Lanthanide complexes of potentially heptadentate Schiff base ligands

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The potentially heptadentate trianionic Schiff base ligands derived from tris(2-aminoethyl)amine and 3 mol of (substituted) salicylaldehyde react with lanthanide metal nitrates to form neutral 1:1 compounds of formula Ln(X-Saltren). Physicochemical measurements are described for the following complexes: Ln = La, Pr, Nd, Eu, Gd, Dy, Ho, Yb, X= 3,5-Cl₂; Ln = La, X = 5-Cl and 5-NO₂; and the analogous complexes, M = Sc, Y, Co, X = 3,5-Cl₂. Discussion of the spectroscopic data focuses on far infrared v(Ln-O) and v(Ln-N) bands, ¹H nmr pseudocontact shifts and hypersensitive *f*-*f* transitions.

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Les ligands du type base de Schiff potentiellement heptadentates et trianioniques provenant de la réaction de la tris(amino-2 éthyl) amine avec trois moles de salicylaldehyde (substitué) réagissent avec les nitrates des métaux de la série des lanthanides en formant des composés neutres 1:1 de formule Ln(X-Saltren). On a effectué les mesures physicochimiques sur les complexes suivants: Ln = La, Pr, Nd, Eu, Gd, Dy, Ho, Yb, X = Cl₂-3,5; Ln = La, X = Cl-5 et NO₂-5 ainsi que sur des complexes analogues, M = Sc, Y, Co, X = Cl₂-3,5. La discussion des données spectroscopiques porte sur les bandes v(Ln—O) et v(Ln—N) dans l'infrarouge lointain, sur la rmn du ¹H des réactifs de pseudo déplacement et sur les transitions hypersensibles f-f.

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Introduction

Studies of metal complexes involving ligands having seven potential donor atoms are relatively rare (1). The number of Schiff base complexes of the lanthanide elements is similarly limited to a few reports (2). In the present work, we accordingly explore the ligating properties of potentially heptadentate Schiff base ligands (I) with several trivalent lanthanide metals.



 $R = H, R' = H \qquad H_3Saltren (Ia)$ $R = H, R' = NO_2 \qquad H_35-NO_2Saltren (Ib)$ $R = H, R' = Cl \qquad H_35-ClSaltren (Ic)$ $R = Cl, R' = Cl \qquad H_33,5-Cl_2Saltren (Id)$

Earlier work in our laboratory (3) described the synthesis of these trianionic ligands derived from tris(2-aminoethyl)amine(tren) and 3 mol of (substituted) salicylaldehydes and the characterization of $M(3,5-Cl_2Saltren)$ (M = Cr, Fe, La), where H₃3,5-Cl₂Saltren represents tris(3,5-dichlorosalicylidene-2-iminoethyl)amine (Id). The present trivalent metal complexes, prepared according to [1]

[1] $M(NO_3)_3 + H_3X$ —Saltren + 3NaOAc $\rightarrow M(X$ —Saltren) + 3NaNO₃ + 3HOAc are expected to have structures represented by the following:



Experimental

Chemicals

Tris(2-aminoethyl)amine was purchased from Ames Laboratories, Inc., salicylaldehyde was a J. T. Baker product, and the substituted salicyladehydes were obtained from the Eastman Kodak Co. The hydrated lanthanide metal nitrates were obtained from Alfa Inorganics Inc. These chemicals and all solvents were used without further purification.

Physical measurements

Elemental analyses were performed by Guelph Chemical Laboratories, Inc., Guelph. Infrared spectra were recorded for Nujol mulls between KBr plates ($4000-400 \text{ cm}^{-1}$ region) and polythene plates ($500-100 \text{ cm}^{-1}$ region) using Beckman Acculab-6 and Perkin-Elmer 180 spectrophotometers, respectively. A Cary 14 spectrophotometer was used to obtain the electronic spectral data, either as mulls on filter paper or in dimethylsulfoxide using 10 cm cells and ca. $10^{-2} M$ solutions. Proton nmr spectra were obtained by Dr. A. Woon-Fat on a Bruker WH-60 FT instrument using dimethylsulfoxide- d_6 solutions with TMS as internal standard. Conductivity measurements were made on dimethylsulfoxide solutions with a Beckman Model RC-18A conductance bridge and a cell with platinized electrodes and a cell constant of 0.20.

