. Burakevich, A. M. Lore and G. P. Volpp, *J. Org. Chem.*, **36**, 1 (1971)
7. H. Cahit Sevindir and R. Mirzaoğlu, *Macromolecular Reports*, A31(Suppl.3&4), 399 (1994).
8. H. E. Ungnade, L. W. Kissenger, A. Narath and D. C. Barham, *J. Org. Chem.*, **28**, 143 (1963).
9. A. Gül and Ö. Bekaroğlu, *J. Chem. soc. Dalton Trans.*, 2537 (1983).
10. F. A. Bovey, "NMR Data Tables for Organic Compounds", Vol.I, p.168, John-Wiley Interscience, 1967.
11. M. E. B. Jones, D. A. Thornton and R. F. Webb, *Macromol. Chem.*, **49**, 6981 (1961).
12. H. Cahit Sevindir, *Synth. React. Inorg. Met.-Org. Chem.*, **24**, 953 (1994).
13. A. Nakamura, A. Konishi and S. Otsuka, *J. Chem. Soc. Dalton Trans.*, 488 (1979).