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SYNTHESIS, CHARACTERIZATION AND ANTI-MICROBIAL ACTIVITY OF AZOMETHINE DERIVATIVE OF 2-AMINO-2-ETHYL-1, 3-PROPANEDIOL AND IT'S METAL COMPLEXES

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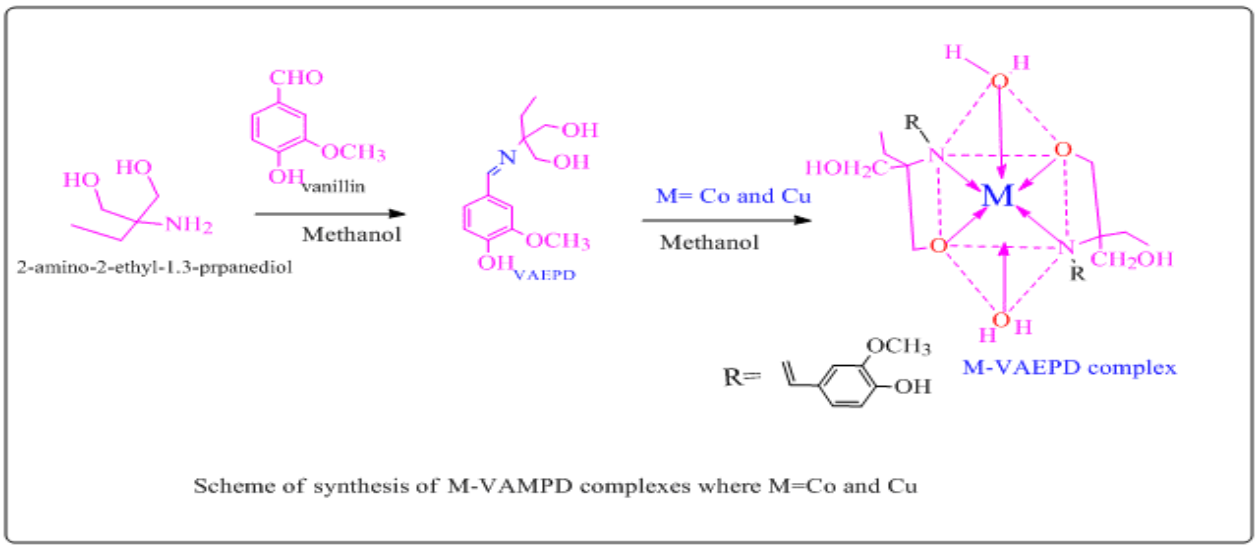
ABSTRACT
In this present investigation we have synthesized cobalt and copper azomethine metal complexes. Azomethine is a derivative of 2-amino-2-ethyl-1,3-propanediol prepared by condensation with vanillin. Azomethine and metal complexes were characterized by elemental analysis, electronic spectra, vibrational spectra, nuclear magnetic resonance, TGA, and Electron Spin Resonance, All these data confirms that the copper complexes exhibit octahedral geometry. These complexes exhibit high potent anti microbial activity against *Bacillus cereus* (MTCC – 1272) Gram positive bacterium and *Salmonella typhi* (MTCC – 3224) Gram negative bacterium.

KEY WORDS: 2-Amino-2-Ethyl-1, 3-Propanediol, azomethine ,Octahedral geometry and Anti microbial activity.

GRAPHICAL ABSTRACT



Scheme of synthesis of M-VAMPD complexes where M=Co and Cu

1. INTRODUCTION
2-amino - 2 - ethyl -1, 3- propanediol is one of the important compounds of a unique series of alkanolamines (or) aliphatic hydroxy amines. A perusal of literature revealed that 2-amino-2-ethyl-l, 3-propanediol and its derivatives have innumerable applications in various important fields. A compound derived from AEPD is useful for the treatment of liver diseases and can be administered orally (or) parenterally.[1] Heteropolyclic aromatic derivative of 2-amino-2-ethyl-l, 3-propanediol was used as antitumor agent.[2] A new class of antitumor DNA inter calators have been prepared from amino alcohols which include AEPD also[3] Oxazoline derivatives of AEPD helped to decrease in blood cholesterol level and in blood triglycerides level.[4] Labrude[5] studied the relative effectiveness of solutions of 2-amino-2-ethyl- l, 3-propanediol and 27 related compounds in protecting hemoglobin dug in freeze-drying. The un protonated forms of the buffers are responsible for the enhancement of GABA uptake and this is a result of the removal of protons from a membrane site in such a manner as to

