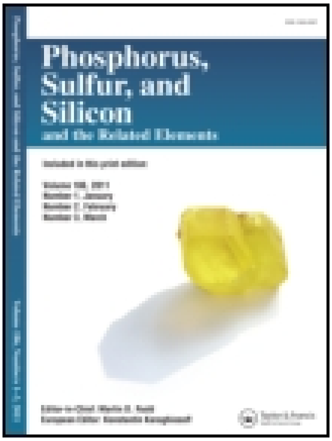

Phosphorus, Sulfur, and Silicon and the Related Elements

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Physicochemical Studies on Some Metal Chelates of Cyclodiphosphazane and Thiourea Monophosphazene Derivatives

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Physicochemical Studies on Some Metal Chelates of Cyclodiphosphazane and Thiourea Monophosphazene Derivatives

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The interaction of Cr(III), Mn(II), and Fe(III) ions with cyclodiphosphazane and thiourea monophosphazene derivatives was followed potentiometrically with the aim of determination of stability constants of (metal : ligand) 1:1 and 1:2 binary, and 1:1:1 ternary chelates at 25°C and $\mu = 0.1$ mole dm^{-3} $NaNO_3$ in 10% (v/v) H_2O-EtOH mixture. The stability of the complexes of both ligands was found to be Fe (III) > Mn(II) < Cr(III). The concentration distribution of the species formed in solution was evaluated. Binary and ternary solid complexes were prepared with the purpose of structural characterization using elemental analyses, molar conductance, IR, ^{1}HNMR and electronic spectra and thermogravimetric analysis. The data show that the ligands behave as neutral bidentate ligands, forming neutral chelates of monomeric nature.

Keywords Cyclodiphosphazane; metal chelates; potentiometry; thioureamonophosphazene

INTRODUCTION

Phosphorus-containing compounds are widely used in phosphate laser glasses, binders and coatings in refractory ceramics, in the intermediate products of the chemical industrial synthesis, in agricultural fertilizers, also, phosphoric acid and phosphate salts can be used to retard corrosion of metals.[1–5] The ester compounds of phosphoric acid play a central role in cellular metabolism.

The literature survey reveals that this class of compounds had considerable attention during the last decade, due to their remarkable

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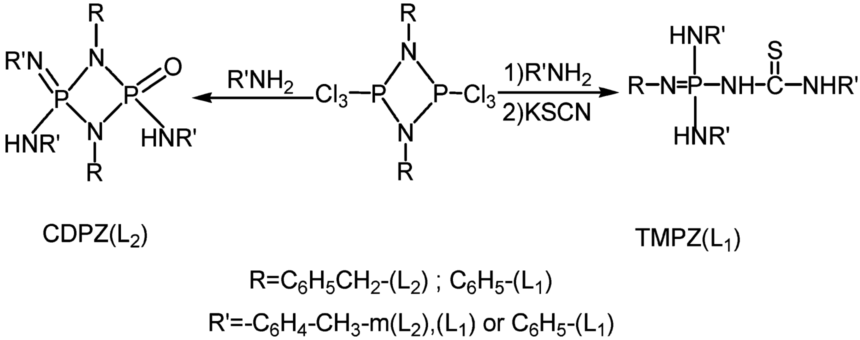
catalytic, medical, polymers, and semiconductor applications[6]. The great use of the compounds is due to the different chemical behavior of N- and P-sites[7–11]. Nitrogen as a hard donor, is capable of stabilizing metals in high oxidation states; the chelate effect may allow unusual coordination numbers and geometries. Phosphorus and sulfur as soft bases are best suited to stabilize metals in low to medium oxidation states. Thus, in view of increasing interest and in continuation of our work on the structure of metal chelates of these compounds,[12,13] we report, herein, the interactions of linear thiourea monophosphazene (TMPZ, L_1) and cyclodiphosphazane (CDPZ, L_2) derivatives (seen below), with Cr(III), Mn(II), and Fe(III) both in solution and in solid phase.

Our goal for this article is to throw more light on the effect of stereochemistry of the ligands on their coordination behavior. Our study involves the determination of stability constants of the chelates formed in solution using pH-metric technique (Scheme 1).



SCHEME 1

EXPERIMENTAL

All chemicals used were of A.R. grade and used without further purification. Thioureamonophosphazene (TMPZ = L_1) and cyclodiphosphazane (CDPZ = L_2), were prepared according to the published procedures,[14,15] and their structures were confirmed with IR and elemental analysis which were carried out at the Microanalytical Center in Cairo University.

