

Synthesis and Characterization of a new Triazole complexes for Cu(II), Ni(II), Co(II), Zn(II) and Fe(II)

Abstract

A new series of complexes containing triazole compound was prepared, triazole compound was prepared by the diazotization of *o*-toluidine then reacting with piperidine to give the corresponding triazole compound (1-(*o*-tolylidiazanyl)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 triazole compound (1-(*o*-tolylidiazanyl)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: Triazole, Complexes, metal complexes, diazenyl, triazene, azo-group.

1. Introduction

Triazenes are a class of organic compounds that containing diazoamino functional group ($N=N-N$) in composition.⁽¹⁾ 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 *N1*- monodentate, *N1,N3*-chelating and *N1,N3*-bridging ligand. These compounds have been used in a variety of ways, ranging from transition metal complexes and polymer synthesis to anticancer drugs.⁽¹⁾ 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.⁽²⁻⁴⁾ In the same way organotellurium compounds have been used as a tool in synthetic chemistry⁽²⁻⁴⁾ and ligand chemistry.⁽⁵⁾ Thus, the present study will describe the synthesis and characterization of new types of complexes containing of organotellurium compounds and 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 $4000-400\text{ cm}^{-1}$. 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*-tolylidiazanyl)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*-tolylidiazanyl)piperidine (*otdip*) (1.5 mmol) in absolute ethanol (10 ml) was prepared and then $CuBr_2$, $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $ZnCl_2$ 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:

Cu[(2-CH₃-C₆H₃-N=N)-N-C₅H₁₀)]₂Br₂ Empirical formula: C₂₄H₃₄CuBr₂N₆; formula weight: 629.92 g mol⁻¹; yield: 85 % ; appearance: brown crystals; m.p. = 95-97°C; Elem. analysis: calc. C, 45.76 %; H, 5.44 %; N, 13.34 %; found: C, 45.67 %; H, 5.12 %; N, 13.20 %; FTIR: 3075-3050 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). ¹H NMR (ppm): 6.23- 7.10 (m, 8H, aromatic), 2.33 (s, 6H, *o*-CH₃), 3.21 (t, 8H, N-CH₂ aliphatic), 1.50-1.55 (m, 12H, (-CH₂)₃ aliphatic).

Fe[(2-CH₃-C₆H₃-N=N)-N-C₅H₁₀)]₂Br₂ Empirical formula: C₂₄H₃₄FeBr₂N₆; formula weight: 622.22 g mol⁻¹; yield: 76 % ; appearance: yellowish brown crystals; m.p. = 101-103°C; Elem. analysis: calc. C, 46.33 %; H, 5.51 %; N, 13.51 %; found: C, 46.20 %; H, 5.40 %; N, 13.43 %; FTIR: 3071-3052 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). ¹H NMR (ppm): 6.63- 7.22 (m, 8H, aromatic), 2.31 (s, 6H, *o*-CH₃), 3.20 (t, 8H, N-CH₂ aliphatic), 1.52-1.57 (m, 12H, (-CH₂)₃ aliphatic).

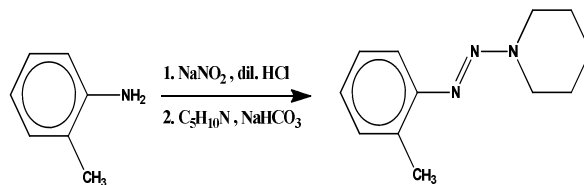
Ni[(2-CH₃-C₆H₃-N=N)-N-C₅H₁₀)]₂Cl₂ Empirical formula: C₂₄H₃₄NiCl₂N₆; formula weight: 536.41 g mol⁻¹; yield: 82 % ; appearance: reddish - brown crystals; m.p. = 141-143°C; Elem. analysis: calc. C, 53.76 %; H, 6.39 %; N, 15.76 %; found: C, 53.56 %; H, 6.13 %; N, 15.52 %; FTIR: 3069-3052 cm⁻¹ v(C-H) aromatic, 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). ¹H NMR (ppm): 6.77- 7.20 (m, 8H, aromatic), 2.31 (s, 6H, *o*-CH₃), 3.20 (t, 8H, N-CH₂ aliphatic), 1.53-1.56 (m, 12H, (-CH₂)₃ aliphatic).

Co[(2-CH₃-C₆H₃-N=N)-N-C₅H₁₀)]₂Cl₂ Empirical formula: C₂₄H₃₄CoCl₂N₆; formula weight: 536.17 g mol⁻¹; yield: 88 % ; appearance: brown crystals; m.p. = 155-157°C; Elem. analysis: calc. C, 53.74 %; H, 6.39 %; N, 15.67 %; found: C, 53.71 %; H, 6.12 %; N, 15.43 %; FTIR: 3077-3052 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). ¹H NMR (ppm): 6.72- 7.55 (m, 8H, aromatic), 2.34 (s, 6H, *o*-CH₃), 3.20 (t, 8H, N-CH₂ aliphatic), 1.51-1.55 (m, 12H, (-CH₂)₃ aliphatic).

Zn[(2-CH₃-C₆H₃-N=N)-N-C₅H₁₀)]₂Cl₂ Empirical formula: C₂₄H₃₄ZnCl₂N₆; formula weight: 542.85 g mol⁻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 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). ¹H 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).

