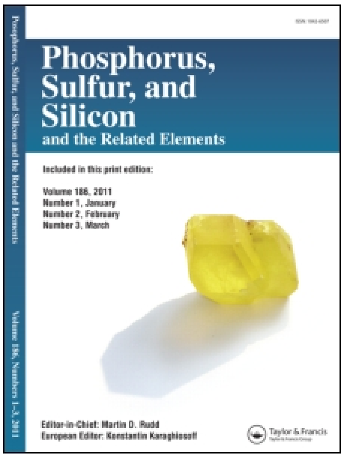

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Physicochemical Investigation on the Complexes of Co(II), Ni(II) and Cu(II) with Aminocyclodiphosph(V)azane Derivative

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PHYSICOCHEMICAL INVESTIGATION ON THE COMPLEXES OF Co(II), Ni(II) AND Cu(II) WITH AMINOCYCLODIPHOSPH(V)AZANE DERIVATIVE

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Co(II), Ni(II), and Cu(II) form 2:1 complexes with aminocyclodiphosph(V)azane derivative. The complexes have been investigated in solution by the spectrophotometric molar ratio and conductometeric methods. The ligand and its complexes have been isolated in solid state and characterized on the basis of microanalytical, infrared, electronic, magnetic moment, ^{1}H NMR and mass spectral data. The cobalt and nickel complexes were assigned to be in tetrahedral structure while the copper complex is assigned to be in square planar.

Keywords: Aminocyclodiphosph(V)azane metal complexes; electronic mass spectra; IR; magnetic moment

INTRODUCTION

The reaction of hexachlorocyclodiphosph(V)azanes with aromatic and aliphatic amines, active methylene containing compounds, and bifunctional reagents have been investigated in some detail.[1–4] Little is known about the interaction of hexachlorocyclodiphosph(V)azane with aminothiophene derivatives and their metal complexes.

EXPERIMENTAL

Starting Materials

The preparation and purification of hexachlorocyclodiphosph(V)-azane(I) has been reported.[3–4] The preparation of 2-amino-3-cyano-4,5,6-trihydrocyclopenteno(b)thiophine (II) was carried out according to the Gewald method.[5]

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Synthesis of Ligand

The solid of 2-amino-3-cyano-4,5,6-trihydrocyclopenteno(b)thiophine (II) (1.64 g, 0.01 mmol) was added in small portions to a well stirred solution of the hexachlorocyclodiphosph(V)azane (I) (3.56 g, 0.005 mmol) in 100 ml acetonitrile over a half-hour period. After the complete addition, the reaction mixture was heated under reflux for 2 h with continuous stirring. After completion of the reaction (HCl) gas ceased to evolve) the reaction mixture was filtered while hot and the filtrate was left to cool at room temperature. The obtained solid was filtered washed several times with acetonitrile, and dried in vacuo to give the corresponding aminocyclodiphosph(V)azane derivative (III) (Figure 1).

