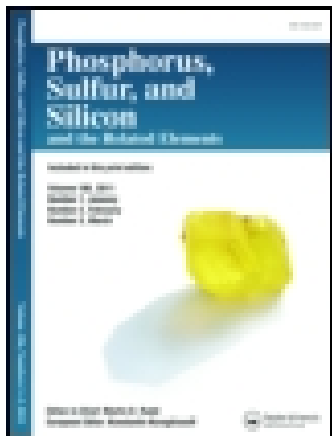




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Preparation and Characterization of Some Novel Diphenylphosphine Hydrazones and Semicarbazones and Their Metal Complex Derivatives

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*Interaction of hydrazones and semicarbazones derivatives I_{a-t} with diphenylchlorophosphine **II**, gave new compounds III_{a-t} , and their complexation ability towards various divalent metal acetates $Mn(OAc)_2 \cdot 4H_2O$, $Co(OAc)_2 \cdot 4H_2O$, $Ni(OAc)_2 \cdot 4H_2O$, and $Cu(OAc)_2 \cdot H_2O$, in organic solvents are described. The metal/ phosphorsemi-carbazones ratios are measured and the results discussed. All these complexes are insoluble in organic solvents and in water. The structures of the isolated products were proposed on the basis of microanalytical data, TGA, IR, (UV/ VIS), (MS), and 1H , ^{13}C , and ^{31}P -NMR spectroscopic analyses and magnetic susceptibility. The proposed structure of the complexes is based on a 1: 2 metal: ligand ratio. All of the complexes are found to have an octahedral geometry, with the exception of the square planar copper (II) complexes. The corrosion inhibition of aluminium and copper in 1 M HCl and chromium–nickel steel in crude oil using III_n have been studied by weight loss method.*

Keywords Diphenylphosphate; magnetic susceptibility; phosphorsemicarbazones; ^{31}P -NMR; (IR)

INTRODUCTION

Coordination chemistry of pentadentate bis-(thiosemicarbazone/semicarbazone)-2,6-diacetylpyridine Schiff base ligands has been intensively studied due to the versatility of the molecular chain in order to obtain very different geometries,¹ as well as their broad therapeutic activity.² Substitution at 4-N position of the thiosemicarbazone arms has been probed to affect the biological activity of the complexes,³ but not much structural information about them has been provided. The

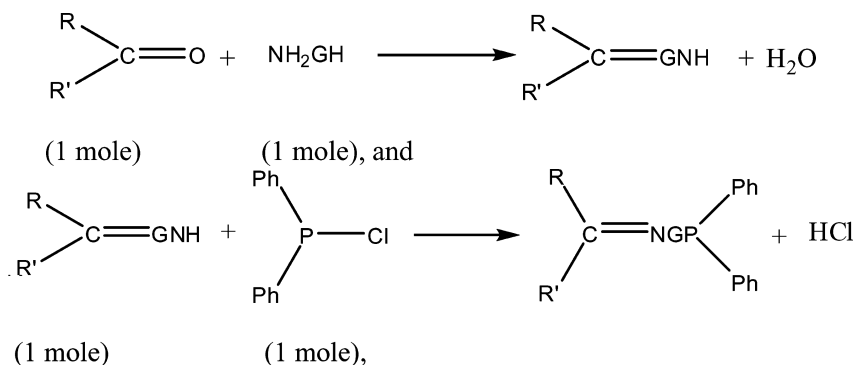
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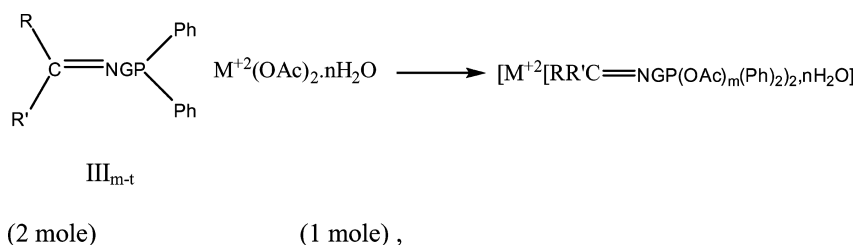
present work was planned to investigate new route for the synthesis of novel diphenylphosphine hydrazones and diphenylphosphine semicarbazones derivatives with potential biological activities.

RESULTS AND DISCUSSION

The reactions of diphenylchlorophosphine with different hydrazone and semicarbazone derivatives containing aliphatic and/ or aromatic alkyl groups may be represented by the Equations (1)–(3).



where G=Ph–N, NO₂C₆H₄N, or HNCONH.



where n = 2, m = 2 for Mn, Co and Ni while m = 0, n = 0, for Cu.

The reactions are quite facile and could be completed within 5–12 hours of refluxing in toluene. The resulting products of complexes are colored solids and insoluble in common organic solvents but soluble in DMSO, THF, and DMF. Phosphorus metal complexes are quite stable. The molecular weight determinations indicate their monomeric nature in Eqs. (1, 2) but dimeric nature in Eq. (3). The low molar conductance values (4.85–16.30 Ω⁻¹ mol⁻¹ cm²) of the prepared complexes in DMF at 10⁻³ M concentrations show them to be nonelectrolytes. The analytical of both the ligand and its metal complexes are listed in Tables I and II.

Infrared Spectra

The IR spectra of hydrazone and semicarbazone derivatives show bands at 1630–1654 cm^{-1} and 1295–1310 cm^{-1} attributed to ν (C=N) and ν (P–N).⁵ ν (P–NH), observed at 2600–2622 cm^{-1} .⁵ Two bands at 1690–1720 cm^{-1} and 3280–3315 cm^{-1} appear in the IR spectra of semicarbazone derivatives assignable to ν (C=O) and ν NH.

