Schiff-base Complexes of the Lanthanoids and Actinoids. Part 1. Lanthanoid(III) Halide Complexes with the Un-ionised Form of *NN'*-Ethylenebis(salicylideneimine) and Related Bases

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The Schiff base *NN'*-ethylenebis(salicylideneimine) and related bases, H_2L, react with hydrated lanthanoid(III) halides to give the complexes $Ln(H_2L)Cl_3{\cdot}nH_2O$ (Ln = La or Ce; n = 0—2), $Ln_2(H_2L)_3Cl_6{\cdot}nH_2O$ (Ln = La, Ce, Pr, Nd, Sm, Gd, Ho, or Yb; n = 0—2), $Ln(H_2L)_2X_3{\cdot}nH_2O$ (Ln = La, Ce, Pr, Nd, Sm, Gd, Ho, or Yb; X = Cl or Br; n = 0—2), and $Ln(H_2L)_3X_3{\cdot}nH_2O$ (Ln = La, Ce, Pr, Nd, Sm, or Gd; X = Cl or Br; n = 0 or 1). Spectroscopic and other evidence has indicated that: (*i*) halide is co-ordinated to the metal ion except in the case of $Ln(H_2L)_3X_3{\cdot}nH_2O$ where the results were ambiguous; and (*ii*) the potentially quadridentate ligands are bidentate in these complexes with the un-ionised phenolic groups being unco-ordinated.

THERE have been a number of reports [1-14] of metal-ion complexes with Schiff bases containing phenolic groups which are either un-ionised or partly ionised. The ligand *NN'*-dihydroxy-*NN'*-diphenylpyridine-2,6-diamine (H_2L) was [1] half-ionised in the complexes $Ln(HL)(NO_3)_2{\cdot}nH_2O$ (Ln^{III} = La, Ce, Pr, Gd, Er, Dy, Yb, Sc, or Y; n = 1 or 2). During the course of the present work, complexes of *NN'*-propane-1,3-diylbis(salicylideneimine) and *NN'*-2-hydroxypropane-1,3-diylbis(salicylideneimine) (H_2L) of the types $Ln(H_2L)_2X_3{\cdot}nH_2O$ and $Ln_2(H_2L)_3X_6$ [Ln^{III} = La—Lu (except Pm); X = Cl or NO_3; n = 0 or 1] were reported.[2] The ligand *NN'*-ethylenebis(*o*-hydroxyacetophenoneimine) (H_2L) yields [3] the complexes $Ln(H_2L)_2(NO_3)_3$ (Ln^{III} = La, Pr, Nd, or Sm), whilst *N*-salicylideneanthranilic acid (H_2L) gave [4] $Ln(HL)(OH_2)Cl$ [Ln^{III} = La—Lu (except Pm)] in which only the carboxylic acid group was ionised. In addition, *NN'*-ethylenebis(salicylideneimine) (H_2salen) gave the complexes $Ti(H_2salen)Cl_4$,[5] $Nb(H_2salen)Cl_4$,[6] $Th(H_2salen)Cl_4{\cdot}thf$ (thf = tetrahydrofuran),[7] and $U(H_2salen)Cl_4{\cdot}thf$.[7,8] Potentially bidentate bases [9-11] such as *N*-salicylideneaniline (HL) gave the complexes $M(HL)_2Cl_4$ (M = Ti, Sn, Zr, Hf, or Th). There are also reports of similar complexes with Co^{II},[12] Fe^{III},[13] and the uranyl ion.[14]

No crystallographic evidence as to the mode of co-ordination of the Schiff bases is available but it is likely [9-11] that the un-ionised phenolic groups are not co-ordinated. However, one sixth of the un-ionised phenolic groups in aquatris(salicylato)samarium(III) are co-ordinated [15] through the oxygen atom, but a dimeric *NN*-diethylsalicylaldimine complex of Ni^{II} containing half-ionised catechol [16] and the 4-nitrophenol adduct [17] of [Cu(salen)] both show non-co-ordination of the un-ionised phenolic groups of catechol and 4-nitrophenol, respectively.