Preparation of the complexes

A solution of the Schiff base ligands (1.0 mmol), hydrated metal nitrate (1.0 mmol), and sodium acetate (1.0 mmol) in absolute ethanol/2,2-dimethoxypropane was stirred and refluxed overnight. The precipitated product was collected by

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	Colour	Calcd.			Found		
Compound ^a		C	Н	N	C	Н	N
Co(3,5-Cl ₂ Saltren)	Dark green	45.0	2.9	7.8	44.2	3.0	7.5
Sc(3,5-Cl ₂ Saltren)	Greenish yellow	45.9	2.9	7.9	46.0	3.0	7.9
Y(3,5-Cl ₂ Saltren)	Yellow	43.2	2.8	7.5	43.6	3.0	7.7
Pr(3.5-Cl ₂ Saltren)	Greenish vellow	40.4	2.6	7.0	40.1	2.8	6.9
Nd(3,5-Cl ₂ Saltren)	Yellow	40.2	2.6	6.9	b	b	b
Eu(3.5-Cl ₂ Saltren)	Yellow	39.8	2.6	6.9	40.1	2.4	6.9
Gd(3.5-Cl ₂ Saltren) ^c	Yellow	37.9	3.2	6.6	37.8	2.5	6.7
$Dv(3.5-Cl_2Saltren)^d$	Yellow	36.9	3.1	6.4	36.7	2.6	6.6
Ho(3,5-Cl ₂ Saltren)	Yellow	40.2	2.8	7.0	39.5	2.5	6.9
Yb(3.5-Cl ₂ Saltren)	Yellow	38.8	2.5	6.7	38.5	2.6	6.4
La(5-ClSaltren)	Yellow	46.5	3.5	8.0	46.9	3.6	8.6
$La(5-NO_2Saltren)^d$	Yellow	41.4	3.9	12.5	41.5	3.6	12.6

TABLE 1. Analytical data for the Schiff base complexes

^aLigands are shown in Ib, Ic, and Id. ⁶Analyses fit for 3H₂O. ⁴Analyses fit for 3H₂O.

filtration, washed with absolute ethanol, then dried over P_4O_{10} for 3h in vacuo at 100°C. The analytical data for the new complexes are given in Table 1. The complexes do not melt, but char at temperatures above 290°C.

Results and Discussion

A series of lanthanide metal complexes of the potentially heptadentate trianionic Schiff base ligands (Id) has been prepared as an extension of our earlier work (3) on $M(3,5-Cl_2Saltren)$ (M = Cr, Fe, La). For comparative purposes, other metal complexes of Id, namely for M = Sc, Y and Co, as well as lanthanum complexes of Ib and Ic were also synthesized. The instability of ligand Ia toward hydrolysis prevented isolation of the analogous lanthanide metal complexes. We had noted earlier that related Schiff base ligands obtained by the condensation of tren with β -diketones are even more susceptible to hydrolysis of the azomethine linkages; however, the in situ isolation of lanthanide shift reagents of this type was reported (4) during the present investigation. Other workers have also recently described the preparation and properties of several first-row metal (III) complexes of ligands Ia and Ic; in particular, X-ray analysis has established essentially octahedral $[M(N_3O_3)]$ geometries for M(5-ClSaltren) (M = Cr, Mn, and Fe) (5). The present work focuses on the spectroscopic characterization of the lanthanide complexes $Ln(3,5-Cl_2Saltren)$ (Ln = La, Pr, Nd, Eu, Gd, Dy, Ho, Yb) with some comparative data being provided for the complexes M(3,5) $Cl_2Saltren$) (M = Cr, Fe, Co, Sc, and Y).

