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Erbium and ytterbium complexes with phosphates and phosphine oxides

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The new complexes of erbium and ytterbium with amine, phosphate and phosphine oxide ligands $\mathrm{Ln(NH_2R)_3Cl_3}$, $\mathrm{Ln[O{=}P(NMe_2)_2NHR]_3Cl_3}$, $\mathrm{Ln[O{=}P(OPh)_2NHR]_3Cl_3}$, $\mathrm{[R{=}CH_2CH_2CH_2Si(OEt)_3]}$, $\mathrm{Ln[O{=}P(OPh)_3]_3Cl_3}$, $\mathrm{Ln[O{=}P(CH_2CH_2CF_3)_3]_3Cl_3}$ and $\mathrm{Ln[O{=}P(CH{=}CHPh)_3]_3Cl_3}$ have been synthesised, and their absorption spectra have been measured in both films and solutions.

Many organometallic compounds and complexes of lanthanides exhibit extraordinarily high photo- and electroluminescence properties. For this reason, lanthanide-doped materials are very promising as gain media for the generation and amplification of intense light pulses.[1–4] For practical applications of lanthanide metal complexes in optoelectronic devices, further development should be focused on obtaining easier fabrication at lower cost, together with better mechanical and thermal stability of the resulting materials. Thus, the preparation of stable rare eath metal complexes incorporated into a solid organic or organosilicon polymer matrix is very challenging.[1,2] Here we report the synthesis of three new phosphorous- and fluorine-containing ligands giving stable complexes with erbium and ytterbium, and the incorporation of these complexes into film-forming polymer composites. The preparation of high optical quality thermostable films doped with Er or Yb cations is also described. The absorption spectra of the Er and Yb complexes are reported.

New ligands **2**, **3** and **5** were prepared. The procedures described previously[5,6] were used for the syntheses of triphenylphosphate $\mathrm{O{=}P(OPh)_3}$ **4** and tris(styryl)phosphine oxide $\mathrm{O{=}P(CH{=}CHPh)_3}$ **6**. Bis(dimethylamido)(3-triethoxysiliylpropylamido)phosphate $\mathrm{O{=}P(NMe_2)_2NHCH_2CH_2CH_2Si(OEt)_3}$ **2** was synthesised by the reaction of 3-aminopropyltriethoxysilane $\mathrm{NH_2CH_2CH_2CH_2Si(OEt)_3}$ **1** (APTES) with bis(dimethylamido)chlorophosphate $\mathrm{(Me_2N)_2P(O)Cl}$. The interaction of APTES with diphenylphosphate $\mathrm{(PhO)_2P(O)Cl}$ gives diphenyl(3-triethoxysilylpropylamido)phosphate $\mathrm{O{=}P(OPh)_2NHCH_2CH_2CH_2Si(OEt)_3}$ **3**. Tris(3,3,3-trifluoropropyl)phosphine oxide $\mathrm{O{=}P(CH_2CH_2CF_3)_3}$ **5** was synthesised by the interaction of 3 equiv. of 3,3,3-triflouropropylmagnesium chloride $\mathrm{F_3CCH_2CH_2MgCl}$ with phosphorous chloroxide in ether.

Compounds **2** and **3** are colourless viscous liquids, and **4**–**6** are colourless crystalline solids relatively stable to oxygen and moisture.[†] The crystal structure and main geometrical parameters of phosphine oxides **5** and **6** are shown in Figure 1.[‡]

Needle crystals suitable for single X-ray analysis were grown from hot acetonitrile (**5**) or hot toluene (**6**). The P atoms have a distorted tetrahedral coordination. The bond angles for the P atoms vary in the ranges 105.53(9)–113.17(8)° for **5** and 104.38(5)–114.18(4)° for **6**. The P–O distances are 1.494(2) and 1.485(2) Å for **5** and **6**, respectively. The corresponding distance for the other compounds is 1.489 Å.[11] The P–C distance for **5** [1.801(2) Å] is longer than that for **6** [1.781(1) Å]. The C(1)–C(2) distance [1.335(2) Å] in **6** lies in the range of C=C distances [1.294–1.345 Å][11] for organic molecules. The C(2)–C(3) distance in **6** is 1.471(2) Å, which is very close to that in molecules containing conjugated $\mathrm{C{=}C{-}C_{ar}}$ fragments (1.470 Å).[11]

