Complexes of Ag^I, Tl^I, Zn^{II}, Cd^{II}, Hg^{II}, Co^{II}, Ni^{II}, Ru^{II}, Pd^{II}, Ru^{III}, Rh^{III} and Pt^{IV} with 4-(pyridine-2-carboxylidineamino)-5-mercapto-1,2,4-triazole

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Abstract : The synthesis and characterization of complexes of Ag^I, Tl^I, Zn^{II}, Cd^{II}, Hg^{II}, Co^{II}, Ni^{II}, Pd^{II}, Ru^{II}, Ru^{III}, Rh^{III} and Pt^{IV} with 4-(pyridine-2-carboxylidineamino)-5-mercapto-1,2,4-triazole (PMT) have been carried out on the basis of chemical and physical methods like elemental analysis, infrared, ^1H NMR and electronic spectral studies, magnetic susceptibility measurements, conductance and thermal studies. Octahedral structures have been proposed for the Co^{II}, Ni^{II}, Ru^{II}, Ru^{III}, Rh^{III} and Pt^{IV} complexes, square-planar for the Pd^{II} complex, tetrahedral for the Zn^{II}, Cd^{II} and Hg^{II} complexes and linear polymeric structures for the Ag^I and Tl^I complexes. The ligand coordinates to the metal ions through thiol sulfur after deprotonation and with nitrogen of the azomethine group. Pyridine nitrogen of PMT is also involved in coordination in Pd^{II}, Ru^{III}, Rh^{III} and Pt^{IV} complexes.

Keywords : Metal complexes, heterocyclic, chelates, PMT.

Introduction

The metal complexes of transition elements with heterocyclic ligands, especially those containing nitrogen and sulfur have diverse applications in various fields including biology. The antimicrobial[1], antiviral[2], antifungal[3], anticonvulsant[4], anticarcinogenic and antiherbicidal activities[5] of thioamide ligands and its metal complexes are well known and gets more attraction recently. Sulfur and nitrogen donor ligands are also used as powerful pesticides[6]. Ruthenium(II) complexes with substituted triazole derivatives find extensive applications as chemical transducers for optical pH sensing[7]. Some of the substituted triazole compounds either alone or in combination with one or more therapeutically active compounds are used as sodium channel blockers to control sodium channel activity for decreasing various types of pain[8]. Due to their extreme volatility and solubility in non-polar solvents, certain metal chelate systems are extensively used in the purification of metals[9]. The metal complexes with Schiff bases of triazole have various industrial applications also[10-12]. In recent years S and N containing triazole derivatives have attracted more attention for their excellent corrosion inhibition activity. These compounds not only possesses very high values of inhibition efficiency but also bring down the permeation current to a considerable extent[13]. In contrast to many commercial acid corrosion inhibitors, which are highly toxic, most of the N- and S-containing triazole derivatives are environmentally benign corrosion inhibitors[14-16]. The present paper reports the synthesis and characterization of the complexes of Ag^I, Tl^I, Zn^{II}, Cd^{II}, Hg^{II}, Pd^{II}, Co^{II}, Ni^{II}, Ru^{II}, Ru^{III}, Rh^{III} and Pt^{IV} with 4-(pyridine-2-carboxylidineamino)-5-mercapto-1,2,4-triazole (PMT).
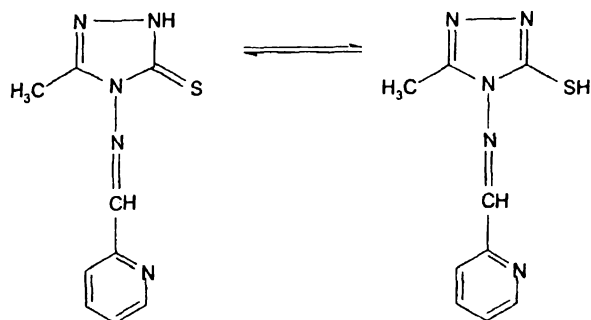
(a)

