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Ethoxy Pyridine- and Methylpyridine-2-Phosphonato Scandium(III), Yttrium(III) and Lanthanide(III) Chelates

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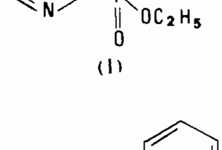
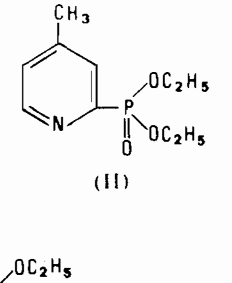
Reaction of MCl_3 (M=Sc, Y, Ln) with diethyl pyridine-2-phosphonate, diethyl 4-methylpyridine-2-phosphonate or diethyl-6-methylpyridine-2-phosphonate at elevated temperatures leads to the precipitation of ML_3 complexes with the corresponding monoethylesters. Characterization studies led to the conclusion that these complexes, unlike their alkoxy alkylphosphonato analogs, which are —O—P—O—bridged polymers, are monomeric metal chelates. The ethoxy pyridine- or methylpyridine-2-phosphonato anions act as bidentate chelating agents, coordinating through one of the POO oxygens and the nitrogen of the pyridine ring. The new complexes are, thus, characterized by MO_3N_3 moieties.

Introduction

In the course of our studies of M^{III} (M=Al, Ga, In, Sc, Y, Ln, Ti, V, Cr, Fe)[1,2] and M^{IV} (M=Th, U)[3] polynuclear (dialkoxyphosphonato) and (alkoxy alkylphosphonato) complexes, we have been interested in preparing and characterizing a number of analogous (ethoxy pyridine-2-phosphonato) metal complexes. Accordingly, we have undertaken synthetic studies, by allowing metal halides to react with the following neutral pyridine-2-phosphonate ethylesters[4] at elevated temperatures:[1-3] diethyl pyridine-2-phosphonate (DEPP; (I)), diethyl 4-methylpyridine-2-phosphonate (DE4MPP; (II)), and diethyl 6-methylpyridine-2-phosphonate (DE6MPP; (III)). The chlorides of the above M^{III} and M^{IV} ions were found to react readily with these neutral esters at 120-150°C to yield metal complexes of the corresponding (ethoxy pyridine-2-phosphonato) ligands, with simultaneous evolution of a mixture of ethyl chloride, hydrogen chloride and ethylene, as expected.[1-3] The present paper deals with the synthesis and characterization of trivalent rare earth metal ion complexes of this type.



(I)



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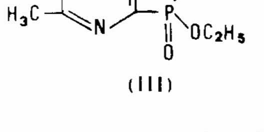

(III)

Experimental Section

The neutral phosphonate esters (I), (II), and (III) were synthesized and purified by the procedures recently reported by Redmore.[4] The new metal complexes were prepared by the general method reported previously;[1-3] i.e., the anhydrous or hydrated metal chloride is suspended in an excess of the neutral phosphonate ester, at room temperature. Gradual increase of the temperature of this mixture leads to the dissolution of the metal salt (60-100°C) and the subsequent reaction between MCl_3 and neutral ester (120-150°C); copius precipitates of tris-(ethoxy pyridine-2-phosphonato) M^{III} or tris-(ethoxy 4- or 6-methylpyridine-2-phosphonato) M^{III} ($M(EPP)_3$, $M(E4MPP)_3$, and $M(E6MPP)_3$, respectively) complexes are obtained during this reaction. These complexes were filtered, washed with acetone and diethyl ether and dried in an evacuated desiccator over P_4O_{10}. The new complexes differ in several respects from analogous polynuclear tris-(alkoxy alkylphosphonato) M^{III} complexes (M=Sc, Y, Ln). In fact, tris-(isopropoxy methylphosphonato) Ln^{III} ($Ln(IMP)_3$) complexes are thermally stable at temperatures exceeding 300°C,[1,5] while the new complexes decompose at 160-220°C. Moreover, in contrast to $M(IMP)_3$ complexes, which are insoluble in water and all common organic solvents,[1,2] the new complexes exhibit the following solubility characteristics in water: $Y(EPP)_3$, LnL_3 (Ln=La to Dy; L=EPP, E4MPP, E6MPP), $Ln(EPP)_3$ (Ln=Ho, Er), $Ln(E4MPP)_3$ (Ln=Ho, Er, Tm) are water-soluble; $Ln(EPP)_3$ (Ln=Tm, Yb), $Ln(E4MPP)_3$ (Ln=Yb, Lu), $Ln(E6MPP)_3$ (Ln=Ho, Er, Tm, Yb) are sparingly soluble in water; and the three Sc^{III} complexes, YL_3 (L=E4MPP, E6MPP) and LuL_3 (L=E6MPP) are

