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Synthetic, Spectral, Thermal, X-ray and Antimicrobial Studies on Metal Complexes of 1,3-*bis*[(5-Mercapto-4-phenyl)-1,2,4-triazol-3-yl]propane

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A series of complexes of Pb(II), Co(II), Cu(II) and Ni(II) with a tetradentate ligand, 1,3-*bis*[(5-mercapto-4-phenyl)-1,2,4-triazol-3-yl] propane, [H_2-(BMPTP)] was synthesized and characterized on the basis of elemental analysis, molar conductance, diffused reflectance, magnetic susceptibility, spectral, thermal and X-ray studies. The antimicrobial and antifungal activity of the metal complexes have been checked. All of the metal-complexes are of 1:1 (M:L) stoichiometry. The IR spectra show that the tetradentate ligand coordinating through the SN-NS donor system. Various ESR parameters for the Cu(II) complex have been calculated. The complexes are polymeric in nature and non-electrolytic in nature. Magnetic moment value indicate diamagnetic nature of Pb(II) complex and paramagnetic nature of cobalt, copper and nickel complexes. The electronic spectral data suggest a tetrahedral geometry for Pb(II) complex, an octahedral geometry for Co(II) and Ni(II) complex and a pseudo-tetrahedral geometry for Cu(II)complex. The metal complexes show high antimicrobial activities and do not show any antifungal activity.

Key Words: Pb(II), Co(II), Cu(II) and Ni(II) complexes, Triazole, Glutaric acid.

INTRODUCTION

Polydentate ligands have the remarkable property of forming metal complexes and serve as the most important class of sculptures-nitrogen donor ligands.1,2,4-Triazole with substituents in 4- and 5-positions and *bis*(1,2,4-triazoles) are classes of compounds with wide technical importance. Polydentate ligands and their metal complexes are becoming increasingly important as analytical[1], industrial[2], biochemical[3] and antibacterial[4], antifungal[5] agents. Prompted by these findings we have been interested in the synthesis of a polydentate ligand in an attempt to synthesize metal complexes of multifarious structures. The present paper describes the synthesis and characterization of polymeric Pb(II), Co(II), Cu(II), Ni(II) complexes using tetradentate ligand derived from fusion of glutaric acid and phenyl thiosemicarbohydrazide (PhTSC) (Fig. 1).

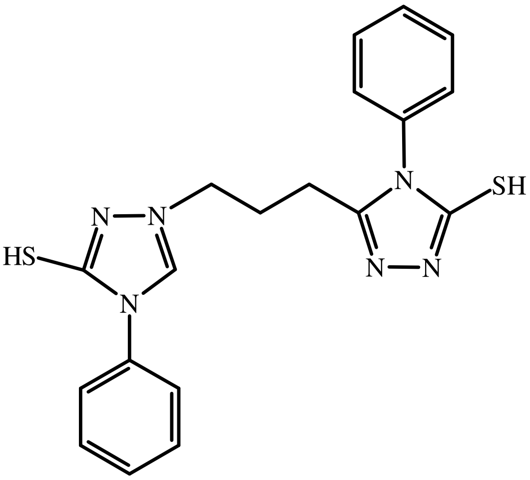
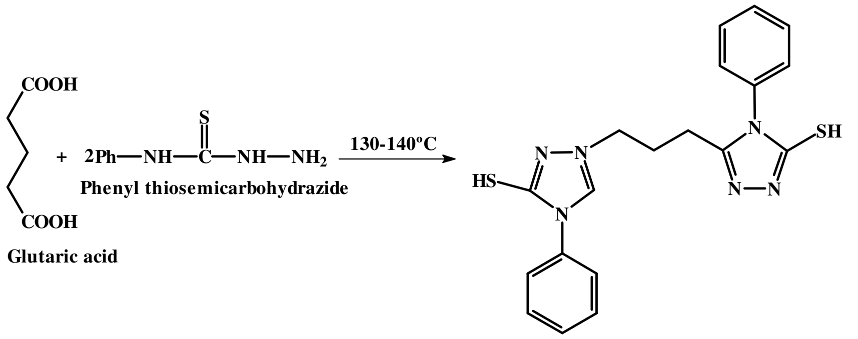


Fig. 1. 1,3-*Bis*[(5-mercapto-4-phenyl)-1,2,4-triazol-3-yl]propane (H_2-[BMPTP])