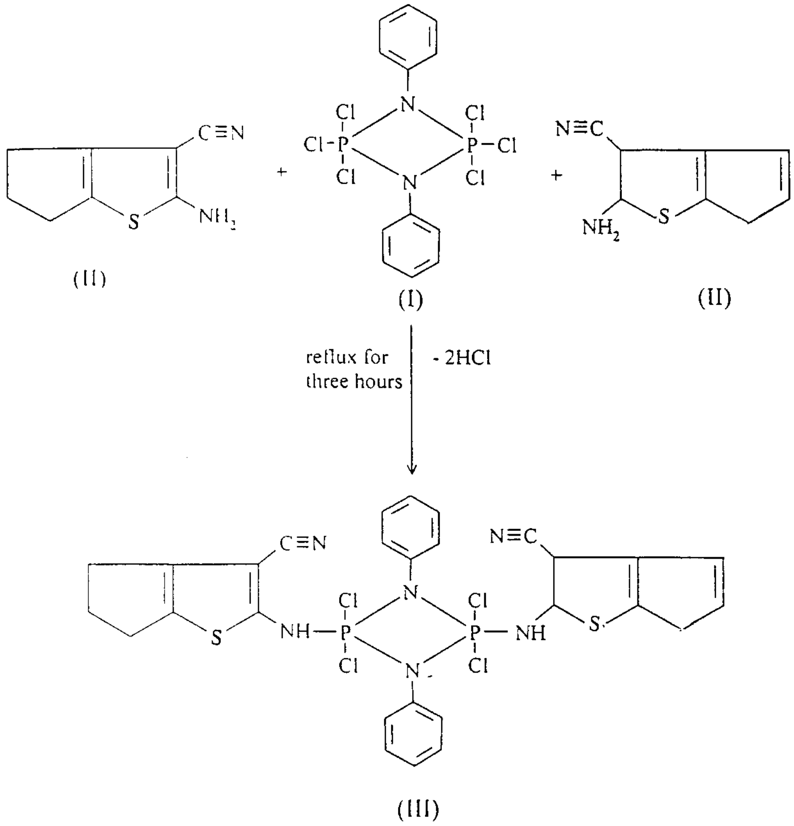


FIGURE 1 Structure of ligand III: 1,3-di(phenyl),2,2,4,4-tetrachloro,2,4-di(2-imino-3-cyano-4,5,6-trihydrocyclopenteno(b)thiophene cyclodiphosphazane).

Preparation of the Solid Metal Complexes

A solution of the metal salt in 50 ml absolute ethanol was added dropwise to a solution of aminocyclodiphosph(V)azane derivative (III) in 100 ml absolute ethanol at room temperature with continuous stirring. After the complete addition of the metal salt solution, the reaction mixture was heated under reflux for 3 h. Then, the reaction mixture evaporated to give solid compounds, which recrystallized from ethanol to give the products IV_{a-c}. The analytical data of both ligand and its metal complexes are listed in Table I.

Methods

Microanalytical analysis of C, H, and N were carried out and phosphorus was determined gravimetrically as phosphoammonium molybdate using the R. Voy method.[6] Infrared spectra were recorded in the solid state on a Mattson 5000 FTIR spectrometer using KBr disc technique. The absorbance of solutions were measured in the UV/VIS range (200–800 nm) using Unicam spectrophotometer model UV 2-100 and 1 cm matched quartz cells. The ^{1}H NMR spectrum of the ligand was recorded on a Varian FT-290.90 MH_z spectrometer in deutrated DMSO using TMS as an internal standard. The Mass spectrum of the ligand was recorded at 70 eV and 300°C on a Hewlett-Packard Mass spectrometer model MS 5988. Magnetic measurements were recorded by the Gouy method at room temperature using a magnetic susceptibility balance (Johnson Mathey), Alfa product, Model No. (MK). Diamagnetic corrections were calculated from Pascal's constants. The conductometric measurements in solutions were carried out using conductivity TDS model 72.

RESULTS AND DISCUSSION

The structure of the organo-phosphorus "ligand" (III) was elucidated by elemental analyses, IR, mass, electronic, and ^{1}H-NMR techniques.

IR Spectra

The assignment of the important bands of the free ligand are given in Table II. The spectra reveal the characteristic bands of the ν_{P-NH} stretching vibrations of the ligand at 2600 cm^{-1} which is similar to those assigned by Abd-Ellah[7] and Pustinger.[8] The band appeared at

TABLE I Elemental Analyses, Yield, Colors, and Melting Points of Ligand III and Its Corresponding Metal Complexes

Compound no. M.F(M.wt)	Elemental analyses found (cal.),%					Yield (%)	Color	m.p. °C
	C	H	N	P	M			
III	46.40	3.9	12.0	8.5	—	71	Green	195
$C_{28}H_{24}Cl_4N_6P_2S_2$ (712)	(47.19)	(3.37)	11.79	(8.7)	—			
IV_a	39.7	3.3	8.50	5.7	10.79	65	Green	285
$C_{36}H_{38}Cl_4N_6O_9P_2S_2Co_2$ (1084.18)	(39.84)	(3.50)	(7.74)	(5.71)	(10.87)			(d)
IV_b	39.6	3.5	8.10	5.8	10.90	70	Dark green	283
$C_{36}H_{38}Cl_4N_6O_9P_2S_2Ni_2$ (1083.74)	(39.97)	(3.86)	(7.38)	(5.45)	(10.35)			(d)
IV_c	28.4	2.1	7.20	5.0	10.23	75	Brownish black	>300
$C_{28}H_{26}Br_4Cl_4N_6OP_2S_2Cu_2$ (1177)	(28.54)	(2.20)	(7.13)	(5.26)	(10.79)			