Stock solutions of the ligands were prepared by dissolving the requisite amounts in 10% (v/v) H_2O-EtOH. The stock solutions of chloride salts of Cr(III), Mn(II), and Fe(III) ions were prepared in doubly distilled water and standardized as given by West[16]. Carbonate-free solution of NaOH (0.1 mol·dm^{-3}) was prepared and standardized against

potassium hydrogen phthalate solution. 1.0 mol·dm^{-3} $NaNO_3$ stock solution was prepared immediately prior to use.
pH-metric titrations were carried out at 25°C ± 0.1°C in a doubly walled glass cell and the temperature was maintained constant by a thermostat. The pH values were determined using a MV-89 digital pH-meter with an accuracy of ±0.005 units. The pH mode was calibrated before and after each titration using standard buffers at pH 4.0 and 7.0. The following mixtures were titrated against CO_2-free 5×10^{-2} mol·dm^{-3} NaOH: HNO_3 1×10^{-2} mol·dm^{-3}(a), a + (L_1) or/and (L_2) 5×10^{-3} mol·dm^{-3} (b), b + metal ion 1×10^{-3} mol·dm^{-3}(c). The total volume was adjusted to 50 cm^3 by adding double–distilled H_2O in each titration and the ionic strength was adjusted to 0.1 mol·dm^{-3} using $NaNO_3$. A magnetic stirrer was performed during all titrations and oxygen-free nitrogen gas was bubbled through the solution before and during the titrations. Multiple titrations were carried out for each system. The pH-meter readings in 10% (v/v) EtOH-H_2O were converted to [H^+] according to the relation of Van Uitert and Hass.[17]

Binary and ternary solid complexes were prepared by mixing, with heating, the requisite amounts, 0.1 mmol (1.96, 2.66, 2.69 g for $MnCl_2.4H_2O$, $CrCl_3.6H_2O$, and $FeCl_3.6H_2O$, respectively) of aqueous metal salts with the appropriate amounts of the ligands (4.99 and 6.05 g for L_1 and L_2, respectively, duplicating the amount of L_1 to prepare the 1:2 Fe^{3+} binary chelate) in ethanol, refluxing for about 5 h. After leaving overnight the complexes were then filtered and dried in vacuo over P_4O_{10}. The solid complexes are soluble in polar organic solvents and in alcohols. The electronic spectra were performed using Shimadzu UV-160-Visible Recording Spectrophotometer using 1 cm width quartz cell. Molar conductance values of ethanol solutions of the synthesized complexes were measured at 25°C using a model 31 YSI conductivity bridge with a conductivity cell constant = 0.10 m^{-1}. The other methods of study were carried out in the Micro analytical Center in Cairo University.

Results and Discussion

It is worth mentioning that the ligands studied do not undergo hydrolysis under the experimental conditions as indicated from the rapid attainment of equilibrium and no change in pH during the time of titration, ruling out any hydrolysis and thus the formation of hydroxo species under the experimental conditions. Figure 1(a) shows representative sets of experimental titration curves obtained according to the sequence described in the experimental section for the different systems studied.

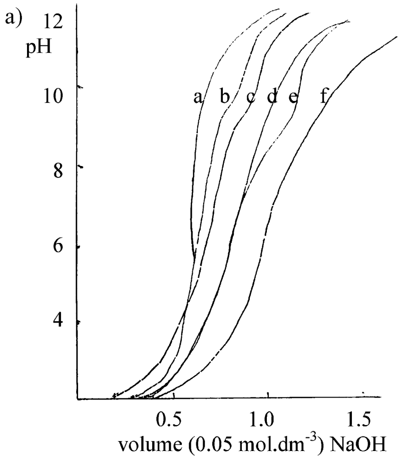


FIGURE 1 Titration curves of: (a) 0.01 mol·dm^{-3} HNO_3, (b) soln. (a) + 0.05 mol·dm^{-3} ligand (L_1); (c) mixture (b) + 0.001 mol·dm^{-3} Cr(III); (d) soln. (a) +0.05 mol·dm^{-3} ligand (L_2); (e) mix. (d) + 0.001 mol·dm^{-3} Cr(III); (f) mixture (e) + 0.05 mol·dm^{-3} ligand (L_1); t = 25°C, $\mu = 0.1$ mol·dm^{-3} $NaNO_3$.

The titration curves of the free ligands Figure 1(b) exhibit three (L_1) or two (L_2) inflections at a ([OH$^-$]/[L]) value of 1, 2, and 3 respectively. The presence of an inflection at a ratio equals 1, which represents the protonation steps of the ligands. The cationic forms are dominant at pH 3.5–6.3, the mono- and bi- anionic forms are dominant species at pH

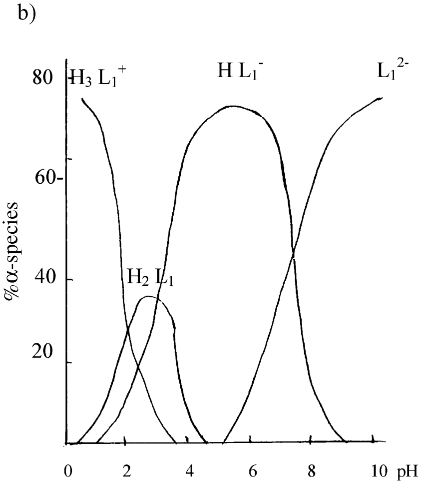


FIGURE 2 pH-species distribution profile for L_1 species.