Table 1. Analytical data of PMT complexes

| Complex | Found (Calcd.) (%) | | | | | Magnetic moment (B.M.) | Molar conductance (Ω^{-1} mol^{-1} cm^2) |
	C	H	N	S	M		
$C_9H_9N_5S$ (Ligand)	49.26 (49.28)	4.13 (4.14)	31.92 (31.94)	14.60 (14.63)	–	–	–
$Zn(C_9H_8N_5S)_2$	43.05 (43.06)	3.20 (3.21)	27.93 (27.91)	12.75 (12.78)	13.01 (13.03)	–	6.0
$Cd(C_9H_8N_5S)_2$	39.35 (39.37)	2.93 (2.94)	25.51 (25.22)	11.68 (11.69)	20.47 (20.49)	–	7.0
$Hg(C_9H_8N_5S)_2$	33.94 (33.92)	2.54 (2.53)	21.97 (21.98)	10.05 (10.07)	31.46 (31.49)	–	8.0
$Ag(C_9H_8N_5S)$	33.13 (33.12)	2.46 (2.47)	21.46 (21.47)	9.83 (9.84)	33.08 (33.09)	–	8.0
$Tl(C_9H_8N_5S)$	25.11 (25.57)	1.83 (1.89)	17.71 (17.76)	7.40 (7.58)	48.02 (48.38)		6.0
$[Pd(C_9H_8N_5S)(H_2O)]Cl$	28.56 (28.57)	2.12 (2.13)	18.51 (18.52)	8.46 (8.48)	28.14 (28.15)	–	210
$Ni(C_9H_8N_5S)_2.2H_2O$	40.67 (40.68)	3.79 (3.80)	26.36 (26.37)	12.05 (12.08)	11.04 (11.05)	3.14	53.0
$Co(C_9H_8N_5S)_2.2H_2O$	40.65 (40.66)	3.79 (3.80)	26.33 (26.35)	12.05 (12.07)	11.07 (11.09)	4.74	57.8
$Ru(C_9H_8N_5S)_2.2H_2O$	40.22 (40.17)	2.98 (2.96)	26.07 (26.01)	11.92 (11.79)	18.80 (18.89)	–	57.0
$[Pt(C_9H_8N_5OS)_2]Cl_2$	31.65 (31.65)	2.12 (2.13)	18.47 (18.46)	8.42 (8.46)	25.71 (25.73)	–	260
$[Ru(C_9H_8N_5S)_2]Cl$	36.31 (36.94)	2.79 (2.76)	23.90 (23.94)	10.87 (10.94)	17.13 (17.29)	1.82	182
$[Rh(C_9H_8N_5S)_2]Cl$	36.81 (36.82)	2.72 (2.75)	23.79 (23.84)	10.86 (10.91)	17.23 (17.54)	–	194

Results and discussion

The analytical results (Table 1) show that Ag^I and Tl^I form ML type complexes while Zn^{II}, Hg^{II} and Cd^{II} form ML$_2$ type complexes with PMT. The Pd^{II} complex contains a molecule of water and is of ML type. The Co^{II}, Ni^{II}, Ru^{II}, Ru^{III}, Rh^{III} and Pt^{IV} form ML$_2$ type complexes and the first three contain two molecules of water coordinated to the metal ion. The presence of coordinated water molecules in the Ni^{II}, Co^{II}, Ru^{II} and Pd^{II} complexes were further confirmed by thermal and spectral data.

Magnetic susceptibility studies : The magnetic susceptibility studies show that all the complexes, except Ni^{II}, Co^{II} and Ru^{III} are diamagnetic. Octahedral Ni^{II} complexes generally show the magnetic moment value slightly higher than the spin-only value of 2.83 B.M. This difference may be due to either the ferromagnetic interaction in the clusters or Jahn-Teller distortion or spin-orbit coupling or due to the combined effects of these. The observed magnetic moment of Ni^{II} complex is 3.14 B.M.,

which is agreeing well with the reported value of other octahedral Ni^{II} complexes[17-19]. A distorted O_h symmetry seems to be more appropriate for the Ni^{II} complex than a perfectly symmetric one. This observation is further supported by the different spectral results. The magnetic moment of Co^{II}-PMT complex is found to be 4.74 B.M. Since the orbital contributions of tetrahedral Co^{II} complexes are much less than octahedral Co^{II} complexes, they have lower magnetic moment values[20]. The observed magnetic moment of Co^{II}-PMT complex lies within the range of high-spin octahedral complexes[18,19].

