Silica supported triethylamine catalyzed synthesis and characterization of 4-aminoantipyrene derived N_2O_2 type of Novel Schiff base metal complexes

Authors & Affiliation:

Sharad D. Dakore[1,*]
Vinod T. Kamble[2]

[1] *Organic Chemistry Research Laboratory, School of Chemical Sciences, Swami Ramanand Teerth Marathwada University, Nanded, Maharashtra, India.*

[2] *Organic Chemistry Research Laboratory, Department of Chemistry, Institute of Sciences, Mumbai, Maharashtra, India*

Corresponding Author

Sharad D. Dakore

Email: ssdakore@gmail.com

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Abstract:

A new series of transition metal complexes Cu(II), Ni (II), Zn(II) and CO(II) were synthesized from the schiff base (L) derived from 4-aminoantipyrine, 3-thiophene carboxaldehyde and acetyl acetone in first step. In second step metal complexes are prepared from synthesized schiff base and divalent metal ions in the presence of silica supported triethylamine catalyst at ambient temperature. The structural features were arrived from their magnetic moment, molar conductance, ^{1}H NMR and ESR, thermal analysis, XRD spectral studies. The synthesized compounds were also screened for their antimicrobial properties.

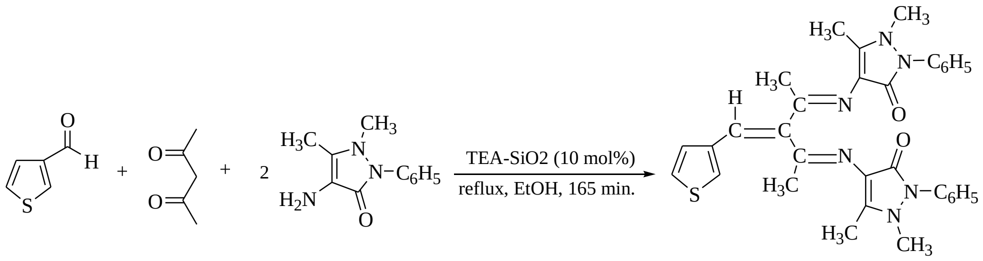
Keywords: 4-aminoantipyrine, 3-thiophene carboxaldehyde, acetyl acetone, silica supported triethylamine

Introduction

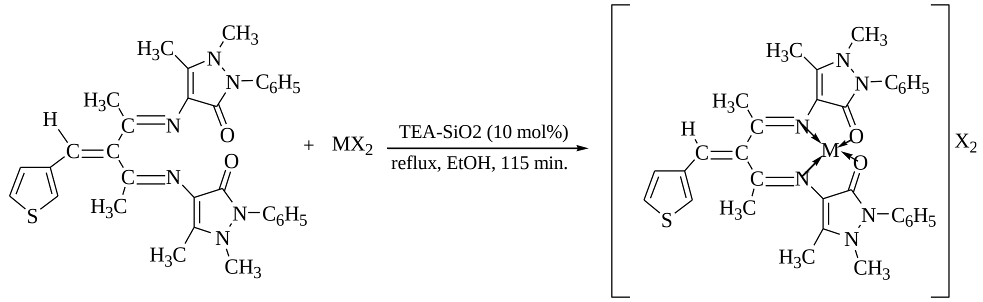
With their versatile structures, redox behavior, and physicochemical properties, transition metal complexes are often useful as chemical nucleases [1-5]. The interaction of these complexes with DNA has gained much attention due to their possible applications as new therapeutic agents. The manipulation of the ligands greatly facilitates the interaction between the complexes and DNA [6-17].

The discovery and development of antibiotics are among the most powerful and successful achievements of modern sciences and technology for the control of infectious diseases. Metal based drugs represent a novel group of antimicrobial agents with potential applications for the control of bacterial infections. Since copper complexes have been proven beneficial against several diseases such as tuberculosis, rheumatoid, gastric ulcer and cancers.