TABLE I pk Values of Thiourea Monophsphazene (L_1) and Cyclodiphosphazan (L_2)

Ligand	Pk_1	Pk_2	Pk_3
Thiourea monophosphazene (L_1)	3.61 (3.50)*	4.95 (5.00)	9.15 (9.15)
Cyclodiphosphazane (L_2)	4.95 (4.80)	8.93 (8.90)	—

*ref. (20).

6.3–8.5. These equilibria can be represented as follows:

$$H_3(TMPZ)^+ \rightleftharpoons H_2TMPZ + H^+ \rightleftharpoons HTMPZ^- + H^+ \rightleftharpoons TMPZ^{2-} + H^+ \quad (1)$$

The values of $\bar{n}_A$ (average number of protons attached per ligand) has been determined making use of Irving and Rossotti[18,19] method using curves of Figure 1(a) and (b). The proton-ligand dissociation constants (pK's) were calculated from the $\bar{n}_A$- pH graphs, where the pK is the pH value corresponding to $\bar{n}_A = 0.5$, 1.5, and 2.5. The obtained pK values are given in Table (1). These pK values are closely in line with those obtained spectrophotometrically.[20]

On the addition of the metal ions to the solution of the free ligand, it is observed that the curve of Figure 1(c) is well separated from curve (b). This is an indication of the liberation of protons during complex-formation, and thus the complex [curve (c)] is located under curve (b), i.e., at lower pH values. The titration curves were used to construct the formation curves as a relation between $\bar{n}$ (average number of ligand molecules attached per metal ion) and pL (free ligand exponent). From these curves, the values of the stability constants were determined and listed in Table II. The titration curves of complexes show inflections at a = 2 in case of Fe(III) complexes, and inflections at a = 1 and 2 for the

TABLE II Stability Constants for Binary Systems in 10% EtOH/H_2O, at 25°C

Complex	Ratio	Log K
Cr^{3+}-L_1	1:1	4.25
	1:2	4.13
Mn^{2+}-L_1	1:1	4.23
	1:2	4.10
Fe^{3+}-L_1	1:2	4.27
Cr^{3+}-L_2	1:1	4.15
	1:2	4.08
Mn^{2+}-L_2	1:1	4.14
	1:2	4.00
Fe^{3+}-L_2	1:1	4.17
	1:2	4.10

Cr(III) and Mn(II) complexes (a = number of moles of base added per mole of metal ion). This indicates that the complexation between the ligand (L) and the metal ion lead to the formation of 1:1 and 1:2 (M:L) complex species for Cr(III) and Mn(II), while only 1:2 can be detected for Fe(III).

As shown in Figure 1(a), the M-CDPZ systems behave similarly to M-TMPZ, except that the L_2-metal complex [curve (d)] is lower in position compared to that of L_1 confirming that the stability of L_2-metal complexes is less than that of L_1(see Table II). Accordingly, we can suggest that the difference in stability of the two types of complexes may be explained in the light of the following: 1) thiourea monophosphazene (L_1) forms chelates of six-member ring, which is more stable than the five-member (open structure) chelates formed by cyclodiphosphazane (L_2); 2) complexes of L_2 contain the four-member cyclodiphosphazane ring which may cause steric hindrance that result in decreasing the stability of the formed complexes; and 3) L_2 has backbone rigidity imposed by the ring system, which is most likely an origin of its weak donor ability.

As can be seen from Table II, the stability constants of the binary complexes decrease generally in the order Fe(III) > Cr(III) > Mn(II), which is in agreement with Irving and Williams order.[21]

From the titration curves of ternary systems studied (Figure 1), one can observe that the ternary system curves (f) are well separated from binary system curves [(c), (e)] at pH > 3.5 for Cr(III)-L_1 binary and at pH > 6 for Cr(III)-L_1–L_2ternary systems. This behavior reveals that in these pH ranges, coordination of secondary ligand with Cr(III) starts. The overall formation constants ($K^{M}_{ML_1L_2}$) of ternary complexes can be calculated considering that complexation takes place in simultaneous manner (Eq. 2) or stepwise manner (Eq. 3) according to the following equilibria:

$$M + L_1 + L_2 \xrightleftharpoons{K^{M}_{ML_1L_2}} ML_1L_2 \tag{2}$$

$$M + L_1 \xrightleftharpoons{K^{M}_{ML_1}} ML_1$$

$$M L_1 + L_2 \xrightleftharpoons{K^{ML_1}_{ML_1L_2}} ML_1L_2 \tag{3}$$

Practically, the binary complex, ML is considered to be completely formed in the lower buffer region followed by the addition of the second ligand in the upper buffer region according to equilibrium (Eq. 2).

