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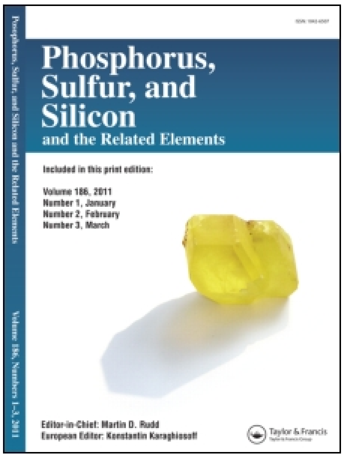

Phosphorus, Sulfur, and Silicon and the Related Elements

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Synthesis and Characterization of Some Novel Diphenyl Phosphate Hydrazones and Semicarbazones and Their Metal Complexes

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Synthesis and Characterization of Some Novel Diphenyl Phosphate Hydrazones and Semicarbazones and Their Metal Complexes

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A group of newly synthesized phosphorus compounds of hydrazone and semicarbazone derivatives IIIa-t have been prepared by reaction of hydrazones and semicarbazones with diphenylchlorophosphate. These compounds have been characterized by means of IR, UV, ^{1}H-NMR, mass spectroscopy and elemental analyses. Their complexation ability toward various divalent metal acetates Mn $(OAc)_2 \cdot 4H_2O$, Co $(OAc)_2 \cdot 4H_2O$, Ni $(OAc)_2 \cdot 4H_2O$, Cu $(OAc)_2 \cdot H_2O$, in organic solvents is described. Metal / phosphosemicarbazones ratios are measured and the results are discussed. The isolated complexes are insoluble in organic solvents and water. Their structures were proposed on the basis of microanalyical data, IR, (UV / VIS), mass spectroscopy and magnetic moments. The proposed structures of these complexes were found to be in ration of 1: 2 (M : L). The electronic spectral data and magnetic moment show that The manganese, cobalt, and nickel complexes are octahedral geometry, while the copper complex is square planner.

Keywords Diphenylphosphate; hydrazones; phosphors; semicarbazones

INTRODUCTION

The hydrazone derivatives and their metal ion complexes have been extensively investigated as a special Schiff base. Many biological and pharmaceutical activities of the hydrazone derivatives such as antitumor, scavenger effects on OH, and O_2^- radicals and inhibitory action for lipid peroxidation has been discovered.[1−3] Moreover, they have been the subject of extensive investigation due to their versatile chelating behavior for which they are widely used in analytical chemistry. Hydrazone derivatives have also, been used in spectroscopic determination of certain transition metals and as a selective metal extracting agent.

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Besides, some hydrazones have been applied as iron chelator drugs in the therapy of anemias and genetic disorders such as thalassemia.[4,5] Thiosemicarbazones and their metal complexes have also, been the subject of extensive studies because of their potential pharmaceutical properties and wide variation in their modes of binding and stereochemistry, whereas their semicarbazones received less attention. However semicarbazones are reported to possess versatile structural features[6] and very good antifungal and antibacterial properties.[7,8] Spectral studies of some semicarbazone complexes have been recently reported.[9,10] We planned the present work to investigate new routes for the synthesis of novel diphenylphosphate hydrazones and diphenylphosphate semicarbazone derivatives, as well as to prepare and investigate metal complexes of one of the semicarbazone derivatives.

EXPERIMENTAL

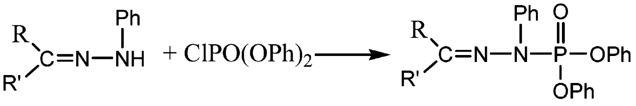
All melting points reported are uncorrected. Elemental analyses of C, H, and N were carried out at the Microanalytical Research Center, Faculty of Science, Cairo University. Phosphorus was determined gravimetrically as phosphoammonium molybdate using R. Voy method.[11] The mid-infrared and the ultraviolet measurements have been carried out at the chemistry Department, Faculty of Science, 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.^{1}HNMR spectra were recorded in $(CD_3)_2SO$ on a Varian Gemini 200 MHz or on a Varian Mercury 300MHz Em-360-60 MHz spectrometer at Cairo University and shifts were expressed in δ units using TMS as internal reference. Mass spectra were recorded on Hewlett-Packard (HP) 5988A (EI, 15eV). Magnetic measurements were recorded by the Gouy method at room temperature using a magnetic susceptibility balance (Johnson Matthey), Alfa product, Model No. (MK).