TABLE II IR Spectra of Ligand and Its Metal Complexes

Compd. no.	ν_{NH}	N_{P-NH}	$\nu_{\text{disubstituted ring}}$	$\nu_{C\equiv N}$	ν_{OCOCH3}	ν_{P-N}	ν_{P-Cl}	ν_{M-N}	ν_{M-O}	ν_{C-H}
III	3351 (br)	2600 (W)	807 (m)	2216 (m)	—	1221 (m)	490 (m)	—	—	3167 (m)
IV$_a$	3321 (br)	2600 (V.W)	842 (w)	2207 (m)	1460 (m), 1575 (s)	1223 (m)	488 (m)	316 (m)	547 (m)	3204 (m)
IV$_b$	3336 (br)	2600 (V.W)	856 (m)	2208 (m)	1465 (m), 1605 (s)	1223 (m)	485 (m)	316 (m)	545 (m)	2930 (br)
IV$_c$	3279 (br)	2600 (V.W)	857 (m)	2209 (m)	—	1223 (m)	485 (m)	265 (m)	—	2930 (br)

3351 cm^{-1} is attributed to the ν_{NH} stretching vibration. The band observed at 2216 cm^{-1} is ascribed to the $\nu_{C\equiv N}$ stretching vibration which appeared at 2197 cm^{-1}[9] in compound (II). The shift of this band to higher frequency in the ligand is considered as an evidence for the ligand formation. The ν_{P-Cl} stretching vibration is observed at 490 cm^{-1}.[10,11] The band at 1221 cm^{-1} was assigned to the ν_{P-N} stretching vibration.[12,13] Bands appear in the range 1654–1402 cm^{-1} may be attributed to $\nu_{C=C}$ of the aromatic rings and attached compounds (II).[14] Moreover, the IR spectra showed weak band at 635 cm^{-1} due to the ν_{C-S} stretching vibration of thiophene ring. Two bands appeared at 2956–2803 cm^{-1} are assigned to the saturated ν_{C-H} and ν_{C-C} of the cyclopentene ring. The weak band observed at 3167 cm^{-1} is due to aromatic C—H stretching vibrations.[15]

Mass Spectrum

The mass spectrum of the ligand (III) shows the fragmentation pattern in Figure 2. The spectrum showed the molecular ion m/e peak at 712.4 (abundance 3.77%) corresponding to molecular weight of the ligand (III). The base peak was observed in the spectrum at 52.

Electronic Spectra

The fact that the expected band at 272 nm,[16] characteristic for the delocalization of the nonbonding electrons on the nitrogen atoms within the phosphazo ring of the dimeric structure was observed in the spectrum of ligand (III), suggested the presence of the phosphazo ring. The bathochromically shifted band observed at 284 nm for the ligand (III) relative to that of the dimer (I) is explained to be due to the replacement for one chlorine atom of each phosphorus atom by the 2-amino-3-cyano-4,5,6,trihydrocyclopent-eno(b)thiophene. The new band observed at 350 nm is attributed to the n-π^* transition of attached compound (II), which is absent in the corresponding dimer (I) and this is considered as an evidence for the ligand formation.

^{1}H-NMR Spectrum

The ^{1}H-NMR spectrum of the ligand (III) showed the following characteristic proton signals at: δ (7.20) ppm is assigned for aromatic protons Ar—H and abroad signal at δ (5.90) ppm is assigned for N—H proton, which disappeared on the addition of D_2O due to the proton exchange. The signal at δ (2.6) ppm can be assigned to the —CH_2— protons of the cyclopentene ring.

