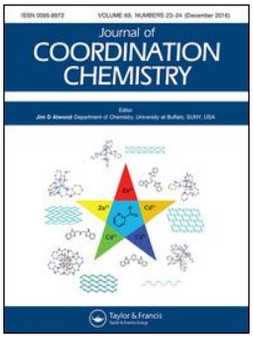

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A.S. Ramasubramanian , B. Ramachandra Bhat & R. Dileep

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Synthesis, characterization, and biological activity of metal complexes of 4-ethyl vanillideneamino-3-methyl-5-mercapto-1,2,4-triazole

A.S. RAMASUBRAMANIAN, B. RAMACHANDRA BHAT*
and R. DILEEP

Catalysis and Material Chemistry Division, Department of Chemistry, National Institute of Technology Karnataka, Srinivasnagar, Surathkal – 575025, Karnataka, India

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A series of transition metal–triazole derivatives have been synthesized and characterized by microanalytical, thermal, magneto-chemical, and spectral studies. The synthesized complexes were screened for biological activities. The complexes of Co(II) and Ni(II) emerged as a good antibacterial agent against Gram-negative bacteria such as *Escherichia coli*, *Pseudomonas aeruginosa*, *Salmonella typhi*, *Bacillus subtilis*, and *Shigella flexneri*.

Keywords: Ethyl vanillin; Metal complexes; Schiff base; Biological studies

1. Introduction

Schiff bases are widely used as analytical reagents since they allow simple and inexpensive determination of several organic and inorganic substances [1]. They also form stable complexes with metals that perform an important role in biological systems [2]. Transition metal Schiff-base complexes have many applications in catalysis, photonics, antitumor, and antibacterial activity [3] and are also used as enzyme models [4]. Schiff bases derived from salicylaldehyde are polydentate ligands, coordinating as deprotonated or neutral forms.

Triazole chemistry is becoming more important due to its excellent biological activity. Triazole antifungal drugs include fluconazole, isavuconazole, itraconazole, voriconazole, pramiconazole, and posaconazole. The triazole plant protection fungicides include epoxiconazole, triadimenol, propiconazole, metconazole, cyproconazole, tebuconazole, flusilazole, and paclobutrazol. Studies have been reported on the synthesis and characterization of metal complexes of Schiff bases involving 1,2,4-mercapto triazoles with salicylaldehyde, *p*-nitro benzaldehyde, *o*-nitrobenzaldehyde, *p*-toluyl aldehyde, and cinnamaldehyde [5–12]. Transition metal complexes of pentadentate ligands [13] coordinate through deprotonated oxygen, thioenolic sulfur, and azomethine nitrogen.

*Corresponding author. Email: chandpoorna@yahoo.com

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Many transition metal complexes of Schiff bases containing 1,2,4-mercapto triazole exhibit greater antibacterial activity against Gram-positive and Gram-negative bacteria. Coordinating metal ions have pronounced effect on the antibacterial activity of the ligand [14, 15].

In this study, the synthesis and characterization of Co(II), Ni(II), Pd(II), and Zn(II) complexes of Schiff-base ethylvanillidene-4-amino-5-mercapto triazole have been undertaken. The antibacterial activities of the ligands and their metal complexes have been screened *in vitro* against bacteria such as *Escherichia coli*, *Pseudomonas aeruginosa*, *Salmonella typhi*, *Bacillus subtilis*, and *Shigella flexneri*.

2. Experimental

2.1. *Methods and materials*

The synthesized complexes were analyzed for metal content using an Atomic Absorption Spectrometer model Varian AA 55B. Carbon–hydrogen–nitrogen–sulfur (CHNS) analysis was carried out on Thermo Flash EA 112 series. Magnetic susceptibilities were measured by a Sherwood Scientific Magnetic Susceptibility meter (UK). Thermogravimetric analyses (TGA) were carried out on a Universal V4.1D TA Instruments TGA analyzer, infrared (IR) spectra in KBr pellets on a Nicolet Fourier transform-infrared (FT-IR) from 4000 to 400 cm^{-1}, UV-Vis spectra on a Shimadzu Pharmaspec, molar conductance measured on an Elico conductivity meter and ^{1}H-NMR spectra were recorded on DSX-300/AMX-400/DRX-500/AV500 NMR spectrometers.