The present work describes a systematic investigation of the complexes formed by the hydrated lanthanoid(III) chlorides and bromides with the potentially quadridentate ligands, *NN'*-ethylenebis(salicylideneimine) (H_2salen), *NN'*-propylenebis(salicylideneimine) (H_2salpn), *NN'*-propane-1,3-diylbis(salicylideneimine) (H_2salpd), and *NN'*-hexane-1,6-diylbis(salicylideneimine) (H_2salhxn) in their un-ionised forms. This was prompted partly by a report [18] that the rapid addition of a Schiff-base solution to a solution of a lanthanoid(III) nitrate in ethanol gave a yellow precipitate which dissolved only with difficulty and could prevent the formation of products containing an ionised Schiff base.

RESULTS AND DISCUSSION

Stoicheiometry of the Complexes.—Since 43 complexes were prepared by a single method, namely by mixing of the components in ethanol, it was necessary to demonstrate that the four analytical stoicheiometries (Table 1), $Ln(H_2L)Cl_3{\cdot}nH_2O$, $Ln_2(H_2L)_3Cl_6{\cdot}nH_2O$, $Ln(H_2L)_2X_3{\cdot}nH_2O$, and $Ln(H_2L)_3X_3{\cdot}nH_2O$, each represented a single complex and not merely mixtures of a smaller number of stoicheiometric types or simple mixtures of the lanthanoid(III) halide and ligand. This was done by *X*-ray powder-diffraction measurements. Typical results † demonstrated that a well ground mixture of a ligand and a salt gave an *X*-ray powder photograph which is a composite of the component parts, whereas the three

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† *X*-Ray, i.r., and magnetic (90—295 K) data are listed in Supplementary Publication No. SUP 22145 (6 pp.). For details see Notices to Authors No.7, *J.C.S. Dalton*, 1977, Index issue.

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lanthanum(III) complexes with H_2salhxn gave photographs quite unlike those of the components or their mixture. Similarly, the photograph of La(H_2salpd)$Cl_3 \cdot H_2O$ contained none of the lines found for H_2salpd.

TABLE 1

Analytical data (%)

