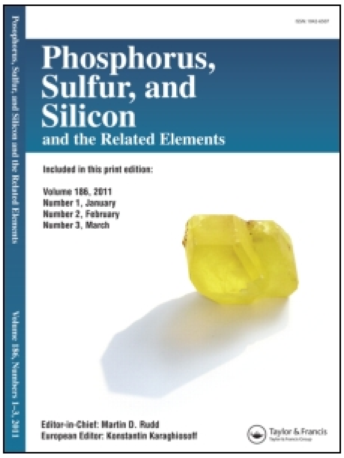


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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

A. M. A. Alaghaz[a]; R. A. A. Ammar[b]
[a] Chemistry Department, Faculty of Science, Al-Azhar University (Boys), Nasr-City, Cairo, Egypt [b] Chemistry Department, Faculty of Science, Al-Azhar University (Girls), Nasr-City, Cairo, Egypt

To cite this Article Alaghaz, A. M. A. and Ammar, R. A. A.(2008) 'Preparation and Characterization of Some Novel Diphenylphosphine Hydrazones and Semicarbazones and Their Metal Complex Derivatives', Phosphorus, Sulfur, and Silicon and the Related Elements, 183: 11, 2827 — 2844

To link to this Article: DOI: 10.1080/10426500802016778

URL: http://dx.doi.org/10.1080/10426500802016778

Phosphorus, Sulfur, and Silicon, 183:2827–2844, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500802016778

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

A. M. A. Alaghaz[1] **and R. A. A. Ammar**[2]
[1]Chemistry Department, Faculty of Science, Al-Azhar University (Boys), Nasr-City, Cairo, Egypt
[2]Chemistry Department, Faculty of Science, Al-Azhar University (Girls), Nasr-City, Cairo, Egypt

Interaction of hydrazones and semicarbazones derivatives $\mathbf{I}_{a-t}$ *with diphenylchlorophosphine* **II**, *gave new compounds* $\mathbf{III}_{a-t}$, *and their complexation ability towards various divalent metal acetates* $Mn(OAc)_2.\ 4H_2O$, $Co(OAc)_2.\ 4H_2O$, $Ni(OAc)_2.\ 4H_2O$, *and* $Cu(OAc)_2.\ H_2O$, *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 microanalyical 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

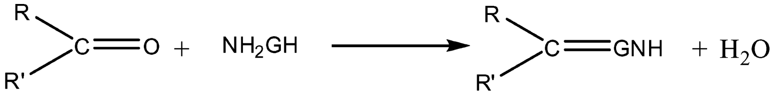
Received 11 December 2007; accepted 27 February 2008.

Address correspondence to A. M. A. Alajhaz, Chemistry Department, Faculty of Science, Al-Azhar University (Boys), Nasr-City, Cairo, Egypt. E-mail: aalajhaz@hotmail.com

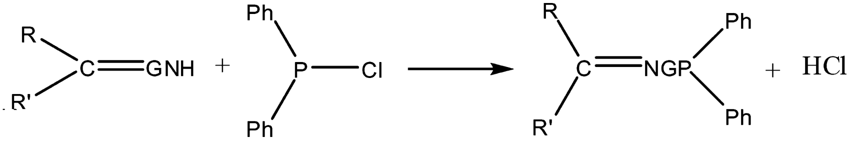
present work was planned to investigate new route for the synthesis of novel diphenylphosphine hydrazones and diphenylphos-phine semicarbazones derivatives with potential biological activities.

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).

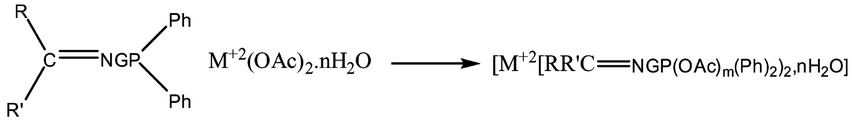


(1 mole) (1 mole), and



(1 mole) (1 mole),

where G=Ph—N, $NO_2C_6H_4N$, or HNCONH.