Thermogravimetric studies : Thermal analysis of the complexes of PMT further confirms the presence of water molecules in the Ni^{II}, Co^{II}, Ru^{II} and Pd^{II} complexes. All the other complexes except these four undergo two step decomposition. The loss in weight in the temperature range 115–220 °C, indicates the loss of coordinated water molecules from these complexes. The thermogram of Ni^{II}, Co^{II} and Ru^{II} complexes with PMT register a loss in weight

Table 2. Electronic spectral bands and their probable assignments of complexes

Complex	Band position (cm^{-1})	Assignment	10 *Dq*	*B*	β
Ni(C$_9$H$_8$N$_5$S)$_2$.2H$_2$O	9078(Ca)	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	9078	940	0.90
	16340	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$			
	25000	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$			
	31056	C.T.			
Co(C$_9$H$_8$N$_5$S)$_2$.2H$_2$O	7309(Ca)	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	9138	989	0.88
	16440	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$			
	20300	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$			
	27460	C.T.			
[Pd(C$_9$H$_8$N$_5$S).H$_2$O]Cl	26600	$^1A_{1g} \rightarrow {}^1T_{2g}$	–	–	–
	29450	$^1A_{1g} \rightarrow {}^1B_{2g}$			
	38320	$^1A_{1g} \rightarrow {}^1E_g$			
[Pt(C$_9$H$_8$N$_5$S)$_2$]Cl$_2$	18622	$^1A_{1g} \rightarrow {}^3T_{1g}$	20486	214.1	0.33
	19802	$^1A_{1g} \rightarrow {}^3T_{2g}$			
	23094	$^1A_{1g} \rightarrow {}^1T_{1g}$			
[Rh(C$_9$H$_8$N$_5$S)$_2$]Cl	16393	$^1A_{1g} \rightarrow {}^3T_{1g}$	22414	335	0.45
	–	$^1A_{1g} \rightarrow {}^3T_{2g}$			
	20408	$^1A_{1g} \rightarrow {}^3T_{1g}$			
	25773	$^1A_{1g} \rightarrow {}^1T_{2g}$			
[Ru(C$_9$H$_8$N$_5$S)$_2$]Cl	13513	$^2T_{2g} \rightarrow {}^4T_{1g}$	28450	429	0.34
	16949	$^2T_{2g} \rightarrow {}^4T_{2g}$			
	25252	$^2T_{2g} \rightarrow {}^2A_{2g}, {}^2T_{1g}$			

corresponds to the loss of two molecules of water, whereas the thermogram of Pd^{II} complex indicates a loss in weight corresponds to the loss of one molecule of water. The sharp decrease in weight occurred in the temperature range of 240-550 °C may be due to the oxidation of the ligand molecule. The final products at 600-800 °C are analyzed to be metal oxides.

Molar conductance studies : The molar conductance values of all the complexes are in the range 5.0-57.8 Ω^{-1} mol^{-1} cm^2 except Pd^{II}, Pt^{IV}, Ru^{III} and Rh^{III} complexes. The relatively low values of molar conductance of most of these complexes indicate the non-electrolytic nature and neutral character of these complexes. The value of molar conductance of Pd^{II} complex is in the range of 210 Ω^{-1} mol^{-1} cm^2 and Pt^{IV} complex is in the range of 260 Ω^{-1} mol^{-1} cm^2. Ru^{III} complex has the value of 182 Ω^{-1} mol^{-1} cm^2 and Rh^{III} complex is in the range of 194 Ω^{-1} mol^{-1} cm^2. These values of molar conductance support the fact that Pd^{II} complex is a 1 : 1 electrolyte and Ru^{III}, Rh^{III} and Pt^{IV}, complexes are 1 : 2 electrolytes.