The new complexes have low solubilities in common organic solvents, necessitating the use of dimethylsulfoxide for solution measurements. Such solutions are non-conducting, with molar conductance values of less than 1 mho cm², confirming the neutral formulation of the complexes. The mass spectrum of La(3,5-Cl₂Saltren) showed the parent ion corresponding to the monomer but attempts to obtain the mass spectra of the other lanthanide metal complexes proved unsatisfactory. In spite of the attempts to dehydrate the complexes by using 2,2-dimethoxypropane as a reagent and by drying the products in vacuo, the presence of lattice water was indicated in a few cases by elemental analysis (Table 1) and broad infrared bands at ca. 3400 cm⁻¹. The existence of lattice water was verified by other workers (5) in the X-ray analyses of M(5-ClSaltren)·3H₂O (Cr, Mn, and Fe).

Infrared studies

The bands near $1600 \,\mathrm{cm}^{-1}$ associated with the v(C=N) and v(C=C) stretching frequencies change in profile in the complexes as compared to those observed for the isolated ligands, with the significant lowering in frequency of the main band also indicating coordination via the azomethine nitrogen atom. The trianionic nature of the ligands in the complexes is shown by the absence of the broad weak hydroxyl bands (3600-2200 cm⁻¹) displayed by the free ligands. All of the complexes showed very similar infrared spectra above 500 cm^{-1} and, therefore, far-infrared spectra were recorded (to $100 \,\mathrm{cm}^{-1}$) in an attempt to assign v(Ln - O) and v(Ln - N) vibrational modes. There is a paucity of such assignments in the literature, though it appears that v(Ln - O) and v(Ln - N)might be expected in the $500-300 \,\mathrm{cm}^{-1}$ and 300- 200 cm^{-1} regions, respectively (6). Some confirmation of this expectation was obtained by recording the far-infrared spectra of two known lanthanide metal complexes of 8-hydroxyquinoline, whose donor atom environments are similar to those in

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TABLE 2. H	Far infrared	bands for	Ln(3.5-	Cl ₂ Saltren) ^a
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La	420s, 408m,	376s, 336m, 302m, 262s, 202s, 160m		
Pr	419s, 406m, 374s, 336m, 307sh, 301m, 260s, 202s, 155bs			
Nd	422s, 408m, 376s, 338m, 310sh, 302m, 266m, 204bys, 170s			
Eu	420s, 410s, 377s, 340m, 303m, 270m, 203s, 162s			
Gd	423vs, 412s, 380vs, 343s, 306s, 276vs, 204vs, 162vs			
Dy	424s, 413m, 381ms, 344m, 316m, 306s, 278s, 205m, 164m			
Ho	424s, 410m, 380m, 340m, 315m, 306s, 277s, 200m, 160m			
Yb	427vs, 412s, 383vs, 348m, 317sh, 310vs, 284vs, 206vs, 166vs, 152s			
Related com	plexes			
H ₃ 3,5-Cl ₂ Sal	tren	433bm, 375bs, 295bs, 130vs		
Cr(3,5-Cl ₂ Sa	ltren)	476vs, 425m, 366m		
Fe(3,5-Cl ₂ Sa	ltren)	470b,sh, 450vs, 415m, 395m, 327b,s, 284m		
Sc(3,5-Cl ₂ Sa	ltren)	462sh, 450vs, 440bvs, 413m, 395s, 343m, 327vs, 302s, 260s,		
· · -		245m, 218s, 205m, 192wm, 134m		
Y(3,5-Cl ₂ Sal	tren)	424s, 412m, 380s, 343m, 306s, 280s, 220s, 167m		
Hoxin		460m, 191m		
Fe(oxin) ₃ ^b		$360(\alpha), 308, 297(\beta)$		
$Al(xin)_3^b$		466, 455, 444(α); 418, 402(β)		
Eu(oxin) ₃		484vs, 365bs, 260vm, 195bvs		
Eu(OPr ⁱ) ₃ ^c		525, 490, 451, 410, 373		
aDanda af mad		•i•		