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Table I. Analytical data for the rare earth complexes[a,b]

	C%		H%		P%		Metal %	
Complex	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
Sc(EPP)$_3$	41.79	41.66	4.51	4.40	15.39	15.55	7.45	7.29
Sc(E4MPP)$_3$	44.66	44.60	5.16	5.02	14.39	14.55	6.96	7.19
Sc(E6MPP)$_3$		44.42		4.88		14.70		7.24
Y(EPP)$_3$	38.96	39.23	4.21	4.04	14.35	14.11	13.73	13.95
Y(E4MMP)$_3$	41.81	42.14	4.83	4.84	13.48	13.70	12.90	12.96
Y(E6MPP)$_3$		42.08		5.12		13.33		13.20
La(EPP)$_3$	36.17	35.89	3.91	4.11	13.32	13.34	19.92	20.08
La(E4MPP)$_3$	38.98	39.42	4.51	4.25	12.56	12.82	18.79	19.01
La(E6MPP)$_3$		38.75		4.40		12.63		18.80
Ce(EPP)$_3$	36.11	35.77	3.89	3.89	13.30	13.42	20.06	19.83
Ce(E4MPP)$_3$	38.92	39.13	4.50	4.61	12.54	12.43	18.92	18.75
Ce(E6MPP)$_3$		39.15		4.59		12.30		19.17
Pr(EPP)$_3$	36.07	35.91	3.89	3.60	13.28	13.07	20.15	20.44
Pr(E4MPP)$_3$	38.88	39.25	4.49	4.72	12.53	12.68	19.00	18.69
Pr(E6MPP)$_3$		39.11		4.73		12.44		18.82
Nd(EPP)$_3$	35.91	35.74	3.87	3.65	13.23	12.97	20.53	20.81
Nd(E4MPP)$_3$	38.70	39.05	4.48	4.72	12.48	12.84	19.37	19.11
Nd(E6MPP)$_3$		38.58		4.41		12.64		19.27
Sm(EPP)$_3$	35.60	35.48	3.84	3.63	13.11	12.93	21.21	21.06
Sm(E4MPP)$_3$	38.39	38.19	4.44	4.59	12.37	12.36	20.02	20.04
Sm(E6MPP)$_3$		38.26		4.37		12.14		20.21
Eu(EPP)$_3$	35.50	35.79	3.83	3.48	13.08	12.74	21.39	21.42
Eu(E4MPP)$_3$	38.30	38.11	4.43	4.24	12.35	12.60	20.19	19.96
Eu(E6MPP)$_3$		38.22		4.55		12.74		20.47
Gd(EPP)$_3$	35.24	35.02	3.80	3.96	12.99	13.27	21.97	22.22
Gd(E4MPP)$_3$	38.04	37.75	4.40	4.46	12.26	12.62	20.75	21.05
Gd(E6MPP)$_3$		37.82		4.70		12.12		20.67
Tb(EPP)$_3$	35.16	34.92	3.79	3.88	12.95	13.14	22.15	22.33
Tb(E4MPP)$_3$	37.95	38.15	4.39	4.14	12.23	12.27	20.93	21.25
Tb(E6MPP)$_3$		38.18		4.03		12.45		20.81
Dy(EPP)$_3$	34.98	34.82	3.77	4.03	12.88	12.73	22.54	22.81
Dy(E4MPP)$_3$	37.78	37.49	4.37	4.17	12.18	11.96	21.30	20.97
Dy(E6MPP)$_3$		37.60		4.20		12.39		21.13
Ho(EPP)$_3$	34.87	34.93	3.76	3.53	12.84	12.70	22.80	22.51
Ho(E4MPP)$_3$	37.66	37.55	4.35	4.21	12.14	12.23	21.55	21.12
Ho(E6MPP)$_3$		37.56		4.29		12.01		21.24
Er(EPP)$_3$	34.75	35.15	3.74	3.72	12.80	12.67	23.05	22.66
Er(E4MMP)$_3$	37.54	37.90	4.34	4.16	12.10	12.12	21.78	22.07
Er(E6MPP)$_3$		37.47		4.53		11.86		21.53
Tm(EPP)$_3$	34.67	34.44	3.74	3.42	12.77	13.03	23.23	23.21
Tm(E4MPP)$_3$	37.46	37.50	4.33	4.15	12.08	11.76	21.95	22.32
Tm(E6MPP)$_3$		37.76		4.24		12.34		21.68
Yb(EPP)$_3$	34.49	34.51	3.72	3.98	12.70	12.72	23.67	23.41
Yb(E4MPP)$_3$	37.26	37.12	4.31	4.12	12.01	11.77	22.37	22.63
Yb(E6MPP)$_3$		37.45		4.48		12.27		22.51
Lu(EPP)$_3$	34.39	34.80	3.71	3.53	12.66	12.95	23.87	24.18
Lu(E4MPP)$_3$	37.17	36.82	4.30	4.32	11.98	12.24	22.56	22.22
Lu(E6MPP)$_3$		36.85		4.10		11.64		22.24