Electronic spectra : Electronic spectral band positions and its assignments in respect of Co^{II}, Ni^{II}, Pd^{II}, Ru^{III} and Pt^{IV} complexes are given in Table 2. For high spin octahedral complexes of Co^{II}, three transitions are expected in the electronic spectra corresponding to, $^4T_{1g}(F)$ to $^4T_{2g}(F)$, $^4A_{2g}(F)$ and $^4T_{1g}(P)$ in the increasing order of energies. The first transition was not recorded, but its position was assigned from the second transition. The values of the crystal field stabilization energy (10 *Dq*), Racah parameter (*B*) and the covalency factor (β) have been evaluated[20,22].

In the case of octahedral and pseudo-octahedral complexes of Ni^{II}, three spin-allowed transitions are expected corresponding to $^3A_{2g}(F)$ to $^3T_{2g}(F)$, $^3T_{1g}(F)$ and $^3T_{1g}(P)$ generally within the range 7000-13000, 11000-22000 and 19000-27000 respectively. The ratio of the frequencies of the second to the first transition would be around 1 : 8. The first transition corresponding to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ is not recorded in the electronic spectra. The assignment of the transitions and various spectral parameters are calcu-

lated and presented. The calculated B value is lower than the free-ion value of 1080 cm^{-1}.

The Pd^{II} metal ion, generally forms square-planar complexes of D_{4h} symmetry. The metal orbitals, s, p and d, span (i) a_{1g}, (ii) e_u and a_{2u} and (iii) b_{1g}, b_{2g}, a_{1g} and e_g respectively. Similarly, the ligand orbitals transform as b_{1g}, a_{1g} and e_u. The sigma bond formation between the metal ion and the ligand units would use one d-orbital (b_{1g}), one s-orbital (a_{1g}) and two p-orbitals (e_u) of the metal ion. The ground state for the low spin d^8 system is therefore $^1A_{1g}$. Assuming D_{4h} symmetry, one should expect three spin-allowed and three spin-forbidden bands in the electronic spectra of the complexes[23], corresponding to the transitions $^1A_{1g}$ to $^1T_{2g}$, $^1B_{2g}$, ^1E_g states and $^1A_{1g}$ to $^3A_{2g}$, ^3E_g, $^3B_{1g}$ states. However, all these possible transitions are not really observed because of the masking effect due to charge transfer or inter-ligand interactions.

The ground state of Pt^{IV} in an octahedral field is $^1A_{1g}$. The excited state corresponding to t_{2g}, e_g configuration

is $^3T_{1g}$, $^3T_{2g}$, $^1T_{1g}$ and $^1T_{2g}$ in the increasing order of energy. Thus four transitions are expected due to $^1A_{1g}$ to $^3T_{1g}$, $^3T_{2g}$, $^1T_{1g}$ and $^1T_{2g}$ transitions. The position of the band observed and the probable assignments are given in Table 2 along with the values of 10 Dq, B and β.
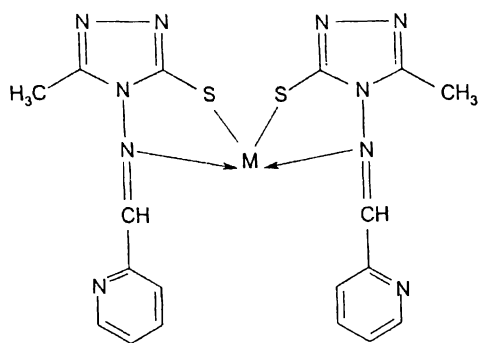
Ruthenium(III) complexes are always six coordinated. The lowest energy transitions are those corresponding to the spin forbidden $^2T_{2g} \rightarrow {}^4T_{2g}$ and $^2T_{2g} \rightarrow {}^4T_{1g}$. According to Tanabe and Sugano, eight different transitions are possible from the ground state $(t_{2g}{}^5, e_g{}^0)$ to the various excited states including the doublet states $(t_{2g}{}^4, e_g{}^1)$ and the quartet states $(t_{2g}{}^4, e_g{}^1)$. So the first two bands are due to the electronic excitation to the $^4T_{1g}$ and $^4T_{2g}$ states and the third band is due to the excitation to the $^2A_{2g}$ and $^2T_{1g}$ states; which is difficult to resolve into two.