allow the GABA transporter of function.[6] Roberts[7] studied the composition of AEPD and other alkanolamines for use in promoting nerve regeneration. The composition further comprises proton withdrawing substances to inhibit growth of glial tissue by increasing the pH at the site of nerve injury. Competition for binding site within the oxygen-evolving complex between various amines including aepd was examined.[8] Fluoranthene derivatives of aepd and other alkanolamines have been prepared and tasted for their antitumour, antiviral, antifungal, antibacterial activities by bair Kenneth.[9] Sandusky[10] and his coworker carried out steady-state kinetic analysis of the inhibition of $_2$ 0_2 oxidation in presence of aepd and other alkanolamines towards chloride-depleted thylakoid membranes. A compound obtained from eyelehexanons and aepd used as the haze inhibitor for lubricating oils and acts as a chelating agent for contaminent metals.[11] The resulting gel was applied to human hair for 30 minutes and dried. An ash, bright, brown nuance was obtained.[12,13] All appeared adequately comparable and could be used as mixtures without harmful effects.[14,15] Aepd along with number of polar group and polar bond compounds was suggested in a thermal printing with excellent thermal transfer characteristics upon a great number of paper surfaces, that can be used for multiple copy productions.[16] Coating compositions forming metal working lubricants of alkanolamines were used as films for drawing heavy gage metals[16] Aepd was also used as aircraft lubricant[17], 2-amino-2-ethyl-l, 3-propanediol-hydrochloride was used as catalyst in presence of aqueous solution of urea and formaldehyde in the manufacture of pressed particleboard and laminated wood articles.[18] Methyl heptenone was prepared from prenyl mesityloxide in presence of aepd as catalyst.[19] Richard employed alkanolamines as amine catalysts in the preparation of poly urethane foams.[20] Aepd was employed in controlling the curing rate of silicone elastomers.[21] Electophotographic plate obtained from the condensation of aepd with polyoxypropylene -2, 2-bis (4- hydroxyphenyl) propane, fumaric acid in presence of hydroquinone yielded 20,000 sharp copies.[22] Durable antistatic film laminates Obtained from unsaturated acid copolymers and alknolamines.

The literature survey revealed that not much work has been carried out in establishing the complexing ability of AEPD towards metal ions. Even the available few references on metal complexes of AEPD not fully established the coordinating ability of AEPD towards metals, but only emphasized the application of those complexes as lubricants and fuel additives. Reaction carried out by Sheldon *et al.*[22] with zinc acetate, polypropenyl succinic anhydride and AEPD yielded a metal complex, which has been used as a lubricant and fuel additive. Competition between chloride ion and Ammonia (or) alkanolamines for binding site within the Oxygen evolving manganese complex of spinach photo system has examined. This competition was a general inhibiting property of amines and was released in their nuclear-felicity which suggests that the binding site was associated with a metal[23,24], Werner coordination complexes[25] prepared by reacting The Charlotte thus obtained was employed as detergent and anti wear additive for lubricants. Synthesis, structural characteristics and magnetic properties of Molybdenum (VI) and copper (II) Schiff base complexes derived from AEPD have been studied by Catherine *et al.*[26]

2. MATERIALS AND METHODS

2.1 Materials

Copper sulphate pentahydrate CuS04.5H20 AR(Loba), Cobalt sulphate.heptahydrate AR(Loba), Sodium acetate trihydrate CH3C00Na.3H20 AR(Merk), 4-Hydroxy-3-methoxybenzaldehyde (Vanillin) Sisco(Chem), 2-Amino-2-ethyl-l,3-propanediol (Ranboxy), Methonal and Double distilled water

2.2. Methods

2.2. 1. Synthesis of imine derivative of 2-amino - 2 - ethyl -1, 3- propanediol (VAEPD)

To the solution of 2-Amino-2-ethy 1-1,3-propanediol (5ml;0.05moles)prepared by using 50ml of water and the 4-Hydroxy -3-methoxybenzaldehyde(0.05moles) solution (Made by using 50ml of methanol) was mixed in a clean 250ml round bottom flask and stirred with a magnetic stirrer and then it was refluxed for one hour on a water bath. On cooling yellow needles were separated out. It was separated by filtration and washed several times with hot water and then dried. The compound was re crystalized from methanol. Yield 72%, Melting point 171-174°C.

