



Synthesis and Characterization of a New Triazene Complexes for Cu(II), Ni(II), Co(II), Zn(II) and Fe(II)

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

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ABSTRACT

A new series of complexes containing Triazene compound was prepared, Triazene compound was prepared by the diazotization of *o*-toluidine then reacting with piperidine to give the corresponding triazene compound (1-(*o*-tolyl diazenyl)piperidine). The complexes $M[(2-CH_3-C_6H_3-N=N)-N-C_5H_{10}]_2X_2^-$ of Cu(II), Ni(II), Co(II), Zn(II) and Fe(II) with triazene compound (1-(*o*-tolyl diazenyl)piperidine) has been synthesized by the reacting between copper bromide, hydrate nickel chloride, hydrate cobalt chloride, zinc chloride, and iron bromide in 1:2 mole ratio. It has been isolated in the solid state and characterized by (C.H.N) data, IR and ¹H NMR spectroscopy. Six coordinate and octahedral complexes were produced and the results are reported and discussed below.

Keywords: Triazene; complexes; metal complexes; diazenyl; azo-group.

1. INTRODUCTION

Triazenes are a class of organic compounds that containing diazoamino functional group (N=N-N) in composition [1a]. This kind of compounds is known as just triazene. The coordination

properties of the triazene ligand with aryl groups as 1,3-substituents (Ar-N=N-NH-Ar) have been intensely studied during the past years. Coordination was found to be *N*1-monodentate, *N*1,*N*3-chelating and *N*1,*N*3-bridging ligand. These compounds have been

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used in a variety of ways, ranging from transition metal complexes and polymer synthesis to anticancer drugs [1b]. The chemistry of triazene compounds have been the subject of increasing attention in recent years, because of their diverse synthetic applications; [2-4] Moreover, they have been widely applied to obtain triazenido complexes with a large range of metals [2-5]. Thus, the present study will describe the synthesis and characterization of new types of complexes containing of triazenes groups.

2. EXPERIMENTAL

2.1 Chemicals and Apparatus

Chemicals obtained from Sigma-Aldrich, Fluka and BDH used without purification. Melting point was determined by using open capillary tube melting point apparatus. ^1H NMR spectra was recorded on Bruker 300 MHz spectrometers with TMS as an internal reference using DMSO-d_6 solvent. Infra-red spectra were recorded with KBr disks using a FTIR spectrophotometer Shimadzu model 8400 S in range $4000\text{-}400\text{ cm}^{-1}$. Elemental analysis for Carbon, Hydrogen and Nitrogen were performed by using a Euro vector EA 3000A Elemental Analysis (Italy). Melting points of all solid compounds were determined using a MPS10 electrically heated melting point apparatus.

2.2 Synthesis

(1-(*o*-tolyl diazenyl)piperidine) was prepared as described in literature [6-8]. The complexes of triazole ligand by 1:3 mole ratio were prepared by the following general method:

A hot solution of the ligand of 1-(*o*-tolyl diazenyl)piperidine (**otdpip**) (1.5 mmol) in absolute ethanol (10 ml) was prepared and then CuBr_2 , $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, ZnCl_2 and FeBr_2 (0.5 mmol) in absolute ethanol (10 mL) was added to the hot solution of triazole ligand. The mixture of ligand and metal halide were refluxed for 3 hrs. The product colored solution was left standing at room temperature to crystallize. The product was filtered to obtain precipitate washed with cooled absolute ethanol. Recrystallized from (1:1) water and methanol then dried. The analytical and physical data of the complexes are:

2.2.1 $\text{Cu}[(2\text{-CH}_3\text{-C}_6\text{H}_3\text{-N=N)-N-C}_5\text{H}_{10}]_2\text{Br}_2$