Thus, the overall stability constant $\beta^{M}_{ML_1L_2}$ may be represented by the following equation:

$$\beta^{M}_{ML_1L_2} = \frac{[ML_1L_2]}{[M][L_1][L_2]} = K^{ML_1}_{ML_1L_2} - K^{M}_{ML_1} \tag{4}$$

The horizontal distance between curves (c) and (f) (Figure 1a) can be used to calculate $\acute{n}_{mix}$ (average number of secondary ligand molecules associated with one $[ML_1]$ ion). From the values of $\acute{n}_{mix}$, the secondary ligand exponent, pL_{mix}, the formation constants $\log K^{ML_1}_{ML_1L_2}$ are obtained from the $\acute{n}_{mix} - pL_{mix}$ plots, and the average values are reported in Table III. The obtained data are treated using least square method[22], the standard deviations are found in the range of 0.2–0.08. The consistency of the resulting parameters and estimated errors associated with measurements are tested as previously reported.[23]

The relative stability of ternary metal complex (ML_1L_2) as compared to that of the corresponding binary complex (ML_1), has been quantitatively expressed in terms of the parameter Δ log K, the difference between the stabilities of binary and ternary chelates, as calculated according to Equation (5):

$$\Delta \log K = \log K^{ML_1}_{ML_1L_2} - \log K^{M}_{ML_2} \tag{5}$$

Δlog K values (Table III) were found to be slightly positive in accordance with statistical consideration.[24] These values suggest that the extent of stabilization due to metal to ligand d_π - p_π back bonding causes metal ion to be more positive (more electronegative).[25] This permits stronger interaction with the secondary ligand, hence there is no effect for the steric and electrostatic factors, which result in lowering the stability of ternary complexes as compared with binary complexes. However, in these ternary systems the magnitude of Δlog K values are not very large, indicating that ternary complexes may exist in both stacked and open forms in equilibrium with each other in solution.

TABLE III Stability Constants and Δlog K Values for 1:1:1 Ternary Complexes in 10% EtOH/H_2 O at 25°C

Complex of	Log $K^{M}_{ML_1}$	Log $K^{ML_1}_{ML_1L_2}$	Δ log K
Cr^{3+}-L_1	4.25	6.16	1.91
Cr^{3+} - L_2	4.15		2.01
Mn^{2+}-L_1	4.23	5.83	1.6
Mn^{2+} - L_2	4.14		1.69
Fe^{3+}-L_1	—	6.46	—
Fe^{3+} - L_2	4.17		2.29

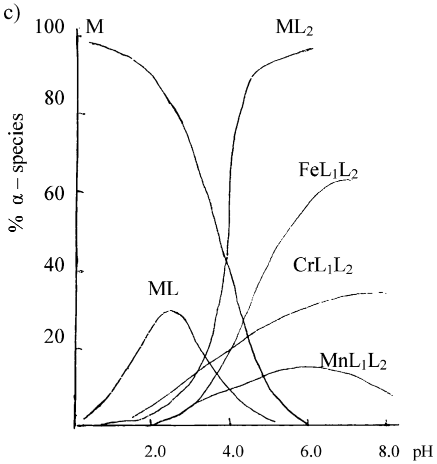


FIGURE 3 pH-species distribution profile for the Binary and ternary M:L_1:L_2 systems.

Analysis of the species distribution plot of the free ligands (Figure 2), clearly indicate that at pH $<$ 2 the ligand molecules become fully protonated [$\alpha(H_3O^+)$ ≈78%]. At pH 2–3, both the protonated and neutral forms coexist in equilibrium. The percentage of deprotonated species HL^- reaches to its maximum at pH ∼ 5. On further increase in the pH values the HL^- species decrease and L^{2-} species increase at the same time. At higher pH, the L^{2-} species predominate, and the HL^- species have a very small extent.

A comparison of the species distribution curves for binary and ternary systems is shown in Figure 3 for Cr(III)- H_2TMPZ and Cr(III)-CDPZ complexes (as representatives). Similar trends were obtained for the other systems. The distribution profiles for these complexes show that at lower pH values $<$ 1.5, almost all Cr(III) ions are present as free ions (98%). In the pH range 2–4.5, the predominant change is the conversion of Cr(III) into Cr(III)- H_2TMPZ complex with a maximum degree of formation (30%). At a pH ∼ 2.5–4.0 the Cr(III) has completely disappeared and Cr(III)- $(L_1)_2$ is present to an extent of (98%). As shown in Figure 1(c), the distribution curves of Cr(III)-L_1-L_2 ternary systems at pH $>$ 8 are greatly different than those of binary system. The values of maximum concentrations for 1:1:1 species were 62.5%, 34%, and 15% for Fe(III), Cr(III), and Mn(II), respectively. At this range, the concentration values of binary systems are of lower values.