2.2. 3. Synthesis of Copper (II)-VAEPD complex metal complex

This complex was prepared by adding requisite(2.2g, 0.009moles) amount of schiff base in 50ml of 50% methanol to the copper metal ion (0.009moles) in water in presence of sodium acetate and refluxed mixture for two hours on a water bath. The reaction mixture was poured in excess of cold water. Colored precipitate of metal complex was obtained with good yield. This product was washed several times with hot water and cold methanol to free them from un reacted metal salt and ligand respectively and finally with ether and dried in a vacuum dessicator.

2.2. 4. Synthesis of cobalt (II)-VAEPD complex

The cobalt complex of Vanillin and 2-Amino-2-ethy 1-1,3-propanediol Azomithine was prepared by heating the reaction mixture in a clean 250ml round bottom flask containing the ligand VAEPD(2g, 0.008moles) dissolved in 50ml of 50% methanol and hydrated cobalt sulphate (0.008moles) dissolved in minimum quantity of 5ml of H2O for two hours. On cooling and slow evaporation, the solid metal complex was formed. It was separated by filtration, and washed several times with hot water and methanol. Then it was dried in vacuum dessicator.

Newly Synthesized metal complexes and Schiff's base were characterized by ir,mass, uv, Protan NMR and TGA

2.2.5 Antimicrobial activity of metal complexes

The Kirby-Bauer disk diffusion susceptibility test is widely used method to determine the sensitivity or resistance of pathogenic bacteria to various antimicrobial compounds. The pathogenic organism is grown on Mueller-Hinton agar in the presence of various antimicrobial impregnated filter paper disks.in this present study we had examined cobalt metal complex against *Bacillus cereus* (MTCC – 1272) Gram + ve bacterium 2. *Salmonella typhi* (MTCC – 3224) Gram – ve bacterium.

3.0. RESULTS AND DISCUSSION

3.1. Elemental analysis

Molecular formula X=H_2O	M.wt	colour	yield%	Melting point	Elemental analysis							
					%carbon		%Hydrogen		%Nitrogen		% metal	
					calc	exp	calc	exp	calc	exp	calc	exp
L=$C_{13}H_{19}NO_4$	253.31	Yellow	72	171-174	61.58	61.56	7.50	7.47	5.52	5.48	---	---
[Cu.L_2.X_2]	604.15	Pale blue	47	311-314	51.64	51.56	6.62	6.57	4.63	4.55	10.51	10.44
[Co.L_2.X_2]	599.65	purple	45	343-346	52.03	52.01	6.67	6.61	4.64	4.64	9.84	9.72

3.1. Interpretation Of Electronic Spectra To Vaepd And Its Metal Complexes

The electronic spectra were recorded on a Thermo Spectronic Heylos a Spectrophotometer. The data are summarized in Table III.2. The data indicates that the energy of the d-d transitions in the complexes is slightly less when compared to the corresponding aqua ions[27, 28, 29], either because of slight covalent interaction of the 3d vacant orbital's with ligands, leading to some delocalization with consequent reduction in inter electronic repulsion[30,31], or by increased nuclear shielding of the orbitals due to slight covalent ligand-metal electron drift. The π-π transitions occur at 290 nm for the ligand. But on complexation with the different metal ions like copper and cobalt, new bands appeared at 328nm, 336nm, respectively corresponding to the transition charge transfer from the ligand of the different metal ions [32,33]. Bands occurring in the region of 372nm to 327nm for all complexes are assigned to charge transfer transition.[34,35,36,37] (L M). Based on the above results octahedral structure is proposed for Cu^{2+} and Co^{2+}complexes.[39]

Table:2. Data of electronic spectras of cu and co metal complexes in comparision with free metal ions and AEPD ligand.

Complexes	λmax of metal ions in nm	λmax of metal complex in nm	λmax of ligand in nm
Cu(VAEPD)2	327	328	290
Co(VAEPD)2	334	336	290