To investigate the mode of coordination, the IR spectra of Acetophenone_{N4} diphenylphosphine semicarbazone (III_n) as one of semicarbazone derivatives and its Mn(II), Co(II), Ni(II), and Cu(II) complexes are compared. Acetophenone_{N4} diphenylphosphine semicarbazone can exist either as keto or enol form or an equilibrium mixture of the two forms since it has an amide –NHC=O function. However, the IR and NMR spectra of III_n indicate that it remains in a keto form in solid state. The IR spectra of the Ni(II), Co(II), Cu(II), and Mn(II) complexes do not show any intense absorption band at around 1705 cm^{-1} , due to the carbonyl stretching of the semicarbazone moiety. This shows that III_n converts to enol form in solution and coordinate to the metals in an enolate form. III_n behaves as a bidentate ligand via azomethine nitrogen and oxygen atom in a deprotonated enolic form—forming a five-membered ring. This structure is supported by disappearance of ν (C=O) band, as well as a new band appearing at $\sim 545 \text{ cm}^{-1}$ due to M–O bond.⁶ The IR spectra of the metal complexes do not show a broad band at 3434 cm^{-1} for O–H stretching mode of the phenolic oxygen. Sharp band at 1635 cm^{-1} in the spectrum of III_n is shifted to lower wavenumber by 10–15 cm^{-1} in the spectra of the metal complexes support the coordination through azomethine nitrogen. This band is abroad and intense compared to that of the ligand and can be attributed to overlapping of the bands of newly formed N=C bond stretching. The band due to ν (P–aryl) and modes in the spectra of the ligands are observed at 1450–1410 cm^{-1} . In addition to the attributed to M–O, a new band appears at about 280 cm^{-1} assigned to M–N,⁷ Table III and IV.

¹H, ¹³C-, and ³¹P-NMR Spectra

¹H-NMR (Table III) of all prepared compounds show peaks assigned to aliphatic and aromatic protons as well as peak at 7.8–8.6 ppm in case of semicarbazone attributed to NH proton. The ¹³C-NMR (Table III) spectral data also support the authenticity of the proposed structures. The considerable shifts in the positions of carbon atoms adjacent to the imine nitrogen [C=N (δ 160.12–162.79 ppm)], enolic oxygen [C=O (δ 164.32–168.84 ppm)] support the proposed coordination in the complexes. Thus the shifts in the position of carbon atoms adjacent to the

TABLE I Analytical Data of the Prepared Ligands

No.	Yield (%)	M.p. (°C)	Color	M. F. (m.wt.)	Elemental analyses calcd. (found)			
					%C	%H	%N	%P
III _a	99	132	Silvery white	C ₃₁ H ₂₅ N ₂ P(456.52)	81.56(81.51)	5.52(5.52)	6.14(6.13)	6.78(6.76)
III _b	94	143	White	C ₂₆ H ₂₃ N ₂ P(394.45)	79.11(79.16)	5.88(5.84)	7.10(7.10)	7.85(7.83)
III _c	92	144	White	C ₃₈ H ₂₇ N ₂ O ₂ P(454.50)	73.99(73.97)	5.99(5.95)	6.16(6.12)	6.81(6.80)
III _d	94	121	Silvery white	C ₃₂ H ₂₇ N ₂ P(470.54)	81.68(81.64)	5.78(5.76)	5.95(5.92)	6.58(6.57)
III _e	95	142	Silvery white	C ₃₀ H ₂₄ N ₃ P(457.51)	78.76(78.75)	5.29(5.25)	9.18(9.15)	6.77(6.75)
III _f	92	124	White	C ₂₅ H ₂₂ N ₃ P(395.44)	75.93(75.92)	5.61(5.60)	7.08(7.03)	7.83(7.84)
III _g	94	112	White	C ₂₇ H ₂₅ N ₂ OP(424.47)	76.40(76.38)	5.94(5.93)	6.60(5.92)	7.30(7.30)
III _h	98	124	White	C ₂₇ H ₂₅ N ₂ OP(424.47)	76.40(76.34)	5.94(5.93)	6.60(6.60)	7.30(7.30)
III _i	95	129	Silvery white	C ₃₁ H ₂₄ N ₃ O ₂ P(501.51)	74.24(74.22)	4.82(4.35)	8.38(7.62)	6.18(5.63)
III _j	96	135	White	C ₂₆ H ₂₂ N ₃ O ₃ P(455.44)	68.57(68.53)	4.87(4.50)	9.23(9.21)	6.80(6.80)
III _k	99	142	Silvery white	C ₂₆ H ₂₁ ClN ₃ O ₂ P(47389)	65.90(65.87)	4.47(4.44)	8.87(8.84)	6.54(6.52)
III _l	97	134	White	C ₃₂ H ₂₆ N ₃ O ₂ P(515.54)	74.55(74.54)	5.08(5.03)	8.15(8.12)	6.01(6.01)
III _m	96	135	White	C ₂₀ H ₁₈ N ₃ OP(347.35)	69.16(69.12)	5.22(5.20)	12.10(12.10)	8.92(8.92)
III _n	98	153	Silvery white	C ₂₁ H ₂₀ N ₃ OP(361.37)	69.80(69.80)	5.58(5.53)	11.63(11.61)	8.57(8.55)
III _o	95	147	Yellow	C ₂₂ H ₂₂ N ₃ O ₂ P(391.40)	67.51(67.51)	5.67(5.63)	10.74(10.74)	7.91(7.90)
III _p	99	154	Pale yellow	C ₂₃ H ₂₄ N ₃ O ₃ P(421.42)	65.55(65.53)	5.74(5.74)	9.97(9.95)	7.35(7.35)
III _q	99	150	Yellow	C ₂₆ H ₂₁ ClN ₃ OP(457.89)	68.20(68.20)	4.60(4.60)	9.18(9.15)	6.76(6.75)
III _r	98	145	Pale yellow	C ₂₆ H ₂₁ ClN ₃ OP(457.89)	68.20(68.20)	4.60(4.60)	9.18(9.16)	6.76(6.75)
III _s	98	153	Yellow	C ₂₅ H ₂₁ N ₄ OP(424.43)	70.75(70.74)	4.99(4.97)	13.20(13.20)	7.30(7.30)
III _t	99	148	Yellow	C ₂₀ H ₁₉ N ₄ OP(362.36)	66.29(66.24)	5.28(5.26)	15.46(15.44)	8.55(8.55)