Synthesis of Ligand IIIa–t

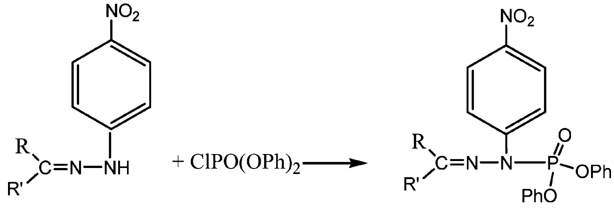
The solid hydrazone or semicarbazone derivatives (0.01 mole, 1.6–3.3 g) was added in small portions to a well stirred solution of (0.01 mol, 2.63–2.68 g) of diphenylchlorophosphate (II) in 100 ml acetonitrile within one-half h. After the complete addition, the reaction mixture was heated under reflux for 4 h with continuous stirring, HCl gas is evolved during the reaction. After the gas ceased to evolve—which means the completion of the reaction—the hot mixture was filtered. The filtrate was left to cool at room temperature. Then, the precipitate was formed, filtered, washed several times with acetonitrile, and diethylether and finally, dried under vacuo to give the corresponding ligands (IIIa-t) (Scheme 1).

(i) The proposed structure of hydrazone derivatives (IIIa-l)



(III a- h)

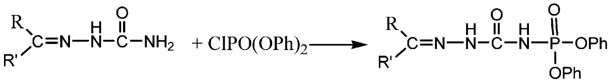
Where;
IIIa R= R′ = Ph
IIIb; R= Me, R′= Ph
IIIc; R= Me, R′= 3, 4-$(MeO)_2C_6H_3$
IIId; R= Me, R′= 4-PhC_6H_4
IIIe; R=Ph, R′=2-Pyridyl
IIIf; R= Me, R′= 4-Pyridyl
IIIg; R= Me, R′= 4-$MeOC_6H_4$
IIIh; R= Me, R′= 2-$MeOC_6H_4$



(III h- l)

Where;
IIIi; R = R′ = Ph
III j; R = H, R′ = 4-$MeOC_6H_4$
IIIk; R = Me, R′ = 4-ClC_6H_4
IIIl; R = Me, R′ = 4-PhC_6H_4

(ii) The proposed structure of semicarbazone derivatives (III m- t)



(III m- t)

Where;
IIIm; R = H, R′ = Ph
IIIn; R = Me, R′ = Ph

IIIo; R = Me, R′ = 4-$MeOC_6H_4$
IIIp; R = Me, R′ = 3,4-$(MeO)_2C_6H_3$
IIIq; R = Ph, R′ = 4-ClC_6H_4
IIIr; R = Ph, R′ = 2-ClC_6H_4
IIIs; R = Ph, R′ = 2-Pyridyl
IIIt; R = Me, R′ = 4-Pyridyl

SCHEME 1

Synthesis of the Solid Metal Complexes

A one mole (0.1 g) of manganese (II), cobalt (II), nickel (II), and copper (II) acetate dissolved in 50 ml absolute ethanol was added drop wise to two moles (0.33–0.41 g) of ADS (IIIn) 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 evaporated to give solid compounds, which recrystallized from ethanol and diethylether and dried under vacuo. The analytical data of both ligand and its metal complexes are listed in Tables I and II.