$III_{m\text{-}t}$

(2 mole) (1 mole) ,

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} cm^2) 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 around1705 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 ~545 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.

^{1}H, ^{13}C-, and ^{31}P-NMR Spectra

^{1}H-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 ^{13}C-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	$C_{31}H_{25}N_2P$(456.52)	81.56(81.51)	5.52(5.52)	6.14(6.13)	6.78(6.76)
III_b	94	143	White	$C_{26}H_{23}N_2P$(394.45)	79.1(79.16)	5.88(5.84)	7.10(7.10)	7.85(7.83)
III_c	92	144	White	$C_{28}H_{27}N_2O_2P$(454.50)	73.99(73.97)	5.99(5.95)	6.16(6.12)	6.81(6.80)
III_d	94	121	Silvery white	$C_{32}H_{27}N_2P$(470.54)	81.68 (81.64)	5.78(5.76)	5.95(5.92)	6.58 (6.57)
III_e	95	142	Silvery white	$C_{30}H_{24}N_3P$(457.51)	78.76 (78.75)	5.29(5.25)	9.18(9.15)	6.77 (6.75)
III_f	92	124	White	$C_{25}H_{22}N_3P$(395.44)	75.93 (75.92)	5.61(5.60)	7.08(7.03)	7.83(7.84)
III_g	94	112	White	$C_{27}H_{25}N_2OP$(424.47)	76.40 (76.38)	5.94(5.93)	6.60(5.92)	7.30 (7.30)
III_h	98	124	White	$C_{27}H_{25}N_2OP$(424.47)	76.40 (76.34)	5.94(5.93)	6.60(6.60)	7.30 (7.30)
III_i	95	129	Silvery white	$C_{31}H_{24}N_3O_2P$(501.51)	74.24(74.22)	4.82(4.35)	8.38(7.62)	6.18 (5.63)
III_j	96	135	White	$C_{26}H_{22}N_3O_3P$(455.44)	68.57 (68.53)	4.87(4.50)	9.23(9.21)	6.80 (6.80)
III_k	99	142	Silvery white	$C_{26}H_{21}ClN_3O_2P$(47389)	65.90(65.87)	4.47(4.44)	8.87(8.84)	6.54(6.52)
III_l	97	134	White	$C_{32}H_{26}N_3O_2P$(515.54)	74.55(74.54)	5.08(5.03)	8.15(8.12)	6.01(6.01)
III_m	96	135	White	$C_{20}H_{18}N_3OP$(347.35)	69.16(69.12)	5.22(5.20)	12.10(12.10)	8.92(8.92)
III_n	98	153	Silvery white	$C_{21}H_{20}N_3OP$(361.37)	69.80(69.80)	5.58(5.53)	11.63(11.61)	8.57 (8.55)
III_o	95	147	Yellow	$C_{22}H_{22}N_3O_2P$(391.40)	67.51 (67.51)	5.67(5.63)	10.74(10.74)	7.91(7.90)
III_p	99	154	Pale yellow	$C_{23}H_{24}N_3O_3P$(421.42)	65.55(65.53)	5.74(5.74)	9.97(9.95)	7.35(7.35)
III_q	99	150	Yellow	$C_{26}H_{21}ClN_3OP$(457.89)	68.20(68.20)	4.60(4.60)	9.18(9.15)	6.76(6.75)
III_r	98	145	Pale yellow	$C_{26}H_{21}ClN_3OP$(457.89)	68.20 (68.20)	4.60(4.60)	9.18(9.16)	6.76 (6.75)
III_s	98	153	Yellow	$C_{25}H_{21}N_4OP$(424.43)	70.75(70.74)	4.99(4.97)	13.20(13.20)	7.30 (7.30)
III_t	99	148	Yellow	$C_{20}H_{19}N_4OP$(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) C%	H%	%N	%P	%M	Λ (Ω^{-1}mol^{-1}cm^{2})
MnIII$_m$	(90) 277	Brown	$C_{44}H_{44}MnN_6O_8P_2$ (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	$C_{44}H_{44}CoN_6O_8P_2$ (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	$C_{44}H_{44}N_6NiO_8P_2$ (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	$C_{40}H_{38}CuN_6OP_2$ (792.26)	60.64 (60.43)	4.83 (4.71)	10.61 (10.29)	7.82 (7.57)	8.02 (7.73)	6.03