TABLE II Analytical Data of the Prepared Metal Complexes

No.	[Yield(%)] m.p. °C	Color	M.F. (m.wt.)	Elemental analyses calcd. (found)				Λ ($\Omega^{-1}\text{mol}^{-1}\text{cm}^2$)	
				C%	H%	%N	%P		%M
MnIII _m	(90) 277	Brown	C ₄₄ H ₄₄ MnN ₆ O ₈ P ₂ (901.74)	58.61 (58.61)	4.92 (4.92)	9.32 (9.28)	6.87 (6.80)	6.09 (6.00)	4.88
CoIII _m	(94) 246	Green	C ₄₄ H ₄₄ CoN ₆ O ₈ P ₂ (905.73)	58.35 (58.12)	4.90 (4.40)	9.28 (9.26)	6.84 (6.45)	6.51 (6.47)	4.90
NiIII _m	(95) 268	Green	C ₄₄ H ₄₄ N ₆ NiO ₈ P ₂ (905.49)	58.36 (58.21)	4.90 (4.43)	9.28 (9.25)	6.84 (6.83)	6.48 (6.44)	6.00
CuIII _m	(97) 274	Green	C ₄₀ H ₃₈ CuN ₆ OP ₂ (792.26)	60.64 (60.43)	4.83 (4.71)	10.61 (10.29)	7.82 (7.57)	8.02 (7.73)	6.03
MnIII _n	(90) 277	Brown	C ₄₂ H ₄₆ MnN ₆ O ₆ P ₂ (847.74)	59.51 (59.50)	5.47 (5.43)	9.91 (9.76)	7.31 (7.30)	6.48 (6.40)	6.83
CoIII _n	(94) 246	Green	C ₄₂ H ₄₆ N ₆ P ₂ O ₆ Co (851.73)	59.23 (59.12)	5.44 (5.40)	9.87 (9.76)	7.27 (6.41)	6.92 (6.87)	12.21
NiIII _n	(95) 268	Olive green	C ₄₂ H ₄₆ N ₆ P ₂ O ₆ Ni (851.49)	59.24 (59.21)	5.45 (5.43)	9.87 (9.26)	7.28 (7.23)	6.89 (6.84)	12.60
CuIII _n	(97) 274	Light green	C ₄₂ H ₄₂ CuN ₆ O ₄ P ₂ (820.31)	61.49 (61.43)	5.16 (5.11)	10.24 (10.22)	7.55 (7.54)	7.75 (7.73)	5.15
MnIII _o	(90) 277	Brown	C ₄₈ H ₅₂ MnN ₆ O ₁₀ P ₂ (989.84)	58.24 (58.23)	5.30 (5.42)	8.49 (8.46)	6.26 (6.30)	5.55 (5.50)	5.17
CoIII _o	(94) 246	Bright green	C ₄₈ H ₅₂ CoN ₆ O ₁₀ P ₂ (993.84)	58.01 (58.00)	5.27 (5.24)	8.46 (8.42)	6.23 (6.20)	5.93 (5.90)	7.92
NiIII _o	(95) 268	Olive green	C ₄₈ H ₅₂ N ₆ NiO ₁₀ P ₂ (993.60)	58.02 (58.00)	5.28 (5.25)	8.46 (8.42)	6.23 (6.23)	5.91 (5.90)	8.06
CuIII _o	(97) 274	Light green	C ₄₄ H ₄₆ CuN ₆ O ₆ P ₂ (880.36)	60.03 (60.03)	5.27 (5.27)	9.55 (9.55)	7.04 (7.04)	7.22 (7.22)	5.55

(Continued on next page)

TABLE II Analytical Data of the Prepared Metal Complexes (Continued)

No.	[Yield(%)] m.p. °C	Color	M.F. (m.wt.)	Elemental analyses calcd. (found)					Λ ($\Omega^{-1}\text{mol}^{-1}\text{cm}^2$)
				C%	H%	%N	%P	%M	
MnIIp	(90) 277	Brown	$\text{C}_{50}\text{H}_{56}\text{MnN}_6\text{O}_{12}\text{P}_2$ (1049.89)	57.20 (57.20)	5.38 (5.38)	8.00 (8.00)	8.00 (8.00)	5.23 (5.23)	16.00
CoIIp	(94) 246	Bright green	$\text{C}_{50}\text{H}_{56}\text{CoN}_6\text{O}_{12}\text{P}_2$ (1053.89)	56.98 (56.98)	5.36 (5.36)	7.97 (7.97)	5.88 (5.88)	5.59 (5.59)	11.11
NiIIp	(95) 268	Olive green	$\text{C}_{50}\text{H}_{56}\text{NiN}_6\text{O}_{12}\text{P}_2$ (1053.65)	57.00 (57.00)	5.36 (5.36)	7.98 (7.98)	5.88 (5.88)	5.57 (5.57)	15.90
CuIIp	(97) 274	Light green	$\text{C}_{46}\text{H}_{50}\text{CuN}_6\text{O}_8\text{P}_2$ (940.42)	58.75 (58.75)	5.36 (5.36)	8.94 (8.94)	6.59 (6.59)	6.76 (6.73)	4.98
MnIIq	(90) 277	Brown	$\text{C}_{56}\text{H}_{50}\text{Cl}_2\text{MnN}_6\text{O}_8\text{P}_2$ (1122.82)	59.90 (59.50)	4.49 (4.49)	7.48 (7.48)	5.52 (5.52)	4.89 (4.40)	7.95
CoIIq	(94) 246	Bright green	$\text{C}_{56}\text{H}_{50}\text{Cl}_2\text{CoN}_6\text{O}_8\text{P}_2$ (1126.82)	59.69 (59.69)	4.47 (4.47)	7.46 (7.46)	5.50 (5.50)	5.23 (5.23)	7.64
NiIIq	(95) 268	Olive green	$\text{C}_{56}\text{H}_{50}\text{Cl}_2\text{NiN}_6\text{O}_8\text{P}_2$ (1126.57)	59.70 (59.21)	4.47 (4.47)	7.46 (7.46)	5.50 (5.50)	5.21 (5.21)	8.00
CuIIq	(97) 274	Light green	$\text{C}_{52}\text{H}_{44}\text{Cl}_2\text{CuN}_6\text{O}_4\text{P}_2$ (1013.34)	61.63 (61.63)	4.38 (4.38)	8.29 (8.29)	6.11 (6.11)	6.27 (6.27)	4.85
MnIIr	(90) 277	Brown	$\text{C}_{56}\text{H}_{50}\text{Cl}_2\text{MnN}_6\text{O}_8\text{P}_2$ (1122.82)	59.90 (59.50)	4.49 (4.49)	7.48 (7.48)	5.52 (5.52)	4.89 (4.40)	4.90
CoIIr	(94) 246	Bright green	$\text{C}_{56}\text{H}_{50}\text{Cl}_2\text{CoN}_6\text{O}_8\text{P}_2$ (1126.82)	59.69 (59.69)	4.47 (4.47)	7.46 (7.46)	5.50 (5.50)	5.23 (5.23)	7.70