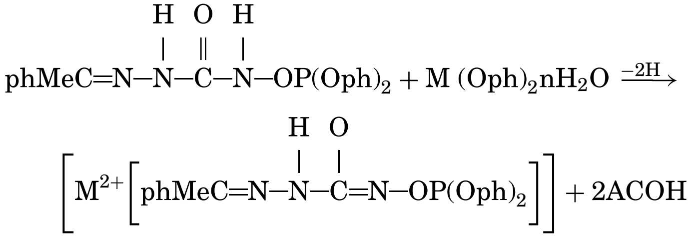
RESULTS AND DISCUSSION

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

$$\underset{\text{(1 mole)}}{RR'C{=}O} + \underset{\text{(1 mole)}}{NH_2GH} \rightarrow RR'C{=}NGH + H_2O \tag{1}$$

$$\underset{\text{(1 mole)}}{RR'C{=}NGH} + \underset{\text{(1 mole)}}{(PhO)_2POCl} \rightarrow RR'C{=}NGOP(OPh)_2 + HCl \tag{2}$$

where; G=Ph−N, $NO_2C_6H_4N$, or HNCONH



$$phMeC{=}N{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{\overset{|}{N}}{-}OP(Oph)_2 + M\,(Oph)_2nH_2O \xrightarrow{-2H} \left[M^{2+}\left[phMeC{=}N{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{|}{C}}{=}N{-}OP(Oph)_2\right]\right] + 2ACOH \tag{3}$$

The reactions are quite facile and could be completed within 4 to 12 h of refluxing in acetonitrile. The resulting products of complexes

TABLE I Characterization Data for Newly Synthesized Compounds (IIIa-t)

No.	Yield %	M.P. °C	Molecular formula (M.wt.)	Elemental analyses calculated (found)			
				%C	%H	%N	%P
IIIa	94	190	$C_{31}H_{25}N_2PO_3$ (504.51)	73.73 (72.93)	4.95 (4.95)	5.55 (5.54)	6.14 (6.14)
IIIb	97	182	$C_{26}H_{23}N_2PO_3$ (442.44)	70.52 (70.53)	5.29 (5.28)	6.32 (6.32)	7.00 (6.98)
IIIc	98	187	$C_{28}H_{27}N_2PO_5$ (502.49)	66.87 (66.52)	5.37 (5.36)	5.57 (5.56)	6.17 (6.17)
IIId	98	165	$C_{32}H_{27}N_2PO_3$ (518.54)	74.05 (74.01)	5.21 (5.21)	5.41 (5.40)	5.97 (5.96)
IIIe	99	172	$C_{30}H_{24}N_2PO_3$ (491.49)	73.24 (73.21)	4.88 (4.87)	5.69 (5.67)	6.31 (6.31)
IIIf	90	172	$C_{25}H_{22}N_2PO_3$ (429.42)	69.86 (69.82)	5.12 (5.12)	6.52 (6.51)	7.22 (7.21)
IIIg	92	150	$C_{27}H_{25}N_2PO_4$ (472.47)	68.57 (68.57)	5.29 (5.27)	5.92 (5.92)	6.56 (6.56)
IIIh	96	148	$C_{27}H_{25}N_2PO_4$ (472.47)	68.57 (68.56)	5.29 (5.28)	5.92 (5.91)	6.56 (6.55)
IIIi	98	175	$C_{31}H_{24}N_3PO_5$ (549.51)	67.69 (67.68)	4.36 (4.36)	7.64 (7.64)	5.64 (5.64)
IIIj	97	183	$C_{26}H_{22}N_3PO_5$ (478.44)	64.00 (63.89)	4.51 (4.50)	8.61 (8.60)	6.36 (6.38)
IIIk	98	175	$C_{26}H_{21}N_3PClO_5$ (504.51)	59.78 (59.72)	4.02 (4.01)	8.05 (8.04)	5.94 (5.92)
IIIl	99	179	$C_{32}H_{26}N_3PO_5$ (563.54)	68.14 (68.12)	4.61 (4.60)	7.45 (7.44)	5.50 (5.50)
IIIm	98	186	$C_{20}H_{18}N_3PO_4$ (395.35)	60.70 (60.68)	4.55 (4.45)	10.62(10.61)	7.84 (7.85)
IIIn	98	179	$C_{21}H_{20}N_3PO_4$ (409.37)	61.56 (61.52)	4.88 (4.87)	10.25 (10.24)	7.57 (7.57)
IIIo	97	180	$C_{22}H_{22}N_3PO_5$ (439.40)	60.08 (60.05)	5.00 (4.98)	9.56 (9.54)	7.05 (7.04)
IIIp	99	172	$C_{23}H_{23}N_3PO_5$ (453.45)	60.86 (60.84)	5.29 (5.28)	9.26 (9.25)	6.83 (6.83)
IIIq	99	188	$C_{26}H_{21}N_3PClO_4$ (505.88)	61.67 (61.64)	4.15 (4.15)	8.30 (8.30)	6.13 (6.12)
IIIr	97	197	$C_{26}H_{21}N_3PClO_4$ (505.88)	61.67 (61.67)	4.15 (4.13)	8.30 (8.28)	6.13 (6.11)
IIIs	96	176	$C_{25}H_{21}N_4PO_4$ (472.43)	33.02 (33.00)	2.54 (2.53)	11.85 (11.83)	6.56 (6.55)
IIIt	98	210	$C_{20}H_{19}N_4PO_4$ (410.36)	23.39 (23.38)	2.43 (2.42)	13.64 (13.63)	7.55 (7.54)