3.2. Interpretation of Esr Spectrum of Copper and Cobalt Complexes of Vaepd

The ESR spectra of the complex in poly crystalline state exhibit only one broad signal which is attributable to dipolar broadening and enhanced spin– lattice relaxation.[40] Anisotropic spectra are obtained for all complexes in DMF at LNT and representative ESR spectra of Cu (II) and Co (II) ion complexes are presented in Fig.6. In this low temperature spectrum, four peaks of small intensity have been identified which are considered to originate from gel component. The g|| and g ⊥ are computed from the spectrum using DPPH free radical as g marker. Kivelson & Neiman[41] have reported that G value is less than 2.3 for covalent character and is greater than 2.3 for the iconic character of the metal- ligand bond in complexes. Applying this criterion, the covalent bond character can be predicted between the metal and ligand for the complexes under study[42,43,44], The trend g|| > g_{ave}> g ⊥> 2.0023 observed in the complex suggests that the unpaired electron is localized in d_{x2-y2} and d_{z2} orbital[45] of the copper (II) and cobalt (II) ions for the complexes respectively.. The G values for all these complexes are greater than four, suggesting that there are no interactions between copper – copper and cobalt - cobalt centres[46,47,48] in DMF medium. The ESR parameters g||, g ⊥, A_u||, and A* of the complexes and the energies of d-d transitions are used[49, 50,51] to evaluate the orbital reduction parameters (Kji, K), the bonding parameters (a_2), the dipolar interaction (P). The observed K || < K indicates the presence of out of plane Pi-bonding.[52] The a_2 values for the present chelates lie in the range 0.41 - 0.48 and support the covalent nature of these complexes. Giordano and Bereman[53,54] suggested the identification of bonding groups from the values of dipole term P. The reduction of P values of the free ion value (0.036cm'1) might be attributable to the strong covalent bonding.[55,56] The values of P obtained for the present complexes lie in between 0.018 - 0. 022cm'1 and are consistent with the bonding of copper and cobalt ions to Oxygen and Nitrogen donor atoms.[57,58,59, 60] The shape of ESR lines, ESR data together with the electronic spectral data suggest an octahedral geometry for copper and cobalt complexes[61,62,63,64 and 65]

3.3. ^{1}H Nuclear Magnetic Resonance Spectra

In the present study, 'H NMR spectra were recorded on 400 MHz NMR spectrometer in IIT Madras in DMSO-d^6 solvent at room temperature Typical NMR spectra are given in Fig..3-5. The ^{1}H NMR spectrum of the ligand

showed a multiple between 6.82- 7.34 ppm due to the aromatic protons of the Vanillin moiety, a singlet at 9.76 ppm due to the resonance peak of the of the azomethine proton[66,67,68] and another singlet at 3.7 ppm due to the methoxyl protons present in the aromatic ring system. Two close peaks are observed at 5.2 ppm due to the two hydroxyl protons of the two hydroxymethyl groups. A group of peaks is observed between 3.37 to 3.63 ppm due to the methyl protons of the two hydroxymethyl groups. In addition to this, two multiples are observed in between 1.48 to 1.60 and 1.76 to 1.90 ppm due to the ethylene methyl protons of the ethyl group respectively. In the case of Cu (II) complex only one peak is observed at 5.2 ppm indicating deprotonation of one hydroxyl proton of one of the hydroxylmethyl group thereby indicating the involvement of that oxygen atom in the coordination. The signal due to the azomethine proton has shifted to 9.2 ppm for copper complex compared to 9.76 ppm in the case of ligand. This up field shift indicates shielding of the azomethine proton on coordination through nitrogen atom of the azomethine group. The singlet at 3.46 ppm in the case of Cu (II) complex indicates the complication of water by coordination with metal ions.[69] The NMR data indicate that the peak corresponding to methoxyl hydrogens undergoes a slight down field[70] in the Copper complex. These results indicate that the ligand behaves in a Bi dentate manner[71], bonding to the metals through the alcoholic oxygen and azomethine nitrogen atoms.

3.4. Interpretation of Mass Spectrum of Vaepd Azomethine

Mass spectrum of VAEPD was recorded using an Autospec Mass spectrometer. Mass spectrum of VAEPD together with other experimental conditions is given in Fig.9. Mass spectrum of the VAEPD was recorded. Different peaks are assigned to various probable fragments according to their m/z values. The difference in stability of different fragments is evidenced from the relative intensity of the corresponding peaks with the base peak. The spectrum shows signal at 253 (m/z) corresponding to its molecular ion peak.[72] The base peak was observed at m/z 222 was assigned to a fragment [M-CH_2OH] and is the most stable fragment. Presuming that the compound has the molecular formula $C_{13}H_{19}NO_4$, Therefore, the compound contains 5 unsaturated sites.

3.6. Interpretation of Tg Spectrum of Metal Complexes of Vaepd

Thermo gravimetric studies of all the complexes were carried out in air at a heating rate of 25°C per minute.[73,74] The calibration of the thermo balance and temperature were checked using standard samples supplied by the Mettler Company. The Cu and Co complexes are thermally stable up to 152°C and 148°C respectively. The thermo gravimetric spectra are presented in Fig.7-8. Then they shows weight loss due to water molecules in the temperature range 152-186°C and 148-188°C[75,76] respectively. The intermediate formed is stable up to 250 °C and 230°C respectively and they undergoes decomposition with the loss of ligand moiety up to 550- 600°C.[77,78,79,80] The solid residue above 600°C was identified as CuO and CoO.[81,82] In all the complexes the final products are metal oxides.