The styrene ligands in **6** have a *trans* conformation. The angle between the C(1)H(1)C(2)H(2) and C(3–8) planes is 34.1° being significantly bigger than analogous angles in $\mathrm{Ph_2PCH{=}CHPh}$ (9.4°)[12] and $\mathrm{(OH)_2(O{=})PCH{=}CHPh}$ (13.5°).[13]

The interaction of dried erbium(III) or ytterbium(III) chloride with amine **1**, phosphates **2**–**4** or phosphine oxides **5**, **6** in diethyl ether, chloroform and acetonitrile afforded 11 new lanthanide complexes: $\mathrm{Er(NH_2R)_3Cl_3}$ **7**, $\mathrm{Er[O{=}P(NMe_2)_2NHR]_3Cl_3}$ **8**,[†] $\mathrm{Er[O{=}P(OPh)_2NHR]_3Cl_3}$ **9**, $\mathrm{Er[O{=}P(OPh)_3]_3Cl_3}$ **10**, $\mathrm{Er[O{=}P(CH_2CH_2CF_3)_3]_3Cl_3}$ **11**, $\mathrm{Er[O{=}P(CH{=}CHPh)_3]_3Cl_3}$ **12**, $\mathrm{Yb(NH_2R)_3Cl_3}$ **13**, $\mathrm{Yb[O{=}P(OPh)_2NHR]_3Cl_3}$ **14**, $\mathrm{Yb[O{=}P(OPh)_3]_3Cl_3}$ **15**, $\mathrm{Yb[O{=}P(CH_2CH_2CF_3)_3]_3Cl_3}$ **16**, $\mathrm{Yb[O{=}P(CH{=}CHPh)_3]_3Cl_3}$ **17**, $\mathrm{R{=}CH_2CH_2CH_2Si(OEt)_3}$. Compounds **7**–**10** and **13**–**15** are viscous liquids, whereas **11**, **12**, **16** and **17** are solids of differing stability towards atmospheric moisture. It is well known[14] that rare earth metal complexes are readily hydrolysed by water. The $\mathrm{H_2O}$ molecule causes strong

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[†] *Bis(dimethylamido)(3-triethoxysilylpropylamido)phosphate* **2**. A solution of APTES (11.4 g, 0.052 mol) in 50 ml of toluene was added drop-by-drop to a solution of $\mathrm{(Me_2N)_2P(O)Cl}$ (8.8 g, 0.052 mol) and $\mathrm{Et_3N}$ (5.25 g, 0.052 mol) in 50 ml toluene with stirring. The reaction mixture was heated for 10 h at 100–110 °C followed by filtering and vacuum distillation to afford 4.2 g (23%) of ligand **2** [colourless transparent liquid, bp 120–123 °C (0.3 Torr)]. ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$) δ: 0.45, 0.49, 0.51, 0.53 (q, 2H, $\mathrm{CH_2Si}$), 0.92 (s, NH), 1.04, 1.05, 1.08, 1.09, 1.11, 1.12 (m, 9H, *Me*–$\mathrm{CH_2OSi}$), 1.43, 1.47, 1.50 (t, 2H, $\mathrm{C}\mathit{H}_2$–$\mathrm{CH_2Si}$), 2.50, 2.51, 2.54, 2.56 (q, 12H, MeN), 2.68, 2.71, 2.73, 2.75, 2.79 (m, 2H, $\mathrm{NCH_2}$), 3.62, 3.66, 3.69, 3.73, 3.75, 3.76, 3.79 (m, 6H, $\mathrm{CH_2OSi}$). IR (ν/cm^{-1}): 3200, 2970, 2920, 2870, 2800, 1450, 1390, 1290, 1200, 1170, 1110, 1080, 980, 955, 770, 740, 660, 470. Found (%): C, 43.21; H, 10.06; P, 9.03; Si, 8.05. Calc. for $\mathrm{C_{13}H_{34}N_3O_4PSi}$ (%): C, 43.92; H, 9.64; P, 8.72; Si, 7.90.