Hence, this work presents the synthesis and characterization of novel ligands and their complexes. A new series of transition metal complexes of Cu (II), Ni(II) Zn (II) & CO (II) are synthesized from the schiff base (L) derived from the 4-aminoantipyrine, 3-thiophene carboxaldehyde and acetyl acetone. The structural features were arrived from their magnetic moment, molor conductance,^{1}HNMR and ESR, TGA-DTA, XRD spectral studies. The synthesized compounds were also screened for their antimicrobial properties.(Scheme-1 and Scheme-2).



Scheme-1



M= Cu(II), CO(II), Ni(II), Zn(II)
X= Cl-, NO3-, CH3COO-

Scheme-2

Experimental

Materials and methods

IR spectra (400–4000 cm-1) were recorded on Shimndzu FTIR spectrophotometer using KBr discs and the absorption bands are expressed in cm^{-1}. ^{1}H NMR spectra were recorded in DMSO-*d*$_6$ with tetramethylsilane as an internal standard. Molar conductivity of 10^{-3} M solution in DMSO was obtained on C-100 Elico digital conductivity meter at room temperature. Magnetic susceptibilities were recorded on Guoy balance using AR grade $CuSO_4$ and $FeSO_4$ as standard. EPR spectra of complexes are performed in solid state at room temperature on Varian-E-4X band EPR spectrophotometer. TG/DTA scans were recorded on Mettler-Toledo-851 TGA-DTA instrument at linear heating rate of 100 per minute under nitrogen atmosphere in a temperature range 25-1000^{0}C.

X-ray powder diffraction patterns of complexes were recorded in the 2θ range of 10-800 on Bruker X-D-8 advanced diffractometer and XRD scans with the help of powder X-programme. Analytical grade chemicals brought from Sigma-Aldrich, INC. were used throughout this work.

Typical procedure

Synthesis of Schiff base

Condensation of acetyl acetone (10mmol), 3-thiophene carboxaldehyde (10mmol), 4-aminoantipyrene (20mmol) was performed by heating (1:1:2) and in presence of 10 mol% of solid supported triethylamine in ethanol (50 ml) on water bath was refluxed until completion of the reaction. The completion of the reaction was monitored by thin layer chromatography (TLC). After completion of the reaction, the catalyst was filtered, washed with ethanol and the filtrate was concentrated under reduced pressure. The crude product was purified by recrystallisation with hot ethanol. The recovered catalyst was activated at 180 ^{0}C for 2 hour and reused four times for the preparation of complexes.

Synthesis of metal complexes

A mixture of schiff base ligand (2mmol) and metal salt (2mmol) along with 10 mol% silica supported triethylamine in ethanol (15 ml) was refluxed for 1hr. The resulting colored complex along with insoluble catalyst was filtered; washed with ethanol, acetone and petroleum ether. Then metal complex was dissolved in DMSO (2x15ml) to separate the catalyst and then filtered. The filtrated was then concentrated under reduced pressure top afford shiny stored complex which was dried over calcium chloride (65% yield). The details of all the synthesized complexes were given in **Table 1**.

Table 1: Analytical dataof Magnetic movements and molar conductivity of complexes