The analytical data of the isolated solid complexes (Table IV), show that the ligands act as neutral bidentate which form monomer chelates of stoichiometric ratios 1:1, 1:2 binary, and 1:1:1 ternary complexes.

TABLE IV Elemental Analysis, Color and Molar Conductivity Values (in mhos·Cm^2/mole), of Binary and Ternary Solid Complexes

	% Found (calculated)						
Complex	C	H	N	S	M.wt.	Color	Λ
L_1–Complexes (binary)							
$[Cr(C_{28}H_{30}N_5PS)Cl_3(H_2O)]$	50,02	4.48	10.46	4.78	676.10	Blue	5.42
Cr-L_1(1:1)	(49.75)	(4.77)	(10.36)	(4.70)			
$[Mn(C_{28}H_{30}N_5PS)Cl_2].2H_2O$	51.13	4.83	10.92	5.01	661.50	Black	4.57
Mn-L_1 (1:1)	(50.84)	(5.18)	(10.58)	(4.84)			
$[Fe(C_{28}H_{30}N_5PS)_2Cl_2]Cl..H_2\,O$	57.85	2.17	12.17	5.50	1179.5	Yellow	72.0
Fe-L_1 (1:2)	(57.03)	(2.73)	(11.87)	(5.42)			
L_2—Complexes (binary)							
$[Cr(C_{35}H_{37}N_5P_2O)Cl_3(H_2O)]$	54.19	5.16	9.19	—	782.16	Black	5.40
Cr-L_2 (1:1)	(53.80)	(5.02)	(8.95)				
$[Mn(C_{35}H_{37}N_5P_2O)Cl_2].2H_2O$	55.29	5.17	9.23	—	767.60	Black	4.37
Mn-L_2 (1:1)	(54.80)	(5.38)	(9.12)				
$[Fe(C_{35}H_{37}N_5P_2O)Cl_3(H_2O)]$	53.90	5.13	9.15	—	786.01	Black	6.53
Fe-L_2 (1:1)	(53.48)	(5.00)	(8.91)				
L_1, L_2—Complexes (ternary)							
$[CrL_1L_2Cl_2]Cl$	60.47	5.53	11.47	2.62	1263.7	Greenish blue	68.4
	(59.88)	(5.34)	(11.08)	(2.53)			
$[Mn\,L_1L_2Cl_2]$	62.03	5.77	11.61	2.65	1231.2	Fair brown	4.56
	(61.46)	(5.49)	(11.38)	(2.60)			
$[Fe\,L_1L_2Cl_2]Cl.H_2O$	58.96	5.67	11.11	2.53	1285.6	Black	64.5
	(58.86)	(5.41)	(10.90)	(2.49)			

The solubility of these complexes in common polar solvents makes one excludes any dimeric or extended polymeric structures.

The molar conductivity values in DMF solution (1×10^{-3} mol·dm^{-3}) are in the range of 4.37 – 6.53 ohm^{-1}·cm^2·mol^{-1}, for binary (1:1) and ternary Mn(II) complexes, revealing that they are non electrolytes. While in case of ternary Cr(III) and Fe(III), as well as binary Fe(III) – L_1 (1:2) complexes they are of higher values (64.5–72.0 ohm^{-1}·cm^2·mol^{-1}), which means the formation of 1:1 electrolytes. The small values reveal the non- ionic neutral nature, whereas the higher molar conductivity values may be due to partial displacement of chloro groups by DMF in coordination sphere of the complex.[26]

IR spectra of binary and ternary complexes are recorded in Tables V–VII and compared with those of the free ligands. The tables show strong, mostly broad, bands in the region 3460–2922 cm^{-1}, indicating the combination of υOH stretching vibration (due to water coordinated or hydrated in the complex molecules) and υNH present in the ligands.

The IR spectra also exhibited a doublet band at 730–782 cm^{-1} assigned to the cyclic υP-N mode of vibration. The other frequency located

TABLE V The Most Important Infrared Bands (cm^{-1}) of Ligand L_1 and Its Binary Complexes

L_1	Fe(III)	Mn(II)	Cr(III)	Assignment of IR bands
	3421 br	3419 br	3450 br	v(OH) of coordinated H_2O
3177, 3022 s	3187, 3065 m	3176, 3021 s	3179, 3023 m	v(NH) stretching
1691s,1602w	1691s, 1608 m	1691s, 1604 m	1691 s, 1606 m	δ(NH) deformation
1493s,1455m	1493, 1451 m	1492, 1455 m	1494, 1455, 1423 m	v(C=S)
1162 m	1165 m	1166 m	1162 m	
1262 s	1265 m	1266s	1263s	v(P=N)
	764 m	763 m	763 m	v of rocking mode of coordinated H_2O
	516 m,465 m	513 m, 478 m	510 m, 467 m	v(M—N)
	250 m	287 m	285 m	v(M—Cl) or$v$(M—S)