TABLE II Analytical Data of the Prepared Metal Complexes

Metal complex M. wt.	(Yield) M.P.°C	μ_{eff} (B.M.) (color)	Elemental analyses calculated (found) %C	%H	%N	%P	%M
[Mn $(L\text{-}H)_2 \cdot (H_2O)_2$] $3H_2O$	(83%)	5.21	52.45	5.03	8.70	6.44	5.72
961.804	268	(Yellow)	(52.93)	(4.95)	(7.72)	(5.82)	(5.16)
[Co $(L\text{-}H)_2$ $(H_2O)_2$] $2H_2O$	(98 %)	4.09	53.23	4.89	8.86	6.54	6.22
947.72	246	(Dark brown)	(53.68)	(5.00)	(8.82)	(5.80)	(5.96)
[Ni $(L\text{-}H)_2$ $(H_2O)_2$] $3H_2O$	(97 %)	3.04	52.25	5.01	8.70	6.42	6.08
965.506	268	(Green)	(51.72)	(5.04)	(8.80)	(5.81)	(6.52)
[Cu $(L\text{-}H)_2$] $4H_2O$	(98 %)	1.84	52.97	4.87	8.82	6.50	6.67
952.338	274	(Yellowish green)	(53.16)	(4.79)	(8.12)	(5.94)	(6.28)

Where L = ADS.

are 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 Equations (1, 2) but dimeric nature in Equation (3). The low molar conductance values (4–11 ohm^{-1} cm^2 mol^{-1}) of the prepared complexes in DMF at 10^{-3} M concentrations show them to be nonelectrolytes.

IR Spectra

The IR spectra of hydrazone and semicarbazone derivatives show bands at 1625–1640 cm^{-1} and 1290–1305 cm^{-1}attributed to ν (C=N) and ν (P=O) stretching, respectively.[12] ν (P—O—C), observed at 1190–1225, 1060–1120, 940–1028 cm^{-1}.[13] Two bands at 1695–1700 cm^{-1} and $\sim$ 3282 cm^{-1} appear in the IR spectra of semicarbazone derivatives assignable to ν C=O and ν NH. ^{1}H-nmr of all prepared compounds show peaks assigned to aliphatic and aromatic protons as well as peak at 8.2–8.8 ppm in case of semicarbazone attributed to NH proton. The structure of these hydrazone and semicarbazone derivatives are supported by elemental analysis (C, H, N, P) and confirmed by mass spectroscopy which show molecular ion peak concise with the calculated molecular weight.

To investigate the mode of coordination, the IR spectra of Acetophenone N4 diphenyl phosphate semicarbazone(ADS) as one of semicarbazone derivatives and its Mn(II), Co(II), Ni(II), and Cu(II) complexes are compared. Acetophenone N4 diphenyl phosphate 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 ADS 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 1700 cm^{-1} due to the carbonyl stretching of the semicarbazone moiety. This shows that ADS converts to enol form in solution and coordinate to the metals in an enolate form. ADS behaves as a bidentate ligand via azomethin nitrogen and oxygen atom in a deprotonated enolic form—forming five-membered ring. This structure is supported by disappearance of ν (C=O) band, as well as a new band appearing at ~540 cm^{-1} due to M—O bond.[14] The IR spectra of the metal complexes do not show a broad band at 3420 cm^{-1} for O—H stretching mode of the phenolic oxygen. Sharp band at 1634 cm^{-1} in the spectrum of ADS is shifted to lower wavenumber by 10–15 cm^{-1} in the spectra of the metal complexes support the coordination through azomethin 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 bands attributed to P=O and P—C—O remain unchanged. In addition to the band attributed to M—O, a new band appear at about 280 cm^{-1} assigned to M–N[15], Table III and IV.