NiIIIr	(95) 268	Olive green	$C_{56}H_{50}Cl_2N_6NiO_8P_2$ (1126.57)	59.70 (59.21)	4.47 (4.47)	7.46 (7.46)	5.50 (5.50)	5.21 (5.21)	7.23
CuIIr	(97) 274	Light green	$C_{52}H_{44}Cl_2CuN_6O_4P_2$ (1013.34)	61.63 (61.63)	4.38 (4.38)	8.29 (8.29)	6.11 (6.11)	6.27 (6.27)	6.70
MnIII _s	(90) 277	Brown	$C_{54}H_{50}MnN_8O_8P_2$ (1055.91)	61.42 (61.42)	4.77 (4.77)	10.61 (10.61)	5.87 (5.87)	5.20 (5.20)	12.98
CoIII _s	(94) 246	Green	$C_{54}H_{50}CoN_8O_8P_2$ (1059.90)	61.19 (61.19)	4.75 (4.75)	10.57 (10.57)	5.84 (5.84)	5.56 (5.80)	1586
NiIII _s	(95) 268	Green	$C_{54}H_{50}N_8NiO_8P_2$ (1059.66)	61.21 (61.21)	4.76 (4.76)	10.57 (10.56)	5.85 (5.85)	5.54 (5.54)	16.30
CuIII _s	(97) 274	Green	$C_{50}H_{44}CuN_8O_4P_2$ (946.43)	63.45 (63.45)	4.69 (4.69)	11.84 (11.82)	6.55 (6.50)	6.71 (6.55)	5.86
MnIII _t	(90) 277	Brown	$C_{44}H_{46}MnN_8O_8P_2$ (931.77)	56.72 (56.72)	4.98 (4.98)	12.03 (12.03)	6.65 (6.65)	5.90 (5.65)	5.19
CoIII _t	(94) 246	Green	$C_{44}H_{46}CoN_8O_8P_2$ (935.76)	56.47 (56.47)	4.95 (4.95)	11.97 (11.97)	6.62 (6.62)	6.30 (6.62)	6.78
NiIII _t	(95) 268	Olive green	$C_{44}H_{46}N_8NiO_8P_2$ (935.52)	56.49 (56.49)	4.96 (4.96)	11.98 (11.98)	6.62 (6.62)	6.27 (6.27)	8.88
CuIII _t	(97) 274	Light green	$C_{40}H_{40}CuN_8O_4P_2$ (822.29)	58.43 (58.43)	4.90 (4.90)	13.63 (13.63)	7.53 (7.50)	7.73 (7.70)	13.64

TABLE III Spectroscopic and Spectrometric Data of the Newly Synthesized Compounds (III_{a-t})

No.	NMR (δ ; ppm)					IR (ν ; cm ⁻¹)			MS				
	¹ H			¹³ C		31P Phosphine	Base		Mole peak				
	NH	OCH ₃	CH ₃	Ar-H	C=O		C=N	C=N	P-NH	Peak (m/z)	Calc.	Found	Abundance%
III _a	—	—	—	7.82–7.22	164.32	160.12	25.57	1630	—	185	456.52	456	0.03
III _b	—	—	1.69	7.86–7.51	165.23	160.23	25.23	1645	—	126	394.45	394.5	0.01
III _c	—	3.82, 3.87	1.78	7.60–7.20	164.78	160.33	25.14	1633	—	122	454.50	454.5	0.05
III _d	—	—	1.97	8.20–8.00	166.21	160.12	21.84	1645	—	185	470.54	470.4	0.02
III _e	—	—	—	7.93–7.32	165.14	160.12	22.37	1636	—	179	457.51	457.1	2.13
III _f	—	—	1.84	7.87–7.12	167.28	160.28	25.22	1642	—	185	395.44	395.4	0.11
III _g	—	3.85	1.76	8.34–8.01	168.84	161.32	23.18	1646	—	212	424.47	424.7	0.04
III _h	—	3.80	1.63	8.22–7.98	165.33	160.38	23.01	1647	—	212	424.47	424.7	0.03
III _i	—	—	—	8.23–8.02	164.55	162.79	22.98	1635	—	250	501.51	501	0.03
III _j	—	3.82	—	7.8–7.24	166.69	162.13	25.68	1632	—	72	455.44	455.4	3.02
III _k	—	—	1.67	7.94–72.20	165.21	161.27	24.68	1630	—	235	473.89	473	0.05
III _l	—	—	1.70	8.33–8.02	168.23	162.30	21.89	1633	—	235	515.54	515.5	0.23
III _m	7.82	—	—	8.28–8.04	166.82	161.74	25.16	1634	2600	126	347.35	347.3	4.82
III _n	7.67	—	1.93	8.26–8.10	167.76	161.86	24.24	1635	2617	180	361.37	361.3	0.92
III _o	8.21	3.84	1.81	8.36–8.12	165.58	160.89	25.69	1630	2615	195	391.40	391.4	0.06
III _p	8.02	3.82, 3.86	1.86	8.15–7.64	167.91	160.37	23.87	1648	2613	210	421.42	421	0.07
III _q	8.26	—	—	8.27–7.74	168.24	160.86	22.64	1640	2619	228	457.89	457	1.13
III _r	8.67	—	—	8.23–8.03	166.63	160.74	22.78	1635	2615	185	457.89	457	0.08
III _s	8.52	—	—	8.22–8.00	167.37	161.53	25.37	1630	2622	212	424.43	424.4	2.63
III _t	8.27	—	1.87	7.96–72.84	168.38	161.86	24.83	1654	2618	185	362.36	362.3	0.02