^aBands of medium or stronge ^bValues taken from ref. 9. ^cValues taken from ref. 10(a). ronger intensity only are ta

our Schiff base ligand of interest. For Nd(oxin)₃ and $Eu(oxin)_3$, prepared according to Aly (7), bands near 485 cm⁻¹ and 365 cm⁻¹ that do not occur in the spectrum of 8-hydroxyquinoline may be assigned to v(Ln-O). The band near 200 cm^{-1} , of greatly increased intensity as compared to the 191 cm⁻¹ band in 8-hydroxyquinoline, may more tentatively be assigned to a v(Ln-N) mode (8). Such assignments are comparable to those made previously for $M(xin)_3$ (M = Al, Fe, Co) (9). Similarly, comparison of the far-infrared spectra of the Ln(3,5-Cl₂Saltren) complexes with the spectra of the uncoordinated ligand and of lighter metal complexes (Table 2, Fig. 1) allows the tentative assignment of v(Ln=0) and v(Ln=N) vibrational modes. Several strong metal-sensitive bands in the 300-450 cm⁻¹ region are probably associated with v(Ln-O) since lanthanide metal isopropoxides and β -diketonates also show strong bands in the same range (6, 10). Of the bands at lower frequency, those near 270 cm^{-1} and 200 cm^{-1} appear to be



FIG. 1. Far-infrared spectrum of Yb(3,5-Cl₂Saltren).

likely candidates for the v(Ln-N) modes (6). Although the complexes $M(3,5-Cl_2Saltren)$ (M = Sc, Cr, Co, Fe) are undoubtedly six-coordinate (5), the apparent decrease in frequency of the farinfrared bands associated with v(Ln-O) and v(Ln-N) nevertheless does not allow a choice in assigning either six- or seven-coordination to these new lanthanide complexes. A comparison of v(M = 0) and v(M = N) modes between the lighter elements and the lanthanide elements is invalidated by the great difference in covalency expected in the metal complexes.

Electronic transitions

An intense intraligand transition occurs for all of the $M(3,5-Cl_2Saltren)$ complexes at ca. 26000 cm⁻¹, with the slight metal dependence signifying the charge-transfer origin of the band. Solid-state spectra show a prominent shoulder centered near 23 000 cm⁻¹ which obscures observations of either d-d or f-f transitions in this region. Strong bands observed near 18000 cm⁻¹ for the iron(III) complexes of ligands I are probably also of chargetransfer (phenol \rightarrow iron(III)) type (11), but the weaker shoulder near 18000 cm⁻¹ for the chromium(III) complexes of I may be the expected $(11)v_1$ transition for octahedral chromium(III) complexes since no shoulder to the 26000 cm⁻¹ band is found for the Sc(3,5-Cl₂Saltren) and La(3,5-Cl₂Saltren) complexes. Similarly, the weak band at $16400 \,\mathrm{cm}^{-1}$ observed in the solid state spectrum of Co(3,5-Cl₂Saltren) may be attributed to the octahedral transition expected (5, 11) in this region, since X-ray analysis has confirmed this geometry for