3.7. Interpretation of Ir Spectra of Vaepd and Its Metal Complexes

The infrared spectrum of the ligand is compared with the spectra of copper and cobalt complexes **fig;1-2**. The infrared spectrum of the ligand has shown a strong band at 1640cm^{-1} due to the (C=N)[83] stretching vibration of the azomethine group. On complexation this band is shifted to 1599cm'1 and 1576cm^{-1} for copper(II) and cobalt(II) complexes respectively, suggesting the involvement of azomethine group (>C=N-) in complexation. Conjugation of this group with the total ion on complexation shifts this band to lower wave numbers due to the reduction in electron density therebyindicating the coordination of the metal ion through the nitrogen atoms.[84.85] The shift in the broad band observed at 2560-3000cm'1 due to the hydroxyl group indicates the participation of this group also in complexation.[86,87] The strong bands present at 1350cm-1 in the ligand 88,89 due to hydroxyl in plane bending vibrations are absent in the IR spectra of complexes, further confirming the participation of this group in complexation. The bands appearing in the regions 415* 425cm and 490-510cm'1 are assigned to the stretching frequencies of M-N[90] and M-0[91] of the metal-ligand bonds respectively[92] for copper complex and 480-495cm'1 and 420-435cm'1 are assigned to the stretching frequencies of M-N[93,94,95,96] and M-0[97] of the metal-ligand bonds respectively.[98] for cobalt complex. The aromatic ether had showed the absorption peaks at 1240cm'1 1226cm'1 in the ligand and metal complexes respectively.[99] The IR spectra of Cu(II) and Co(II) complexes exhibited a broad band around 3400cm'1 which can be assigned to (OH) of water molecules associated in the complex formation.[100] The two weaker bands at 800-750 and 720-700cm'1 are assigned respectively to OH rocking and wagging vibrations of coordinated water in the complexes. These results indicate that the ligand coordinate with the metal ions through the nitrogen and the deprotonated oxygen of the hydroxyl group and the suggested structures of the complexes are given in Fig.

4.0. ANTI MICROBIAL ACTIVITY

The test cobalt metal complex shows significant antibacterial activity against pathogenic bacterial strain (*Salmonella typhi)* causes infectious diseases in humans. Zone of inhibition was shown in the below table.

Table 3: Antibacterial activity of cobalt metal complex against *Bacillus cereus* and *Salmonella typhi*.

S.No	Micro-organism	Inhibition zone (mm^{-1}) Concentrations mg/ml (dissolved in DMSO)				Standard µg/disc
		1	2	5	15	
1	*Bacillus cereus*	7	8	8	10	22^{A}
4	*Salmonella typhi*	6	8	8	10	22^{A}
Ampicillin,						

FIGURES

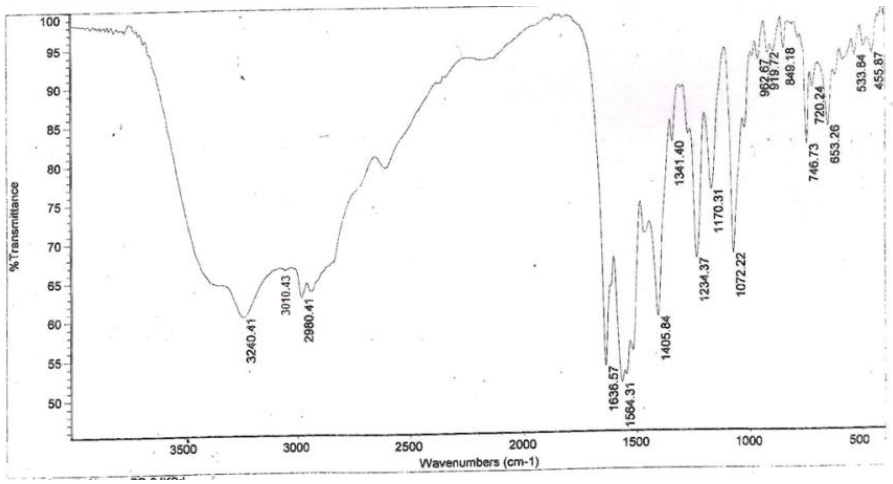


Figure 1: IR spectrum of Cu-VAEPD.