MnIIIn	(90) 277	Brown	$C_{42}H_{46}MnN_6O_6P_2$ (847.74)	59.51 (59.50)	5.47 (5.43)	9.91 (9.76)	7.31 (7.30)	6.48 (6.40)	6.83
CoIIIn	(94) 246	Green	$C_{42}H_{46}N_6P_2O_6Co$ (851.73)	59.23 (59.12)	5.44 (5.40)	9.87 (9.76)	7.27 (6.41)	6.92 (6.87)	12.21
NiIIIn	(95) 268	Olive green	$C_{42}H_{46}N_6P_2O_6$ 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
CuIIIn	(97) 274	Light green	$C_{42}H_{42}CuN_6O_4P_2$ (820.31)	61.49 (61.43)	5.16 (5.11)	10.24 (10.22)	7.55 (7.54)	7.75 (7.73)	5.15
MnIIIo	(90) 277	Brown	$C_{48}H_{52}MnN_6O_{10}P_2$ (989.84)	58.24 (58.23)	5.30 (5.42)	8.49 (8.46)	6.26 (6.30)	5.55 (5.50)	5.17
CoIIIo	(94) 246	Bright green	$C_{48}H_{52}CoN_6O_{10}P_2$ (993.84)	58.01 (58.00)	5.27 (5.24)	8.46 (8.42)	6.23 (6.20)	5.93 (5.90)	7.92
NiIIIo	(95) 268	Olive green	$C_{48}H_{52}N_6NiO_{10}P_2$ (993.60)	58.02 (58.00)	5.28 (5.25)	8.46 (8.42)	6.23 (6.23)	5.91 (5.90)	8.06
CuIIIo	(97) 274	Light green	$C_{44}H_{46}CuN_6O_6P_2$ (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) C%	H%	%N	%P	%M	Λ (Ω^{-1}mol^{-1}cm^2)
MnIIIp	(90) 277	Brown	$C_{50}H_{56}MnN_6O_{12}P_2$ (1049.89)	57.20 (57.20)	5.38 (5.38)	8.00 (8.00)	8.00 (8.00)	5.23 (5.23)	16.00
CoIIIp	(94) 246	Bright green	$C_{50}H_{56}CoN_6O_{12}P_2$ (1053.89)	56.98 (56.98)	5.36 (5.36)	7.97 (7.97)	5.88 (5.88)	5.59 (5.59)	11.11
NiIIIp	(95) 268	Olive green	$C_{50}H_{56}N_6NiO_{12}P_2$ (1053.65)	57.00 (57.00)	5.36 (5.36)	7.98 (7.98)	5.88 (5.88)	5.57 (5.57)	15.90
CuIIIp	(97) 274	Light green	$C_{46}H_{50}CuN_6O_8P_2$ (940.42)	58.75 (58.75)	5.36 (5.36)	8.94 (8.94)	6.59 (6.59)	6.76 (6.73)	4.98
MnIIIq	(90) 277	Brown	$C_{56}H_{50}Cl_2MnN_6O_8P_2$ (1122.82)	59.90 (59.50)	4.49 (4.49)	7.48 (7.48)	5.52 (5.52)	4.89 (4.40)	7.95
CoIIIq	(94) 246	Bright green	$C_{56}H_{50}Cl_2CoN_6O_8P_2$ (1126.82)	59.69 (59.69)	4.47 (4.47)	7.46 (7.46)	5.50 (5.50)	5.23 (5.23)	7.64
NiIIIq	(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)	8.00
CuIIIq	(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)	4.85
MnIIIr	(90) 277	Brown	$C_{56}H_{50}Cl_2MnN_6O_8P_2$ (1122.82)	59.90 (59.50)	4.49 (4.49)	7.48 (7.48)	5.52 (5.52)	4.89 (4.40)	4.90
CoIIIr	(94) 246	Bright green	$C_{56}H_{50}Cl_2CoN_6O_8P_2$ (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
CuIIIr	(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
MnIIIt	(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
CoIIIt	(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
NiIIIt	(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
CuIIIt	(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})

