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A Study on Chelation and Antimicrobial Activity of The Complexes of 4-Amino-5-Phenyl-3-Mercapto-1,2,4-Triazole and Its Benzylidene Derivatives

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ABSTRACT

Solid metal complexes of mercapto triazoles with biologically significant metal ions were synthesized and characterized by various spectro-analytical techniques viz. elemental analyses (CHNS & ICPMS), IR, TG-DTA, XPS, ESR and magnetic susceptibility measurements. On the basis of physico-chemical data the formation of polynuclear metal complexes of 3-mercapto-1,2,4-triazoles is ascertained. The antibacterial activity of mercapto triazoles and their Cu(II) complexes has also been evaluated. Further Potentiometric titrations were carried out adopting Irving –Rossotti technique for the formation of complexes of 3-mercapto-1,2,4-triazoles in 70% v/v dioxan–water medium with Fe(II), Co(II), Ni(II), Zn(II), Cd(II) and Pb(II) metal ions at 0.1M (KNO₃) ionic strength and 303K temperature.

Key words: ICPMS, TG-DTA, XPS, ESR, magnetic susceptibility measurements.

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INTRODUCTION

The antimicrobial [1], antiviral [2], antifungal [3], anticonvulsant [4], anti-carcinogenic and anti-herbicide activities [5] of thioamide ligands and their metal complexes are well known and have drawn attention recently. The 1, 2, 4-triazole nucleus is associated with pharmacological activities such as hypoglycemic, antihypertensive and analgesic properties [6-10]. The sulphur and nitrogen donor chelating agents are also used as powerful pesticides [11]. The transition metal complexes of substituted triazole derivatives find extensive application as chemical transducers for optical pH sensing [12]. Metal complexes with thiols containing additional hydroxyl groups exhibit increased biological activity [13]. The substituted triazole compounds either alone or in combination with therapeutically active compounds are used as sodium channel blockers to control sodium channel activity for decreasing various types of pains [14]. Due to their extreme volatility and solubility in non-polar solvents, their metal chelates are extensively used in the purification of metals [15]. The coordinating properties of mercapto triazoles towards metal ions appeared interesting and hence we undertook the present study.

MATERIALS AND METHODS

All the chemicals and solvents used were of AnalaR grade or guaranteed reagents.

Synthesis of ligands

The benzylidene derivatives 4-benzylidene amino-5-phenyl-3-mercapto-1,2,4-triazole (BPMT), 4-(2'-hydroxy) benzylideneamino-5-phenyl-3-mercapto-1,2,4-triazole (HBPMT) and 4-(4'-methyl) benzylideneamino-5-phenyl-3-mercapto-1,2,4-triazole (MBPMT) were synthesised by refluxing 4-amino-5-phenyl-3-mercapto-1,2,4-triazole (APMT) with benzaldehyde, salicylaldehyde and 4-methyl benzaldehyde in acidified ethanolic medium in 1:1 molar ratio [16]. The compounds obtained were recrystallized from ethanol-water mixture and the purity was checked by TLC and melting point.

Synthesis of complexes

The solid complexes of APMT, BPMT, HBPMT and MBPMT were synthesized using metal chlorides of Cu(II), Mn(II), Ni(II), Co(II), Zn(II) and VO(II) by adding aqueous solution of metal salt to the hot ethanolic solution of the ligand in 1:2(M:L) molar ratio. The reaction mixture was refluxed for 6-7 hours. The pH of the solution for complexation was maintained by adding few drops of dilute ethanolic ammonium hydroxide solution. The solid complexes separated were filtered in hot condition, washed with hot ethanol, petroleum ether and then with water to remove unreacted ligand and metal. Finally the solid complexes were dried in an oven at 110 °C.