Empirical formula: $\text{C}_{24}\text{H}_{34}\text{CuBr}_2\text{N}_6$; formula weight: 629.92 gmol^{-1} ; yield: 85%; appearance:

brown crystals; m.p. = $95\text{-}97^\circ\text{C}$; Elem. analysis: calc. C, 45.76%; H, 5.44%; N, 13.34%; found: C, 45.67%; H, 5.12%; N, 13.20%; FTIR: $3075\text{-}3050\text{ cm}^{-1}$ $\nu(\text{C-H})$ aromatic, 2825 cm^{-1} $\nu(\text{C-H})$ aliphatic, 1020 cm^{-1} $\nu(\text{C-N})$ aliphatic, 1280 cm^{-1} $\nu(\text{C-N})$ aromatic, 1481 cm^{-1} $\nu(\text{C=C})$ aromatic, 1449 cm^{-1} $\nu(\text{N=N})$. ^1H NMR (ppm): 6.23- 7.10 (m, 8H, aromatic), 2.33 (s, 6H, *o*- CH_3), 3.21 (t, 8H, N- CH_2 aliphatic), 1.50-1.55 (m, 12H, ($-\text{CH}_2$) $_3$ aliphatic).

2.2.2 $\text{Fe}[(2\text{-CH}_3\text{-C}_6\text{H}_3\text{-N=N)-N-C}_5\text{H}_{10}]_2\text{Br}_2$

Empirical formula: $\text{C}_{24}\text{H}_{34}\text{FeBr}_2\text{N}_6$; formula weight: 622.22 gmol^{-1} ; yield: 76%; appearance: yellowish brown crystals; m.p. = $101\text{-}103^\circ\text{C}$; Elem. analysis: calc. C, 46.33%; H, 5.51%; N, 13.51%; found: C, 46.20%; H, 5.40%; N, 13.43%; FTIR: $3071\text{-}3052\text{ cm}^{-1}$ $\nu(\text{C-H})$ aromatic, 2835 cm^{-1} $\nu(\text{C-H})$ aliphatic, 1021 cm^{-1} $\nu(\text{C-N})$ aliphatic, 1283 cm^{-1} $\nu(\text{C-N})$ aromatic, 1485 cm^{-1} $\nu(\text{C=C})$ aromatic, 1445 cm^{-1} $\nu(\text{N=N})$. ^1H NMR (ppm): 6.63- 7.22 (m, 8H, aromatic), 2.31 (s, 6H, *o*- CH_3), 3.20 (t, 8H, N- CH_2 aliphatic), 1.52-1.57 (m, 12H, ($-\text{CH}_2$) $_3$ aliphatic).

2.2.3 $\text{Ni}[(2\text{-CH}_3\text{-C}_6\text{H}_3\text{-N=N)-N-C}_5\text{H}_{10}]_2\text{Cl}_2$

Empirical formula: $\text{C}_{24}\text{H}_{34}\text{NiCl}_2\text{N}_6$; formula weight: 536.41 gmol^{-1} ; yield: 82%; appearance: reddish - brown crystals; m.p. = $141\text{-}143^\circ\text{C}$; Elem. analysis: calc. C, 53.76%; H, 6.39%; N, 15.76%; found: C, 53.56%; H, 6.13%; N, 15.52%; FTIR: $3069\text{-}3052\text{ cm}^{-1}$ $\nu(\text{C-H})$ aromatic, 2835 cm^{-1} $\nu(\text{C-H})$ aliphatic, 1021 cm^{-1} $\nu(\text{C-N})$ aliphatic, 1295 cm^{-1} $\nu(\text{C-N})$ aromatic, 1450 cm^{-1} $\nu(\text{C=C})$ aromatic, 1433 cm^{-1} $\nu(\text{N=N})$. ^1H NMR (ppm): 6.77- 7.20 (m, 8H, aromatic), 2.31 (s, 6H, *o*- CH_3), 3.20 (t, 8H, N- CH_2 aliphatic), 1.53-1.56 (m, 12H, ($-\text{CH}_2$) $_3$ aliphatic).