2.2. *Synthesis of 4-ethyl vanillideneamino-3-methyl-5-mercapto-1,2,4-triazole*

This ligand (shortly EVAMMT) was synthesized in two stages. In the first stage, thiocarbohydrazide was refluxed with glacial acetic acid for 2 h [5]. The white-colored product, 3-methyl-4-amino-5-mercapto-1,2,4-triazole (MAMT) was filtered, washed, and recrystallized. In the second stage, the MAMT (0.02 mmol) was dissolved in ethyl alcohol and refluxed with (0.002 mmol) of ethyl vanillin for 4 h. The reaction mixture was cooled, filtered, washed, and recrystallized from alcohol. The ligand was characterized by elemental analysis, IR, UV, and ^{1}H-NMR. Yield: 89%, m.p.: 214°C.

^{1}H-NMR (400 MHz, ppm, from TMS in DMSO): 11.2 (s, 1H, –SH), 8.1 (s, 1H, –CH=N–), 10.3 (s, 1H, –OH), 6.24–8.76 (m, 4H, Ar), 3.8 (q, 2H, $–OCH_2–$), 2.3 (s, 3H, $–CH_3$, triazole), and 1.8 (t, 3H, $–CH_3$). FT-IR (KBr pellets, in cm^{-1}): 3150 (N–H), 1604 (C=N azomethine), and 1430 (thioamide), 800 (C–S thiomide). Elemental Anal. Calcd (%): C (52.4), H (5.1), N (20.8), and S (11.7); Found (%): C (52.2), H (5.1), N (21.0), and S (11.6).

2.3. *Synthesis of complexes*

EVAMMT complexes were prepared by refluxing a solution of 0.004 mmol EVAMMT in ethyl alcohol with 0.002 mmol solution of respective transition metal salt

($NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $PdCl_2$, and $ZnCl_2 \cdot 2H_2O$). The complexes formed were filtered, washed with ether, and dried *in vacuo*. EVAMMT complexes of Ni(II), Co(II), Pd(II), and Zn(II) were slightly soluble in dimethylformamide (DMF) and soluble in DMSO.

2.3.1. *bis*(1,2,4-triazole-3-methyl-4 ethylvanillideneamino 5-thiolato)zinc(II). ^{1}H-NMR (400 MHz, ppm, from TMS in DMSO): 8.5 (s, 1H, –CH=N–), 10.8 (s, 1H, –OH), 6.24–8.76 (m, 4H, Ar), 3.8 (q, 2H, –OCH_2–), 2.3 (s, 3H, –CH_3, triazole), and 1.8 (t, 3H, –CH_3). FT-IR (KBr pellets, in cm^{-1}): 2987 (N–H), 1591 (C=N azomethine), 1433 (thioamide), and 800 (C–S thiomide). Elemental Anal. Calcd (%): C (46.5), H (4.5), N (18.2), and S (10.3); Found (%): C (46.3), H (4.4), N (18.1), and S (10.2).

2.3.2. Diaquo*bis*(1,2,4-triazole-3-methyl-4 ethylvanillideneamino 5-thiolato)nickel(II). ^{1}H-NMR (400 MHz, ppm, from TMS in DMSO): 8.6 (s, 1H, –CH=N–), 10.7 (s, 1H, –OH), 6.24–8.76 (m, 4H, Ar), 3.8 (q, 2H, –OCH_2–), 2.3 (s, 3H, –CH_3, triazole), and 1.8 (t, 3H, –CH_3). FT-IR (KBr pellets, in cm^{-1}): 3525 (N–H), 1591 (C=N azomethine), 1450 (thioamide), 733 (C–S thiomide). Elemental Anal. Calcd (%): C (47.3), H (4.3), N (18.4), S (10.4); Found (%): C (47.11), H (4.23), N (18.36), and S (10.3).

2.3.3. Diaquo*bis*(1,2,4-triazole-3-methyl-4 ethylvanillideneamino 5-thiolato)cobalt(II). ^{1}H-NMR (400 MHz, ppm, from TMS in DMSO): 8.5 (s, 1H, –CH=N–), 10.8 (s, 1H, –OH), 6.24–8.76 (m, 4H, Ar), 3.8 (q, 2H, –OCH_2–), 2.3 (s, 3H, –CH_3, triazole), and 1.8 (t, 3H, –CH_3). FT-IR (KBr pellets, in cm^{-1}): 3500 (O–H), 3197 (N–H), 1597 (C=N azomethine), 1445 (thioamide), and 681 (C–S thiomide). Elemental Anal. Calcd (%): C (47.3), H (4.3), N (18.4), and S (10.7); Found (%): C (47.2), H (4.3), N (18.6), and S (10.5).