EXPERIMENTAL

All the chemicals used were of AR grade. Various solvents used were of S.D. Fine Chemicals and of Merck made. The compounds were analyzed for C, H, N, S contents on Thermo Finnigan elemental analyzer, Model No. FLASH EA 1112 Series at SAIF, I.I.T. Mumbai. The metal content in the complexes were determined by ICPAES (Inductively Coupled Plasma Analysis) technique as well as volumetrically by standard procedure[6]. The molar conductance values were measured in DMF (10^{-3}) on an Equiptronics digital conductivity meter. Room temperature magnetic susceptibilities were measured by a Gouy balance using $Hg[Co(SCN)_4]$ as a calibrant. The effective magnetic moments were calculated after diamagnetic correction for ligand components using Pascal's constants[7]. Infrared spectra were recorded on a model 160 Perkin Elmer FTIR spectrophotometer using KBr Pellets. Far IR spectra were recorded on Magna IR 550, Make of Nicolet. Reflectance spectra of the solid complexes in the UV-Visible spectral region were recorded against $BaSO_4$ as reference in the Jasco 560 solid state UV/VIS spectrophotometer. ESR Spectra of Cu(II) complexes were recorded on an E-112 Varian-E-LINE, electron spin resonance spectrometer at room temperature and low temperature for the samples using TCNE as marker. Thermogravimetric studies (TGA and DTA) of the complexes were made on Perkin-Elmer diamond TG-DTA instrument at SAIF, IIT Mumbai, by recording the change in weight on increasing the temperature from room temperature to 900ºC in the nitrogen atmosphere. X-ray diffraction studies for the complexes have been done at IIT, Mumbai.

The ligand, H_2-(BMPTP) is prepared by the procedure reported below. Phenyl thiosemicarbohydrazide is fused with glutaric acid on an oil bath by maintaining the temperature between 130-140ºC. The pasty mass is separated out by filtration and purified by giving washings with hot water and dried overnight (Yield: 80 %, m.p. 155°C).



1,3-*bis*[(5-mercapto-4-phenyl)-1,2,4-triazol-3-yl]propane H_2-[BMPTP]

Preparation of complexes: The ligand (0.03 mol) was suspended in 15 mL DMF. The solution of corresponding metal acetate (0.03 mol) was dissolved in 15 mL distilled water which was added to the ligand solution drop wise under stirring. The solid product obtained was stirred for 0.5 h and filtered by suction, washed with distilled water, repeatedly and dried in vacuum.

Biological activities: The antibacterial and antifungal activities of the complexes were screened against some of the bacteria and fungi. The Pour Plate method was used to assay antibacterial and anti fungal activity against *E. coli, S. typhi, S. aureus* and *A. niger*. The solvent used was 0.1 N HCl and the sample concentration was 100-0.1 μg/mL.

Outlay of the Pour Plate method: The analysis is carried out in 2 steps: (a) *Qualitative analysis:* To detect whether the samples are active against specific organisms at ambient conditions. (b) *Quantitative analysis*: To calculate the minimum inhibitory concentrations (MIC) of the active samples.

Procedure: The test compounds have been subjected to *in vitro* screening by pour plate technique against Gram-positive and Gram-negative bacteria *viz.*, *E. coli* ATCC 11108, *S. typhi* ATCC 786, *S. aureus* ATCC 29737 using Himedia Antibiotic No. 8 as the culture medium. This medium is boiled and filtered through an ordinary filter paper and finally through a Whatman filter paper. To this filterate agar is added. The medium thus prepared is used for the growth of bacteria after sterilization in an autoclave at 15 lbs/121ºC/15 min. After sterilization, the medium is mixed with respective cultures (diluted in 0.9 % saline) and poured in sterile petri-dishes. After setting, small bores are made on the plates. 0.1 mL of the sample dilutions are added in these bores and allowed to diffuse for 1 h at 10ºC and incubated at 37ºC for 24 h and then examined for the presence or absence of growth of the test organisms. The lowest concentration at which there was no visible growth was taken as an end point known as minimum inhibitory concentration (MIC). Next day the zones of inhibition are measured in mm.

Dilutions: (a) *Qualitative test:* Concentration of 100 µg/mL is prepared in 0.1N HCl. (b) *Quantitative test:* Various concentrations *viz.*, 100, 50, 40, 30, 20, 10, 5, 0.5, 0.25, 0.125, 0.1, *etc.* are prepared in 0.1 N HCl.

Ampicilin and cephalexin were used as standard drugs against Gram-positive and Gram-negative bacteria respectively and were subjected to similar screening programs. MIC of ampicilin is 0.01 µg/mL against *S. aureus* and that of cephalexin is 1 µg/mL against *S. typhi*.