Compound **3** was synthesised in an analogous way to that used for **2**.

Tris(3,3,3-trifluoropropyl)phosphine oxide **5**. Mp 193–195 °C. ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$) δ: 2.01, 2.03, 2.04, 2.07, 2.09 (m, 6H, $\mathrm{CH_2P}$), 2.37, 2.40, 2.42, 2.43, 2.44, 2.46, 2.47, 2.48, 2.49, 2.50 (m, 6H, $\mathrm{CH_2C}$). ^{31}P NMR (200 MHz, $\mathrm{CD_3CN}$) δ: 45.17. IR (ν/cm^{-1}): 1305, 1255, 1230, 1200, 1150, 1125, 1110, 1065, 1020, 925, 835, 785, 640, 615, 550, 440, 375, 355. Found (%): C, 31.94; H, 3.90. Calc. for $\mathrm{C_9H_{12}F_9OP}$ (%): C, 31.98; H, 3.58.

Tris(styryl)phosphine oxide **6**. ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$) δ: 6.53, 6.61, 6.64, 6.72 (q, 6H, CH=CH), 7.37, 7.39, 7.40, 7.41, 7.42 (m, 6H, CH=CH–P), 7.50, 7.52, 7.53, 7.55, 7.57, 7.60 (m, 15H, Ph). ^{31}P NMR (200 MHz, $\mathrm{CDCl_3}$) δ: 20.90. IR (ν/cm^{-1}): 1610, 1575, 1230, 1170, 980, 835, 800, 740, 690, 600, 505, 460. UV [λ/nm (ε/dm^3 mol^{-1} cm^{-1})]: 214 (sh.), 220 (sh.), 281 (42000).

Trichloro-tris[bis(dimethylamido)(3-triethoxysilylpropylamido)phosphate]erbium(III) **8**. A solution of amidophosphate **2** (1.82 g, 0.0051 mol) in diethyl ether (5 ml) was dropped onto $\mathrm{ErCl_3}$ (0.47 g, 0.0017 mol) *in vacuo* resulting in an exothermal reaction accompanied by the dissolution of the erbium chloride. The solid product was separated by centrifuging and the diethyl ether was removed *in vacuo* affording 1.66 g of complex **8** (yield 73%, viscous pink liquid). IR (ν/cm^{-1}): 3250, 2970, 2920, 2875, 2800, 1480, 1450, 1390, 1300, 1270, 1210, 1170, 1130, 1110, 1060, 1000, 990, 955, 770, 755, 690, 475. Found (%): C, 35.38; H, 8.04; Cl, 7.24; Er, 12.75; P, 7.08; Si, 6.42. Calc. for $\mathrm{C_{39}H_{102}Cl_3ErN_9O_{12}P_3Si_3}$ (%): C, 34.95; H, 7.67; Cl, 7.95; Er, 12.48; P, 6.94; Si, 6.29. Complexes **9**, **10**, **14** and **15** were obtained analogously.

Table 1 Absorption spectra [ν/cm^{-1} (ε/dm^3 mol^{-1} cm^{-1})] of erbium complexes **7**–**9**, **11** and **12**.[a]

Transition	**7**	**8**	**9**	**11**	**12**	Er^{3+} aqua cation
$^4I_{15/2} \rightarrow {}^2K_{15/2}$	27400 (2.63)	27500	27400			
$^4I_{15/2} \rightarrow {}^4G_{11/2}$	26400 (18.42)	26550 (15.73)	26400 (8.25)	26500 (16.08)		26370 (6.90)
$^4I_{15/2} \rightarrow {}^4F_{7/2}$	20600 (2.63)	20550	20400 (1.68)			20530 (2.03)
$^4I_{15/2} \rightarrow {}^2H_{11/2}$	19200 (11.58)	19300 (6.11)	19100 (5.73)	19210 (9.46)	19230 (15.58)	19120 (3.28)
$^4I_{15/2} \rightarrow {}^4F_{9/2}$	15400 (2.11)	15400	15250 (1.96)		15310 (1.25)	15.326 (2.04)
$^4I_{15/2} \rightarrow {}^4I_{9/2}$	12500 (0.35)		12200 (0.98)		11330 (4.90)	
$^4I_{15/2} \rightarrow {}^4I_{11/2}$	10200 (1.06)	10250 (0.82)			9850 (9.02)	
$^4I_{15/2} \rightarrow {}^4I_{13/2}$	6540 (2.83)	6530 (2.34)				