	NMR (δ; ppm)										MS		
	^1H				^{13}C			IR (ν; cm^{-1})			Mole peak		
No.	NH	OCH_3	CH_3	Ar—H	C=O	C=N	^{31}P Phosphine	C=N	P—NH	Base 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 $\mathbf{III_{a-t}}$ adds further substantial evidence supporting the proposed structures. The ^{31}P-NMR (Table III) spectra showed one signals at $\delta = 21.84-25.57$ 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 $\mathbf{III_{a-t}}$, as well as the ligand $\mathrm{III_n}$ and its complexes are carried out in DMF and show bands at 37,580–30,100 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 cm^{-1} is corresponding to n-π^* transitions of the azomethine (> CH=N) group. However, in the spectra of the complexes the bands are found to be broadened and can be explained as a combination of O → M and N → 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 cm^{-1} assigned to the $^6\mathrm{A_{1g}}$ $(F) \rightarrow {}^4\mathrm{T_1}(^4G)$ (ν_1) and $^6\mathrm{A_{1g}} \rightarrow {}^4\mathrm{T_{2g}}(^4G)$ 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 cm^{-1} assigned to the $^4\mathrm{T_{1g}}$ $(F) \rightarrow {}^4\mathrm{T_{2g}}(F)$ (ν_1), $^4\mathrm{T_{1g}}$ $(F) \rightarrow {}^4\mathrm{A_{2g}}(F)$ (ν_2), and $^4\mathrm{T_{1g}} \rightarrow {}^4\mathrm{T_{2g}}(P)$ (ν_3) transitions, respectively. The band observed at 26,520 cm^{-1} refers to L→MCT band.[9]From the observed magnetic moment value ($\mu_{\mathrm{eff}} = 5.11$ 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 cm^{-1}, which are assigned to the $^3\mathrm{A_{2g}} \rightarrow {}^3\mathrm{T_{1g}}(P)$ (ν_1), $^3\mathrm{A_{2g}} \rightarrow {}^3\mathrm{T_{1g}}(F)$ (ν_2), and

$^3A_{2g} \rightarrow {}^3T_{2g}$ (P) (ν_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 cm^{-1}, was assigned to $^2B_2 \rightarrow {}^2E$ transition. The bands observed in the range 23,809–23,864 cm^{-1} were assigned to the charge transfer via L→M (Cu^{2+}). The observed magnetic moment of the Cu(II) complex is 1.89 B.M., which confirms the square planner 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 Mn < Co < Ni < 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 conductivity[13] 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 $\sigma = eN$m, $e$is the electron charge. The charge carrier concentration was determined using the relation,

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

where $m^*$is the effective mass of charge carrier. The calculated mobilities are ranged from 10^{-5} to 10^{-9} cm^2/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 (70–110°C). The initial mass loss observed for Ni(II) complex of III_o in the temperature range (80–120°C) corresponds to two water molecules attributed as water of hydration. In the temperature range (180–210°C). For Cu(II) complex of III_t, the TGA analysis indicates the complex contains two hydrated water molecules (60–115°C), hence, the