[a] The calculated values for E4MPP and E6MPP complexes are, of course, the same. [b] The colors of the new complexes are as follows: E6MPP complexes: Sc^{3+}, dark yellow; Ce^{3+}, lt. pink; Nd^{3+}, lt. brick red; all others, white. E4MPP complexes: Sc^{3+}, cherry red; Pr^{3+}, lt. green; Nd^{3+}, brick red; all others, lt. pink. EPP complexes: Sc^{3+}, beige; Pr^{3+}, lt. green; Nd^{3+}, red-brown; Dy^{3+} and Ho^{3+}, creme; Er^{3+}, lt. pink; all others, white.

water-insoluble. In various organic solvents, such as chloroform, acetone, ethanol, nitromethane, acetonitrile, N,N-dimethylformanide and dimethyl sulfoxide, the new complexes are either insoluble or slightly soluble.

Analytical data (Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany) are given in Table I. Infrared spectra (Nujol mulls and KBr pellets; Table II), magnetic susceptibility measurements (Table III) and X-ray powder diffraction patterns were obtained by methods described elsewhere.[1-3] The ir spectra of the new complexes are generally devoid of coordinated or residual water bands.

Discussion

The ligands examined during this work may act as bidentate chelating or bridging agents by coordinating either through the two oxygen atoms of the POO group[1-3] or through one oxygen of this group and the nitrogen of the pyridyl substituent.[6,7] For the corresponding alkoxy alkylphosphonato ligands only the former possibility exists, and their metal complexes are generally polynuclear, characterized by the exclusive presence of –O–P–O– bridges between neighboring metal ions.[1-3] As already mentioned (*vide supra*) the new complexes differ from their alkoxy alkyl-

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Table II. Pertinent infrared data for the rare earth complexes (cm^{-1}).