Sl. No.	**Mol. Formula of Complex**	**Mol. Wt.**	**Colour**	**Melting Point**	**%C**	**%H**	**%N**	**ΛMohm^1 cm^{2}mol^1**	**M.M B.M**
1	$[Cu(C_{32}H_{32}N_6O_2S)]\ Cl_2$	699.15	Faint Blue	227	54.97 (54.65)	4.61 (4.52)	12.02 (12.36)	10	1.72
2	$[Cu(C_{32}H_{32}N_6O_2S)](\ NO_3)_2$	751.54	Blue	231	51.09 (51.50)	4.29 (4.62)	14.90 (15.10)	09	1.73
3	$[Cu(C_{32}H_{32}N_6O_2S)](CH_3COO)_2$	746.33	Dark Blue	229	57.93 (57.58)	5.13 (5.25)	11.26 (11.33)	08	1.72
4	$[Co(C_{32}H_{32}N_6O_2S)]\ Cl_2$	694.54	Brown	237	55.35 (55.50)	4.64 (4.32)	12.10 (12.35)	10	2.83
5	$[Co(C_{32}H_{32}N_6O_2S)](NO_3)_2$	747.64	Dark Brown	233	51.41 (51.48)	4.31 (4.35)	14.99 (15.01)	15	2.83
6	$[Co(C_{32}H_{32}N_6O_2S)](CH_3COO)_2$	741.72	Black	240	58.29 (58.90)	5.16 (5.54)	11.33 (11.64)	14	2.81
7	$[Ni(C_{32}H_{32}N_6O_2S)]\ Cl_2$	694.3	Green	241	55.36 (55.08)	4.65 (4.01)	12.10 (12.40)	13	---
8	$[Ni(C_{32}H_{32}N_6O_2S)](NO_3)_2$	747.4	Dark Green	247	51.42 (51.12)	4.32 (4.09)	14.99 (15.20)	12	---
9	$[Ni(C_{32}H_{32}N_6O_2S)](CH_3COO)_2$	741.48	Faint Green	250	58.31 (57.97)	5.17 (4.83)	11.33 (12.03)	16	---
10	$[Zn(C_{32}H_{32}N_6O_2S)]\ Cl_2$	698.1	Buff	246	54.83 (55.10)	4.60 (4.90)	11.99 (12.30)	07	---
11	$[Zn(C_{32}H_{32}N_6O_2S)](\ NO_3)_2$	754.1	Buff	255	50.97 (51.12)	4.28 (4.42)	14.86 (14.35)	09	---
12	$[Zn(C_{32}H_{32}N_6O_2S)](CH_3COO)_2$	748.18	Buff	253	57.79 (58.04)	5.12 (5.26)	11.23 (11.77)	12	---

Result and Discussion

Novel Schiff base complexes of N_2O_2 type have been synthesized by non template method utilizing solid supported tri ethyl amine catalyst as a catalyst. The investigated complexes were characterized and evaluated for their antimicrobial activity against four bacterial stains.

IR Spectra

The Infrared spectra of complex (Table 2) exhibit strong bands at 1654 cm^{-1} which is characteristics for azomethine group (C=N) in free Schiff base, in complex this bands shifts to lower frequency 1582-1597 cm^{-1} which indicates that azomethine nitrogen is one of the coordinating atom in schiffs base. The metal-nitrogen and metal-oxygen bonds showed the 655 cm^{-1} and 528 cm^{-1} frequencies respectively.

Table 2: IR spectra of complexes

Compound	$\nu(\mathrm{C=N})$	**ν (C = O)**	$\nu(\mathrm{M-N})$	**ν (M-O)**
$[Cu(C_{32}H_{32}N_6O_2S)]\ Cl_2$	1654	1582-1597	655	528

NMR Spectra

The NMR spectrum of the all the metal complexes exhibits a singlet at δ 2.40–2.50 ppm of $=C–CH_3$, singlet at δ 3.01–3.10 ppm of $N–CH_3$ and singlet at δ 2.75–2.82 ppm of $–N=C–CH_3$ regions which showed the formation and confirmation of the metal complexes. The remaining aromatic protons are appeared at 6.60-7.60 ppm range (Table 3).

Table 3: ^{1}H NMR Spectroscopic data of the complexes

Complex	**=C-CH_3**	**-N-CH_3**	**N = C-CH_3**	**Phenyl Multiplate**
$[Co(C_{32}H_{32}N_6O_2S)]\ Cl_2$	2.40-2.50	3.01-3.10	2.75-2.82	6.60-7.60

EPR Spectra:

The EPR spectra of the $[Cu(C_{32}H_{32}N_6O_2S](NO_3)_2$ complex in powder form at room temperature shows isotropic signals with $g\|=2.0015$, $g^{\perp} = 1.9995$, and giso = 2.0001, $A\| = 3.33G$, $A^{\perp} = 6.66G$ and exchange coupling interaction constant G = 0.2000. This finding indicates that the observed ‘g’ values for the complex are less than 2.3 in agreement with the covalent character of the metal ligand bond. The trend $g\|> g_{\perp}> 2.0023$ observed for the Cu(II) complexes indicates that unpaired electron is localized in the dx^2-y^2 orbital and spectral features are characteristic of axial symmetry tetragonal elongated structure is conformed for the complex (Table 4a).