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

No.	$\sigma(\Omega^{-1}cm^{-1})$	E (eV)	$n(cm^{-3})$	$\mu(cm^2/Vs)$
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}	$9.88 \times 10-8$
$NiIII_o$	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}	$9.67 \times 10-8$
$NiIII_q$	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:

$$M(CH_3COO)_2 + 2HL + 4H_2O = ML2(CH_3COO)_2 \text{ for M} = \text{Co(II), Ni(II), and} \quad (2)$$

$$M(CH_3COO)_2 + 2HL + H_2O = ML_2 \text{ for M} = \text{Cu(II)}. \quad (3)$$

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 effciency ($\eta\%$) and the corrosion rate (R) were calculated as follows[15]:

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

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

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

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 IIIn 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 IIIn Concentrations

Inhibitor conc. (M)	Wt. loss (mg cm^{-2})	R (mg cm^{-2}h^{-1})	θ	η%
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 (η%) 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 IIIn Concentrations

Inhibitor conc. (M)	Wt. loss (mg cm^{-2})	R (mg cm^{-2}h^{-1})	θ	η%
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 EImer Lambda-3B Ultraviolet-Visible spectrophotometer using DMF as a solvent.^{1}H and ^{13}C-NMR spectra were recorded in $(CD_3)_2SO$ 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°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.

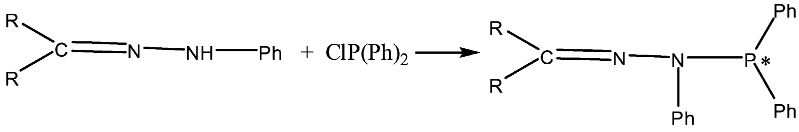
Measurement of the Dark Conductivity

The dark conductivity, which ranges from 10^{-16} to 10^{5}(ohm^{-1} 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 mm and thickness 1–2 mm, coated with silver paint (BDH) and checked several times for good contact.

Synthesis of Ligand III_{a-t}

The solid of hydrazone or semicabazone 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})



(III_{a-h})

Where;

III_a; R= R'= Ph

III_b; R= Me, R'= Ph

III_c; R= Me, R'= 3, 4-$(MeO)_2C_6H_3$

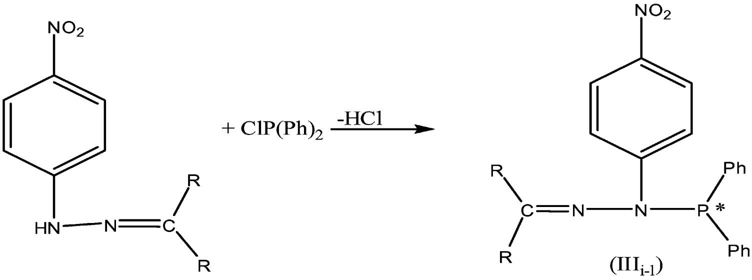
III_d; R= Me, R'= 4-PhC_6H_4

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

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

III_g; R= Me, R'= 4-$MeOC_6H_4$

III_h; R= Me, R'= 2-$MeOC_6H_4$



Where;

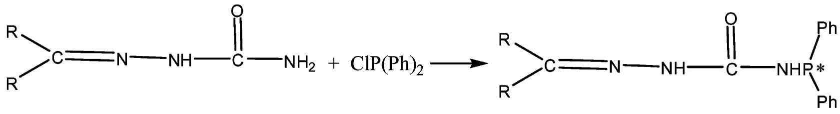
III_i; R=R'=Ph

III_j; R=H, R'=4-$MeOC_6H_4$

III_k; R= Me, R'=4-ClC_6H_4

III_l; R= Me, R'=4-PhC_6H_4

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



(III_{m-t})