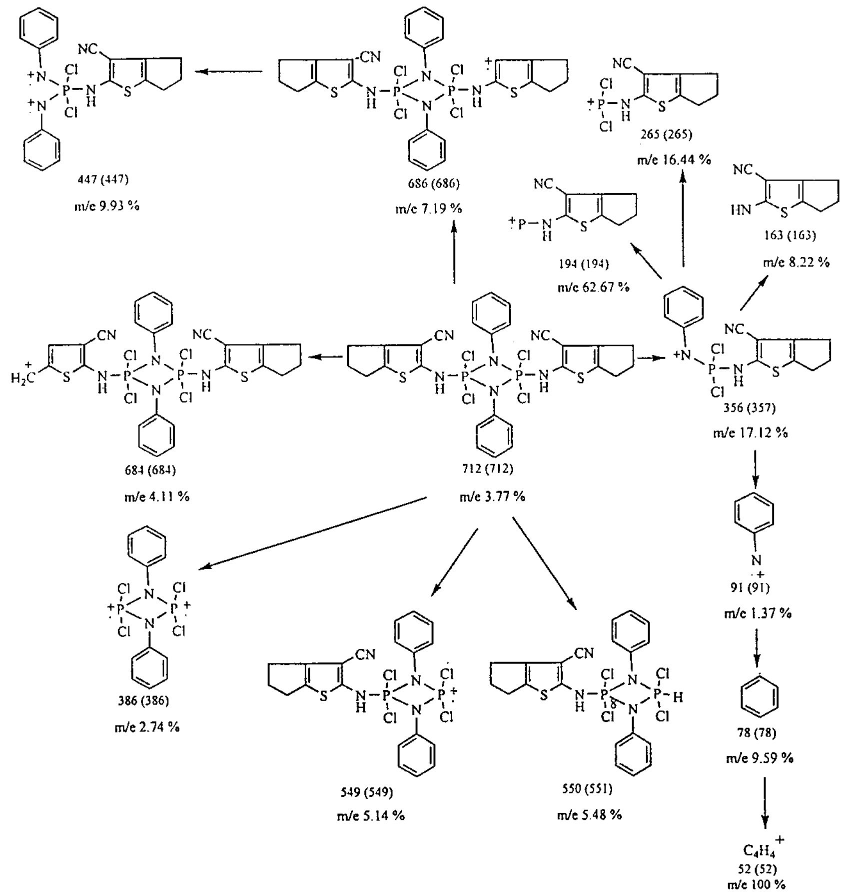


FIGURE 2 Fragmentation of the mass for the ligand III.

Spectrophotometric Measurements of Solution Stoichiometry (17)

The absorption spectra of the Co^{2+}, Ni^{2+}, and Cu^{2+} complexes $IV_{a\text{–}c}$ are shown in Figure 3. The diagrams in Figure 4, consist of two linear portions intersecting at 1:2 [ligand]/[M^{2+}], where M^{2+} corresponding to Co^{2+}, Ni^{2+}, and Cu^{2+} respectively, indicating the formation of 2M: IL species. This is in agreement with the elemental analyses and conductometric analyses data.

Magnetic and Electronic Spectral Studies

The electronic spectra of the free ligand exhibit bands at 350 and 284 nm which could be assigned to n-π^* and π-π^* transitions respectively. On

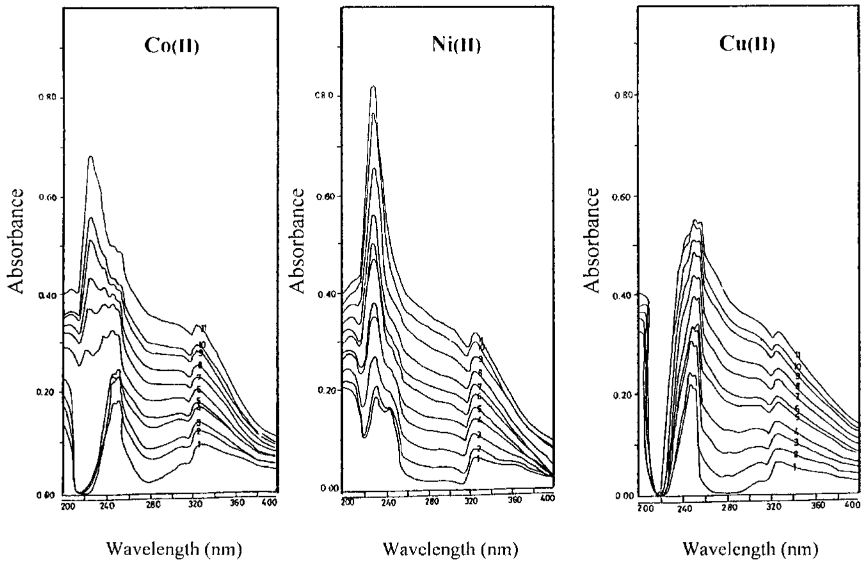


FIGURE 3 Absorption spectra for (a) Co(II), (b) Ni(II) and (c) Cu(II) Complexes.

complexation, the lower-energy band is shifted to a red shift, while the transition π-π^* is slightly shifted to a blue shift.