Complex	Found					Calc.				
	M	C	H	N	Halide	M	C	H	N	Halide
La(H_2salen)$_2Cl_3$	17.8	49.2	4.2	7.2	13.4	17.8	49.2	4.1	7.2	13.6
La(H_2salen)$Cl_3 \cdot H_2O$	26.0	37.0	3.6	5.3	19.7	26.1	36.1	3.4	5.3	20.0
La(H_2salpn)$_2Cl_3 \cdot 2H_2O$	16.3	48.2	4.4	6.8	12.4	16.4	48.3	4.8	6.6	12.6
La(H_2salpd)$_2Cl_3 \cdot 2H_2O$	16.5	48.2	4.6	6.5	12.6	16.4	48.3	4.8	6.6	12.6
La(H_2salpd)$Cl_3 \cdot H_2O$	24.6	36.1	3.6	4.8	18.8	24.8	36.1	3.9	4.9	18.8
La_2(H_2salhxn)$_3Cl_6$	19.3	50.1	5.2	5.9	14.4	19.0	49.2	5.0	5.7	14.5
La(H_2salhxn)$_2Cl_3$	15.4	53.8	5.6	6.1	11.8	15.5	53.7	5.4	6.3	11.9
La(H_2salhxn)$_3Cl_3 \cdot H_2O$	11.1	58.5	6.1	6.7	8.5	11.2	58.3	6.0	6.8	8.6
Ce(H_2salen)$_2Cl_3 \cdot 2H_2O$	16.9	46.3	4.2	6.8	13.1	17.1	46.9	4.4	6.8	13.0
Ce(H_2salpd)$Cl_3 \cdot 2H_2O$	24.6	36.1	3.6	4.8	18.8	24.8	36.1	3.9	4.9	18.8
Ce(H_2salhxn)$_2Cl_3$	15.8	53.8	5.5	6.2	11.8	15.7	53.7	5.4	6.3	11.9
Ce(H_2salhxn)$_3Cl_3$	11.3	59.0	5.7	6.8	8.6	11.5	59.1	5.9	6.9	8.7
Pr(H_2salen)$_2Cl_3 \cdot H_2O$	17.4	48.1	4.5	6.7	13.0	17.6	48.0	4.3	7.0	13.3
Pr(H_2salpn)$_2Cl_3 \cdot H_2O$	16.9	49.6	4.4	6.8	12.7	17.0	49.2	4.6	6.8	12.8
Pr(H_2salpd)$_2Cl_3 \cdot 2H_2O$	16.5	48.1	4.7	6.4	12.4	16.6	48.2	4.8	6.6	12.5
Pr_2(H_2salhxn)$_3Cl_6$	19.1	49.2	4.9	5.7	14.3	19.2	49.1	4.9	5.7	14.5
Pr(H_2salhxn)$_2Cl_3 \cdot 2H_2O$	14.8	51.3	5.2	6.0	11.2	15.1	51.5	5.6	6.0	11.4
Pr(H_2salhxn)$_3Cl_3$	11.4	58.9	5.9	6.9	8.6	11.5	59.0	5.9	6.9	8.7
Nd(H_2salen)$_2Cl_3 \cdot 2H_2O$	17.4	45.4	4.2	6.7	12.8	17.5	46.7	4.4	6.8	12.9
Nd(H_2salpn)$_2Cl_3 \cdot H_2O$	17.1	49.1	4.4	6.8	12.7	17.4	49.2	4.6	6.8	12.8
Nd(H_2salpd)$_2Cl_3 \cdot H_2O$	17.2	48.4	4.4	6.6	12.6	17.4	49.2	4.6	6.8	12.8
Nd_2(H_2salhxn)$_3Cl_6 \cdot H_2O$	19.2	47.6	5.2	5.4	13.9	19.1	47.7	5.1	5.6	14.1
Nd(H_2salen)$_2Br_3 \cdot 2H_2O$	14.9	40.7	3.6	5.5	24.8	15.1	40.2	3.8	5.9	25.1
Nd(H_2salpd)$_2Br_3 \cdot 2H_2O$	14.6	41.2	3.9	5.6	24.2	14.7	41.5	4.1	5.7	24.3
Nd(H_2salhxn)$_2Br_3 \cdot H_2O$	13.6	45.3	4.7	5.3	22.5	13.7	45.7	4.8	5.3	22.8
Nd(H_2salhxn)$_3Br_3$	10.7	53.1	5.3	5.9	17.5	10.6	53.1	5.3	6.2	17.7
Nd(H_2salhxn)$_2Cl_3 \cdot 2H_2O$	15.3	51.5	5.2	6.0	11.2	15.4	51.4	5.6	6.0	11.4
Nd(H_2salhxn)$_3Cl_3 \cdot H_2O$	11.9	57.7	5.8	6.6	8.4	12.0	57.7	6.0	6.7	8.5
Sm(H_2salen)$_2Cl_3$	18.8	48.4	4.1	7.1	13.3	19.0	48.4	4.1	7.1	13.4
Sm_2(H_2salpn)$_3Cl_6$	21.9	45.2	4.1	6.2	15.5	22.1	45.0	4.0	6.2	15.6
Sm(H_2salpn)$_2Cl_3 \cdot 2H_2O$	17.7	46.7	4.2	6.2	12.3	17.5	47.6	4.7	6.5	12.4
Sm(H_2salpd)$_2Cl_3 \cdot 2H_2O$	17.4	47.0	4.4	6.4	12.3	17.5	47.6	4.7	6.5	12.4
Sm(H_2salhxn)$_3Cl_3 \cdot H_2O$	11.9	57.7	5.8	6.6	8.4	12.0	57.7	6.0	6.7	8.5
Gd_2(H_2salen)$_3Cl_6$	23.2	43.9	3.7	6.5	15.9	23.6	43.3	3.6	6.3	16.0
Gd(H_2salpn)$_2Cl_3 \cdot 2H_2O$	17.9	46.7	4.2	6.1	12.2	18.2	47.2	4.7	6.5	12.3
Gd(H_2salpd)$_2Cl_3 \cdot 2H_2O$	18.0	46.5	4.4	6.3	12.2	18.2	47.2	4.7	6.5	12.3
Gd(H_2salhxn)$_3Cl_3 \cdot H_2O$	12.4	57.6	5.9	6.5	8.3	12.5	57.4	5.9	6.7	8.5
Ho_2(H_2salen)$_3Cl_6$	24.0	43.0	3.4	6.0	15.6	24.5	42.8	3.6	6.2	15.8
Ho(H_2salpn)$_2Cl_3 \cdot H_2O$	19.1	48.2	4.4	6.4	12.2	19.3	47.8	4.5	6.6	12.5
Ho(H_2salpd)$_2Cl_3 \cdot H_2O$	19.2	48.2	4.6	6.1	12.3	19.3	47.8	4.5	6.6	12.5
Yb_2(H_2salen)$_3Cl_6 \cdot H_2O$	24.5	41.3	3.8	6.0	15.0	24.7	41.2	3.4	6.0	15.2
Yb(H_2salpn)$_2Cl_3 \cdot 2H_2O$	19.5	46.7	4.2	6.1	12.0	19.7	46.4	4.6	6.4	12.1
Yb(H_2salhxn)$_2Cl_3$	18.7	51.9	5.2	5.9	11.4	18.6	51.8	5.2	6.0	11.5