Physical measurements

The elemental analysis (C, H, N&S) of metal complexes under study were carried out on Perkin-Elmer 240C elemental analyzer. The percentages of metal content in complexes were determined by inductively coupled plasma mass spectrometry (ICPMS) on Perkin

Elmer Sciex ELAN DRC II by open acid digestion method. The chloride estimation in metal complexes was done by Volhard's method [17]. IR spectra (KBr) were recorded on a Perkin-Elmer 435 Spectrophotometer. Thermogravimetric (TG) and differential thermal analyses (DTA) of complexes was carried on Mettler Toledo Star system in the temperature range 0-1000°C. ESR spectra were scanned on JEOL JES-FA 200 ESR Spectrometer X-band microwave unit instrument at room temperature. The magnetic susceptibilities of the metal complexes were measured on a Faraday balance model 7550. The calibration constant was first determined by taking a measurement on standard substance Hg [Co (SCN)₄]. The binding energies of the atoms in the complexes were measured on Kratos axis 165 XPS electron spectrometer by using the source of MgK α radiation (1253.6eV). The pH measurements were made using a digital Digisun electronic model DI-707 pH meter in conjunction with a combined glass and Calomel electrode.

Potentiometric titrations

Potentiometric titrations have been carried out with the ligands APMT, BPMT, HBPMT and MBPMT in 70% v/v dioxan-water medium at 303K and 0.1M (KNO₃) ionic strength. The concentrations of Fe (II), Co (II), Ni (II), Zn (II), Cd (II) and Pb (II), stock solutions were estimated volumetrically by titrating against standard solution of disodium salt of ethylenediamine tetracetic acid using suitable indicators. The dissociation constant of ligands have been determined by measuring the pK_a values [16] in 70% dioxan-water medium.

RESULTS AND DISCUSSION

All the complexes are quite stable to air and moisture and have excellent shelf life. From the analytical data it is evident that all the complexes are in 1:1 ratio except in VO (II)-MBPMT complex, wherein 1:2 composition is observed. The analytical data obtained for the complexes are in good agreement with the proposed structures (Table 1).

Thermogravimetric and Differential thermal analyses.

The TG and DT analyses have been carried out in temperature range of 0-1000°C. Thermograms of the complexes showed weight loss in 2-3 steps, a small loss in weight in the range of 80-120°C, a considerable weight loss in the range of 260°-300°C and gradual and maximum weight loss in the range of 350°-1000°C which are attributed to loss of lattice as well as coordinated water [18-20] molecules and partial decomposition of the complex. The residue left at 1000°C approximately corresponds to the weight of metal oxide indicating 1:1 composition of the complexes. In VO (II)-MBPMT complex the total weight loss (91%) observed is equal to two moles of ligand indicating the composition of the complex as 1:2, which is also evident from C, H, N, S and ICPMS analyses. The DTA of the complexes showed endothermic peaks, which are attributed to various transitional changes accompanied by energy absorptions at different steps of decomposition.

Table 1. Physical and Analytical data of APMT, BPMT, HBPMT, MBPMT and their metal complexes