Complex	Phosphonato moiety [a]	Aromatic amine moiety [b]	ν_{M-O}	ν_{M-N}
Sc(EPP)$_3$	1190s,sh,1080s,545m	624m,420m,sh	397s	273s
Y(EPP)$_3$	1190s,sh,1072s,537m	627m,417m,sh	364m,340m	224s
La(EPP)$_3$	1210s,1069s,541m	630s,412m	350m,318m	209m
Ce(EPP)$_3$	1208s,1062s,540m,b	630s,411m	352m,320m	211m
Pr(EPP)$_3$	1202s,1070s,540s	631s,413m	353s,320m	211m-s
Nd(EEP)$_3$	1200s,b,1072s,537m	631m,416m	356m,323m,b	212m
Sm(EPP)$_3$	1200s,1073s,538m	631m,415m	359m,324m	212m
Eu(EPP)$_3$	1198s.1072s,540m	630s,413m	360m,328m,b	212m
Gd(EPP)$_3$	1209s,1077s,542m	632m,418m	361m,330m,b	212m
Tb(EPP)$_3$	1200s,sh,1070s,535m	626m,413m,sh	360m,335m-s	209m
Dy(EPP)$_3$	1207s,sh,1070s,535m,b	623m,416w,sh	359m,330m-s	209m
Ho(EPP)$_3$	1204s,sh,1068s,530m	622m,412w,sh	358m,328m	208m
Er(EPP)$_3$	1200s,sh,1071s,532m	623m,414m,sh	361m,333m-s	208m
Tm(EPP)$_3$	1200s,sh,1073s,530m	621m,411w	360m,330m	207w
Yb(EPP)$_3$	1193s,sh,1072s,531m	621m,411w	350m,vb	209w
Lu(EPP)$_3$	1190s,1080s,533m	624m,414w,sh	364m,336m-s	205w
Sc(E4MPP)$_3$	1190s,sh,1076s,519s	530m	399s,377s	264s
Y(E4MPP)$_3$	1187s,sh,1073s,521s	529m,sh	361s,339s	222s
La(E4MPP)$_3$	1200s,1069s,519m	530s	358m,319m	208w,sh
Ce(E4MPP)$_3$	1202s,1071s,520m	531m	362m,321m	211w,sh
Pr(E4MPP)$_3$	1202s,1070s,518m	531m	355m,320m	210w,sh
Nd(E4MPP)$_3$	1207s,1072s,520sh	531m	359m,326m	213w,b,sh
Sm(E4MPP)$_3$	1210s,b,1076s,522m	535m	361m,329m-s	215m,sh
Eu(E4MPP)$_3$	1206s,1073s,521m	532m	360m,330m	215m,sh
Gd(E4MPP)$_3$	1208s,1079s,521m	534m	361m,331m	216m,sh
Tb(E4MPP)$_3$	1205s,sh,1072s,520m	532m,sh	360m,333m-s	216m,sh
Dy(E4MPP)$_3$	1207s,sh,1070s,519m	528m,sh	359m,335m-s	217m,sh
Ho(E4MPP)$_3$	1204s,sh,1071s,521s	529m,sh	360m,339s	219m,b
Er(E4MPP)$_3$	1199,sh,1073s,520m	530m,sh	360m,b,337m-s	220m,b
Tm(E4MPP)$_3$	1209m,sh,1079s,519m	529m,sh	357m,332m	212m,sh
Yb(E4MPP)$_3$	1206m,sh,1079s,520m-s	528m,sh	362m,339m-s	214m,sh
Lu(E4MPP)$_3$	1199m,sh,1080s,521m	531m	359m,335m,b	213m
Sc(E6MPP)$_3$	1210m,sh,1088s,546s	561s,sh	410s,390s	268s
Y(E6MPP)$_3$	1209m,sh,1078s,544s	567s,sh	338vs	221s
La(E6MPP)$_3$	1204s,sh,1070s,544s	578s	355m,b,321s	213m,b
Ce(E6MPP)$_3$	1197s,sh,1068s,545s	579s	350m,b,321s	214m,b
Pr(E6MPP)$_3$	1196m,sh,1060s,547s	578s,sh	350m,sh,328s	217m
Nd(E6MPP)$_3$	1200s,1070s,547s	574s	355m,sh,326m,b	215m,b
Sm(E6MPP)$_3$	1201s,sh,1064s,548s	575s,sh	356m,sh,327s	220m-s
Eu(E6MPP)$_3$	1199m,sh,1069s,548s	577s,sh	358m,sh,329s	221m,b
Gd(E6MPP)$_3$	1192s,sh,1069s,548s	578s,sh	356m,sh,330s	221m
Tb(E6MPP)$_3$	1189s,sh,1070s,550s	581s,sh	355m,sh,331s	222m
Dy(E6MPP)$_3$	1190s,sh,1080s,550s	580s,sh	354m,sh,331s	223m
Ho(E6MPP)$_3$	1188s,1080s,549s	579s,sh	354m,330s	222m
Er(E6MPP)$_3$	1189s,1081s,547s	578s,sh	352m,330s	219m,b
Tm(E6MPP)$_3$	1190s,1082s,548s	577s,sh	350m,sh,337s	217m,b
Yb(E6MPP)$_3$	1189s,1087s,549s	570s	349m,sh,340s	214m,b
Lu(E6MPP)$_3$	1191s,1089s,549s	574s,sh	348m,sh,341s	211m,b