The zones of inhibition found around each disc were measured by means of calipers. The end point was taken as the complete inhibition of growth as it appeared to the unaided eye. The diameters of zones were recorded and reported as resistant or sensitive to each microbial tested.

The complexes have been tested for their antibacterial activity with the help of Pour Plate method. Results are shown in Tables 9 and 10.

RESULTS AND DISCUSSION

The analytical and physical data of the metal complexes are presented in Table-1. The complexes are intensively coloured and thermally stable at least upto 275ºC. They are insoluble in water and show almost negligible solubility in common organic solvents, though they are more soluble in DMF at room temperature. The analytical data of the metal complexes indicate that the complexes have 1:1 metal-ligand stoichiometry. The elemental analysis data of the complexes show the presence of the one metal atom for the ligand. Thus, the complexes can be formulated as [ML] where M = Pb(II), Co(II), Cu)(II), Ni(II) and L represents deprotonated ligand, *i.e.* H_2(BMPTP).

The FT-IR spectra of the complexes were recorded over a range of 4000-100 cm^{-1}. The assigned values of the structurally important bands due to ν(C=N), ν(C-S), ν(M-S) and ν(M-N), ν(O-H) are given in Table-2.

IR spectra of the metal complexes quite complex and it is not possible to assign all the bands without ambiguity. However, structurally important bands (Table-2) due to ν(C-N), ν(M-S), ν(M-N) modes are distinguishable and provide unequivocal evidence regarding structural features and manner of their bonding with metal ions. Some common features of the infrared spectra are noteworthy: (1) In all the complexes the ν(C-N)

TABLE-1
MAGNETIC, PHYSICAL AND ANALYTICAL DATA FOR LIGAND AND ITS METAL COMPLEXES

Compound	m.f.	m.w.	Colour	Yield (%)	m.p. (ºC)	Elemental analysis found (calcd.) %					μ_{eff} (BM)
						M	C	N	H	S	
H_2-(BMPTP)	$C_{19}H_{18}N_6S_2$	394.00	White	80.0	155	- -	56.21 (57.86)	20.97 (21.32)	4.6 (4.57)	7.10 (6.24)	-
[Pb(BMPTP)]$_n$	$C_{19}H_{16}N_6S_2Pb$	599.20	Yellow	89.2	220d	21.14 (20.89)	37.58 (38.06)	11.73 (10..9)	3.95 (4.47)	14.60 (15.68)	1.77
[Co(BMPTP)·2H_2O]$_n$	$C_{19}H_{16}N_6S_2Co$	450.93	Greenish gray	89.0	235d	14.07 (13.09	51.03 (50.56)	17.80 (18.62)	3.97 (4.10)	13.71 (14.19)	3.69
[Cu(BMPTP)]$_n$	$C_{19}H_{16}N_6S_2Cu$	455.54	Gray	76.8	230d	21.05 (20.99)	49.98 (50.05)	17.91 (18.43)	3.93 (3.51)	7.81 (7.02)	1.03
[Ni(BMPTP)·2H_2O]$_n$	$C_{19}H_{16}N_6S_2Ni$	450.69	Brown	78.0	260d	19.37 (19.26)	49.50 (50.58)	17.26 (18.63)	4.36 (4.43)	8.69 (7.10)	2.64

d = decomposed.

TABLE-2
SELECTIVE IR BANDS (cm^{-1}) OF LIGAND AND COMPLEXES

Compound	ν(C=N)	ν(Ar–N)	ν(C–S)	ν(O–H)	ν(C=C) aromatic	ν(M–S)	ν(M–N)
H_2-BMPTP	1601	1446	1191 (s) 1253 (w)	-	1546	-	-
[Pb(BMPTP)]$_n$	1598	-	1179	–	-	692	497
[Co(BMPTP)·2H_2O]$_n$	1601	-	1152	3461	-	608	497
[Cu(BMPTP)]$_n$	1600	-	1154	–	-	606	498
[Ni(BMPTP)·2H_2O]$_n$	1600	-	1069	3456	-	691	498