The room temperature magnetic susceptibility measurement of the green Co(II) complex, $Co_2L2AC.H_2O$ IV$_a$ gave magnetic moment value μ_{eff} of 5.0 B.M., corresponding to three unpaired electrons are expected for a weak field ligand. The electronic spectra of the Co(II) complex as nujol mulls and/or solution in ethanol (Table III) were recorded in the range 280–900 nm. The spectra exhibit peaks at 705–633 nm region, which may be assigned to $^4A_2 \rightarrow {}^4T_1$ (p) (ν_3) and is consistent with the tetrahedral geometry.[18] The peaks observed at 466–299 nm and 286–240 nm regions, were assigned to n-π^* and π-π^* transitions respectively.

TABLE III Magnetic Moment and Electronic Spectral Data, nm for the Ligand III and Its Metal Complexes

Compound no.	μ_{eff} (B.M.)	π-π^*, n-π and charge transfer transitions	d $\rightarrow$ d transitions
III	—	284, 350	—
IV$_a$	5.0	247, 264, 299, 314, 386, 411, 454	585, 698
IV$_b$	3.0	243, 273, 298, 318, 360, 398, 489	596, 709
IV$_c$	1.8	280, 325, 425, 496	689

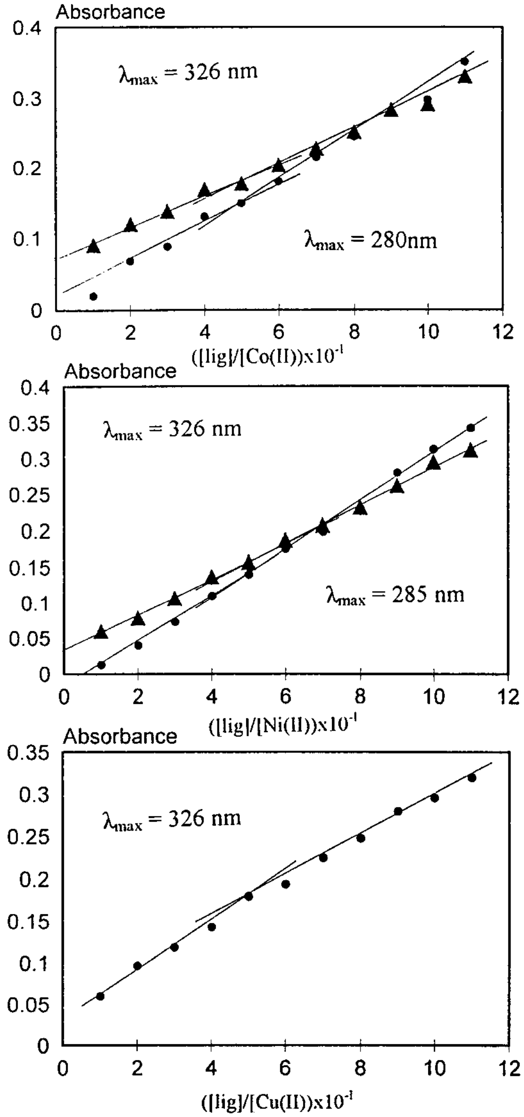
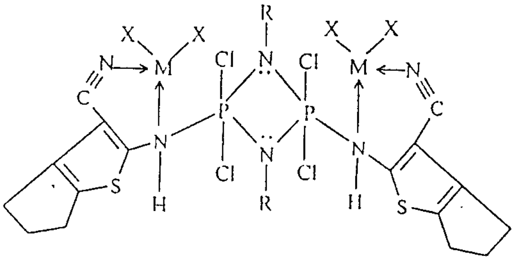


FIGURE 4 Results of molar ratio method for (a) Co(Il), (b) Ni(II) and (c) Cu(II) Complexes respectively.

The green Ni-complex IV_b gives value μ_{eff} of 3.0 B.M. which is indicative of two unpaired electrons. The electronic spectra of the Ni(II) complex IV_b exhibit absorption band near 666 nm which may be attributable to the $^3T_1 \rightarrow {}^3T_1$ (p), weak bands observed on the high and low energy sides of the 666 nm band have been assigned to spin-forbidden bands.



IVa–c

FIGURE 5 The proposed structure of the Co(ll), Ni(II) and Cu(lI) Complexes. Where X = acetate or Br, M = Co^{2+}, Ni^{2+} or Cu^{2+}, R = $C_6 H_5$.