Abbreviations: s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder. [a] ν_{POO} asymmetric and symmetric at *ca.* 2110 1190 and 1090-1060 cm^{-1} respectively; the band at 550-518 cm^{-1} is characteristic of alkyl arylphosphonic acids[25] and occurs at 540, 519 and 544 cm^{-1} in compound (I), (II) and (III), respectively. [b] ν_{6a} and ν_{16b} modes (see text) occur at 599 and 400 cm^{-1} in compound (I); the ν_{6a} made in compounds (II) and (III) overlaps with the 519 and 544 cm^{-1} bands of the phosphonato ligand[25] (cf. footnote a).

phosphonato analogs in that they are considerably less thermally stable and, in most cases, water-soluble. The solubility characteristics of the new complexes are suggestive of a monomeric or oligomeric structure,[8-11] whereas their relatively low thermal stability may be indicative of involvement of the nitrogen of the pyridine ring in coordination. In fact, Ln^{III} chelates with bidentate nitrogen ligands reportedly decompose at temperatures ranging between 80° and 240°C for 2,2-dipyridyl complexes and 150° and 340 °C for 1,10-phenanthroline complexes.[12]

The infrared spectra (Table II) of the EPP, E4-MPP, and E6MPP complexes are suggestive of coordination of the ligands through one of the POO oxygens and the pyridine nitrogen. Tris-(alkoxy alkylphosphonato) Sc^{III}, Y^{III}, or Ln^{III} polynuclear complexes exhibit the ν_{POO} asymmetric and symmetric vibrational modes at 1183-1122 and 1088-1059 cm^{-1}, respectively.[1,13] In the spectra of the new complexes the higher frequency ν_{POO} band occurs at significantly

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Table III. Representative μ_{eff} values for the complexes with paramagnetic Ln(III) ions (298°K.) [a].

Complex	$10^6\chi_M^{corr}$, cgsu	μ_{eff}, BM
$Ce(EPP)_3$	3,051	2.69
$Pr(E6MPP)_3$	5,759	3.70
$Nd(E4MPP)_3$	5,917	3.76
$Sm(EPP)_3$	922	1.49
$Eu(E6MPP)_3$	6,622	3.97
$Gd(E6MPP)_3$	28,596	8.25
$Tb(E6MPP)_3$	40,620	9.83
$Dy(E6MPP)_3$	50,379	10.94
$Ho(E6MPP)_3$	49,405	10.84
$Er(E4MPP)_3$	39,067	9.66
$Tm(E4MPP)_3$	24,688	7.68
$Yb(E4MPP)_3$	8,958	4.62

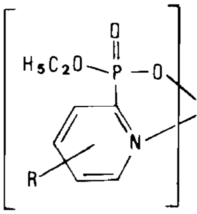
[a] The μ_{eff} values of the other complexes of a given Ln^{3+} ion are in the same range as those reported in the Table; *e.g.*, $Nd(E6MPP)_3$, 3.91; $Gd(E4MPP)_3$, 8.33; $Dy(E4MPP)_3$, 11.10; and $TM(E6MPP)_3$, 7.74BM.