Ligand/ Complex	Colour	mp (°C)	μ_{eff} (BM)	Analysis Found (Calc) %				
				C	H	N	S	M
APMT	Cream	202-205	-	49.01 (50.0)	4.20 (4.16)	29.06 (29.16)	16.54 (16.66)	-
Co(II)-APMT	Brown	Dp	2.93	29.84 (29.77)	3.52 (3.41)	17.41 (17.37)	9.81 (9.92)	18.54 (18.27)
Ni(II)-APMT	Fluorescent green	Dp	2.31	29.82 (29.79)	3.46 (3.41)	17.44 (17.38)	9.86 (9.93)	18.32 (18.22)
Cu(II)-APMT	Light green	Dp	0.76	29.46 (29.35)	3.48 (3.36)	17.22 (17.12)	9.69 (9.78)	20.0 (19.42)
Zn(II)-APMT	White	Dp	Dia	29.23 (29.19)	3.38 (3.34)	17.14 (17.03)	9.70 (9.73)	20.0 (19.88)
BPMT	White	168-172	-	64.10 (64.28)	4.15 (4.28)	20.39 (20.00)	11.38 (11.42)	-
Mn(II)-BPMT	Light brown	Dp	5.59	44.40 (44.30)	3.72 (3.69)	13.85 (13.78)	7.80 (7.87)	13.60 (13.52)
Cu(II)-BPMT	Dark green	Dp	0.97	43.42 (43.37)	3.53 (3.61)	13.56 (13.49)	7.65 (7.71)	15.92 (15.31)
HBPMT	Cream	197-200	-	60.54 (60.81)	4.21 (4.05)	18.78 (18.91)	10.78 (10.81)	-
Mn(II)-HBPMT	Golden yellow	Dp	5.88	42.52 (42.61)	3.57 (3.55)	13.31 (13.25)	7.50 (7.57)	13.50 (13.0)
Cu(II)-HBPMT	Light green	Dp	1.02	41.83 (41.76)	3.51 (3.48)	13.10 (13.00)	7.34 (7.42)	15.02 (14.74)
MBPMT	Pale yellow	223-225	-	65.17 (65.30)	4.53 (4.76)	19.23 (19.04)	10.78 (10.88)	-
VO(II)-MBPMT	Dirty green	Dp	Zero	58.98 (58.63)	4.06 (4.27)	16.59 (17.10)	7.60 (7.68)	8.02 (7.78)
Co(II)-MBPMT	Blue	Dp	3.78	45.54 (45.24)	4.10 (4.00)	13.42 (13.19)	7.47 (7.53)	14.0 (13.88)
Ni(II)-MBPMT	Yellowish green	Dp	2.85	50.12 (49.01)	4.48 (4.34)	14.64 (14.30)	7.46 (7.54)	15.60 (14.99)
Cu(II)-MBPMT	Dull green	Dp	0.97	44.56 (44.75)	3.65 (3.96)	13.48 (13.05)	7.34 (7.45)	15.04 (14.80)
Zn(II)-MBPMT	White	Dp	Dia	44.62 (44.56)	3.90 (3.94)	13.08 (13.0)	7.31 (7.42)	15.64 (15.17)

Infrared spectra

The IR spectra of Co (II), Ni (II), Cu (II) and Zn (II) complexes of APMT indicated a broad trough ranging from 3100-3600 cm^{-1} which is attributed to the presence of coordinated water in the complexes. The band at 1609 cm^{-1} assigned to $\nu_{\text{C}=\text{N}}$ of the triazole ring is shifted to higher wave number in the complexes showing the involvement of heterocyclic nitrogen in coordination. The thioamide bands at 1065 and 964 cm^{-1} shifts towards lower wave numbers in all the complexes indicating the bonding through sulphur. The IR spectra of all the complexes of BPMT, HBPMT and MBPMT exhibited peaks which are attributable to $\nu_{\text{C}=\text{N}}$ of the azomethine indicating the coordination of its nitrogen with the metal ion. The bands corresponding to $\nu_{\text{C}=\text{N}}$ of triazole ring indicate the involvement of its

nitrogen in coordination. The thioamide band which is mainly due to the stretching modes of vibrations including C–N, C=S in the spectra of the ligands is shifted to lower wave number side in their complexes [21, 22]. The above observed changes in the spectra of metal complexes of benzylidene derivatives indicate that there are three potential donor sites in the ligands, where sulphur of thiol group and nitrogen of azomethine bind with one metal ion to form a five-membered chelate ring and nitrogen of triazole ring other side binds with second metal ion. Thus each ligand moiety is attached to two metal ions and forms a polymeric chain.

Magnetic susceptibility

The low magnetic moment value in Ni (II), Co (II) and Cu (II)-APMT complexes than the expected theoretical values may be due to anti parallel alignment of electron spin on adjacent metal atoms at room temperature which indicate polynuclear nature of metal complexes [23]. In Cu (II) complexes of BPMT, HBPMT and MBPMT the observed magnetic moments are 0.97, 1.02 and 0.97 BM respectively. The magnetic moment values 5.59, 5.88 BM for Mn(II) of BPMT and HBPMT complexes indicate the presence of five unpaired electrons. The magnetic susceptibility measurements of Ni (II)-MBPMT complex showed the magnetic moment of 2.85BM indicating the presence of two unpaired electrons. For Co (II)-MBPMT the magnetic moment is 3.78BM. The magnetic moment value for Zn (II)-MBPMT is zero indicating diamagnetic nature of complex.