Table 4a: EPR parameters for $[Cu(C_{32}H_{32}N_6O_2S)](NO_3)_2$ complexes

Compound	**Gyromatric ratio G**	**A gauss**	**G**	**e/gm*10^{21}**
$[Cu(C_{32}H_{32}N_6O_2S)](NO_3)_2$	$g\|$=2.0015 g+= 1.9995 gav= 2.0001	$A\|$ = 3.33 $A^{\perp}$= 6.66	0.200	1.5075

The EPR spectra of the $[Co(C_{32}H_{32}N_6O_2S]Cl_2$ complex in powder form at room temperature shows isotropic signals with $g\|=1.9954$, $g^{\perp} = 1.9965$ and giso = 1.9959, $A\| = 8.33G$, $A^{\perp} = 3.33G$ and exchange coupling interaction constant G = 1.1553. This finding indicates that the observed ‘g’ values for the complex are less than 2.3 in agreement with the covalent character of the metal ligand bond. The trend $g\|> g_{\perp}> 2.0023$ observed for the Co(II) complexes indicates that unpaired electron is localized in the dx^2-y^2 orbital and spectral features are characteristic of axial symmetry tetragonal elongated structure is conformed for the complex (Table 4b).

Table 4b: EPR parameters for $[Co(C_{32}H_{32}N_6O_2S)]Cl_2$ complexes

Compound	**Gyromatric ratio G**	**A gauss**	**G**	**e/gm*10^{21}**
$[Co(C_{32}H_{32}N_6O_2S)]Cl_2$	$g\|$=1.9954 g+= 1.9965 gav= --------	$A\|$= 8.33 $A^{\perp}$= 3.33	1.1553	1.5057

The EPR spectra of the $[Ni(C_{32}H_{32}N_6O_2S](CH_3COO)_2$ complex in powder form at room temperature shows isotropic signals with parameters $g\|=2.0004$, $g^{\perp} = 1.9990$ and giso =1.9997, $A\| = 4.08\ G$, $A^{\perp} = 8.18\ G$ and exchange coupling interaction constant G = 0.6596. This finding indicates that the observed ‘g’ values for the complex are less than 2.3 in agreement with the covalent character of the metal ligand bond. The trend $g\|> g_{\perp}> 2.0023$ observed for the Ni(II) complexes indicates that unpaired electron is localized in the dx^2-y^2 orbital (Table 4c).

Table 4c: EPR parameters for $[Ni(C_{32}H_{32}N_6O_2S)](CH_3COO)_2$ complexes

Compound	**Gyromatric ratio G**	**A gauss**	**G**	**e/gm*10^{21}**
$[Ni(C_{32}H_{32}N_6O_2S)](CH_3COO)_2$	$g\|$=2.0004 g+=1.9990 gav= 1.9997	$A\|$= 4.08 $A^{\perp}$=8.18	0.6596	1.5077

Powder X-ray analysis:

Powder XRD diffractogram of Co(II) complexes were recorded in the range 20-80^0 at wavelength 1.5447 ^{0}A. In conclusion the complexes Co(II) have orthorhombic crystal system. The experimental density values of complexes were determined using specific gravity method and found to be 0.7732 g cm^{-3} for the Co(II) complex (Table 5).

Table 5:Millar indices and interplanardistances

Complex	hkl	2θ observed	2θ calculated	D
$[Zn(C_{32}H_{32}N_6O_2S)](NO_3)_2$	1 1 0	10.250	10.258	8.6229
	200	12.939	12.931	6.8366
	120	17.209	17.237	5.1487
	002	18.158	18.193	4.8817
	112	20.925	20.929	4.2419
	202	22.348	22.353	3.9749
	320	25.274	25.262	3.5210
	031	25.749	25.748	3.4572

Thermal analysis

From TG analysis, presence of lattice water, and breakdown pattern of complexes are evaluated.In complex of Cu (II) three step decomposition. First step from 30 to 50^0C with mass loss of 11.12% (calcd.10.89%) accompanied by endothermic peak with 50^0C on the DTA curve, may be attributed to the decomposition of lattice water ,The second step, from 50 to 410^0C with loss 55.55% (calcd.57.19%) corresponds to removal of chloride and partial ligand moiety. For this a exothermic peak in the DTA at 320^0C was observed. The third step, from 410 to 610^0C with mass loss 26.5% (calcd.24%) corresponds to removal of coordinated part of ligand which was observed a broad exothermic peak in DTA. Decomposition completed at 770^0C, leading final product of copper oxide. Amount of copper oxide found in residue is close agreement with calculated. (**Table 6**).