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Ln	Ground term	Excited term	Lnag	Observed ^a
Pr	³ H ₄	${}^{3}P_{2}, {}^{3}P_{1} + {}^{1}I_{6}$ ${}^{3}P_{0}, {}^{1}D_{2}$	17 300– 23 200°	19 900 20 200 20 500
Nđ	4I _{9/2}	${}^{2}P_{1/2}$ ${}^{4}G_{5/2,7/2}$	23 400 17 500 17 460	С
Eu	${}^{7}F_{0,1,2}$	${}^{5}D_{0,1,2}$	16 920 21 500	None ^d
Gd	⁸ S _{7/2}	⁶ PIDG	е	(35 700) ^e (40 000) ^e
Dy	⁶ H _{15/2}	⁶ <i>F</i> _{11/2}	7 700	7 7 50
Но	⁵ <i>I</i> ₈	⁵ G ₆ , ³ G ₆	22 100 27 700	21750
Yb	${}^{2}F_{7/2}$	${}^{2}F_{5/2}$	10 300	10 280 10 580

TABLE 3. Hypersensitive transitions for Ln(3,5-Cl₂Saltren)

^aAll complexes have a ligand band at ca. 26000 cm⁻¹ in DMSO, and additionally a shoulder in the 22700– 25600 cm⁻¹ region in the solid state. ^bFour peaks are observed, see Fig. 2. The pattern of peaks is distinctly different from those observed for either Nd(NO₃)₃: 5H₂O or Nd₂O₃. ^dBands observed by fluorescence spectroscopy, see text. ^cAssignments are tentative, broad multiplets in ultraviolet region expected.

 $M(5-ClSaltren) \cdot 3H_2O$ (M = Cr, Mn, Fe) (5). The absence of a shoulder to the intense 26000 cm⁻¹ $(\varepsilon \approx 2 \times 10^3 \text{ mol}^{-1} \text{ L cm}^{-1})$ band for dimethylsulfoxide solutions of the Ln(3,5-Saltren) complexes doubtless implies an increase in coordination number upon dissolution, since the complexes are also insoluble in other common organic solvents.

Changes in the intensity and fine structure of certain "hypersensitive" absorption bands in the absorption spectra of trivalent lanthanide complexes have been related to changes in the symmetry of the ligand field around the lanthanide ions (12). Accordingly, the occurrence of such f-ftransitions was observed in the solid state for the Ln(3,5-Cl₂Saltren) complexes to allow a comparison with those bands reported for the aqueous Ln^{3+} ions (Table 3). A qualitative indication of significant covalency in the ligand-to-metal bonds, as compared to the aquo ions, is given by calculations of the nephelauxetic parameter β for the complexes. For example, the red shift of 350 cm^{-1} for the Ho(3,5-Cl₂Saltren) complex represents a nephelauxetic effect of 0.98. More quantitative information on the degree of covalency and site symmetry in the complexes via a comparison of oscillator strengths of these hypersensitive bands is precluded by the low solubility of the complexes, even in dimethylsulfoxide.

The coordination number of neodymium has been related to the shape and intensity of the hypersensitive transition, ${}^{4}I_{9/2} \rightarrow {}^{4}G_{5/2}$, ${}^{2}G_{7/2}$, which occurs near 17000 cm⁻¹ (12, 13). Thus, $Nd(NO_3)_3 \cdot 5H_2O$, known to be 10-coordinate (14), shows a single solid state visible band at 17400 cm^{-1} . A prominent shoulder at 17500 cm^{-1} to the more intense 17300 cm⁻¹ band is observed in the visible spectrum of Nd(oxin)₃. An assignment of either 6- or 7-coordination is possible for this 8-hydroxyquinoline complex by comparison with the spectral profiles of tri- β -diketonate complexes (and their adducts) studied by Karraker (13). Because of the similarity in donor atom environment between ligands I and 8-hydroxyquinoline, the spectrum of Nd(3,5-Cl₂Saltren) was expected to be similar. Although the shoulders on the high energy side of the hypersensitive transition centered at $17000 \,\mathrm{cm}^{-1}$ (see Fig. 2) signify a low coordination number, the more extensive splitting indicates a lower symmetry site for the Nd³⁺ ion. Whether or not this low symmetry environment results only from the (expected) trigonal field imposed by a pseudooctahedral environment or from the additional asymmetry due to coordination by the apical nitrogen atom cannot be ascertained from the visible spectra. An X-ray analysis of a Ln(3,5-Cl₂Saltren) complex has been initiated in order to answer the question of apical nitrogen coordination. The observance of less extensive splitting of the ${}^{4}I_{9/2} \rightarrow {}^{4}G_{5/2}$, ${}^{2}G_{7/2}$ transition for Nd(3,5-ClSaltren) in dimethylsulfoxide solution is compatible with an increase in coordination number. It is ALYEA ET AL.