TABLE VI The Most Important Infrared Bands (cm^{-1}) of Ligand L_2 and Its Binary Complexes

L_2	Fe(III)	Mn(II)	Cr(III)	Assignment
	3419 br	3397 s	3393 br	v(OH)
2922 s	2962, 2927 w	2980,2922 s	2923 s	v(NH)
2586 s	—	2583 s	2588 s	exocyclic
2362 m	2362 m	2363 m	2363 m	v(P-NH)
1543 s	1647, 1513 s	1578, 1492 s	1543, 1492 s	δ(NH)
1181 s	1179 s	1132 s	1177,1102 s	v(P=O)
1261 s	1262 s	1277 s	1277 s	v(P=N)
730 m	782 m	777 m	768 m	cyclic v(P—N)
	545 m, 450 m	521 m, 432 m	578 m, 454 m	v(M—N) or v(M—O)
	307 m	305 m	310 m	v(M—Cl)

TABLE VII THe Most Important Infrared Bands (cm^{-1}) of the Ternary Complexes

Fe(III)	Mn(II)	Cr(III)	Assignments
3419 s	3420 br	3460 br	v(OH) or$v$(NH)
3187, 3022 m	3176-3023 m	3179, 3020 m	
1661 s	1691s	1692 s	δ(NH)
1605 s	1603 s	1607 s	
1450 m	1455 m	1455 m	v(C=S)
1261 m	1238 m	1240 m	v(P=N)
1173 s	1175 s	1176 s	v(P=O)
755 m	782 m	768 m	v(P—NH)
508 m, 475 m	513 m, 470 m	510 m, 470 m	v(M—O) or$v$(M—N)
290 w	288 w	289 w	v(M—S) or v(M—Cl)

at 1238–1277 cm^{-1} region is attributed to exocyclic υP=N stretching. The band observed at 2588–2362 cm^{-1} is characteristic of exocyclic υP-NH ,and that at 1181–1102 cm^{-1} is due to υP=O mode of CPDZ ligand. The new bands observed in the IR spectra of the complexes at 432–578 cm^{-1} region can be tentatively assigned to υM-L originated from υM-O, coupling with υM-N.[27] The band that is assigned to δN-H, and appearing at about 1492–1692 cm^{-1} is unusually broad in the complexes compared to that of the free ligand. The spectra of the complexes also show a band in the 250–310 cm^{-1} range that can be assigned to the trans-coordinated chloride atom (M-Cl). In TMPZ complexes, the υC=S band, located at 1494–1423 cm^{-1} is slightly positively shifted. This is an indication of the involvement of the S-atom in coordination. The M-S stretching vibrations are expected to be found in the region 290–250 cm^{-1}. The appearance of this band in the present study confirms coordination through the sulfur atom of TMPZ ligand.[28–30]

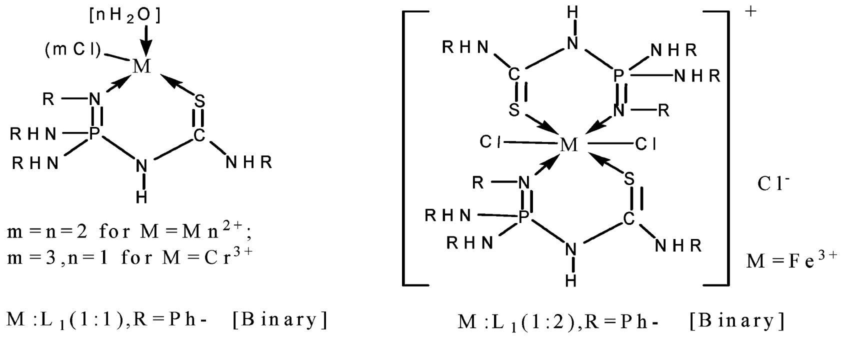
The ^1H NMR spectral data agree well with the IR results in that, the NH signals (four for L_1 and two for L_2) occur as high field signals located at 5.2 and 4.8 ppm. The coordinated H_2O molecules associated to all binary complexes are evidenced by signals at about 4.0 ppm.[31]

Thermogravimetric analyses of the prepared binary and ternary complexes have been carried out to confirm the suggested molecular formulae of the prepared complexes. The obtained data reveal that the binary Fe-L_1(1:2) and ternary Fe-L_1-L_2 show weight losses in the temperature range 110–120°C due to loss of a molecule of hydrated H_2O from each type. The percentages of weight losses are 1.51 and 1.45%, and the calculated values are 1.56 and 1.49%, respectively. Also, binary Mn(II) complexes lose two hydrated water of crystallization.

The TG thermograms show also degradation for some chelates occurring at about 165–215°C with percentage weight losses equivalent to two or one coordinated water molecules. Binary complexes of Cr(III) with both ligands and Fe(III)-L_2, have one coordinated H_2O. At higher temperatures ($> 300°C$), all binary and ternary complexes display rapid and successive weight loss steps revealing their decomposition yielding the corresponding metal oxides or pyrophosphates.