2.2.4 $\text{Co}[(2\text{-CH}_3\text{-C}_6\text{H}_3\text{-N=N)-N-C}_5\text{H}_{10}]_2\text{Cl}_2$

Empirical formula: $\text{C}_{24}\text{H}_{34}\text{CoCl}_2\text{N}_6$; formula weight: 536.17 gmol^{-1} ; yield: 88%; appearance: brown crystals; m.p. = $155\text{-}157^\circ\text{C}$; Elem. analysis: calc. C, 53.74%; H, 6.39%; N, 15.67%; found: C, 53.71%; H, 6.12%; N, 15.43%; FTIR: $3077\text{-}3052\text{ cm}^{-1}$ $\nu(\text{C-H})$ aromatic, 2835 cm^{-1} $\nu(\text{C-H})$ aliphatic, 1025 cm^{-1} $\nu(\text{C-N})$ aliphatic, 1283 cm^{-1} $\nu(\text{C-N})$ aromatic, 1485 cm^{-1} $\nu(\text{C=C})$ aromatic, 1449 cm^{-1} $\nu(\text{N=N})$. ^1H NMR (ppm): 6.72- 7.55 (m, 8H, aromatic), 2.34 (s, 6H, *o*- CH_3), 3.20 (t, 8H, N- CH_2 aliphatic), 1.51-1.55 (m, 12H, ($-\text{CH}_2$) $_3$ aliphatic).

2.2.5 $\text{Zn}[(2\text{-CH}_3\text{-C}_6\text{H}_3\text{-N=N)-N-C}_5\text{H}_{10}]_2\text{Cl}_2$

Empirical formula: $\text{C}_{24}\text{H}_{34}\text{ZnCl}_2\text{N}_6$; formula weight: 542.85 gmol^{-1} ; yield: 75%; appearance:

yellowish brown crystals; m.p. = 130-132°C; Elem. analysis: calc. C, 53.10%; H, 6.31%; N, 15.48%; found: C, 52.93%; H, 6.12%; N, 15.33%; FTIR: 3095-3088 cm^{-1} $\nu(\text{C-H})$ aromatic, 2825 cm^{-1} $\nu(\text{C-H})$ aliphatic, 1025 cm^{-1} $\nu(\text{C-N})$ aliphatic, 1284 cm^{-1} $\nu(\text{C-N})$ aromatic, 1481 cm^{-1} $\nu(\text{C=C})$ aromatic, 1444 cm^{-1} $\nu(\text{N=N})$. $^1\text{H NMR}$ (ppm): 6.77- 7.20 (m, 8H, aromatic), 2.31 (s, 6H, *o*-CH₃), 3.25 (t, 8H, N-CH₂ aliphatic), 1.53-1.59 (m, 12H, (-CH₂)₃ aliphatic).

3. RESULTS AND DISCUSSION

Triazene compound 1-(*o*-tolylidiazanyl)piperidine was prepared by diazotization of *o*-toluidine and piperidine based on literature with minor modification [6-8], To obtain the corresponding triazene, [Scheme 1].

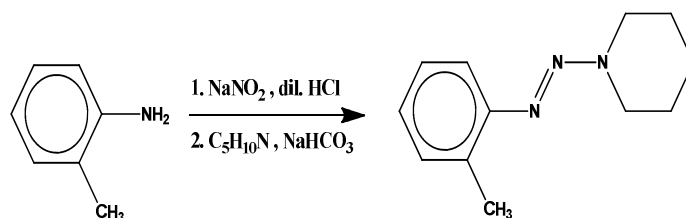
The complexes were prepared at 1:2 molar ratio and obtained in pure form. Reactions of (Cu-, Fe-, Ni-, Co- and Zn- halides) with ligand [1-(*o*-tolylidiazanyl)piperidine] (**otdpip**) in 1:2 molar ratio in ethanol are represented in Scheme 2.

The complexes are air- stable, insoluble in water, partly soluble in ethanol and soluble in DMSO and DMF, non hygroscopic and colored solids crystals. The elemental analysis data (CHN) of

ligands and all their complexes are in a good agreement with the calculated values as shown in Table 1.