X-ray photon spectroscopy

In the complexes of mercapto triazoles the peaks corresponding to 1s binding energies of C, N, O and $^2P_{1/2}$, $^2P_{3/2}$ binding energies of S, Cu, Mn, V, Ni and Zn atoms were recorded. The C 1s spectrum showed three distinct peaks at 284.58, 286.34 and 288.47eV respectively corresponding to benzene ring, triazole ring and azomethine carbon [24-26]. The N 1s binding energies were observed at 398.4 and 399.6eV. The sulphur 2p spectrum exhibited peaks at 162.60 and 161.63eV for $^2P_{1/2}$ and $^2P_{3/2}$ spin states. The peak at 533.21eV is assigned for the coordinated water molecule thus supporting TGA. The 2p spectrum of Cu is spin split into two peaks at 950.8 and 931.1eV respectively which indicates that copper is in +2 oxidation state and infer the participation of sulphur and nitrogen in bonding. The binding energy at 530.64eV corresponds to Mn–O interaction [27] indicating the coordination of phenolic oxygen to Mn in Mn(II)-HBPMT complex. The binding energies at 652.78, 644.17 and 654.60, 641.24eV were observed for $^2P_{1/2}$, $^2P_{3/2}$ of Mn. The increase in binding energy from 639 to 641.24 and 644.17eV indicate Mn–N and Mn–S interactions [28, 29]. Hence it can be concluded that Cu (II)-APMT has two binding sites viz. Cu–N and Cu–S whereas Mn(II)-HBPMT complex has Mn–O, Mn–N and Mn–S as binding sites. In VO (II)-MBPMT the V 2p spectrum showed two distinct peaks at 524.9 and 517.8eV. The higher binding energy from 513.4 to 517.8eV indicates coordinated [30] vanadium. The binding energy 531.7eV corresponds to O 1s of oxygen attached to vanadium. The 2p binding energies at 870.62 and 853.05eV were observed for $^2P_{1/2}$ and $^2P_{3/2}$ energy levels of Ni [31] indicating Ni–S interaction in Ni (II)-MBPMT complex. The 2p spectrum of Zn in Zn (II)-MBPMT complex is spin split into two peaks at 1044.58eV for $^2P_{1/2}$ and 1021.50eV for $^2P_{3/2}$ spin states. The value 1021.50eV for Zn–S interaction³¹ is in agreement with the literature value 1022eV.

ESR studies

The ESR spectrum of Cu (II)-APMT, BPMT and HBPMT exhibited two g values corresponding to anisotropy indicating tetragonal geometry in APMT, non-cubic geometry in HBPMT and rhombohedral geometry in BPMT and MBPMT. The peak corresponding to g_y exhibited hyperfine splitting in the copper complexes due to interaction of an electron spin with nuclear spin of Cu ($I=3/2$). The ESR spectrum of Mn (II)-APMT, BPMT, HBPMT and MBPMT complexes indicate nearly isotropic ' g ' values. The g_{\parallel} and g_{\perp} values observed for VO (II)-MBPMT complex are 1.98129, 1.96384 respectively indicating tetragonal distorted geometry.

From all the spectral investigations and results tentatively the structures are predicted for the metal complexes of APMT, BPMT, HBPMT and MBPMT as (Fig. I-V)