vibrations undergo a shift to lower energy as compared to the free ligand, indicating coordination of the azomethine nitrogen to the metal ion which is further confirmed by the appearance of new bands due to ν(M-N).in the lower wave number region[9]. (2) The significant shifts of the free ligand ν(C-N) band to the lower wave number side in the complexes point to bonding of the ligand to the metal ion though the nitrogen and support the tetradentate nature of the ligand. (3) The strong band due to ν(C=S) observed at 1191 cm^{-1} in the spectrum of the ligand was shifted towards lower wave number in the complexes suggesting bonding of ligand to metal ion through sulphur. This was further supported by the appearance of new peaks due to ν(M-S) at *ca.* 692 cm^{-1} in the spectra of the complexes. (4) Peaks corresponding to the ν(O-H) stretching was observed in the complexes at *ca.* 3461 cm^{-1}. (5) Inference can be made that these were due to the presence of coordinated water molecules, which is generally expected in the Co(II) and Ni(II) complexes, to have water molecules coordinated to the metal ion. However, the Co(II) complex exhibited a weak band, which can be attributed to the adsorbed water, which was further supported by thermal studies.

The magnetic moment value of the Co(II) complex is 3.69 BM. Although the μ_{eff} value of high-spin octahedral and tetrahedral cobalt complexes overlap considerably, tetrahedral Co(II) complexes generally have lower μ_{eff} values, often in the range of 4.2-4.5 BM. Cu(II) shows pseudo tetrahedral geometry[10] and Ni(II) shows an octahedral geometry[11].

The X-band room temperature ESR spectra of poly-crystalline samples of copper(II) complex could not show $\Delta Ms = \pm 2$ transition at half field, indicating the absence of intermolecular antiferromagnetic interactions[12]. There are several examples of pseudo-tetrahedral Cu(II) complexes[12,13], where the ESR spectra do not show any resolved hyperfine splitting. The absence of hyperfine splitting is attributed to dipolar line broadening and to the much reduced nuclear hyperfine coupling constant for pseudo-tetrahedral copper(II) complexes[13].

The ESR spectrum of present Cu(II) complex exhibit two g values ($g_{\parallel} = 2.27$, $g_{\perp} = 2.08$) are less than 2.3 and are in agreement with the covalent character of the metal-ligand bond. The values of the hyperfine splitting parameters $A_{\parallel}$ and $A_{\perp}$ are calculated[13] by taking one third of the line widths at half height and A_O as $1/3[A_{\parallel} + 2A_{\perp}]$. The deviation from planar to tetrahedral geometry is reflected in the $A_{\parallel}$ and $A_{\perp}$ values[14]. In the case of severe distortion from square planar towards tetrahedral geometry, the A_0 values are lowered by a factor of two or three. The A_0 values for the present complexes compare very well with the values reported for pseudo-tetrahedral Cu(II) complexes. These observations support the previously discussed results that the copper ion environment is highly distorted towards tetrahedral configuration. The ESR data further support the prediction made from magnetic and electronic spectral data that the geometry around the Cu(II) center is pseudo-tetrahedral.

The thermogravimetric curves recorded for the complexes listed in Table-3 shows that all the complexes decomposed on heating to form the product, following a sequence of steps. The complexes of Pb(II), Co(II), Cu(II) and Ni(II) showed two steps in the TG prior to the formation of final stable product.

TABLE-3
THEMOANALYTICAL DATA FOR METAL COMPLEXES

Complex	Temp. range (ºC)	Weight loss (%)		Group/ moiety lost
		Calculated	Observed	
$[Pb(BMPTP)]_n$	Rt. 220	5.074	4.850	-$C_{19}H_{14}N_6$
	220-875	1.027	1.212	- S_2H_2
	875-900	2.988	3.262	-$(SO_4)_2$
$[CO(BMPTP)\cdot 2H_2O]_n$	Rt. 235	0.980	0.935	$2H_2O$
	235-675	8.891	8.680	-$C_{19}H_{12}N_6$
	675-850	1.811	1.336	-S_2H_2
	850-900	2.097	2.405	-COO
$[Cu(BMPTP)]_n$	Rt. 230	5.292	5.540	$C_{19}H_{14}N_6$
	230-805	1.071	0.960	- S_2H_2
	805-900	1.290	0.890	-CuO
$[Ni(BMPTP)\cdot 2H_2O]_n$	Rt. 260	1.198	1.290	$2H_2O$
	260-780	10.852	10.369	-$C_{19}H_{14}N_6$
	780-875	2.197	1.944	- S_2H_2
	875-900	2.480	2.592	-NiO

The first mass loss step in each of these complexes initiated at about 150-250ºC and tapered in the temperature range 300-400ºC. This was followed by other steps involving the major mass loss. The complexes show a clear separation between the first and further steps. The values deduced from the TG curves for the number of constitutional water were found to be two for Co(II) and Ni(II) complexes. The mass loss in case of copper complex was very negligible, which could be accounted for the adsorbed moisture on exposure to atmosphere. From the amount of weight loss shown by the TG curves, it could be concluded that the moisture content in the Cu(II) complex was found to be relatively less than that in the complexes of Co(II) and Ni(II). The presence of constitutional water in complexes of Co(II) and Ni(II) was evident from the IR patterns recorded for these samples.