TABLE IV IR Spectral Data of the Ligands III_(m-t) and Its Metal Complexes

No.	NH (cm ⁻¹)	P—N (cm ⁻¹)	P—NH (cm ⁻¹)	M—N (cm ⁻¹)	M—O (cm ⁻¹)	C≡N (cm ⁻¹)	P—aryl (cm ⁻¹)
III _m	3283(br)	1184(m)	2600(w)	—285(s)	—543(w)	1634(m)	1453(m)
MnIII _m	3234(br)	1212(m)	2589(v.w)			1625(m)	1447(m)
CoIII _m	3254(br)	1221(m)	2591(v.w)	283(m)	540(w)	1622(m)	1442(m)
NiIII _m	3245(br)	1215(m)	2592(v.w)	280(w)	553(s)	1623(m)	1447(m)
CuIII _m	3237(br)	1215(m)	2686(v.w)	280(w)	554(w)	1624(m)	1432(m)
III _n	3280(br)	1186(m)	2617(w)	—285(w)	—544(s)	1635(m)	1450(m)
MnIII _n	3215(br)	1214(m)	2604(v.w)			1223(m)	1447(m)
CoIII _n	3220(br)	1220(m)	2604(v.w)	283(w)	542(m)	1224(m)	1445(m)
NiIII _n	3225(br)	1215(m)	2601(v.w)	280(m)	551(s)	1226(m)	1449(m)
CuIII _n	3220(br)	1215(m)	2600(v.w)	280(w)	550(w)	1226(m)	1432(m)
III _o	3269(br)	1184(m)	2615(w)	—285(m)	—540(m)	1635(m)	1450(m)
MnIII _o	3235(br)	1214(m)	2600(v.w)			1222(m)	1443(m)
CoIII _o	3240(br)	1222(m)	2600(v.w)	282(w)	543(w)	1225(m)	1445(m)
NiIII _o	3230(br)	1213(m)	2600(v.w)	282(m)	555(w)	1223(m)	1442(m)
CuIII _o	3230(br)	1214(m)	2602(v.w)	280(w)	555(m)	1223(m)	1430(m)
III _p	3275(br)	1178(m)	2613(w)	—286(m)	—543(m)	1648(m)	1453(m)
MnIII _p	3219(br)	1201(m)	2602(v.w)			1224(m)	1444(m)
CoIII _p	3244(br)	1200(m)	2601(w)	284(w)	542(m)	1223(m)	1442(m)
NiIII _p	3234(br)	1205(m)	2600(w)	283(m)	551(s)	1222(m)	1445(m)
CuIII _p	3236(br)	1205(m)	2602(v.w)	282(m)	556(w)	1225(m)	1433(m)
III _q	3276(br)	1182(m)	2619(w)	—288(w)	—548(m)	1640(m)	1452(m)
MnIII _q	3213(br)	1213(m)	2605(v.w)			1221(m)	1442(m)
CoIII _q	3227(br)	1202(m)	2602(v.w)	285(m)	544(m)	1221(m)	1444(m)
NiIII _q	3228(br)	1212(m)	2601(w)	284(w)	554(m)	1223(m)	1445(m)
CuIII _q	3226(br)	1211(m)	2601(w)	284(m)	555(v.w)	1224(m)	1433(m)
III _r	3278(br)	1168(m)	2615(w)	—286(v.w)	—550(m)	1635(m)	1458(m)
MnIII _r	3245(br)	1213(m)	2602(v.w)			1222(m)	1443(m)
CoIII _r	3233(br)	1211(m)	2602(w)	286(m)	544(m)	1222(m)	1445(m)
NiIII _r	3242(br)	1211(m)	2600(v.w)	288(m)	553(m)	1223(m)	1447(m)
CuIII _r	3243(br)	1212(m)	2600(v.w)	280(w)	555(s)	1221(m)	1442(m)
III _s	3276(br)	1188(m)	2622(w)	—287(s)	—548(m)	1630(m)	1464(m)
MnIII _s	3245(br)	1210(m)	2606(v.w)			1215(m)	1445(m)
CoIII _s	3243(br)	1221(m)	2607(v.w)	283(s)	544(m)	1214(m)	1442(m)
NiIII _s	3242(br)	1217(m)	2605(w)	282(s)	552(m)	1226(m)	1444(m)
CuIII _s	3242(br)	1216(m)	2600(v.w)	280(m)	550(s)	1224(m)	1446(m)
III _t	3282(br)	1188(m)	2618(w)	—285(s)	—542(s)	1654(m)	1452(m)
MnIII _t	3213(br)	1211(m)	2606(v.w)			1223(m)	1447(m)
CoIII _t	3262(br)	1222(m)	2604(w)	283(m)	540(s)	1224(m)	1445(m)
NiIII _t	3264(br)	1202(m)	2602(v.w)	281(m)	550(m)	1222(m)	1449(m)
CuIII _t	3269(br)	1205(m)	2602(v.w)	280(m)	550(m)	1223(m)	1431(m)

coordinating atoms clearly indicate the bonding of the imine nitrogen and amido oxygen to the manganese, cobalt, nickel or copper atom. The ^{31}P -NMR chemical shifts for the phosphorus compounds ligands **III**_{a-t} adds further substantial evidence supporting the proposed structures. The ^{31}P -NMR (Table III) spectra showed one signals at $\delta = 21.84\text{--}25.57$ ppm, corresponding to the one phosphorus environment (*) designated in the above structure. The structure of these hydrazone and semicarbazone derivatives are supported by elemental analysis (C, H, N, P) and confirmed by mass spectroscopy, which show a molecular ion peak corresponding to the calculated molecular weight.

Electronic and Magnetic Properties

Electronic spectral data of phosphorus compounds **III**_{a-t}, as well as the ligand **III**_n and its complexes are carried out in DMF and show bands at $37,580\text{--}30,100\text{ cm}^{-1}$ assigned to $\pi - \pi^*$ electronic transitions within the benzene ring. These bands remain almost unchanged in the spectra of the complexes. Another band is observed at $27,150\text{ cm}^{-1}$ is corresponding to $n\text{--}\pi^*$ transitions of the azomethine ($> \text{CH}=\text{N}$) group. However, in the spectra of the complexes the bands are found to be broadened and can be explained as a combination of $\text{O} \rightarrow \text{M}$ and $\text{N} \rightarrow \text{M}$ LCT transitions.

The electronic spectra and magnetic moment values for all complexes are consistent with the proposed structures. The diffuse reflectance spectrum of the Mn(II) complex displays two bands at $12,950$ and $15,250\text{ cm}^{-1}$ assigned to the ${}^6\text{A}_{1g}(\text{F}) \rightarrow {}^4\text{T}_1(4\text{G})(\nu_1)$ and ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(4\text{G})$ transitions, respectively, considering an octahedral symmetry.⁸ In addition, the octahedral configuration is also supported by the measured magnetic moment of such complex, 5.34 B.M.

The diffuse reflectance spectrum of the Co(II) complex displays three bands at $13,501$, $18,250$, and $22,953\text{ cm}^{-1}$ assigned to the ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})(\nu_1)$, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})(\nu_2)$, and ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{P})(\nu_3)$ transitions, respectively. The band observed at $26,520\text{ cm}^{-1}$ refers to $\text{L} \rightarrow \text{MCT}$ band.⁹ From the observed magnetic moment value ($\mu_{\text{eff}} = 5.11\text{ B.M.}$) together with the band position in the solid reflectance spectra, the Co(II) complex is octahedral with largely covalent bonds between the organic ligand and Co(II) ion.