FIG. 2. Visible absorption spectrum of $Nd(3,5-Cl_2Saltren)$: A, solid state; B, dimethylsulfoxide solution.

worth noting that an asymmetric tetramethylurea complex of neodymium, $Nd(tmu)_5(F_3CSO_3)_3$, also presumably either 6- or 7-coordinate, shows similar splitting of this hypersensitive band (15).

Hypersensitive transitions in europium complexes are often observed by fluorescence spectroscopy, with information on the local symmetry of the Eu³⁺ ion coming from the number of ${}^{5}D_{0} \rightarrow$ ${}^{7}F_{J}$ transitions. For example, the single ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition observed at 17000 cm⁻¹ is compatible with other evidence for octahedral coordination in $Eu(tmu)_6(CF_3SO_3)_3$ (15). A lower symmetry site for the europium ion in $Eu(3,5-Cl_2Saltren)$ is implied by the presence of several peaks in the 16000-17800 cm⁻¹ region. These peaks are superimposed upon a broad fluorescence band centred at 20000 cm⁻¹ which is also observed for the other Ln(3,5-Cl₂Saltren) complexes. Consideration of the possible allowed components for the ${}^5D_J \rightarrow {}^7F_J$ transitions in the feasible crystal field symmetries

TABLE 4. ¹H nmr spectra for (3,5-Cl₂Saltren)

	Assignments, $\delta ppm^{a,b}$				
Ln	N—CH ₂	$-CH_2N=$	Ar—H	N=C-H	
н	2.92	3.70	(7.00- 7.60)	8.40	
La	2.95	3.68	(7.30 - 7.60)	8.03	
Pr	1.51	-10.32	9.33 13.40	25.90	
Nd	4.54	-1.11	9.01 10.43	24.84	
Eu	-0.21	-1.40	4.44 5.30	-16.85	

^aSatisfactory integration obtained for all spectra. ^bPeaks due to undeuterated dimethylsulfoxide occur at 2.52 for the free ligand and in the range 2.52–2.59 for the lanthanide complexes.



FIG. 3. Proton nmr spectrum of Eu(3,5-Cl₂Saltren) in dimethylsulfoxide- d_6 solution.

(16) does not allow an unambiguous assignment of the coordination number in $Eu(3,5-Cl_2Saltren)$.

¹H nmr studies

Proton nuclear magnetic resonance spectra were recorded for the Ln(3,5-Cl₂Saltren) complexes in order to characterize the ligating ability of the ligand. As indicated for the diamagnetic lanthanum complex in Table 4, coordination of the azomethine nitrogen atom results in an upfield shift of the azomethine proton, with the magnitude of the shift being comparable to a solvent shift (3). For the paramagnetic praseodymium, neodymium, and europium compounds, well-resolved spectra are observed (Table 4, Fig. 3) which exhibit large pseudocontact shifts (17). As expected from the distance-shift relationship, the azomethine proton undergoes the greatest shift, with a shielding difference of about 42 ppm between the signals for the europium (upfield) and the two other lanthanide complexes (downfield). The well-resolved resonance peaks due to the ethylene and aromatic protons (${}^{4}J = 2.9 \,\text{Hz}$ for the Eu case) indicate a rigid chelated structure with potential, after modification to improve solubility and eliminate proton peaks, for applications as lanthanide shift reagents. Investigations are underway with suitably modified analogous ligands.

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