higher frequencies (in many cases above 1200 cm^{-1}, cf. Table II). This is indicative of the presence of uncoordinated POO oxygens.[9,14,15] ($\nu_{P=O}$ occurs at 1220-1170 cm^{-1} in monoacidic phosphonate esters[14,15]). It should be noted that in certain cases ν_{POO} asymmetric appears as a shoulder of the strong $\nu_{C-O-(P)}$ bands,[14] which are observed in the 1170-1130 cm^{-1} region in compounds (I)-(III). The ν_{POO} (symmetric) bands occur in the 1090-1060 cm^{-1} region in the new complexes, and to not overlap with the $\nu_{P-O-(C)}$ absorptions which appear at 1050-1025 cm^{-1}.[14]

Ppridine and picoline coordination through the ring nitrogen results in characteristic shifts of certain infrared band of these ligands.[16-22] Thus, in the case of the pyridine, most sensitive are the ν_{6a} (ring in-plane-deformation) and ν_{16b} (ring out-of-plane deformation)[23] modes, which occur at 604 and 405 cm^{-1}, respectively, in the free base, and exhibit substantial positive frequency shifts upon metal complex formation.[16,17,22] Likewise, the ν_{6a} mode of 2– and 4–picolines, ocurring, respectively, at 546 and 515 cm^{-1} in the free bases,[24] exhibits positive frequency shifts in the metal complexes of these ligands.[19-21] Positive shifts of the above bands are generally observed in the spectra of the new complexes (Table II); these bands are sharp and can be easily distinguished from the broad absorptions of the phosphonato moiety in this region;[25] in the case of E4MPP complexes the ν_{6a} mode of the 4-picoline substituent overlaps partially with the sharp absorption at ca. 520 cm^{-1}, which occurs invariably in alkyl arylphosphonic acids,[25] but no problem arises as far as distinction between these two bands is concerned. In the 1400-800 cm^{-1} region the absorption of the pyridine ring are generally masked by the strong ν_{POO}, $\nu_{P-O-(C)}$, $\nu_{C-O-(P)}$ and $\nu_{P-C(aryl)}$ bands[14] of the coordinated ligands. Thus, for instance, the shifts of the ν_1 mode of pyridine and the picolines (from 998-991 cm^{-1} in the free ligands [23,24] to 1035-1005 cm^{-1} in the metal complexes[16-22]) was not detected, owing to the strong $\nu_{P-O-(C)}$ and $\nu_{PC(aryl)}$ absorptions in this region. Finally, the intense ν_{8a} mode of the aromatic amine substituents, occuring at 1578, 1593 and 1580 cm^{-1} in compounds (I), (II) and (III), respectively, shows small positive shifts (2-10 cm^{-1})[16-22] in the metal complexes of the corresponding monoacidic pyridine-2-phosphonato ethylesters.

Coordination of the EPP, E4MPP and E6MPP ligands through one of the POO oxygens and the aromatic ring nitrogen is also favored by the presence of metal-sensitive bands at both the 400-300 and the 300-200 cm^{-1} regions (Table II). The tentative assignment of the bands at 400-300 cm^{-1} as ν_{M-O}[1,26,27] and those at 300-200 cm^{-1} as ν_{M-N}[27-29] (Table II) is considered as justified, on the basis of analogous ν_{M-O} and ν_{M-N} ($M=Sc^{III}$, Y^{III}, Ln^{III}) assignments, appearing in the literature.[1,26-29]