Certain types of complex could not be prepared for some metal salts and ligands; the range is illustrated in Table 2. Contrary to an earlier report,[2] H_2salpd, gave 1 : 1 and 2 : 1 rather than 3 : 2 and 2 : 1 stoicheiometries. Mol ratios (Ln : L) of 1 : 2.5 were used [2] in the previous study, together with a material described as anhydrous ethanol but no details as to its use were given. There was probably more water present in our solutions.

TABLE 2

Stoicheiometries of the complexes

Ligand : metal ratio	Halide	Metal							
		La	Ce	Pr	Nd	Sm	Gd	Ho	Yb
1 : 1 [a]	Cl	S [b]	S						
3 : 2	Cl	S	S	S	S	S	S	S	S
2 : 1	Cl,Br	S	S	S	S	S	S	S	S
3 : 1 [c]	Cl,Br	S	S	S	S	S	S		

[a] H_2L = H_2salen (La) or H_2salpd (La or Ce); these ligands did not give 3 : 2 complexes with La or Ce. [b] S = Synthesised. [c] H_2L = H_2salhxn only.

Infrared Spectra.—(*a*) 2 500—4 000 cm^{-1}. The ligand spectra showed evidence of strong intramolecular hydrogen bonding [19] with the O–H stretching vibration appearing as a broad absorption centred at *ca.* 2 700 cm^{-1}. In the cases of the 1 : 1 and 2 : 1 complexes with chloride, absorption due to water was not sufficiently strong to mask a sharp, non-hydrogen-bonded, O–H stretching frequency [19] between 3 500 and 3 600 cm^{-1}, which indicates that the metal ion has opened the intramolecular hydrogen-bonded system and that the phenolic group is un-ionised in these cases. The broad ligand band centred at *ca.* 2 700 cm^{-1} was not observed for the complexes. Absorption due to water was observed as a broad band at *ca.* 3 400 cm^{-1} and in many cases this masked the phenolic O–H stretching frequency. The remaining bands were assigned to aromatic and aliphatic C–H stretching vibrations.