The Ni(II) complex reported herein is high spin with a room temperature magnetic-moment value of 2.93 B.M. , which confirms the octahedral structure of this complex. The solid reflectance spectrum of the complex shows three bands at $14,993$, $17,483$, and $21,552\text{ cm}^{-1}$, which are assigned to the ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})(\nu_1)$, ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})(\nu_2)$, and

$^3A_{2g} \rightarrow ^3T_{2g} (P) (\nu_3)$ transitions, respectively, confirming the octahedral geometry of the Ni(II) complex.^{10,11}

The solid reflectance spectrum of the Cu(II) complex gave a band at $17,361\text{ cm}^{-1}$, was assigned to $^2B_2 \rightarrow ^2E$ transition. The bands observed in the range $23,809\text{--}23,864\text{ cm}^{-1}$ were assigned to the charge transfer via $L \rightarrow M$ (Cu^{2+}). The observed magnetic moment of the Cu(II) complex is 1.89 B.M., which confirms the square planar structure of this complex.⁵

Solid-State Electrical Conductivity

The conductivity of the free ligands (III_{m-t}) is increased on complexing with transition metal ions. This behaviour is attributed to the inclusion of the various metal cations in the π -electron delocalization of the ligands.¹² The observed conductivities follow the order $\text{Mn} < \text{Co} < \text{Ni} < \text{Cu}$. Theoretically, if we consider the charge/radii, the stability of the metal complexes increases as the size of the metal ion decreases or the value of the ratio charge/radii increases. This means that the stability increases towards the copper complexes. It is apparent that increasing stability of the complexes will increase the number of dislocated electrons on the ligand molecule and then increase the conductivity¹³ as given in (Table V). To explain the conduction mechanism of the ligand and its complexes, it is necessary to determine the mobility of charge carriers μ . If the density of charge carriers is known, then the mobility can be calculated using the relation $\sigma = eNm$, e is the electron charge. The charge carrier concentration was determined using the relation,

$$n = 2[2\mu m * kT/h_2]^{1/2} \exp(-E/kT), \quad (1)$$

where m^* is the effective mass of charge carrier. The calculated mobilities are ranged from 10^{-5} to $10^{-9}\text{ cm}^2/\text{V s}$ suggesting that the conduction of Acetophenone N_4 diphenylphosphine semicarbazones (III_{m-t}) ligands and its metal complexes takes place by hopping mechanism.¹⁴

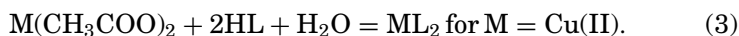
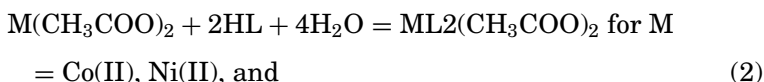
The Thermal Analyses of the Complexes

The thermogram of Co(II) complex of III_n shows that there is two water molecules as water of hydration, the decomposition range was ($70\text{--}110^\circ\text{C}$). The initial mass loss observed for Ni(II) complex of III_o in the temperature range ($80\text{--}120^\circ\text{C}$) corresponds to two water molecules attributed as water of hydration. In the temperature range ($180\text{--}210^\circ\text{C}$). For Cu(II) complex of III_t , the TGA analysis indicates the complex contains two hydrated water molecules ($60\text{--}115^\circ\text{C}$), hence, the

TABLE V Values of the Electrical Conductivity (σ) and Thermal Activation Energy of the Ligands $\text{III}_{(\text{m}-\text{t})}$ and Its Metal Complexes at 303 K

No.	$\sigma(\Omega^{-1}\text{cm}^{-1})$	E (eV)	$n(\text{cm}^{-3})$	$\mu(\text{cm}^2/\text{Vs})$
III_{m}	1.42×10^{-8}	0.32	8.54×10^{19}	1.11×10^{-7}
MnIII_{m}	1.92×10^{-8}	0.35	12.32×10^{18}	0.71×10^{-9}
CoIII_{m}	2.11×10^{-8}	0.42	12.21×10^{18}	9.82×10^{-8}
NiIII_{m}	3.22×10^{-8}	0.42	12.41×10^{18}	3.63×10^{-6}
CuIII_{m}	4.54×10^{-8}	0.55	1.25×10^{16}	2.33×10^{-5}
III_{n}	1.44×10^{-8}	0.33	8.56×10^{19}	1.14×10^{-7}
MnIII_{n}	1.94×10^{-8}	0.36	12.8×10^{18}	0.72×10^{-9}
CoIII_{n}	2.13×10^{-8}	0.41	12.0×10^{18}	9.81×10^{-8}
NiIII_{n}	3.21×10^{-8}	0.46	12.8×10^{18}	3.65×10^{-6}
CuIII_{n}	4.53×10^{-8}	0.57	1.28×10^{16}	2.36×10^{-5}
III_{o}	1.44×10^{-8}	0.33	8.56×10^{19}	1.18×10^{-7}
MnIII_{o}	1.94×10^{-8}	0.36	12.84×10^{18}	0.77×10^{-9}
CoIII_{o}	2.13×10^{-8}	0.41	12.05×10^{18}	9.88×10^{-8}
NiIII_{o}	3.21×10^{-8}	0.46	12.83×10^{18}	3.69×10^{-6}
CuIII_{o}	4.53×10^{-8}	0.57	1.28×10^{16}	2.36×10^{-5}
III_{p}	1.49×10^{-8}	0.31	8.53×10^{19}	1.14×10^{-7}
MnIII_{p}	1.87×10^{-8}	0.36	11.86×10^{18}	0.75×10^{-9}
CoIII_{p}	2.16×10^{-8}	0.40	12.08×10^{18}	9.87×10^{-8}
NiIII_{p}	3.23×10^{-8}	0.46	12.84×10^{18}	3.66×10^{-6}
CuIII_{p}	4.57×10^{-8}	0.57	1.28×10^{16}	2.34×10^{-5}
III_{q}	1.49×10^{-8}	0.32	8.58×10^{19}	1.15×10^{-7}
MnIII_{q}	1.98×10^{-8}	0.35	12.82×10^{18}	0.76×10^{-9}
CoIII_{q}	2.16×10^{-8}	0.40	12.05×10^{18}	9.67×10^{-8}
NiIII_{q}	3.28×10^{-8}	0.45	12.86×10^{18}	3.70×10^{-6}
CuIII_{q}	4.50×10^{-8}	0.58	1.26×10^{16}	2.23×10^{-5}
III_{r}	1.46×10^{-8}	0.34	8.55×10^{19}	1.23×10^{-7}
MnIII_{r}	1.98×10^{-8}	0.37	12.86×10^{18}	0.74×10^{-9}
CoIII_{r}	2.14×10^{-8}	0.42	12.02×10^{18}	9.87×10^{-8}
NiIII_{r}	3.31×10^{-8}	0.47	12.83×10^{18}	3.70×10^{-6}
CuIII_{r}	4.55×10^{-8}	0.56	1.31×10^{16}	2.42×10^{-5}
III_{s}	1.43×10^{-8}	0.30	8.43×10^{19}	1.17×10^{-7}
MnIII_{s}	1.94×10^{-8}	0.35	12.92×10^{18}	0.87×10^{-9}
CoIII_{s}	2.16×10^{-8}	0.40	12.01×10^{18}	9.93×10^{-8}
NiIII_{s}	3.31×10^{-8}	0.47	12.82×10^{18}	3.74×10^{-6}
CuIII_{s}	4.56×10^{-8}	0.58	1.31×10^{16}	2.45×10^{-5}
III_{t}	1.49×10^{-8}	0.31	8.62×10^{19}	1.24×10^{-7}
MnIII_{t}	1.93×10^{-8}	0.36	12.72×10^{18}	0.83×10^{-9}
CoIII_{t}	2.14×10^{-8}	0.42	12.32×10^{18}	9.97×10^{-8}
NiIII_{t}	3.25×10^{-8}	0.46	12.83×10^{18}	3.68×10^{-6}
CuIII_{t}	4.54×10^{-8}	0.59	1.34×10^{16}	2.43×10^{-5}