Results and discussion

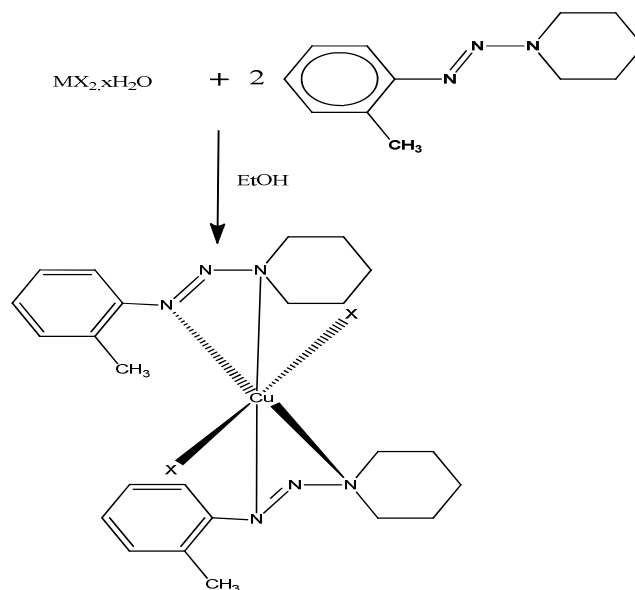
Triazole compound 1-(*o*-tolyl diazenyl)piperidine was prepared by diazotization of *o*-toluidine and piperidine based on literature with minor modification⁽⁶⁻⁸⁾, to obtain the corresponding triazole, [Scheme 1.].



SCHEME 1. Preparative methods for 1-(*o*-tolyl diazenyl)piperidine

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*-tolyl diazenyl)piperidine] (*otdpip*) in 1:2 molar ratio in ethanol are represented in Scheme 2.

107



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

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.

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

Comp.	color	Melting point (°C)	Analysis (%) ^a			Yield %
			C	H	N	
C₂₄H₃₄CuBr₂N₆ (1)	Brown	95-97	45.76 (45.67)	5.44 (5.12)	13.34 (13.20)	85
C₂₄H₃₄FeBr₂N₆ (2)	yellowish brown	101-103	46.33 (46.20)	5.51 (5.40)	13.51 (13.43)	76
C₂₄H₃₄NiCl₂N₆ (3)	reddish - brown	141-143	53.76 (53.56)	6.39 (6.13)	15.76 (15.52)	82
C₂₄H₃₄CoCl₂N₆ (4)	brown	155-157	53.74 (53.71)	6.39 (6.12)	15.67 (15.43)	88
C₂₄H₃₄ZnCl₂N₆ (5)	yellowish brown	130-132	53.10 (52.93)	6.31 (6.12)	15.48 (15.33)	75

^a calculated values are in parentheses

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.

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

Ligand/ complexes IR (cm^{-1})	λ_{max} in nm (ϵ in $\text{M}^{-1}\text{cm}^{-1}$)
C₂₄H₃₄CuBr₂N₆ (1)	3075-3050 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} $\nu(\text{N=N})$.
C₂₄H₃₄FeBr₂N₆ (2)	3071-3052 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} $\nu(\text{N=N})$.
C₂₄H₃₄NiCl₂N₆ (3)	3069-3052 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} $\nu(\text{N=N})$.
C₂₄H₃₄CoCl₂N₆ (4)	3077-3052 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} $\nu(\text{N=N})$.
C₂₄H₃₄ZnCl₂N₆ (5)	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} $\nu(\text{N=N})$.

¹H NMR spectra of compounds **1-5** were recorded in DMSO-d₆ and shows in Table 3. The ¹H 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, 10, 11-13) The protons in (-CH₂)₃ can be appeared at the range (1.50 – 1.59) ppm as a multiple signal,^(9, 11-15).

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

Ligand/ complexes	Chemical shift (ppm)
C₂₄H₃₄CuBr₂N₆ (1)	6.23- 7.10 (m, 8H, aromatic), 2.33 (s, 6H, <i>o</i> -CH ₃), 3.21 (t, 8H, N-CH ₂ aliphatic), 1.50-1.55 (m, 12H, (-CH ₂) ₃ aliphatic).
C₂₄H₃₄FeBr₂N₆ (2)	6.63- 7.22 (m, 8H, aromatic), 2.31 (s, 6H, <i>o</i> -CH ₃), 3.20 (t, 8H, N-CH ₂ aliphatic), 1.52-1.57 (m, 12H, (-CH ₂) ₃ aliphatic).
C₂₄H₃₄NiCl₂N₆ (3)	6.77- 7.20 (m, 8H, aromatic), 2.31 (s, 6H, <i>o</i> -CH ₃), 3.20 (t, 8H, N-CH ₂ aliphatic), 1.53-1.56 (m, 12H, (-CH ₂) ₃ aliphatic).
C₂₄H₃₄CoCl₂N₆ (4)	6.72- 7.55 (m, 8H, aromatic), 2.34 (s, 6H, <i>o</i> -CH ₃), 3.20 (t, 8H, N-CH ₂ aliphatic), 1.51-1.55 (m, 12H, (-CH ₂) ₃ aliphatic).
C₂₄H₃₄ZnCl₂N₆ (5)	6.77- 7.20 (m, 16H, aromatic), 2.31 (s, 6H, <i>o</i> -CH ₃), 3.25 (t, 8H, N-CH ₂ aliphatic), 1.53-1.59 (m, 12H, (-CH ₂) ₃ aliphatic).

In conclusion, several new coordination compounds containing triazole were prepared in this study. These new compounds may be used as dyes for industrial processes.

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