The IR spectra of the complexes synthesized are shows two strong bands appeared at range (1020-1025) cm^{-1} and (1280-1295) cm^{-1} due to stretching aliphatic (C-N) and aromatic (C-N) respectively [9,10] The IR spectra of compounds 1-5 showed a strong band in range (1433-1449) cm^{-1} can be attributed to (N=N) bond [9,10]. The sharp band of medium intensity occurred at range (1450-1485) cm^{-1} is attributed to (C=C) aromatic. All the IR data suggest that the metal was bonded to the ligand through the azo - groups in triazole. As shown in Table 2.

$^1\text{H NMR}$ spectra of compounds 1-5 were recorded in DMSO-*d*₆ and shows in Table 3. The $^1\text{H NMR}$ spectrum of compounds shows a multiple broad signal at the range 6.23-7.55 ppm can be assigned to protons in aromatic ring of phenyl groups. The protons in N-(CH₂)₂ can be obtained at range (3.20-3.25) ppm as triplet signal, also a singlet signal can be appeared at range (2.31-2.34) ppm due to *o*-methyl group in triazene [9-13]. The protons in (-CH₂)₃ can be appeared at the range (1.50 – 1.59) ppm as a multiple signal, [9,11-15].

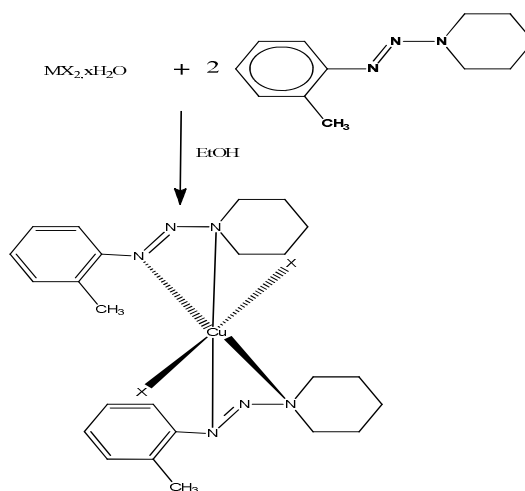


Scheme 1. Preparative methods for 1-(*o*-tolylidiazanyl)piperidine

Table 1. Physical and analytical data for compounds 1-5

Comp.	Color	Melting point (°C)	Analysis (%) ^a			Yield %
			C	H	N	
C ₂₄ H ₃₄ CuBr ₂ N ₆ (1)	Brown	95-97	45.76 (45.67)	5.44 (5.12)	13.34 (13.20)	85
C ₂₄ H ₃₄ FeBr ₂ N ₆ (2)	yellowish brown	101-103	46.33 (46.20)	5.51 (5.40)	13.51 (13.43)	76
C ₂₄ H ₃₄ NiCl ₂ N ₆ (3)	reddish - brown	141-143	53.76 (53.56)	6.39 (6.13)	15.76 (15.52)	82
C ₂₄ H ₃₄ CoCl ₂ N ₆ (4)	brown	155-157	53.74 (53.71)	6.39 (6.12)	15.67 (15.43)	88
C ₂₄ H ₃₄ ZnCl ₂ N ₆ (5)	yellowish brown	130-132	53.10 (52.93)	6.31 (6.12)	15.48 (15.33)	75

^a calculated values are in parentheses



Where $MX_2 \cdot xH_2O = CuBr_2; NiCl_2 \cdot 6H_2O; ZnCl_2; CoCl_2 \cdot 6H_2O$ or $FeBr_2$