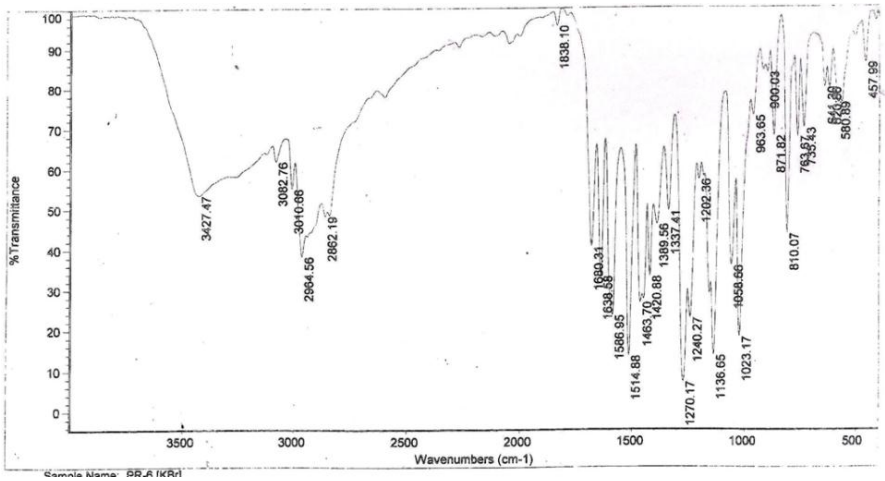


Figure 2: IR spectrum of Co-VAEPD.

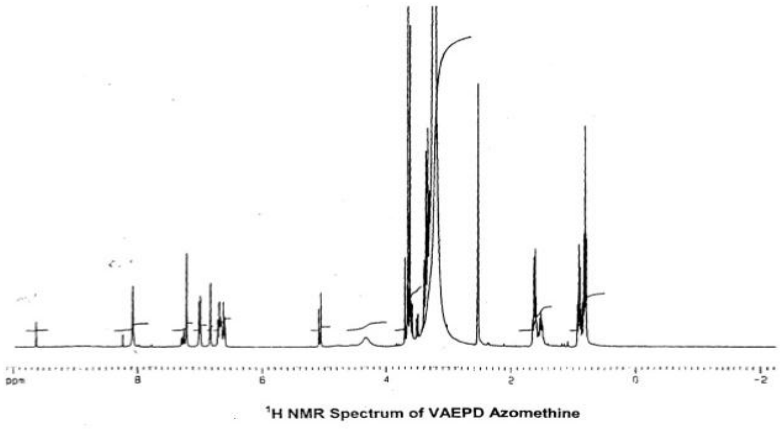


Figure 3: Proton NMR spectra of VAEPD ligand.

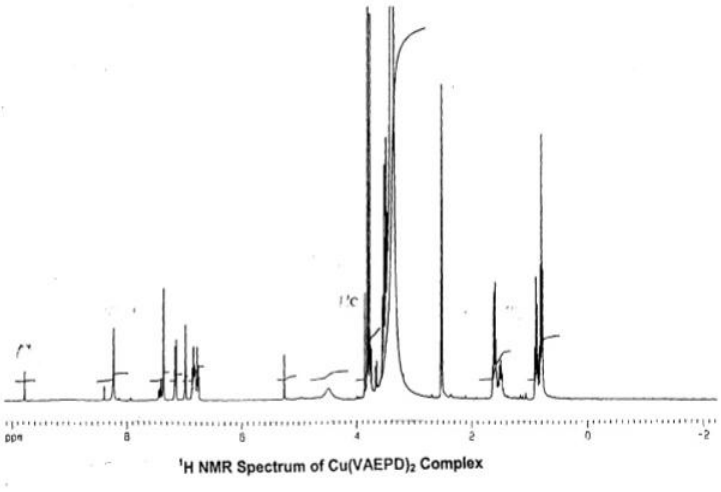


Figure 4: Proton NMR spectra of Cu-VAEPD complex.