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[19] L. J. Bellamy, 'Advances in Infrared Group Frequencies,' Methuen, London, 1968.

(*b*) 650—2 500 cm^{-1}. The main features of this region relevant to the present discussion were (*i*) a sharp absorption at *ca.* 1 650 cm^{-1} assignable [19] to a stretching vibration mainly involving the C=N group and (*ii*) a sharp absorption at *ca.* 1 280 cm^{-1} assignable [19] to a 'C–O stretching' vibration. The C=N stretching vibration in the spectra of the complexes was invariably at a higher frequency than in the ligand spectra ($\Delta\bar{\nu}$ 7—37 cm^{-1}), whilst the C–O absorption was unchanged or slightly increased in frequency in the spectra of the complexes ($\Delta\bar{\nu}$ 0—10 cm^{-1}). Such results are said [9-11] to indicate co-ordination through the azomethine nitrogen atoms only. There is no confirmatory crystallographic evidence for the C–O vibrations. However, all the four nitrogen atoms of the organic ligand are co-ordinated [20] in ten-co-ordinate [*NN'*-ethylenebis(pyridine-2-aldimine)]trinitratogadolinium(III) and here the frequency of the C=N(azomethine) vibration increases on complex formation.

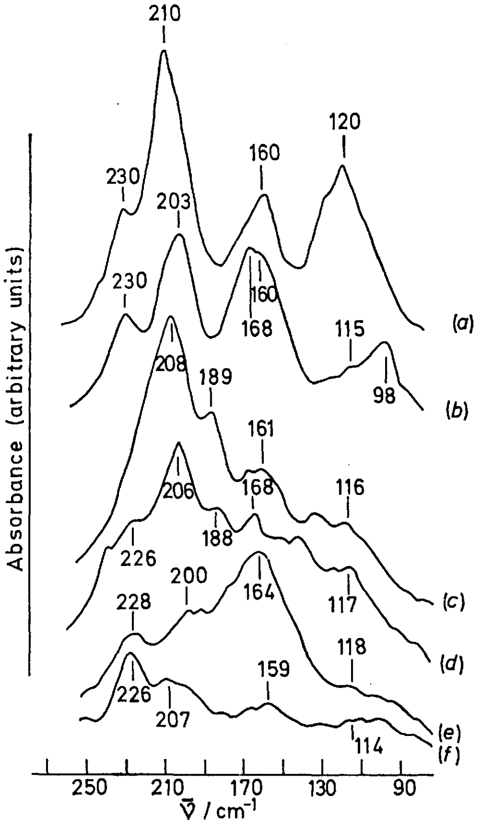
For complexes of the ionised form of H_2salen, the C=N vibration decreases [7] in frequency compared to that of the free ligand {except [21] for [Cu(salen)] and [Zn(salen)]} and the C–O vibration decreases considerably ($\Delta\bar{\nu}$ −25 to −80 cm^{-1}) for the complexes. Here crystallographic evidence shows that co-ordination takes place through both phenolic oxygen and azomethine nitrogen atoms.

The reasons for the spectral changes are poorly understood in the case of the un-ionised bases and crystallographic studies are needed (but see Experimental section).

(*c*) *Far-i.r.* Few reliable studies of the vibrational spectroscopy of lanthanoid halide compounds have been made at <400 cm^{-1}. Metal–halide stretching vibrations (cm^{-1}) have been assigned as follows: for anhydrous halides, La–Cl,[22,23] 210 and 165; Nd–Cl,[23] 207; Sm–Cl,[23] 210; Eu–Cl,[23] 210; Er–Cl,[23] 220; Yb–Cl,[23] 225; Pr–Br,[24] 144, 120, and 96; Nd–Br,[24] 166, 148, 140, and 96; Tm–Br,[24] 157, 135, and 74 cm^{-1}; for $ErBr_3\cdot6H_2O$, 132, 114, and 98; for complexes with organic ligands,[25] Dy–Cl, 240; Lu–Cl, 244.