The Cu(II) complex IV_c absorbs at 692–683 nm was assigned to $^2B_2 \rightarrow ^2E$ transition. The bands observed in the range 426–414 nm were assigned to the charge transfer via L → M (Cu^{2+}). The observed band at 280 nm was attributable to π-π^* the magnetic moment of the Cu(II)-complex of μ_{eff} value of 1.8 B.M. is in accord with one unpaired electron which is indicative to square planner structure. We propose that the coordination with metal ions occurs through the nitrogen of the NH and CN groups to the following structure Figure 5.

IR Spectra

The most characteristic IR spectral bands of the metal chelates together with those of the free ligand are collected in Table II. The IR spectra of the metal complexes show a shift to lower frequencies of both $\nu_{C\equiv N}$ and ν_{N-H_2} indicating that both the C≡N and NH groups coordinate via nitrogen atoms to the cations (Table II). In all metal complexes, there are new medium to weak bands appeared at lower frequencies between 316–265 cm^{-1} were assigned to ν_{M-N} and two bands at 547, 545 cm^{-1} were attributed to ν_{M-O} for IV_a and IV_b respectively.[19] The bands observed at 1460, 1575 cm^{-1} and 1465, 1605 cm^{-1} in both Co(II) and Ni(II)-complexes were assigned to $\nu_{sym.OCO}$ and $\nu_{asym \cdot OCO}$, respectively, which indicated that the acetate groups coordinate as a monodentate to the central metal cation in Co(II) and Ni(II) complexes respectively. This is supported with the observed characteristic ν_{M-O} band. The characteristic bands corresponding to the ν_{P-NH}, ν_{P-N} and ν_{P-Cl} which were associated with all the investigated complexes are collected in Table II.

Conductometric Titration

In order to follow up the behavior of the ligand III in solution with Co(II), Ni(II), and Cu(II), we investigated these systems using conductometric titration method.

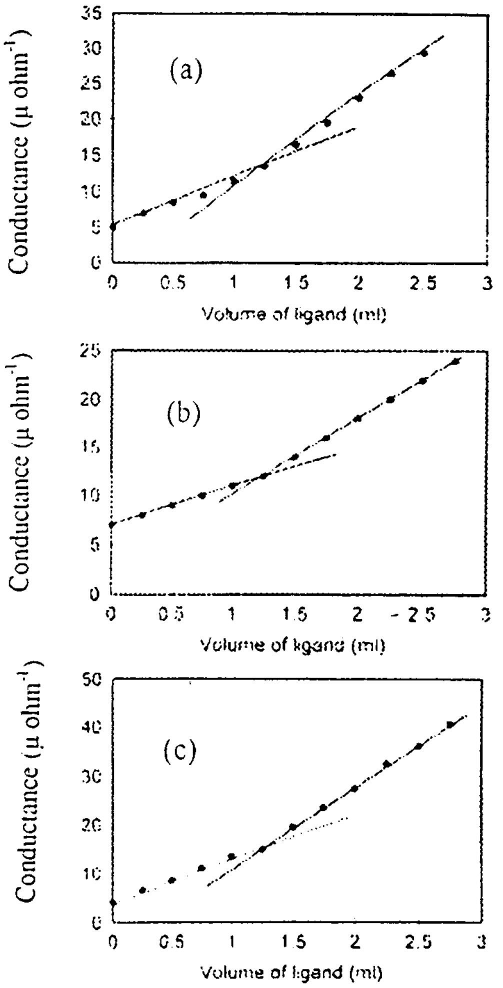


FIGURE 6 Conductometric titrations for (a) Co(II), (b) Ni(II) and (c) Cu(II) Complexes respectively.

In this method 25 ml (10^{-4} M) of M(II) where M(II) is Co(II), Ni(II), or Cu(II) solution in absolute ethanol was titrated with (10^{-3} M) of III solution absolute ethanol at room temperature 25°C and represented in Figure 6. The curves were plotted between the conductance of the solution and the volume of ligand added. The results show that the break in the curve occurred when the 2:1 (M:L) species are formed in solution. The conductance of the reaction mixture was increase continuously with increasing the amount of the ligand III added in all the complexes under investigation. The reason for increase in conductivity after 2:1 (M:L) complex forms may be due to the presence of the ligand in ionic form in the medium (ethanol) which arises the conductivity.

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