TABLE III Spectral Data of the Newly Synthesized Compounds (IIIa-t)

	NMR		IR		MS	
Compound	^{1}H (ppm)	P=O (cm^{-1})	P—O—C (cm^{-1})	P—NH (cm^{-1})	Base peak (m/z)	M$^+$ -(m/z)
IIIa	7.5,8.2	1299	1223, 1106, 940	—	272	504.51
IIIb	7.2, 8.3	1290	1227, 1104, 942	—	—	—
IIIc	4.1, 7.4, 8.1	1299	1227, 1106, 1023	—	286	—
IIId	4.3, 7.8	1298	1199, 1106, 1021	—	179	518.54
IIIe	7.2, 8.3	1297	1203, 1108, 1020	—	179	491.49
IIIf	4.0, 7.3, 8.2	1299	1198, 1105, 1019	—	329	—
IIIg	4.8, 7.2, 7.4, 7.8	1298	1222, 1102, 1018	—	331	472.47
IIIh	4.7, 7.3, 7.5, 7.9	1302	1211, 1109, 1019	—	—	—
IIIi	7.3, 7.6	1302	1213, 1108, 1020	—	329	549.50
IIIj	4.8, 7.3, 8.9	1302	1218, 1106, 1013	—	289.5	487.44
IIIk	4.2, 7.5, 7.6	1305	1223, 1109, 1015	—	331	——
IIIl	4.2, 7.6, 7.9	1300	1227, 1104, 1020	—	163	563.54
IIIm	6.4, 7.2, 8.7	1302	1224, 1101, 1028	2611	—	—
IIIn	4.2, 7.5, 8.2	1306	1225, 1102, 1023	2617	177	409.37
IIIo	4.2, 4.8, 7.2, 8.6	1300	1207, 1105, 1021	2615	207	—
IIIp	4.2,4.7, 7.4, 8.8	1299	1230, 1108, 1019	2613	221	453.45
IIIq	7.6, 8.2	1302	1229, 1106, 1017	2619	273.5	—
IIIr	7.6,8.2	1299	1228, 1108, 1023	2615	—	—
IIIs	7.5, 8.4	1297	1226, 1109, 1028	2619	240	472.43
IIIt	4.2, 7.6, 8.3	1305	1228, 1106, 1020	2618	178	—

TABLE IV IR Spectral Data of the Metal Ion Complexes

Compound	C=N cm^{-1}	NH (cm^{-1})	P=O (cm^{-1})	P—NH (cm^{-1})	M—N (cm^{-1})	M—O (cm^{-1})
ADS	1635	3282	1290	2604	—	—
[Mn (L-H)$_2$. (H$_2$O)$_2$] 3H$_2$O	1620	3220	1290	2600	280	545
[Co (L-H)$_2$ (H$_2$O)$_2$] 2H$_2$O	1623	3215	1290	2605	285	542
[Ni (L-H)$_2$ (H$_2$O)$_2$] 3H$_2$O	1624	3220	1294	2604	283	540
[Cu (L-H)$_2$] 4H$_2$O	1620	3220	1292	2600	280	550