2.3.4. *bis*(1,2,4-Triazole-3-methyl-4 ethylvanillideneamino 5-thiolato)palladium(II). ^{1}H-NMR (400 MHz, ppm, from TMS in DMSO): 8.5 (s, 1H, –CH=N–), 10.6 (s, 1H, –OH), 6.24–8.76 (m, 4H, Ar), 3.8 (q, 2H, –OCH_2–), 2.2 (s, 3H, –CH_3, triazole), and 1.8 (t, 3H, –CH_3). FT-IR (KBr pellets, in cm^{-1}): 3200 (N–H), 1591 (C=N azomethine), 1440 (thioamide), and 750 (C–S thiomide). Elemental Anal. Calcd (%): C (47.5), H (4.6), N (17.0), and S (9.8); Found (%): C (47.3), H (4.5), N (17.1), and S (9.6).

2.4. *Biological activity*

Preliminary screening of Co(II), Ni(II), and Zn(II) complexes of EVAMMT for their *in vitro* antibacterial activity against pathogenic strains of bacteria such as *E. coli*, *P. aeruginosa*, *S. typhi*, *B. subtilis*, and *S. flexneri* using plate technique was performed. The bacteria were cultured (15 mm diameter) in a previously sterilized Mueller–Hinton agar medium in a petri dish and used as an inoculum for the study. The components to be tested were dissolved in DMF to a final concentration of 0.5% and 1% and soaked in filter paper disks of 5 mm diameter and 1 mm thickness. These disks were placed on

the previously seeded plates and incubated at $35 \pm 2°C$ for 24 h. The diameter (mm) of the inhibitory zone around each disk was measured after 24 h.

3. Results and discussion

3.1. *UV spectra*

Electronic spectra of the synthesized complexes (10^{-3} mol L^{-1} in DMSO) are given in table 1. The Co(II) complex shows three bands at 7273, 14,285, and 19,638 cm^{-1} due to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1), $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2), and $^4T_{1g}(P) \rightarrow {}^4T_{1g}(F)$ (ν_3) transitions, respectively, suggesting octahedral environment around Co(II). The $\nu_3 : \nu_2$ value for the compound is 2.70, leading to (from appropriate energy level diagram)

$$D_q/B' = 0.96$$

and to,

$$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)/B' = 7273/B' = 8.2$$

$$B' = 887$$

Hence, $D_q = 851.5$.

Consequently, the spectral parameters of the compounds are: $10D_q = 8515\,cm^{-1}$, $B' = 887\,cm^{-1}$, and $\beta = 0.79$. The reduction of Racah parameter from the free ion value of 1120 to 887 cm^{-1} and the value of β (0.79) indicates covalence in the compound. The Ni(II) complex shows three bands at 13,984, 16,090, and 23,772 cm^{-1}, which are assigned to the spin-allowed transitions, $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1), $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2), and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_3), respectively, suggesting an octahedral geometry [16–18]. The $\nu_1 : \nu_2$ value for the present compound is 1.74 and corresponds to usual range (1.6–1.82). The spectral parameters are $10D_q = 8565\,cm^{-1}$, $B' = 874\,cm^{-1}$, $\beta = 0.81$, and the β^0 value is 19%. The reduction of Racah parameter from the free ion value of 1080 to 874 cm^{-1} and β value of 0.81 indicates the covalent nature of the compound [19, 20]. The above discussion very strongly indicates octahedral geometry around the central

Table 1. Analytical results.

Complex	Molar conductance (μS)	μ_{eff}	Frequency (cm^{-1})	Assignments	$10D_q$ (cm^{-1})	B (cm^{-1})	β	B (%)
EVAMMT	–	–		–				
Zn-EVAMMT	21.0	Diamagnetic		–				
Ni-EVAMMT	26.6	3.12	16,090	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	8565	874	0.81	19
			13,984	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$				
			25,000	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$				
Co-EVAMMT	20.8	5.20	14,285	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	8515	887	0.79	21
			7273	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$				
			23,772	$^4T_{1g}(P) \rightarrow {}^4T_{1g}(F)$				
Pd-EVAMMT	22.2	Diamagnetic						

metal ion in these two complexes (Ni and Co), requiring occupation of two coordination sites by H_2O.