[a] **7**–**9**, films on silica; **11**, an acetonitrile solution; **12**, a chloroform solution.

luminescence quenching.[15] We monitored the concentration of hydroxyl groups by IR spectroscopy, which showed that the trend to hydration depends on the ligand and increases in the order **6** < **2** < **3** < **1** < **5** < **4**. The hydroxyl bands at 3300 and 1600 cm^{-1} are absent for complexes **8**, **9**, **12**, **14**, **17** with triamidophospate, diphenylamidophosphate and styrylphosphine oxide ligands and are very weak for complexes **7**, **11**, **13**, **16** with amine and trifluoropropylphosphine oxide ligands. However, the bands are quite intense for complexes **10**, **15** with the triphenylphosphate ligand. Note that the addition of free triphenyl phosphate decreases the hydroxyl band intensities for **10** and **15**.

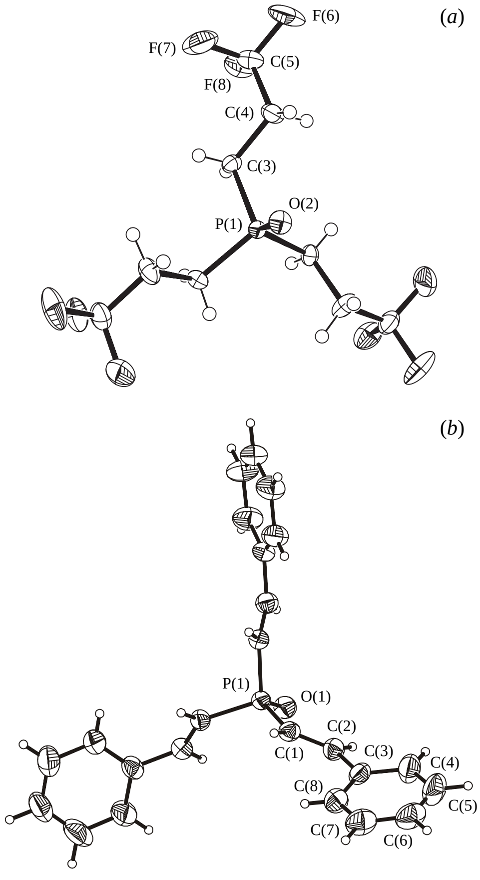

Figure 1 Molecular structures of compounds (*a*) **5** and (*b*) **6**. Important distances (Å) and angles (°) for **5**: P(1)–C(3) 1.801(2), P(1)–O(2) 1.494(2), C(5)–F(8) 1.341(3), C(5)–F(7) 1.335(3), C(5)–F(6) 1.340(3); C(3)–P(1)–O(2) 113.17(8), C(3)–P(1)–C(3) (2 – *x* + *y*, 1 – *x*, *z*) 105.53(9) and for **6**: P(1)–O(1) 1.485(2), P(1)–C(1) 1.781(1), C(1)–C(2) 1.335(2), C(2)–C(3) 1.471(2); O(1)–P(1)–C(1) 114.18(4), C(1)–P(1)–C(1) (–*x* + *y* + 1, –*x* + 1, *z*) 104.38(5).

APTES is an excellent precursor for the production of sol–gel films. We found that this useful feature is transferred to metal complexes **7**–**9**, **13** and **14** synthesised from ligands **2** and **3**. High optical quality sol–gel films were obtained from the compositions containing the amidophosphate erbium complex, oligodimethylsiloxane-α,ω-diols HO(SiMe$_2$O)$_n$H (n = 3–7) and trifunctional organoalkoxysilanes [MeSi(OMe)$_3$, PhSi(OMe)$_3$, NH$_2$CH$_2$CH$_2$CH$_2$Si(OEt)$_3$] with a weight ratio from 1:0.5:0.2 up to 1:1:0.5. The films are formed within 5–15 h and they remained transparent up to 200 °C.