Electronic Spectra

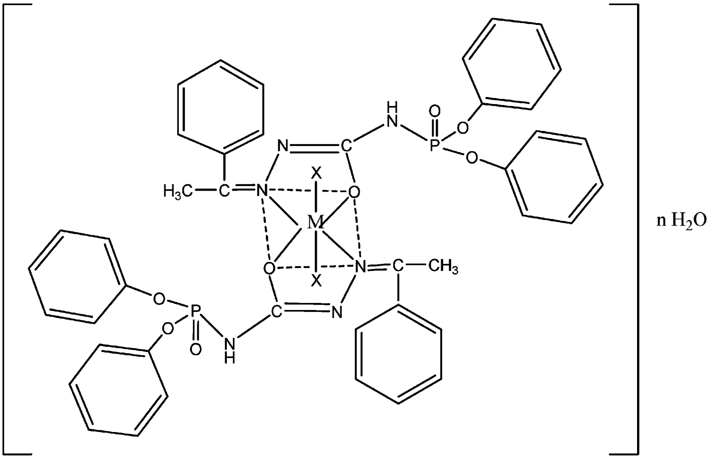
Electronic spectral data of phosphorous compounds IIIa-t, as well as the ligand ADS and its complexes are carried out in DMF and show bands at 37,700–30,000 cm^{-1} assigned to $\pi \rightarrow \pi^*$ electronic transitions within the benzene ring. These bands remain almost unchanged in the electronic spectra of the complexes. Another bands observed at ~27000 cm^{-1}, due to the n $\rightarrow \pi^*$ transitions of the azomethine (> CH=N) group. However, in the spectra of the complexes these bands are found to be abroad and explained as a combination of O → M and N → M LMCT transitions.

The electronic spectra and magnetic moment values for all complexes are consistent with the proposed structures. The electronic spectra of the manganese complex exhibit bands at 12,930 and 15,840 cm^{-1} which are assigned to the $^6A_1g \rightarrow {}^4T_1g$ (^4G) and $^6A_1g \rightarrow {}^4T_2g$ (^4G) transitions respectively, considering an octahedral symmetry.[16] In addition, the octahedral configuration is also supported by the measured magnetic moment of such complex, 5.21 B.M.

[Co(L-2H)$_2$ (H$_2$O)$_2$]2H$_2$O shows two bands at 14,300 and 21,800 cm^{-1}, may be assigned to ^4T_1g (F) $\rightarrow {}^4A_2g$ (F) and ^4T_1g (F) $\rightarrow {}^4T_1g$ (P) transitions, respectively; this is characteristic to an octahedral geometry around the cobalt (II) ion. [17] The magnetic moment 4.09 B.M. are typical of high-spin octahedral complex.

The magnetic moment 3.04 B.M. for [Ni (L-2H)$_2$ (H$_2$O)$_2$]3H$_2$O is in a good accordance with high-spin species, establishing the triplet ground state. Its spectrum gives two main bands at 15300 cm^{-1} and 24700 cm^{-1} assigned to ^3A_2g (F) $\rightarrow {}^3T_1g$ (F) and ^3A_2g (F) $\rightarrow {}^3T_1g$ (P) transitions respectively, consistent with the presence of octahedral geometry around the nickel (II) ion. [18,19]

The electronic spectrum of [Cu (L-H)$_2$] 4H$_2$O shows a broad band central at ca. 16,000 cm^{-1}, which may be ascribed to $^2B_1 \rightarrow {}^2A_1$ transition with two weak shoulders. These shoulders are attributed to $^2B_1 \rightarrow {}^2B_2$ and $^2B_1 \rightarrow {}^2E$ transitions respectively, suggesting a square



Where;

M	X	n
Mn	H_2O	3
Co	H_2O	2
Ni	H_2O	3
Cu	----	4

FIGURE 1 The structure of the prepared complexes.

planar geometry around the copper (II) ion.[20,21] This geometry is supported by the value of the magnetic moment, 1.84 B.M.[22] All these previous data, together with the elemental analyses C, H, N, P, and M%, proved the formation of complexes with molar ratio 2: 1 (ligand: metal) and support the proposed structures shown in the Figure 1.

CONCLUSION

In this study, we have prepared a group of newly synthesized phosphorus compounds of hydrazone and semicarbazone derivatives IIIa-t by reacting hydrazones and semicarbazones derivatives with diphenylchlorophosphate. These compounds have been characterized by means of IR, UV, ^{1}H-NMR, mass spectroscopy, and elemental analyses. The mode of binding to the metal has been investigated by reacting

ADS with Mn(II), Co(II), Ni(II), and Cu(II) to form metal complexes. ADS behaves as a bidintate ligand and converts to enol form in solution and coordinate to the metal in enolate form. The manganese, cobalt, and nickel complexes are found to be octahedral while the copper complex is square planner.

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