3.2. *FT-IR spectra*

IR positions of the ligand and the complexes given in table 2 have bands in the region of 2900 cm^{-1}, assigned to ν(C–H). The thioamide moiety in the ligand is confirmed by four thioamide bands present in the IR spectra of the ligand [21]. In the complexes, the thioamide band IV at 800 cm^{-1} shifts lower by 30–40 cm^{-1}; thioamide band III at 1180 cm^{-1} shifts 20–30 cm^{-1} higher; thioamide band I at 1500 cm^{-1}, and thioamide band III have less intensity compared to the ligand. These systematic shifts support bond formation through both nitrogen and sulfur [22–26]. Ni(II) and Co(II) complexes exhibit a broad band at 3500 and 910 cm^{-1} indicating that the metal ion is coordinated to water.

3.3. *^{1}H-NMR spectra*

Ni(II) and Co(II) complexes have been investigated in the context of dynamic combinatorial libraries. The kinetic lability of the d^7 cobalt(II) center and d^8 nickel(II) center combined with the strength of the Co–N and Ni–N bonds allows for the construction of thermodynamically stable, but labile, libraries of complexes from the reaction of cobalt and nickel salts with mixtures of ligands. The ^{1}H-NMR spectra of these complexes are paramagnetically shifted, but only modestly, broadened and are characteristic of the individual complexes providing a fingerprint of the speciation [27].

The ^{1}H-NMR spectra of the free ligands and complexes have been recorded in DMSO. The ligands exhibit singlets at 11.24. The disappearance of these signals in the spectra of the complexes clearly suggests deprotonation of the functional group during the complexation and coordination through sulfur. The singlet at 8.1 ppm in the ligand is altered to that in the complex at 8.5 ppm. In spectra of the ligands, multiplets due to aromatic protons appear in the range δ 6.24–8.76 ppm and remain unchanged in spectra of the complexes. The peak corresponding to –O–H– at 10.8 ppm in the free ligand is unaltered in the complexes. Also, the peaks at 1.8 ppm (–CH_3) and 3.8 ppm (–OCH_2–) in the ligand are unaltered in the complexes. A peak due to –CH_3 (triazole) at 2.3 ppm in the ligand remains unchanged in the complexes.

3.4. *Magnetic susceptibility measurements*

At room temperature, Ni(II) and Co(II) complexes exhibit paramagnetic behavior (3.12 and 5.20 B.M., respectively) which are in good agreement with the theoretical values for octahedral complexes [28–31]. All other complexes are diamagnetic.

3.5. *TGA studies*

TGA analyses of Ni(II) and Co(II) complexes show weight loss starting from 100°C indicating coordinated water investigated in nitrogen and dynamic air atmospheres

Table 2. IR spectral positions of EVAMMT and its metallic complexes.

	ν(O–H) water (cm^{-1})	ν(N–H) (cm^{-1})	ν(C–H) (cm^{-1})	ν(C=N) (cm^{-1})	Thioamide I (cm^{-1})	Thioamide II (cm^{-1})	Thioamide III (cm^{-1})	Thioamide IV (cm^{-1})	ν(N–H) triazole (cm^{-1})	Characteristic of coordinated water (cm^{-1})	Thioamide band IV and phenyl with 5 adjacent H (cm^{-1})	Aromatic ring (cm^{-1})	ν(M–N) (cm^{-1})
$C_{12}H_{14}N_4SO_2$	–	3150(b)	2900(s)	1604(s)	1499(s)	1433(s)	1180(s)	800(s)	1030(m)	–	800(s)	700(m)	
$Zn(II)(C_{12}H_{14}N_4SO_2)_2$	–	2987	2900	1591	1500	1450	1200	750	1030	–	750	700	550
$Ni(II)(C_{12}H_{14}N_4SO_2)_2 2H_2O$	3525(b)	3050	2900	1597	1469(m)	1445(m)	1223(m)	681(m)	1055	900	681	700	571(m)
$Co(II)(C_{12}H_{14}N_4SO_2)_2 2H_2O$	3500(b)	3197	2979	1598	1550	1440+10	1190	770	1030	912	770	720	550
$Pd(II)(C_{12}H_{14}N_4SO_2)_2$	–	3200	2900	1591	1500	1440	1290	750	1030	–	750	700(s)	550

Table 3. Antibacterial activity of metal(II) complexes.