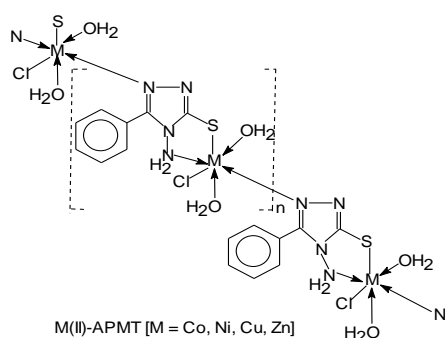


Fig 1

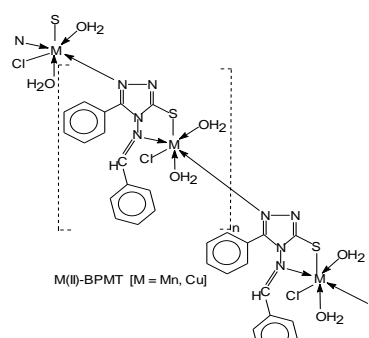


Fig 2

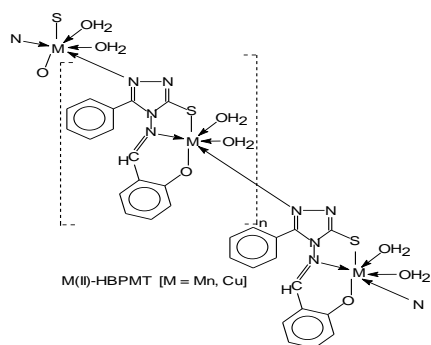


Fig 3

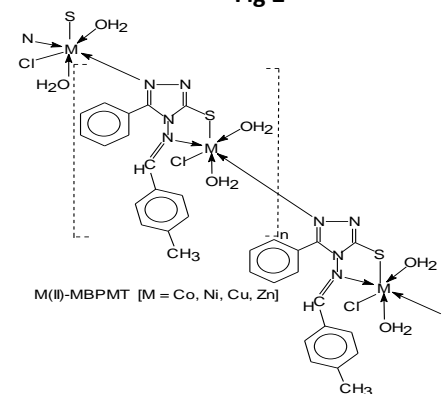


Fig 4

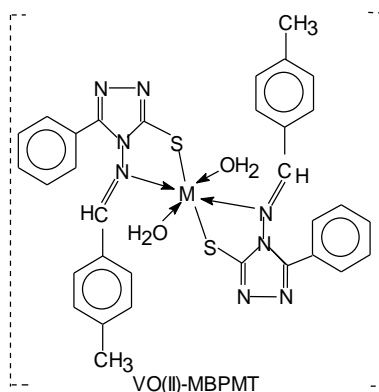


Fig 5

DETERMINATION OF STABILITY CONSTANTS OF BINARY COMPLEXES OF APMT, BPMT and MBPMT

The stability constants were calculated from linear plots of $\log (1-\bar{n})/\bar{n}$ Vs pL and $\log (2-\bar{n}) / (\bar{n} -1)$ Vs pL. The metal ligand formation curves data for APMT indicated the formation of 1:1 and 1:2 complexes except Pb (II) – APMT system wherein 1:2 stability constants are not obtained. (The \bar{n} values of M(II)-BPMT and M (II)-MBPMT systems vary from 0.1 to 1.9 indicating formation of 1:1 (ML) and 1:2 (ML₂) complexes in all the systems except with Co(II) and Ni(II) where only 1:1 complexes are formed. A comparison of stabilities in APMT, BPMT and MBPMT Table 2, 3, 4) with respect to metal ions Fe (II), Co(II), Ni(II), Zn(II), Cd(II) and Pb(II) revealed that Fe(II) complexes have higher stabilities. The order with respect to Ni (II) and Co (II) followed the Irving and William [32] and Muller and Maley [33, 34] order of stabilities. The higher stability of Cd (II) and Pb(II) complexes than Ni(II) and Co(II) in condensed systems is due to invariably soft acid character of Cd and Pb as per Pearson's HSAB principle.

Table 2. Metal Ligand Stability Data for M (II)-APMT in 70% v/v Dioxan-Water Medium at 303K Temperature and 0.1M Ionic strength

M (II)-APMT	Log K ₁	Log K ₂	Log β ₂	Composition
Fe(II)	5.55	4.12	9.67	1:1, 1:2
Co(II)	3.85	3.29	7.14	1:1, 1:2
Ni(II)	4.42	3.40	7.82	1:1, 1:2
Zn(II)	4.12	3.35	7.47	1:1, 1:2
Cd(II)	4.56	3.35	7.91	1:1, 1:2
Pb(II)	3.83	-	-	1:1

Table 3. Metal Ligand Stability Data for M (II)-BPMT in 70% v/v Dioxan-Water Medium at 303K Temperature and 0.1M Ionic strength