synthesis of the complexes may be explained according to the equations:



It should be indicated that the Co(II), Ni(II) and Cu(II) ions forms 2 : 1 ligand to metal ratio.

Corrosion Inhibition

The inhibitive action of III_n on the dissolution of aluminium and copper in 1 M HCl, as well as chromium–nickel steel in crude oil are investigated (Tables VI–VIII). III_m is impracticable to study because the precipitation occurred. Aluminium, copper, and chromium–nickel steel were selected for this study due to their numerous industrial applications. The degree of surface coverage (θ), the percentage inhibition efficiency ($\eta\%$) and the corrosion rate (R) were calculated as follows¹⁵:

$$\theta = 1 - w/w_0, \quad (4)$$

$$\eta\% = [w_0 - w/w_0] \times 100, \text{ and} \quad (5)$$

$$R = \text{weight loss (mg)/area(cm}^2\text{)} \times \text{time(h)}, \quad (6)$$

where w and w_0 are the weight losses of the test specimens in absence and presence of the inhibitor. The inhibition efficiency of additive compound depends on many factors, which include the number of adsorption sites and their charge density, molecular size, heat of hydrogenation, mode of interaction with the metal surface, and formation of metallic complexes. The weight loss data were determined and listed in (Tables VI–VIII). Careful inspection of these results showed that, by

TABLE VI Corrosion Parameters of Copper in 1M HCl at Different III_n Concentrations

Inhibitor conc. (M)	Wt. loss (mg cm ⁻²)	R (mg cm ⁻² h ⁻¹)	θ	$\eta\%$
Blank	0.04	0.035	—	—
1×10^{-5}	0.03	0.025	0.31	31
5×10^{-5}	0.026	0.022	0.37	37
1×10^{-4}	0.024	0.020	0.44	44
5×10^{-4}	0.020	0.012	0.65	65
1×10^{-3}	0.011	0.010	0.82	82

TABLE VII Corrosion Parameters of Aluminum in 1M HCl at Different III_n Concentrations

Inhibitor conc. (M)	Wt. loss (mg cm ⁻²)	R (mg cm ⁻² h ⁻¹)	θ	$\eta\%$
Blank	0.11	0.09	—	—
1×10^{-5}	0.10	0.08	0.12	12
5×10^{-5}	0.09	0.07	0.15	15
1×10^{-4}	0.06	0.05	0.41	41
5×10^{-4}	0.05	0.04	0.52	52
1×10^{-3}	0.01	0.01	0.86	86

increasing the inhibitor concentration, both (θ) and ($\eta\%$) increased while (R) reduced. So, the dissolution of aluminium, copper and chromium–nickel steel in the presence of the investigated inhibitor can be interpreted on the basis of interface inhibition mode, the inhibitor acts effectively at the metal solution interface.¹⁶ Weight loss data determination after 70 min. yielded convincing evidence for the application of III_n as an active corrosion inhibitor (Tables VI–VIII). The maximum efficiencies at higher III_n concentration values are 88, 87, and 88% for aluminum, copper, and chromium–nickel steel, respectively. These results indicate a reasonable corrosion inhibition for specimens.

EXPERIMENTAL

All melting points reported are uncorrected. Elemental analyses of C, H, and N were carried out at the Microanalytical Research Center, Faculty of Science, Cairo University and phosphorus was determined gravimetrically as phosphoammonium molybdate using R. Voy method.¹⁷ The mid-infrared and the Ultraviolet measurements have been carried out

TABLE VIII Corrosion Parameters of Chromium-Nickel Steel in Crude Oil at Different III_n Concentrations

Inhibitor conc. (M)	Wt. loss (mg cm ⁻²)	R (mg cm ⁻² h ⁻¹)	θ	$\eta\%$
Blank	0.07	0.06	—	—
1×10^{-5}	0.04	0.04	0.37	37
1×10^{-4}	0.02	0.02	0.67	67
5×10^{-4}	0.01	0.01	0.87	87

at the chemistry Department, Faculty of Science, and Al-Azhar University. IR spectra recorded in (KBr disk) on a Bruker, vector 22, Germany, or on a Shimadzu FT- 8201 PC spectrophotometer. Ultraviolet spectra were recorded on Perkin Elmer Lambda-3B Ultraviolet-Visible spectrophotometer using DMF as a solvent. ^1H and ^{13}C -NMR spectra were recorded in $(\text{CD}_3)_2\text{SO}$ on a Varian Gemini 200 MHz or on a Varian Mercury 300MHz Em-360-60 MHz spectrometer and shifts were expressed in δ units using TMS as internal reference. Mass spectra were recorded on Hewlett-Packard (HP) 5988A (EI, 15eV). ^{31}P NMR spectra were run, relative to external H_3PO_4 (85%), with a Varian FT-80 spectrometer at 365MHz. Magnetic measurements were recorded by the Gouy method at room temperature using a magnetic susceptibility balance (Johanson Mathey), Alfa product, Model No. (MK). The thermogravimetric analyses (TGA) were recorded on a Shimadzu TGA -50 H. TGA was carried out in a dynamic nitrogen atmosphere (20 mL min^{-1}) at a heating rate of $10^\circ\text{C min}^{-1}$. The conductometric measurements in solutions were carried out using conductivity TDS model 72. Metal contents were determined by titration against standard EDTA after complete decomposition of the complexes with aqua regia in a Kjeldahl flask several times.