Infrared spectra : The infrared spectrum of the ligand has bands at 3150–3065 (v_{N-H}) and 2860 cm^{-1} (v_{C-H}). The ligand bands at 1595 cm^{-1} is assigned to $v_{C=N}$ of the azomethine linkage[19-21]. The slight shift of the band to lower wave number side in the complexes indicates the coordination of this nitrogen with the metal ions.

The ligand molecule containing thioamide moiety is expected to exist in tautomeric thiol and thione forms (Fig. 1). Due to the presence of thioamide moiety, four characteristic bands are expected in the spectra of the ligands. The position of the thioamide band I mainly due to the bending modes of N–H and C–H at 1545 cm^{-1} in the spectrum of the ligand is not shifted appreciably in the spectra of the complexes. But the position of thioamide band II due to the stretching modes of vibrations of C=S and C=N of the ligand (1420 cm^{-1}) suffered a considerable shift towards higher wave number side in the complexes (1445–1450 cm^{-1}). In the spectrum of the ligand PMT, a band at 1595 cm^{-1} is observed due to $v_{C=N}$ of the pyridine ring. The band due to the pyridine ring vibrations is also appeared at 1475 cm^{-1} and 1440 cm^{-1}. In the spectra of some of the complexes the band at 1595 cm^{-1} is shifted to lower wave number side indicating coordination through nitrogen of the pyridine ring while in some other complexes this shift was not observed and hence pyridine ring nitrogen is not involved in bonding[25]. The thioamide band IV which is mainly due to stretching modes of vibrations including C-N, C=S and ring deformations (760–790 cm^{-1}) in the spectra of the ligand is shifted to lower wave number side in their complexes[24]. The increased intensity of the thioamide band IV in the spectra of the ligands may be due to the mixing of thioamide band IV and the band characteristic of the
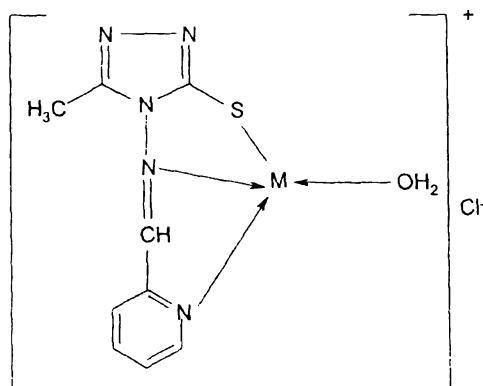
Table 3. Infrared bands (cm^{-1}) of PMT and its complexes

Ligand	Tl^I, Ag^I, Zn^{II}, Cd^{II}, Hg^{II}, Ru^{III}, Rh^{III}, Pt^{IV} complexes	Co^{II}, Ni^{II}, Pd^{II}, Ru^{II} complexes	Assignment
		3400B	v_{O-H}
3150–3065	3060±10	3050±10	v_{N-H}
2860M	2860±10	2890±10	v_{C-H}
1595M	1580±10	1575±10	$v_{C=N}$
1545M	1540M	1540±10M	Thioamide band I
1420M	1445±10	1450M	Thioamide band II
1172M	1180±10	1220±10	Thioamide band III
1039M	1020±10	1010±5	v_{N-N} triazole ring
–	–	900±10	Characteristic of coordinated water
760S	710±5M	710±5M	Thioamide band IV and aromatic ring
667M	670±5	670±5	Aromatic ring
–	480±10W	470±10W	v_{M-N}
–	330±10	320±10	v_{M-S}
–	240±10	250±10	Coordinated pyridine ring

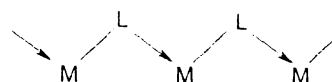M = Zn^{II}, Cd^{II}, Hg^{II}

(b)

M = Pd^{II}

(d)

pyridine ring. The presence of a band around 790 cm^{-1} in the spectra of some of the complexes is due to the presence of pyridine ring. The IR band corresponding to the coordinated pyridine ring is also observed in the region 240–260 cm^{-1} in complexes of Pd^{II}, Ru^{III}, Rh^{III} and Pt^{IV}.

New bands are also observed in the spectra of the complexes due to v_{M-N} and v_{M-S} coupled with other modes of vibrations of the ligand molecules. Bands due to coordinated water molecule are also observed in the spectra of the Co^{II}, Ni^{II}, Ru^{II} and Pd^{II} complexes around 3400 and 890 cm^{-1}.