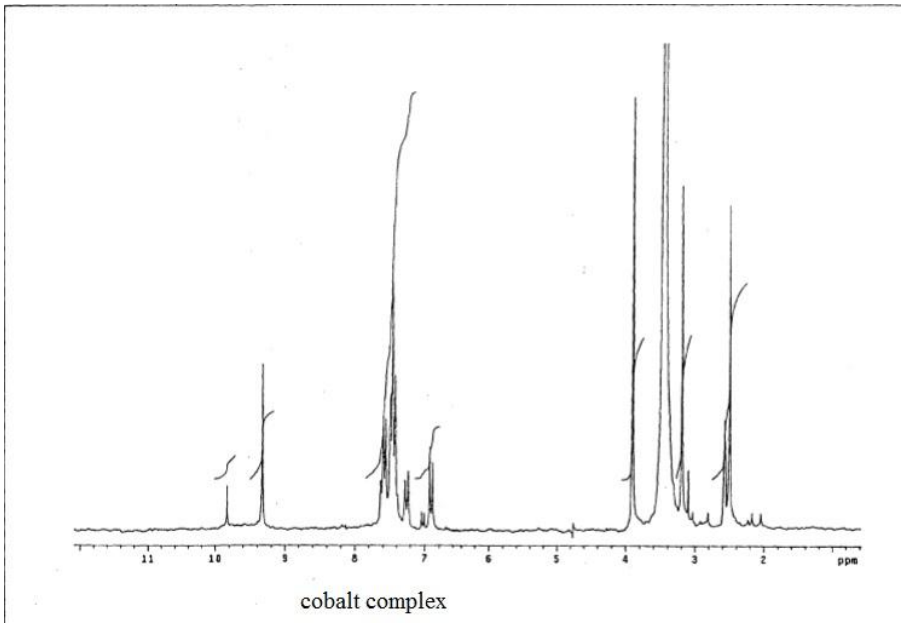


Figure 5: Proton NMR spectra of Co-VAEPD complex.

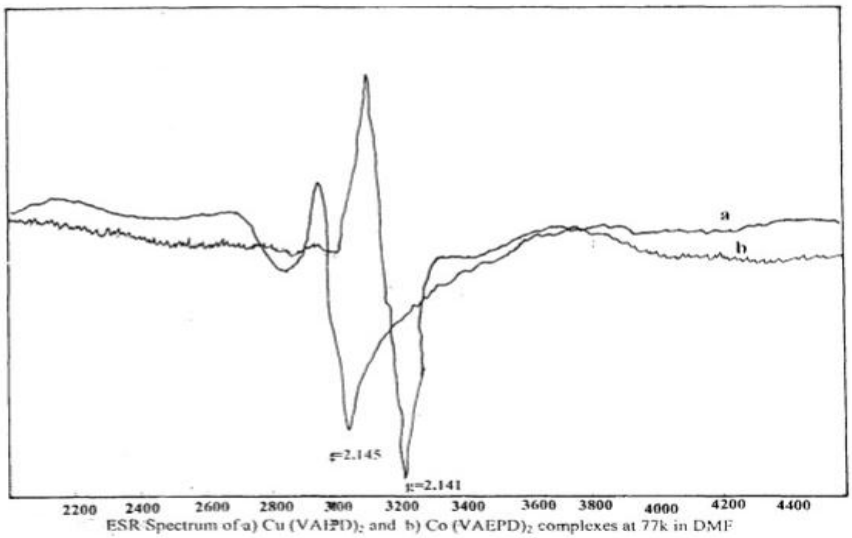


Figure 6. ESR spectras of a).Cu-VAEPD, b)Co-VAEPD complexes.