Scheme 2. Preparative methods for complexes (1:2) molar ratio

Table 2. IR Spectroscopic data for Ligand and compounds 1-10

Ligand/ complexes IR (cm^{-1})	λ_{max} in nm (ϵ in $M^{-1}cm^{-1}$)
$C_{24}H_{34}CuBr_2N_6$ (1)	3075-3050 cm^{-1} v(C-H) aromatic, 2825 cm^{-1} v(C-H) aliphatic, 1020 cm^{-1} v(C-N) aliphatic, 1280 cm^{-1} v(C-N) aromatic, 1481 cm^{-1} v(C=C) aromatic, 1449 cm^{-1} v(N=N).
$C_{24}H_{34}FeBr_2N_6$ (2)	3071-3052 cm^{-1} v(C-H) aromatic, 2835 cm^{-1} v(C-H) aliphatic, 1021 cm^{-1} v(C-N) aliphatic, 1283 cm^{-1} v(C-N) aromatic, 1485 cm^{-1} v(C=C) aromatic, 1445 cm^{-1} v(N=N).
$C_{24}H_{34}NiCl_2N_6$ (3)	3069-3052 cm^{-1} v(C-H) aromatic, 2835 cm^{-1} v(C-H) aliphatic, 1021 cm^{-1} v(C-N) aliphatic, 1295 cm^{-1} v(C-N) aromatic, 1450 cm^{-1} v(C=C) aromatic, 1433 cm^{-1} v(N=N).
$C_{24}H_{34}CoCl_2N_6$ (4)	3077-3052 cm^{-1} v(C-H) aromatic, 2835 cm^{-1} v(C-H) aliphatic, 1025 cm^{-1} v(C-N) aliphatic, 1283 cm^{-1} v(C-N) aromatic, 1485 cm^{-1} v(C=C) aromatic, 1449 cm^{-1} v(N=N).
$C_{24}H_{34}ZnCl_2N_6$ (5)	3095-3088 cm^{-1} v(C-H) aromatic, 2825 cm^{-1} v(C-H) aliphatic, 1025 cm^{-1} v(C-N) aliphatic, 1284 cm^{-1} v(C-N) aromatic, 1481 cm^{-1} v(C=C) aromatic, 1444 cm^{-1} v(N=N).

Table 3. 1H NMR Spectroscopic data for Ligand and compounds 1-10

Ligand/ Complexes	Chemical shift (ppm)
$C_{24}H_{34}CuBr_2N_6$ (1)	6.23- 7.10 (m, 8H, aromatic), 2.33 (s, 6H, o-CH ₃), 3.21 (t, 8H, N-CH ₂ aliphatic), 1.50-1.55 (m, 12H, (-CH ₂) ₃ aliphatic).
$C_{24}H_{34}FeBr_2N_6$ (2)	6.63- 7.22 (m, 8H, aromatic), 2.31 (s, 6H, o-CH ₃), 3.20 (t, 8H, N-CH ₂ aliphatic), 1.52-1.57 (m, 12H, (-CH ₂) ₃ aliphatic).
$C_{24}H_{34}NiCl_2N_6$ (3)	6.77- 7.20 (m, 8H, aromatic), 2.31 (s, 6H, o-CH ₃), 3.20 (t, 8H, N-CH ₂ aliphatic), 1.53-1.56 (m, 12H, (-CH ₂) ₃ aliphatic).
$C_{24}H_{34}CoCl_2N_6$ (4)	6.72- 7.55 (m, 8H, aromatic), 2.34 (s, 6H, o-CH ₃), 3.20 (t, 8H, N-CH ₂ aliphatic), 1.51-1.55 (m, 12H, (-CH ₂) ₃ aliphatic).
$C_{24}H_{34}ZnCl_2N_6$ (5)	6.77- 7.20 (m, 16H, aromatic), 2.31 (s, 6H, o-CH ₃), 3.25 (t, 8H, N-CH ₂ aliphatic), 1.53-1.59 (m, 12H, (-CH ₂) ₃ aliphatic).

4. CONCLUSION

Several new coordination compounds containing triazene were prepared in this study. The FTIR, CHN and 1H NMR studies for the complexes

showed significant evidence of complexation 1:2 when the complexes are prepared by the reflux technique these new compounds may be used as dyes for industrial processes.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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