The overall evidence provided by the infrared spectra and the solubility and thermal stability characteristics of the new complexes is, therefore, suggestive that these compounds are monomeric hexacoordinated metal chelates (IV) and that the monoacidic phosphonate esters act as bidentate O,N-ligands. The mechanism of their formation most probably involves the following reaction sequence:[1-3,13,30] Initially a 3:1 adduct between the neutral phosphonate ester and the MCl_3 is formed; the neutral ester may act as a mono- or bi-dentate ligand, coordinating through the P=O oxygen, the pyridine nitrogen or both.[6,7] Adducts of neutral alkoxyphosphoryl ligands with metal halides are generally not easily isolable;[1-3,13] the metal trichloride-neutral phosphonate ester adduct remains, therefore, in solution and decomposes in the following manner at higher temperatures:[13,30]



(IV)

$$M[(R{-}C_5H_4N)PO(OC_2H_5)_2]_3Cl_3 \rightarrow M[(R{-}C_5H_4N)P(O)O(OC_2H_5)]_3 + 3C_2H_5Cl$$

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The new complex precipitated during this reaction is stabilized in the monomeric form shown by structure (IV), which involves formation of five-membered chelate rings, rather than the polynuclear –O–P–O– bridged, configuration which is common in the analogous complexes of R_2POO^- ligands, when R=alkyl, aryl or alkoxy group.[1-3,8,9,13,31] Part of the ethyl chloride formed during the above reaction decomposes to yield $HCl + C_2H_4$.[13]

The magnetic moments of the new complexes are generally within the range of values predicted and observed in compounds of paramagnetic trivalent lanthanide ions.[1,32] The whole series of the E6MPP complexes were obtained in crystalline form; the X-ray powder diffraction patterns of these compounds exhibit noticeable changes with variation of the central metal ion; isomorphism is observed for the complexes of metal ions whose ionic raddi are of about the same magnitude, i.e.: La, Ce, Pr and Nd; Sm, Eu, and Gd; Y, Tb, Dy, Ho and Er; Tm, Yb and Lu; the pattern of $Sc(E6MPP)_3$ is in a class by itself. In the cases of the EPP and E4MPP complexes, only certain compounds were obtained in crystalline form, while the rest of the complexes were amorphous powders with the exception of $Pr(E4MPP)_3$, which was precipitated in the form of a viscous liquid. The fact that the complexes of certain rare earth ions are crystalline, while their analogs with other rare earth ions are amorphous may be due to differences in the temperatures of precipitation of these compounds (cf. experimental section). An analogous case was reported for (isopropoxy methylphosphonato) metal complexes ($M(IMP)_n$), which were obtained as crystalline powders at relatively low temperatures (50-180 °C), and as rubber-like materials at higher temperatures (above (200°C).[13] The x-ray patterns of the crystalline $M(EPP)_3$ complexes (M=Y, La, Tb, Dy, Ho, Er, Tm, Yb, Lu) suggest that these compounds are of about the same structure. The crystalline $M(E4MPP)_3$ complexes exhibit X-ray patterns indicating that the following groups of metal ions form isomorphous complexes: Ce^{3+} and Nd^{3+}; Y^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+} and Lu^{3+}.

In conclusion, a series of trivalent rare earth ion complexes with the EPP, E4MPP and E6MPP ligands were synthesized and characterized as monomeric hexacoordinated metal chelates, involving coordination of these ligands through one of the POO oxygens and the aromatic ring nitrogen. The novel feature introduced by the present study is that it demonstrates the possibility of isolation of monomeric complexes of appropriately substituted monoacidic organophosphates, phosphonates and -phosphinates. Ligands of this type containing alkyl, aryl, alkoxy, aryloxy or halo substituents on phosphorus form invariably polynuclear –O–P–O– bridged metal complexes.[1-3,8,9,13,31,33] Nevertheless, analogs charactezed by a heterocyclic ring (aromatic or saturated) with a $-PO(R)OH_1$ $-CH_2PO(R),OH$, $-OPO(R)OH$ etc. (R=alkyl, aryl, alkoxy, aryloxy or halo group) *ortho*-substituent, would most probably act as bidentate O,X-ligands (X=heteoroatom, i.e. N,O,S, etc.), forming monomeric metal chelates, as suggested by the evidence presented in the present work. Research in this direction would certainly be rewarding.

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