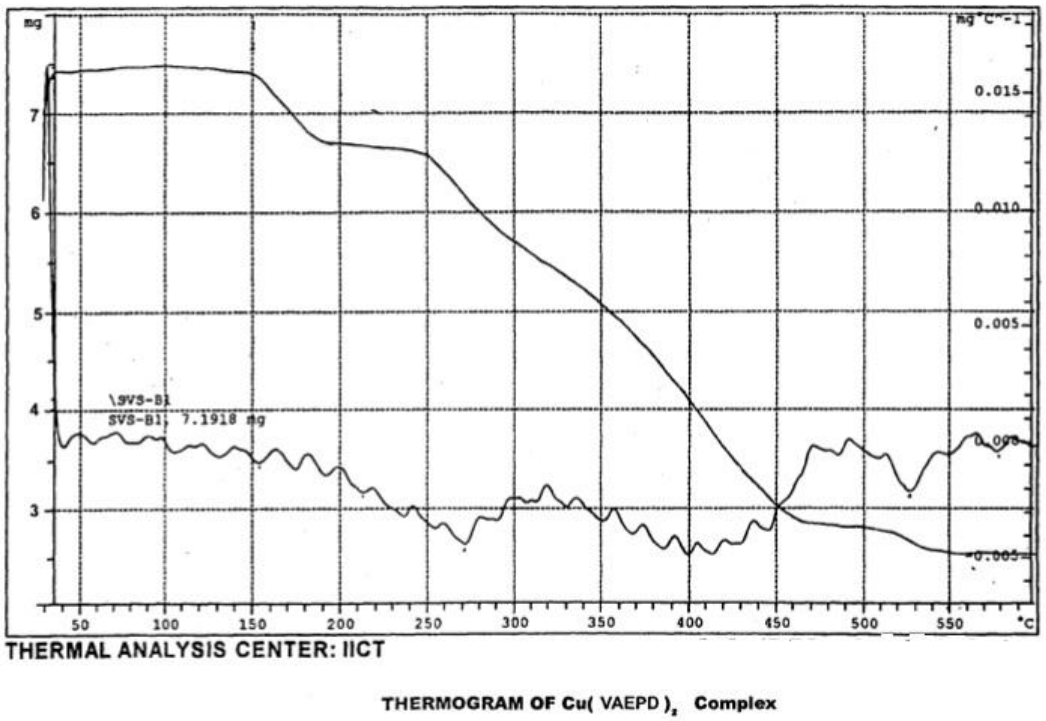


Figure 7: Thermogram of Cu-VAEPD.

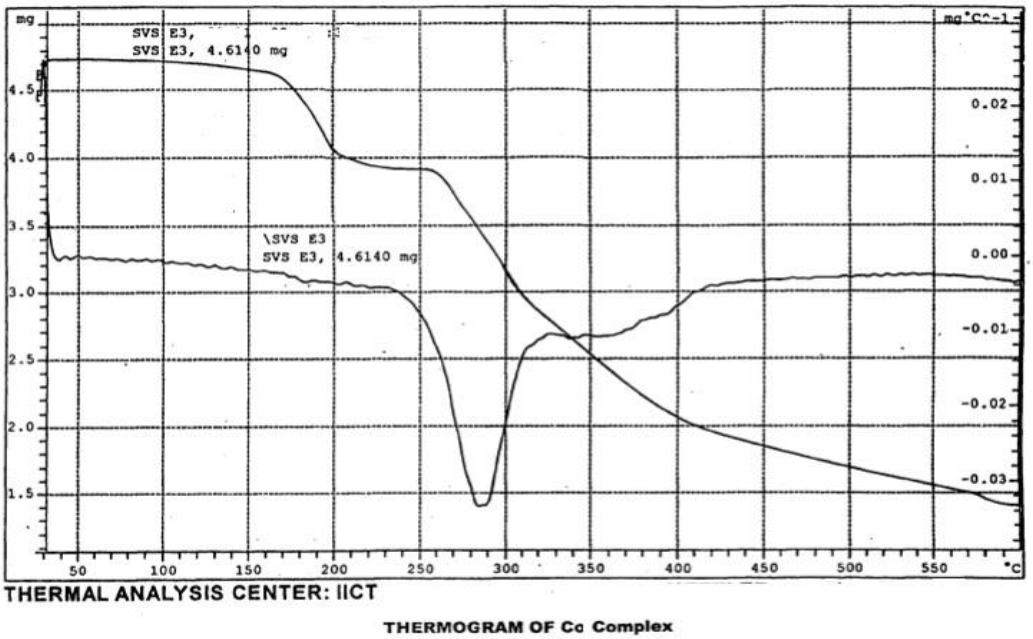


Figure 8. Thermogram of Co-VAEPD.

5.0. CONCLUSION

TGA data explains the two metal complexes were thermally stable up to 250 °C and weight loss in the temperature range 152-186°C and 148-188°C. is due to water molecules. in the temperature range 152-186°C and 148-188°C. Vibrational spectral data confirms that oxygen of propanediol moiety and nitrogen atom of azomethine function were involved in coordination. Up field shift in NMR indicates shielding of the azomethine proton on coordination through nitrogen atom of the azomethine group. The singlet at 3.46 ppm in the case of Cu (II) complex indicates the complication of water by coordination with metal ions. From the above data it was very clear that two metal complexes were shown octahedral geometry. We hope this study is helpful for the development of alkanolamine chemistry.

6.0. CONFLICT OF INTEREST; The author has no conflict of interest.

7.0. ACKNOWLEDGEMENT: Authors are very thankful to department of chemistry . sk university. Ananthapuram. for providing research facilities.

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