The reflectance electronic spectra of the absorption bands recorded in ethanolic solutions for solid binary complexes display an absorption band at 320 nm (for M-L_1) and at 276 nm (for M-L_2). These bands are assigned to the intramolecular charge transfer (CT) transition from the ligand to the unfilled orbital localized on the metal ion (L →M). The bands are broad and ascribed to combination of some transitions, namely, $^4A_2 \rightarrow {}^4T_2$, $^4A_2 \rightarrow {}^4T_1(F)$, $^4A_2 \rightarrow {}^4T_1(P)$ for Cr^{3+} chelates, and $^4T_1 \rightarrow {}^4E_1$, $^4A_1$,$^4T_1 \rightarrow {}^4T_2$ for Fe^{3+} and Mn^{2+} chelates. These transitions indicate octahedral stereochemistry for all complexes except those binary complexes of manganese which attain the tetrahedral structure. This result is evidenced from the colors and the absorptivity values, which are deeper and greater, respectively for binary (tetrahedral) and the reverse for ternary (octahedral). It is worth mentioning that binary Fe-L_2 and ternary Fe-L_1-L_2 complexes show a small splitting in their electronic spectra appearing at 340 nm and indicating the occurrence of some distortion in t_{2g} orbitals due to Jahn Teller effect.[32]

Generally, the data of microanalyses, conductivity measurements, ^{1}H NMR, IR, and reflectance spectra and TGA analysis, reveal that the neutral ligand is coordinated to the metal ion as bidentate P=N and P=O or C=S forming neutral monomeric metal chelates as represented by Scheme 2.

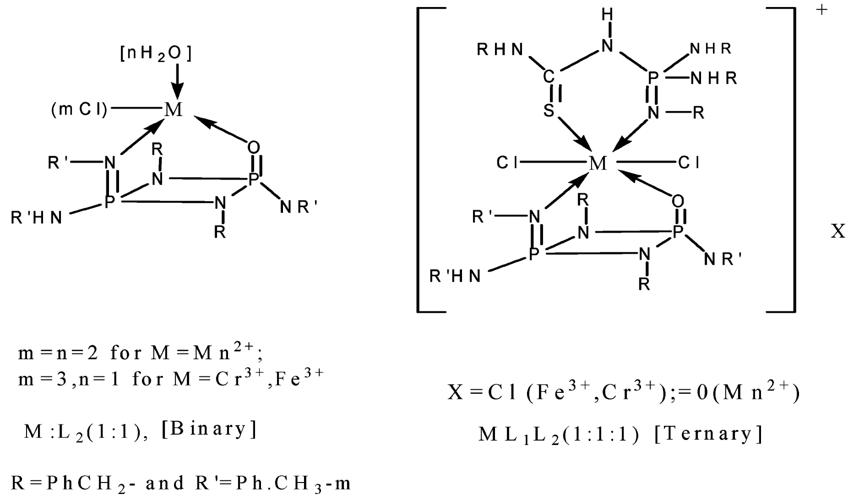


m = n = 2 for M = Mn^{2+};
m = 3, n = 1 for M = Cr^{3+}

M : L_1(1:1), R = Ph- [Binary]

M = Fe^{3+}

M : L_1(1:2), R = Ph- [Binary]



m = n = 2 for M = Mn^{2+};
m = 3, n = 1 for M = Cr^{3+}, Fe^{3+}

M : L_2(1:1), [Binary]

X = Cl (Fe^{3+}, Cr^{3+}); = 0 (Mn^{2+})

M L_1L_2(1:1:1) [Ternary]

R = PhCH_2- and R' = Ph.CH_3-m

SCHEME 2

The structures of the complexes are suggested depending on the following facts:

1) in agreement with a previous work,[12,13] these ligands can be coordinated with transition metal ions via other atoms than phosphorus atom;
2) the nitrogen atom of the P—N are stronger bases compared to that of P-NH, due to the hyper conjugation between nitrogen lone pair and adjacent P—N σ^* orbitals; and
3) the proposed structure has less steric hindrance, thus the less sterically hindered substituents allow easier complexation and leading to its higher stability constant.

Conclusion

Stability and structural characterization of some metal complexes of bidentate phosphorus ligands possessing varying steric and environments have been determined. From the previous discussion, it is concluded that the ligands bond to metal ions through the imino nitrogen atom of P=N and oxygen atom of P=O (CDPZ) or sulfur atom of C=S (TMPZ).