Co-ordinated chloride and bromide might be distinguished by the absence of strong absorption at *ca.* 200 cm^{-1} in the spectra of the bromides. This result was found (Figure) on comparing $Nd_2(H_2salhxn)_3Cl_6\cdot H_2O$, $Nd(H_2salhxn)_2Cl_3\cdot 2H_2O$, and $Nd(H_2salhxn)_2Br_3\cdot H_2O$. It is not conclusive since weak ligand absorption could have been intensified on complex formation. However, a similar result was found for $Nd(H_2salpd)_2Br_3\cdot 2H_2O$ for which by far the strongest feature was at 172 cm^{-1} (with weaker absorption at 234 and 214 cm^{-1}), whilst the corresponding lanthanum(III) chloride absorbed very strongly at 226 and 159 cm^{-1} (H_2salpd: 220w, 190vw, 178w, and 160w cm^{-1}). We conclude that these complexes contain co-ordinated chloride (3 : 2 and 2 : 1) and bromide (2 : 1).

The situation with the 3 : 1 complexes is even less clear (Figure). There is a general similarity between the spectra which might suggest unco-ordinated halide. However, the relative intensities of the bands at *ca.* 210 and 165 cm^{-1} change such that the chloride absorption at 210 cm^{-1} is by far the strongest feature, whereas the absorption centred at 167 cm^{-1} is apparently stronger and broader in the bromide than that at 165 cm^{-1} in the chloride spectrum. There are more marked differences at low frequency. Clearly, ligand absorption could interfere with these assignments, but for H_2salhxn the strongest ligand band (226 cm^{-1}) had only medium intensity in the complexes except for $Nd_2(H_2salhxn)_3Cl_6\cdot H_2O$ where it did not appear at all. On balance, perhaps, halide is co-ordinated in the 3 : 1 complexes also.



Far-i.r. spectra: (*a*) $Nd(H_2salhxn)_3Cl_3\cdot H_2O$; (*b*) $Nd(H_2salhxn)_3Br_3$; (*c*) $Nd_2(H_2salhxn)_3Cl_6\cdot H_2O$; (*d*) $Nd(H_2salhxn)_2Cl_3\cdot 2H_2O$; (*e*) $Nd(H_2salhxn)_2Br_3\cdot H_2O$; and (*f*) H_2salhxn

Durham and Hart [25] found no significant absorption assignable to Lu^{III}–N vibrations; we found the same result.

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Electronic Spectra (5 000—50 000 cm^{-1}).—These were recorded by diffuse reflectance at room and near liquid-nitrogen temperatures. The charge-transfer and *f–f* transitions were in keeping with the previously well characterised energy-level diagrams [26] for the metal ions concerned. For Nd^{III}, however, hypersensitive transitions can be used in some circumstances as a guide to co-ordination number; Karraker [27–29] has shown that four transitions are sensitive to environment but one, $^4I_{\frac{9}{2}}\rightarrow{}^4G_{\frac{5}{2}},{}^2G_{\frac{7}{2}}$ (at *ca.* 17 000 cm^{-1}), is particularly so.