The electronic absorption spectra for the complexes were measured in films of thickness 70–170 μm for **7**–**9**, and **14** and in acetonitrile or chloroform solutions in the case of **11** or **12**, respectively (Table 1). The series of narrow bands in the region 28000–15000 cm^{-1} corresponds to *f*–*f* transitions in Er^{3+}. Their position depends very slightly on the ligand (the variation being no more than 200 cm^{-1}) and no splitting or broadening is observed. However, an increase in the value of ε by a factor of 2.7–3.5 (relative to the erbium aqua cation[15]) is observed for the supersensitive transition bands at 26370 ($^4I_{15/2} \rightarrow {}^4G_{11/2}$) and 19120 cm^{-1} ($^4I_{15/2} \rightarrow {}^2H_{11/2}$). The strongest absorption was revealed for erbium amine complex **7**. The narrow bands arising from the *f*–*f* transitions to the exited levels $^2H_{11/2}$, $^4F_{9/2}$, $^4I_{9/2}$ and $^4I_{11/2}$ were revealed in the absorption spectrum of erbium complex **12** with the tris(styryl)phosphine oxide ligand in the region 500–1100 nm (20000–9090 cm^{-1}). The region 250–420 nm (40000–23800 cm^{-1}) is occupied by an intense absorption band of ligand **6**. The $^4I_{15/2} \rightarrow {}^4I_{9/2}$ and $^4I_{15/2} \rightarrow {}^4I_{11/2}$ transition absorption bands also have high intensities and in comparison with the corresponding transitions in the amide and phenylphosphate complexes are shifted to longer wavelengths. The absorption spectrum of ytterbium complex **14** was measured in the region 50000–12000 cm^{-1}. Only the ligand absorption band (triplet at 38900, 38100 and 37200 cm^{-1}) was observed.[15]

The near-IR absorption spectra were measured for films prepared from amine **7** and amidophosphate **8** complexes, siloxanediols and phenyltrimethoxysilane (all the films contained the same concentration of erbium). The spectra of the complexes are very similar in the region 800–2000 nm (12500–5000 cm^{-1}) in spite of the essential difference in the chemical structures of the ligands. The transition $^4I_{15/2} \rightarrow {}^4I_{13/2}$ at 1530 nm (6530 cm^{-1}) overlaps with the absorption of the N–H and O–H bonds. Note that the degree of the overlap is greater for amine complex **7** containing a higher concentration of N–H groups. At the same time, the transition $^4I_{15/2} \rightarrow {}^4I_{11/2}$ at 975 nm (10250 cm^{-1}) is almost free from overlap with the bands of the overtone absorption for the C–H bonds normally observed in the region 850–950 nm (11760–10530 cm^{-1}).

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‡ C$_9$H$_{12}$F$_9$OP **5**: trigonal, a = 15.170(2), c = 9.979(1) Å, V = 1988.8(4) Å^3, space group $R3c$, Z = 6, μ = 0.307 mm^{-1}, number of reflections measured, 12831; number of independent reflections, 1440; R_{int} = 0.05, R_{all} = = 0.0575, wR_{all} = 0.0568. Structure solution by direct methods[7] and structure refinement using CRYSTALS.[8]

C$_{24}$H$_{21}$OP **6**: trigonal, a = 18.0896(8), c = 5.0536(4) Å, V = 1432.2(1) Å^3, space group $R3$, Z = 3, μ = 0.153 mm^{-1}, number of reflections measured, 3410; number of independent reflections, 1644; R_{int} = 0.02, R_{all} = 0.0363, wR_{all} = 0.0876. Structure solution by direct methods SHELXS-97[9] and structure refinement using SHELXL-97.[10]

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference numbers 229549 (for **5**) and 230016 (for **6**). For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2004.

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