	B. subtilis (μg)		*S. typhi* (μg)		*P. aeruginosa* (μg)		*E. coli* (μg)		*S. flexneri* (μg)	
Compound	30	50	30	50	30	50	30	50	30	50
Ligand	–	8	–	7	9	11	5	9	7	9
Ni(II) complex	12	18	14	16	16	20	13	18	10	13
Co(II) complex	9	14	10	12	10	11	13	15	8	12
Zn(II) complex	20	24	16	18	20	22	13	21	12	15
Ampicillin	25	27	18	20	24	26	22	24	13	18
DMF	–	–	–	–	–	–	–	–	–	–

Zone inhibition are given in mm.

using TGA and differential thermal analysis (DTA). The complexes decompose in three or four decomposition steps. The first step is elimination of water. The endothermic peaks at 60–100°C correspond to the evolution of the crystal water ($\Delta H = 100$–$250\,\mathrm{J\,g^{-1}}$), while those at 110–160°C are consistent with coordinated water ($\Delta H = 150$–$330\,\mathrm{J\,g^{-1}}$) [32, 33]. Afterwards, continuous decomposition sets in with varying decomposition peaks. Some decomposition could be correlated with decomposition products. Decomposition of all complexes in dynamic air ends with oxide formation. The percentage weight of the residue agrees well with oxide formation. However, higher percentages of the residue than calculated for oxide have been observed in nitrogen flow. This may be attributed to contamination of the oxide with some carbon. From 250°C, decomposition of the complex starts and ends at around 900°C.

The molar conductance values of all the complexes in DMF are less than 30 μS at room temperature confirming that the complexes are non-ionic. From the analytical data, it was confirmed that the complexes were ML_2.

3.6. *Biological activity*

Preliminary *in vitro* antimicrobial activities of the investigated compounds were tested against bacteria *E. coli*, *P. aeruginosa*, *S. typhi*, *B. subtilis*, and *S. flexneri*. Ampicillin was used as a standard. Ni(II), Co(II), and Zn(II) complexes showed good activity. From table 3, it is clear that the inhibition zone of the metal chelates is higher than that of the ligand. Such increased activity of the metal chelates is due to the lipophilic nature of the metal ions in complexes [34]. The increase in activity of metal chelates, with increase in concentration, is due to the effect of metal ions on cell process [35]. Furthermore, the mode of action of the compounds may involve the formation of a hydrogen bond through the azomethine nitrogen with the active centers of cell constituents, resulting in interference with the normal cell process [36].

4. Conclusions

On the basis of analytical and spectral data, octahedral structures have been proposed for Co(II) and Ni(II) complexes (figure 1a), square planar geometry for Pd(II) complex

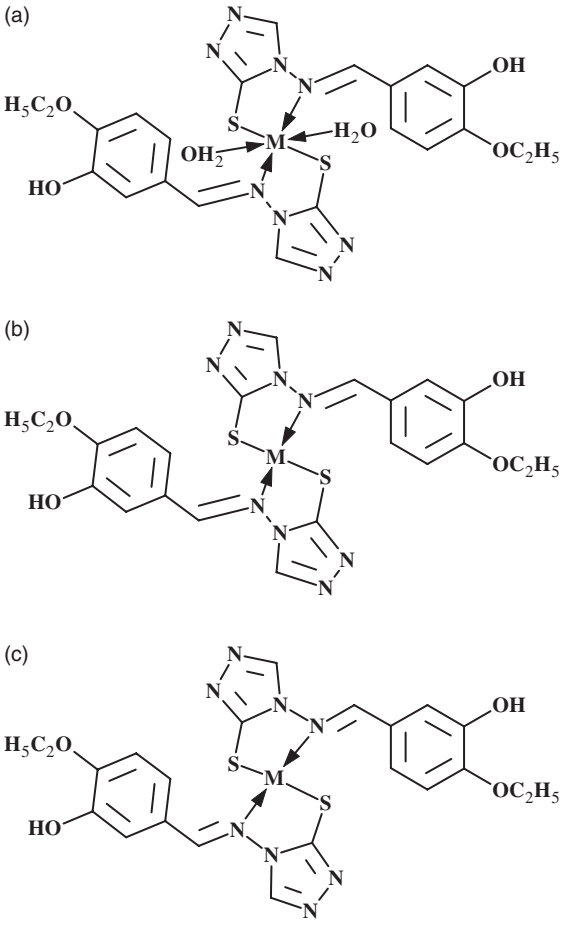

Figure 1. (a) M = Ni(II), Co(II); (b) M = Pd(II); and (c) M = Zn(II).

(figure 1b), and tetrahedral structure for Zn(II) (figure 1c). Zn(II), Co(II), and Ni(II) complexes show antibacterial activity against Gram-negative bacteria such as *E. coli*, *P. aeruginosa*, *S. typhi*, *B. subtilis*, and *S. flexneri*.

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