III_m; R= H, R'= Ph

III_n; R= Me, R'= Ph

III_o; R= Me, R'= 4-$MeOC_6H_4$

III_p; R=Me, R'= 3, 4-$(MeO)_2C_6H_3$

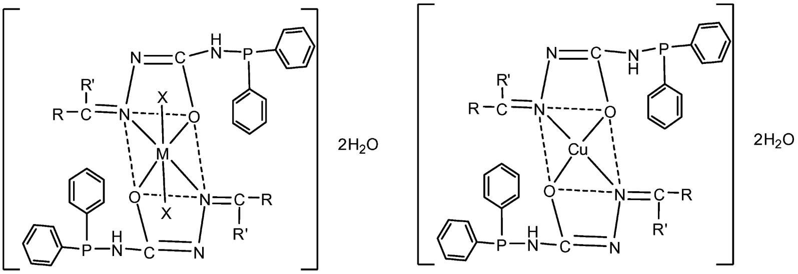
III_q; R= Ph, R'= 4-ClC_6H_4

III_r; R= Ph, R'= 2-ClC_6H_4

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-$MeOC_6H_4$(III_o) R=Me, R'= 3, 4-$(MeO)_2C_6H_3$ (III_p)

R= Ph, R'= 4-ClC_6H_4(III_q) R= Ph, R'= 2-ClC_6H_4 (III_r)

R= Ph, R'= 2-Pyridyl (III_s) R= Me, R'= 4-Pyridyl(III_t)

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.

REFERENCES

[1] J. S. Casas, M. S. G. Tasende, and J. Sordo, *Coord. Chem. Rev.*, **209,** 197 (2000).

[2] M. Belicchi, F. Bisceglie, G. Gasparri, G. Pelosi, P. Tarasconi, R. Albertini, and S. Pinelli, *J. Inorg. Biochem.*, **89,** 36 (2002).

[3] M. Maji, S. Ghosh, and S. K. Chattopadhyay, *Trans. Metal Chem.*, **23,** 81 (1998).

[4] G. M. Abu El Reash, M. A. Kattaab, and U. I. El-Ayaan, *Synth. React. Inorg. Met. Org. Chem.*, **22,** 1417 (1992).

[5] I. M. Abd-Ellah, B. A. El-Sayed, M. A. El-Nawawy, and A. M. A. Alajhaz, *Phosphorus, Sulfur, and Silicon*, **177,** 2895 (2002).

[6] A. D. P. Lever, *Inorganic Electronic Spectroscopy* (Elsevier, Amsterdam, 1963).

[7] I. Cohen, A. Ha, X. Zhao, M. Lee, T. Fischer, M. J. Strouse, and D. Kivelson, *J. Phys.Chem.*, **100,** 8518 (1996).

[8] G. Dyer and D. W. Meek, *J. Amer. Chem. Soc.*, **81,** 3983 (1967).

[9] F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, (Inter Science Publishers, New York, 1972.

[10] M. M. Patel and R. Manvalan, *J. Macromol. Sci. Chem.*, **19,** 951 (1973).

[11] A. S. Aswar, R. G. Mahale, P. R. Kakde, and S. G. Bhadange, *J. Indian Chem. Soc.*, **75,** 395 (1998).

[12] N. F. Mott, and E. A. Davis, *Electronic Processes in Non-Crystalline Materials* (Clarendon Press, Oxford, 1971).

[13] M. G. Abd El-Wahed, A. M. Hassan, H. A. Hammad, and M. M. El-Dessoky, *Bull. Korean Chem. Soc.*, **13,** 113(1992).

[14] D. A. Seanor, *Electrical Properties of Polymers* (Academic Press, New York, 1982).

[15] M. A. Migahed, *Prog. Org. Coat.*, **54,** 91 (2005).

[16] I. Sekin, T. Shimodo, M. Yuasa, and K. Takaoko, *Ind. Eng. Chem. Res.*, **29,** 1460 (1990).

[17] R. Voy, *Chem. Ztg. Chem. Apparatus*, **21,** 441(1897).

[18] M. A. Ahmed and F. A. Radwan, *J. Phys. Chem. Solids*, **49**, 1385 (1988).