The salt Nd[BrO$_3$]$_3$·9H$_2$O is nine-co-ordinate to water molecules [30] and NdCl$_3$·6H$_2$O contains [31] the eight-co-ordinate cation [NdCl$_2$(OH$_2$)$_6$]$^+$. The spectra [29] of these two compounds are different in the region mentioned above and very much different from those of Nd(bipy)$_2$(NO$_3$)$_3$ (bipy = 2,2′-bipyridyl) and Nd$_2$Mg$_3$(NO$_3$)$_{12}$·24H$_2$O which probably contain ten- and twelve-co-ordinate Nd^{III}, respectively, by analogy with the crystal structures of the corresponding compounds [32,33] of La^{III}, Tb^{III}, and Ce^{III}. By comparing the spectra of these four compounds with those of our neodymium(III) complexes, we concluded that all the latter are either eight- or nine-co-ordinate. It would be unwise to be more specific than this because the chromophores of our complexes are different from those used as standards. This was illustrated in part by Nd(H$_2$salpd)$_2$Br$_3$·2H$_2$O, the spectrum of which resembled [28] that of Nd(O$_2$CMe)$_3$·1.5H$_2$O more closely than those of the compounds mentioned above. However, this was also eight- or nine-co-ordinate.

It is often the case [see,[15] for example, aquatris(salicylato)samarium(III)] that lanthanoid(III) complexes containing a small number of water molecules (say one or two) have all this water co-ordinated. If this is the case then the results from the i.r. and electronic spectra show some consistency. For Nd(H$_2$L)$_2$X$_3$·*n*H$_2$O (n = 1 or 2), eight- or nine-co-ordination is possible in a monomeric species using four nitrogen, three halogen, and one or two oxygen (H$_2$O) atoms as donors, whilst the 3 : 1 complexes would be nine- (or, possibly, ten-) co-ordinate if halide is acting as a ligand. For the 3 : 2 stoicheiometry sufficient donor atoms are available to form dimers or larger polymeric species to give eight- or nine-co-ordination with no need to use the phenolic oxygen atoms if we assume chloride to be co-ordinated.

Holmium(III) compounds also have a hypersensitive transition [29] but this occurs in a region where overtone or combination bands from the i.r. appeared for our complexes. This was deduced from the spectra of the complexes of La^{III}, Ce^{III}, and Gd^{III} and from those of the ligands alone.

Paramagnetic Susceptibilities.—These were in keeping with literature observations and with theoretical values. There was no evidence that the complexes could be classified by stoicheiometry by this method.

EXPERIMENTAL

Of the lanthanoid(III) halide–Schiff-base complexes reported here only Nd(H$_2$salpd)$_2$Cl$_3$·H$_2$O has been previously described.[2] Analytical results are in Table 1. Most of the complexes were prepared by the addition of the stoicheiometric amount of the hydrated lanthanoid(III) halide in absolute ethanol (containing *ca.* 1% water) to a hot solution of the ligand in absolute ethanol. A yellow precipitate formed almost immediately. This was filtered off, washed with cold ethanol several times, and dried (CaCl$_2$). None of the compounds could be recrystallised. They dissolved in dimethylformamide and dimethyl sulphoxide to give conducting solutions which precipitated the ligands on standing. Halide could be determined gravimetrically in the filtrate. Both solvents are good ligands for lanthanoid(III) ions. The complexes are stable in moist air.

Ligand : metal ion ratios of 1 : 1 were used in the preparation of the complexes Ln$_2$(H$_2$L)$_3$Cl$_6$·*n*H$_2$O; ligands forming this type of complex could not be used to prepare Ln(H$_2$L)Cl$_3$·*n*H$_2$O which were synthesised with solvents at room temperature. Only H$_2$salhxn gave Ln(H$_2$L)$_3$Cl$_3$·*n*H$_2$O. Many unsuccessful attempts were made to prepare the complexes Ln(H$_2$L)Br$_3$·*n*H$_2$O and Ln$_2$(H$_2$L)$_3$Br$_6$·*n*H$_2$O; Ho and Yb would not give 3 : 1 complexes with bromide or chloride.

The ligands were prepared by routine methods and the hydrated lanthanoid(III) halides were prepared from the oxides (99.9%).

Standard analytical methods were used. Spectroscopic and magnetic properties and the *X*-ray powder photographs were observed routinely. For some complexes, water was determined using an automatic Stanton–Redcroft TG-750 thermorecording balance. Close agreement (*ca.* 5%) was found between calculated and experimental values.

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