M (II)-BPMT	Log K ₁	Log K ₂	Log β ₂	Composition
Fe(II)	6.55	5.20	11.75	1:1,1:2
Co(II)	4.07	-	-	1:1
Ni(II)	4.67	-	-	1:1
Zn(II)	6.37	4.95	11.32	1:1, 1:2
Cd(II)	6.12	4.72	10.84	1:1, 1:2
Pb(II)	5.82	4.52	10.34	1:1, 1:2

Table 4. Metal Ligand Stability Data for M (II)-MBPMT in 70% v/v Dioxan-Water Medium at 303K Temperature and 0.1M Ionic strength

M (II)-MBPMT	Log K ₁	Log K ₂	Log β ₂	Composition
Fe(II)	7.42	6.72	14.14	1:1, 1:2
Co(II)	4.58	-	-	1:1
Ni(II)	4.83	-	-	1:1
Zn(II)	6.91	6.10	13.01	1:1, 1:2
Cd(II)	6.42	5.85	12.27	1:1, 1:2
Pb(II)	6.22	5.60	11.82	1:1, 1:2

The order of stabilities of M (II)-APMT with respect to metal ions is

Log K₁: Fe (II) > Cd (II) > Ni (II) > Zn (II) >Co (II) = Pb(II)

Log K₂: Fe (II) > Ni (II) > Cd (II) =Zn (II) > Co (II)

Log β₂: Fe (II) > Cd (II) > Ni (II) > Zn (II) >Co (II)

The order of stabilities ofM(II)-BPMT and M(II)-MBPMT with respect to metal ions is

Log K₁: Fe (II) > Zn (II) > Cd (II) > Pb(II) Ni(II) >Co(II)

Log K₂: Fe (II)> Zn (II)> Cd (II) Pb(II)

Log β₂: Fe (II) > Zn (II) > Cd (II) > Pb(II)

BIOLOGICAL ACTIVITY

The antimicrobial activity of copper complexes of APMT, BPMT, HBPMT and MBPMT compounds were tested by applying the broth dilution method [35, 36] against Gram-positive and Gram-negative bacteria. The widely used rich medium called Luria-Bertani broth is popular because it permits fast and good growth yields for many bacterial species. A set of sterilized test tubes with nutrient broth medium capped with cotton plugs were used. The compounds under investigation were dissolved in DMSO solvent to obtain a 1mg/mL solution. A fixed volume of 0.5mL overnight culture is added in all the test tubes and the inhibition zones of microbial growth produced were measured in millimeters at the end of an incubation period of 48h at 28°C. The DMSO alone showed no inhibition zone. The minimum inhibition concentration (MIC) was determined using spread plate method by which a pure culture of an individual bacterial species can be developed. The comparison of activity of the ligands with that of the complexes revealed that all the copper complexes are inactive towards Gram-negative bacteria and moderately or highly active towards Gram-positive bacteria (Table 5). Further the activity of APMT, BPMT and HBPMT against Gram-positive bacteria is enhanced on complexation, while that of MBPMT is lowered.

Table 5. Antibacterial activity of the copper complexes of mercapto triazoles

Tested compounds	E. coli (Gram-ve)	Bacillus subtilis (Gram + ve)
APMT	++	++
APMT Cu(II)	-	+++
BPMT	+	-
BPMT Cu(II)	-	++
MBPMT	+	+++
MBPMT Cu(II)	-	++
HBPMT	+	++
HBPMT Cu(II)	-	+++

+ > 5mm slightly active, ++ >7mm moderately active, +++ > 9mm highly active

CONCLUSION

The spectro-analytical techniques employed provided valuable and complementary data in the present study to understand the structural features of title compounds and their metal complexes. The formation of polynuclear metal complexes is predicted on the basis of magnetic as well as ESR studies and their structures have been assigned based on analytical and various spectral data. The equilibrium studies are informative to identify the potential donor sites in the compounds under study. Biological studies on the title compounds and their Cu (II) complexes indicated their potential to act against bacteria.

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