The stereochemistry of the ligand appears to play a significant role in determination of its coordination sites. In addition, steric hinderance and greater π-accepting nature of the phosphorus centers governs the stability of the formed chelates. The increasing stability constants of the ternary complexes can be attributed to the intramolecular stacking interaction.[33] Thus, the cyclodiphosphazane (L_2) is rigid and is also a good π-acceptor molecule, while the ring system of thiomonophosphazene (L_1) is attached to side chain. When L_1 and L_2 coordinate to the same metal ion, the L_1 reaches easily to the rigid L_2 molecule producing intramolecular aromatic ring stacking.[34]

REFERENCES

[1] B. Morosin and G. A. Samara, *Ferroelectrics*, **3,** 49 (1971).
[2] H. Grimm, H. Stiller, and Th. Plesser, *Phys. Status Solidi*, **42,** 207 (1970).
[3] R. G. Aziev, S. I. Volfkovich, G. A. Dudkina, and T. K. Mikhaleva, *Zh. Fiz. Khim.*, **46,** 188 (1972).
[4] F. Ackermann, H. Lefebvre-Brion, and A. L. Roche, *Can. J. Phys.*, **50,** 692 (1972).
[5] (a) A. G. Kloeckner-Humboldt-Deutz and Multi-Minerals Ltd., German Patent, 1, 301, 998 (1969); (b) L. W. Cochran, German Patent, 1, 285, 466 (1968).
[6] M. Witt and H. W. Roesky, *Chem. Rev.*, **94,** 1163 (1994).
[7] M. S. Balakrishna, V. S. Reddy, S. S. Krishnamuthy, J. F. Nixon and J. C. T. R. Burckett St. Laurent, *Coord. Chem. Rev.*, **129,** 1 (1994).

[8] K. Raghuraman, S. S. Krishnamuthy, and M. Nethaji, *J. Organomet. Chem.*, **669,** 79 (2003).

[9] R. P. K. Babu, K. Aparna, S. S. Krishnamuthy, and M. Nethaji, *Phosphorus, Sulfur, Silicon*, **103,** 39 (1995).

[10] R. P. K. Babu, K. Aparna, S. S. Krishnamuthy, and M. Nethaji, *Polyhedron*, **15,** 2689 (1996).

[11] Li Jin, Kattesh V. Katti, Ronald G. Cavell, A. Alan Pinkerton, and Herbert Nar, *Can. J. Chem./Rev. Can. Chim.* **74**(11), 2378–2385 (1996).

[12] A. E. Arifien and E. H. Ibrahim, *Polish J. Chem.*, **58,** 41 (1984).

[13] A. E. Arifien, *Commun. Fac. Sci. Univ. Ank.*, **37**(B), 95–101 (1991).

[14] E. H. Ibrahim and A. S. Lashine, *Indian J. Chem.*, **18**(B), 368 (1979).

[15] A. E. Arifien, *Indian J. Chem.*, **24**(A), 694 (1985).

[16] T. S. West, *Complexometry With EDTA and Related Reagents* (Broglia Press, London, 1969).

[17] L. G. Van Uitert and G. G. Hass, *J. Am. Chem.Soc.*, **75,** 451 (1953).

[18] H. Irving and H. S. Rossotti, *J. Chem. Soc.*, 3397–3405 (1953).

[19] H. Irving and H. S. Rossotti, *J. Chem. Soc.*, 2904–2910 (1954).

[20] A. E. Arifien, G. M. Taha, A. A. M. Gad, and M. Sh. Zoromba, *Acad. J.*, **11**(7), 3 (2004).

[21] H. Irving and P. J. R. Williams, *J. Chem. Soc.*, 3192 (1953).

[22] J. C. Sullivan, J. Rydperg, and W. F. Miller, *Acta. Chem. Scand.*, **13,** 2023 (1959).

[23] J. Rydperg and J. C. Sullivan, *Acta. Chem. Scand.*, **13,** 2059 (1959).

[24] H. Sigel, *Coordination Chemistry* (Pergamon Press, Oxford, 1980) Vol. 20.

[25] S. Mohan, *Ind. J. Chem.*, **20**(A), 252 (1981).

[26] W. J. Geary, *Coord. Chem. Rev.*, **7,** 81 (1971).

[27] R. A. Shaw, R. Keat, and M. C. Miller, *J. Chem. Soc.*, 1404 (1967).

[28] C. D. Flint and M. Good Game, *J. Chem. Soc.*, **A,** 744 (1966).

[29] William Kemp *Organic Spectroscopy* (Macmillan Edu. Ltd., Hong Kong, 1987), 2nd ed., p. 86.

[30] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds* (John Wiley & Sons, New York, 1986), 4th ed., 228, 229, 237–239 (1986).

[31] E. C. Okafor, *Spectrochim. Acta*, **38**(A), 981 (1982).

[32] F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry* (John Wiley & Sons, Inc., New York, 1980), 4th ed., p. 679.

[33] H. Sigel, B. E. Fischer, and B. Brijs, *J. Am. Chem. Soc.*, **99,** 4489 (1977).

[34] B. E. Fischer and H. Sigel, *J. Am. Chem. Soc.*, **102,** 2998 (1980).