^1H NMR spectra : The ^{1}H NMR spectra of the Schiff base ligand PMT have the expected characteristic signals. The SH signal around 3.2 of the ligand is absent in the spectra of all the complexes indicating the replacement of this SH proton by a metal atom. Signal observed in the region of 8.18–8.23 due to the azomethine proton are either remained unaffected or shifted slightly to higher field with reference to those of the parent ligand. The

chemical shift values noted for the aromatic ring as well as the ring protons (7.3–7.6) remain unaffected in all the complexes except Pd^{II} complex.

M = Ag^I, Tl^I

(e)

On the basis of the above results octahedral structures have been proposed for the Co^{II}, Ni^{II}, Ru^{II} (Fig. c), Ru^{III}, Rh^{III} and Pt^{IV} (Fig. f) complexes, square-planar for the Pd^{II} complex (Fig. d), tetrahedral for the Zn^{II}, Cd^{II} and Hg^{II} complexes (Fig. b) and linear polymeric structures for the Tl^I and Ag^I complexes (Fig. e). The ligand molecules coordinate to the metal ions through thiol sulfur

M = Ni^{II}, Co^{II}, Ru^{II}

(c)
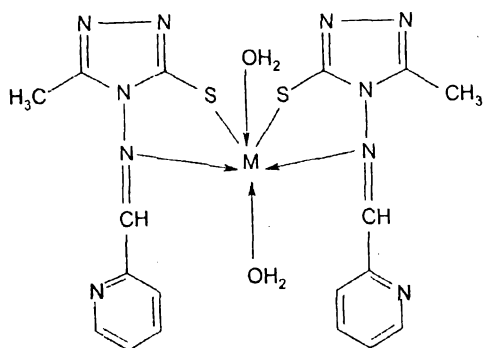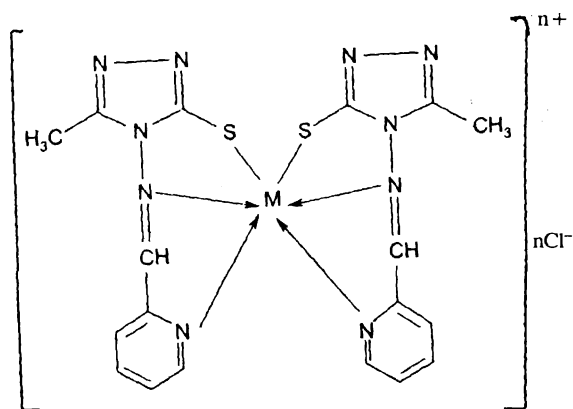
M = Ru^{III}, Rh^{III}, Pt^{IV}

(f)

after deprotonation and with azomethine nitrogen. Pyridine nitrogen of PMT is also involved in bonding in Pd^{II}, Ru^{III}, Rh^{III} and Pt^{IV} complexes.

Experimental

The chemicals used were all of AnalaR or chemically pure grade. The ligand was synthesized[17] by condensing 5-mercapto-1,2,4-triazole with pyridine-2-carboxaldehyde. The product was recrystallized from ethanol, and characterized by various physical and chemical methods. The complexes were prepared by refluxing the respective metal chlorides/acetates (0.01 mol) and the ligand (0.02 mol) in ethanol (75 ml) for 1–5 h. The separated solid was washed with hot water, warm ethanol and ether and dried at 110–120 °C.

The metal contents were determined by the standard AAS method. C, H, N and S were analyzed at STIC, CUSAT, Cochin. The magnetic susceptibility was determined with a Gouy balance at room temperature. Thermo gravimetric analysis was carried out on a Mettler TA 4000 thermal analyzer by heating the complexes in air at a rate of 10°/min up to 850 °C at STIC, CUSAT, Cochin. The molar conductivity of the complexes (in 1×10^3 mol dm^{-3} DMF solution) was measured using an Elico conductivity meter. Electronic spectral studies (Beckmann) and infrared spectral studies (KBr/CsI, Perkin-Elmer 1330 spectrophotometer) were carried out in the Department of Chemistry, Mangalore University.

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