The IR patterns recorded for the samples prior to thermogravimetric studies did show the presence of water in all the compounds. A sharp -OH frequency band was observed for Co(II) and Ni(II) complexes, confirming the presence of water molecule in coordination sphere[15]. However, the Cu(II) complex showed a weak band which could be due to the adsorbed water by the complex on exposure to the ambient atmosphere. Hence, the possibility for the elimination of water from the compounds during thermolysis could be well expected.

The loss corresponding to the second steps in complexes resulted in the formation of their sulphate from the dried complexes, which on further heating transformed progressively to the oxides except lead complexes. The thermal stability of anhydrous complexes deduced from the TG curves suggest that the temperatures of thermal decomposition of Pb(II), Co(II), Cu(II) and Ni(II) were *ca.* 220, 235, 230, 260ºC, respectively.

Differential thermal analysis was done by heating at the programmed heating rate for the samples in nitrogen atmosphere. The temperature was allowed to increase at a rate of 10ºC min^{-1}. The high decomposition temperature of the chelates indicates that they are thermally quite stable, suggesting stronger metal-ligand bonding and also their polymeric existence. This is further supported by the very low solubility in all the common solvents.

The DTA curves recorded for the samples showed endothermic peak followed by broad exothermic peak for all the complexes. The endothermic peak could be in general be attributed to the loss of water in case of Co(II) complex, the twin endothermic peak preceding the exothermic peak in the range 200 to 300ºC could be due to loss of water and partial decomposition of the metal complex which subsequently merges with the peak caused by the burning of the metal complex.

The IR spectrum recorded prior to thermal analysis showed the presence of water in all the compounds, very resolved peaks for Co(II) and Ni(II) and a very weak band for Cu(II) complex in the (O-H) frequency band region. The peak intensities suggest that the Cu(II) complex adsorbed moisture, where as Co(II) and Ni(II) complexes have coordinated water molecules, which was corroborated by TG and DTA.

X-Ray diffraction technique can be used to determine the crystallinity of the complexes. The X-Ray diffraction patterns show few intense reflections followed reflections of rapidly decreasing intensities at higher angles.

All the observations are indexed and lattice constants are determined. The crystallographic results such as 'd' values, Miller indices and relative percentage intensities are reported in Tables 4-7. The position of each sharp reflux was measured in terms of 2θ value.

TABLE-4
$[Pb(BMPTP)]_n$

Peak no.	2θ	Miller indices	d_{obs} (Å)	D_{cal} (Å)	I (%)
1	5.120	020	17.245	17.3	37.5
2	5.579	110	15.828	15.73	39.8
3	7.920	100	11.153	11.16	100.0
4	16.439	953	5.388	5.43	25.3
5	21.179	953	4.192	4.18	31.3

Average lattice constants = 34.151.

TABLE-5
$[Co(BMPTP)\cdot 2H_2O]_n$

Peak no.	2θ	Miller indices	d_{obs} (Å)	D_{cal} (Å)	I (%)
1	6.380	020	13.842	13.85	5.5
2	7.920	110	11.154	11.14	100.0
3	8.440	100	10.468	10.49	4.7
4	12.997	953	6.806	6.83	5.5
5	16.378	953	5.408	5.42	10.3

Average lattice constants = 36.980.

TABLE-6
$[Cu(BMPTP)]_n$

Peak no.	2θ	Miller indices	d_{obs} (Å)	D_{cal} (Å)	I (%)
1	7.920	020	11.153	11.16	100.0
2	14.801	110	5.980	5.95	8.1
3	16.400	100	5.401	5.45	12.7
4	19.380	953	4.576	4.58	21.0
5	21.140	953	4.199	4.18	25.1

Average lattice constants = 26.055.

TABLE-7
$[Ni(BMPTP)\cdot 2H_2O]_n$

Peak no.	2θ	Miller indices	d_{obs} (Å)	D_{cal} (Å)	I (%)
1	6.160	020	14.337	14.31	19.4
2	7.001	110	12.617	12.65	17.8
3	7.960	100	11.098	11.12	100.0
4	19.460	953	4.558	4.56	5.5
5	21.158	953	4.196	4.18	7.1

Average lattice constants = 30.297.