Measurement of the Dark Conductivity

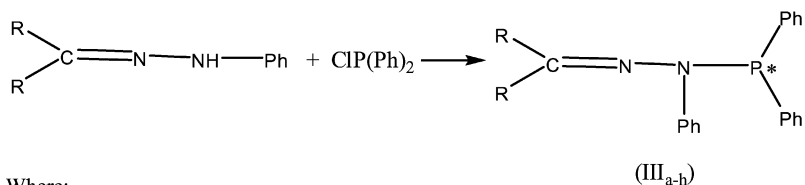
The dark conductivity, which ranges from 10^{-16} to $10^5(\text{ohm}^{-1}\text{ cm}^{-1})$, is usually measured by the following cell arrangements: sandwich cells in which the sample is arranged between two electrodes.

The electrical conductivity (dc) data were collected at different temperatures, from room temperature up to near the melting point of each sample in the ohmic region by using the potential probe method.¹⁸ The samples were in the form of pellets pressed at 4 tons /cm^2 , diameter $\cong 10\text{ mm}$ and thickness $1\text{--}2\text{ mm}$, coated with silver paint (BDH) and checked several times for good contact.

Synthesis of Ligand III_{a-t}

The solid of hydrazone or semicarbazone derivatives (I_{a-t}) (0.01 mmol) was added in small portions to a well stirred solution of the diphenylchlorophosphine (**II**) (0.01 mmole) in 100 ml acetonitrile over a half-hour period. After the complete addition, the reaction mixture was heated under reflux for 4 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,

i) The proposed structure of hydrazone derivatives (III_{a-h})



Where;

III_a; R = R' = Ph

III_b; R = Me, R' = Ph

III_c; R = Me, R' = 3, 4-(MeO)₂C₆H₃

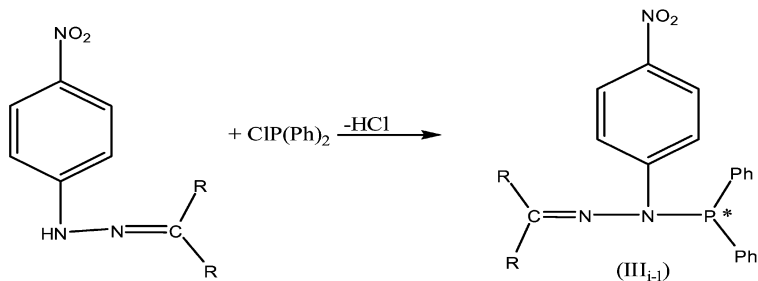
III_d; R = Me, R' = 4-PhC₆H₄

III_e; R = Ph, R' = 2-Pyridyl

III_f; R = Me, R' = 4-Pyridyl

III_g; R = Me, R' = 4-MeOC₆H₄

III_h; R = Me, R' = 2-MeOC₆H₄



Where;

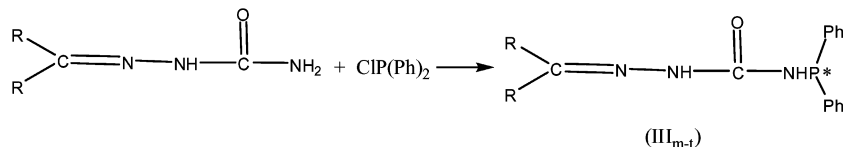
III_i; R = R' = Ph

III_j; R = H, R' = 4-MeOC₆H₄

III_k; R = Me, R' = 4-ClC₆H₄

III_l; R = Me, R' = 4-PhC₆H₄

(ii) The proposed structure of semicarbazone derivatives (III_{m-t})



III_m; R = H, R' = Ph

III_n; R = Me, R' = Ph

III_o; R = Me, R' = 4-MeOC₆H₄

III_p; R = Me, R' = 3, 4-(MeO)₂C₆H₃

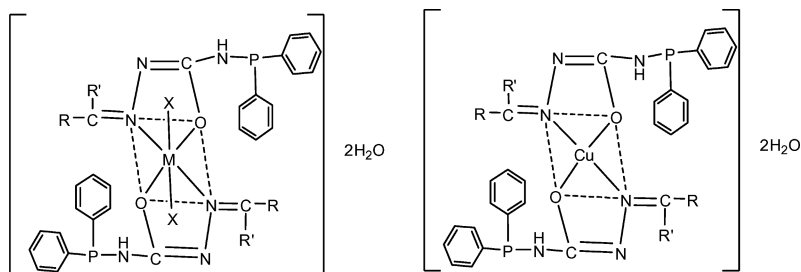
III_q; R = Ph, R' = 4-ClC₆H₄

III_r; R = Ph, R' = 2-ClC₆H₄

III_s; R = Ph, R' = 2-Pyridyl

III_t; R = Me, R' = 4-Pyridyl

SCHEME 1



Where:

M = Mn(II), Co(II), or Ni(II) and Cu(II)

R = H, R' = Ph (III_m)

R = Me, R' = Ph (III_n)

R = Me, R' = 4-MeOC₆H₄ (III_o)

R = Me, R' = 3, 4-(MeO)₂C₆H₃ (III_p)

R = Ph, R' = 4-ClC₆H₄ (III_q)

R = Ph, R' = 2-ClC₆H₄ (III_r)

R = Ph, R' = 2-Pyridyl (III_i)

R = Me, R' = 4-Pyridyl (III_j)

SCHEME 2 The proposed structure of the metal complexes.

diethylether and dried under vacuo to give the corresponding ligands (III_{a-t}) (Scheme 1).

Synthesis of the Solid Metal Complexes

A one molar equivalent (0.1 mol) of manganese (II), cobalt (II), nickel (II), and copper (II) acetate dissolved in 50 ml absolute ethanol was added to two molar equivalent (0.2 mol) of III_{m-t} dissolved in 100 ml absolute ethanol at room temperature with continuous stirring. The reaction mixture was heated under reflux for 3 h. Then, the reaction mixture was evaporated to give solids, which were recrystallized from ethanol and diethylether and dried under vacuo. The analytical data of both the ligands and their metal complexes are listed in Tables I and II.

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