Table 6: Thermal decomposition and kinetic parameters

Complex	DTA peak 0C	Temp. range 0C	Mass loss (%) observer (calculated)	Nature of decomposition	Order of reaction	△E kg/mole	△S JK/ mole	GKJ / mole free	Frequency factor Z
[CuL1]Cl2	50	0-50	11.12(10.88)	Water	1.9	9.068	-267.721	24.738	1.058x10-1
	320	50-410	55.55(57.19)	Chloride+Ligand	1.9	23.279	-241.872	41.797	3.098
	580	410-610	26.5(24.0)	Ligand	0.5	15.832	-267.501	45.087	2.030x10-1

Antimicrobial activity:

The *in vitro* antibacterial activities of synthesized complexes have been studied by disc diffusion method. The antibacterial activities were done at 100 µg/ml concentrations in DMF solvent using method four bacterial strains (*S.typhi*, *S. aureus*, *E. coli and B. subtilis*) by the minimum inhibitory concentration (MIC). These bacterial strains were incubated for 72 h at 27^0C. Standard antibacterial (Cefodox and Linazoid) were used for comparison under similar conditions. Activity was determined by measuring the diameter of the zone of inhibition (mm). The data of antibacterial activities tabulated in Table 5 indicated that Zn(II) and Cu(II) complexes are more active against the bacterial strains *S. coli* and *S.typhi*as compared to other bacterial strains. Cu (II) and Zn (II) complexes were found to be moderately active against all bacterial strains.

Table7: Antibacterial activity of complexes of type $[M(C_{32}H_{32}N_6O_2S)X_2]$

Sr. No.	Complex	*S. typhi*	*S. aureus*	*E. coil*	*B. subtilis*
1	$[Cu(C_{32}H_{32}N_6O_2S)]Cl_2$	15.6	12.3	14.0	14.5
2	$[Cu(C_{32}H_{32}N_6O_2S)](NO_3)_2$	15.4	12.4	14.1	14.3
3	$[Cu(C_{32}H_{32}N_6O_2S)](CH_3COO)_2$	15.9	12.2	13.9	14.6
4	$[Co(C_{32}H_{32}N_6O_2S)]Cl_2$	12.8	13.1	13.1	13.2

5	$[Co(C_{32}H_{32}N_6O_2S)](NO_3)_2$	13.0	13.0	12.9	13.5
6	$[Co(C_{32}H_{32}N_6O_2S)](CH_3COO)_2$	13.2	13.1	13.2	13.6
7	$[Ni(C_{32}H_{32}N_6O_2S)]Cl_2$	13.2	13.0	13.3	13.3
8	$[Ni(C_{32}H_{32}N_6O_2S)](NO_3)_2$	13.0	13.2	13.1	13.5
9	$[Ni(C_{32}H_{32}N_6O_2S)](CH_3COO)_2$	13.1	12.9	13.3	13.3
10	$Zn(C_{32}H_{32}N_6O_2S)]Cl_2$	14.3	12.6	13.2	14.6
11	$[Zn(C_{32}H_{32}N_6O_2S)](NO_3)_2$	14.1	12.4	13.1	14.7
12	$[Zn(C_{32}H_{32}N_6O_2S)]CH_3COO)_2$	14.2	12.5	13.3	14.5
13	Cefodox	10.8	10.3	10.5	10.6
14	Linazoid	11.3	10.8	10.8	13.0

Conclusion:

In summary, we have synthesized new schiff base ligand complexes of Cu (II), Co (II), Ni (II) and Zn (II). The Schiff base ligands are prepared from 4-amino antipyrine, 3- thiophene carboxaldehyde & acetyl acetone using tri ethylamine catalyst is used at room temperature. The antimicrobial activity showed that Cu (II) and Zn (II) complexes were found to be moderately active against all bacterial strains.

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