X-Ray diffractometric study of metal complexes provides information about their crystallization. Each diffractogram is well resolved into sharp refluxes suggesting highly crystalline nature for the complexes

The results of the Pour Plate method shown in the Table-8 indicate that the complexes are highly active for the selected organisms. Compared with the standard compound Cephalexin, the present complexes are less active against the respective strains of microorganisms. (Table-9). The present complexes are not at all active against the antifungal organism *Aspergillus niger*.

TABLE-8
QUALITATIVE RESULTS (Concentration -100 μg/mL)

Complex	Organism			
	E. coli (gram -ve)	*S. typhi* (gram -ve)	*S. aureus* (gram +ve)	*A. niger* (gram +ve)
H_2-(BMPTP)	No growth	No growth	No growth	Growth observed
$[Pb(BMPTP)]_n$	NG	NG	NG	G
$[Co(BMPTP)\cdot 2H_2O]_n$	NG	NG	NG	G
$[Cu(BMPTP)]_n$	NG	NG	NG	G
$[Ni(BMPTP)\cdot 2H_2O]_n$	NG	NG	NG	G

NG: No growth (Inhibition zones observed).
G: Growth observed (No inhibition zones observed).

TABLE-9
MINIMUM INHIBITORY CONCENTRATION (MIC) RESULTS

Sample	Conc. (μg/mL)	*E. coli* zone (mm)	Conc. (μg/mL)	*S. typhi* zone (mm)	Conc. (μg/mL)	*S. aureus* zone (mm)
H_2-(BMPTP)	0.50	10.74	0.750	10.86	0.50	10.44
$[Pb(BMPTP)]_n$	1.00	12.22	1.000	10.66	1.00	10.70
$[Co(BMPTP)\cdot 2H_2O]_n$	1.50	10.22	1.125	11.48	1.00	10.26
$[Cu(BMPTP)]_n$	1.00	13.48	1.250	14.06	1.25	13.96
$[Ni(BMPTP)\cdot 2H_2O]_n$	0.75	12.80	0.750	12.68	0.50	11.38

Conclusion

Based on the above discussion and information available in the literature, the following conclusions may be drawn. (1) The magnetic moment values, together with the electronic spectral data, are in favour of an octahedral stereochemistry for Co(II) and Ni(II) complexes, a pseudo-tetrahedral geometry for Cu(II) complex and tetrahedral geometry for Pb(II) complex. (2) The analytical data shows the presence of one metal ion per ligand molecule, with a polymeric structure, further supported by the high decomposition temperature and poor solubility of the compounds. (3) The complexes are highly active as microbial agent but comparatively Cu(II) and Ni(II) complexes are more microbial agent than Pb(II) and Co(II). (4) The complexes are not at all active as antifungal agents. (5) From X-ray studies, each diffractogram is well resolved into sharp refluxes suggesting highly crystalline nature for the complexes. (6) The spectral data confirms that in the complexes, the metal ligand coordinate bonding is through the nitrogen atom.In all the four cases, the sulphur formed strong covalent bond with the metal ion.

On the basis of the physico-chemical studies, the bonding and structure for the metal complexes may be represented as shown in Fig. 2.

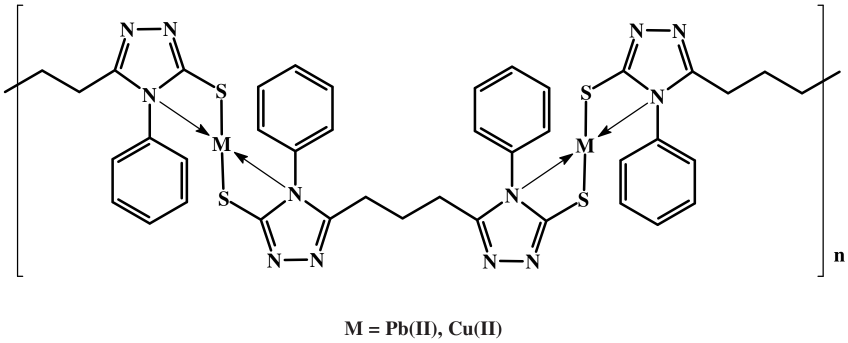


Fig. 2. Proposed bonding and structure of the metal complexes

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