Partial Hydrolysis of Homodinuclear Macrocyclic Complexes of Lanthanides with a 2:2 Phenolic Schiff's Base and the Crystal and Molecular Structure of Resulting Open Mononuclear 3:1 Schiff's Base Complexes of Praseodymium(III) and Neodymium(III)

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Abstract

Partial hydrolysis of a 2:2 Schiff base (L) which is derived from 2,6-diformyl-*p*-cresol (HP) and triethylenetetramine (TETA) and coordinated to lanthanide cations (Ln^{3+}) yields acyclic mononuclear complexes of a zwitterionic Schiff base $H_n L'^{(n-3)+}$, $n = 3, 4$. L′ is a condensation product of three molecules of HP and one of TETA. TETA employs a pair of adjacent secondary amines and two primary amines to condense with one of the aldehyde groups on each molecule of HP. The syntheses, crystal and molecular structure of the partial hydrolysis/condensation products of L, *i.e.* $[Pr(H_3L')(NO_3)(OH)]_2(ClO_4)_2 \cdot NaNO_3 \cdot 2H_2O$ and $[Nd(H_3L')(NO_3)(OH_2)](NO_3)_2$ are reported along with a template synthesis of $[Nd(H_4L')(NO_3)(OH_2)]Cl_3$. The hydrolytic/condensation products crystallize in the triclinic (Pr) and monoclinic (Nd) systems in space groups $P\bar{1}$ (Pr) and $P2_1/m$ (Nd). The coordination polyhedron is in each case a distorted monocapped dodecahedron to which L′ contributes phenolic and carbonyl groups only; a bidentate nitrate and a water molecule or OH⁻ ion result in coordination number nine for each central metal species.

Introduction

Recently we reported the syntheses of trimorphic homodinuclear lanthanide (Ln) complexes of the 2:2 macrocyclic phenolate Schiff's base ligand L [1, 2] showing significant $Ln^{3+}-Ln^{3+}$ antiferromagnetic coupling and predominant ligand-to-Ln^{3+} energy transfer processes [3].
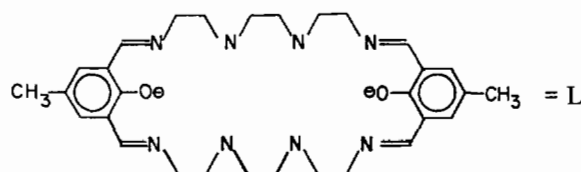

Currently, however, our attempts to grow X-ray diffraction quality crystals of those lanthanide dinuclear complexes of L by recrystallization and other procedures have not been successful. Even attempts to obtain a reduced free ligand $H_2(H_8L)$ have yielded oligomeric products. Furthermore, transmetallation reactions of the dinuclear complexes and d-block cations did not lead to well defined products. This extreme instability of ligand L and its dinuclear lanthanide complexes stands in sharp contrast to the remarkable stability of mononuclear complexes of several pyridino tetraimine or hexaimine Schiff's base complexes in (even boiling) aqueous solutions [4–9] and/or organic solvents [10–15]. Unlike the complexes of L, mononuclear complexes of smaller Schiff's base macrocycles exchange Ln^{3+} for d-block cations quite readily [7, 10, 12]. Experiments designed to facilitate our understanding of the essential origin of the solution instability of L and its dinuclear lanthanide complexes have now revealed that one metal ion is readily leached out of L and this is accompanied by facile hydrolysis of L to 2,6-diformyl-*p*-cresol in water. But in mildly acidic alcoholic solutions (with limited amounts of water) partial hydrolysis of L occurs along with condensation at the adjacent secondary nitrogen sites. This is evidenced by the isolation (from a mixture of several products) and characterization by single crystal X-ray crystallography of mononuclear praseodymium and neodymium complexes of a 3:1 zwitterionic Schiff's base $H_n L'^{(n-3)+}$. The praseodymium complex was obtained from an ethanolic sodium acetate solution of yellow $Pr_2L(NO_3)_4$ whereas the neodymium complex was obtained by reacting 2,6-diformyl-*p*-cresol in methanol with solid off-white $Nd_2L(NO_3)_4 \cdot 2H_2O$. The complex

[Nd(H$_4$L')(NO$_3$)(OH$_2$)]Cl$_3$ was subsequently prepared by a template procedure from 2,6-diformyl-p-cresol and triethylenetetramine in the presence of Nd^{3+}. These results and the report of Fregona *et al.* [16] confirm an extensive, though complex, chemistry of secondary amine (NH) sites with neighboring reactive groups which could be helpful in the design and fabrication of novel ligands.

We herein report the preparation, crystal and molecular structures of [Pr(H$_3$L')(NO$_3$)(OH)]$_2$-(ClO$_4$)$_2$·NaNO$_3$·2H$_2$O and [Nd(H$_3$L')(NO$_3$)(OH$_2$)]-(NO$_3$)$_2$ which identify the vulnerability of C=N to hydrolysis as well as the reactivity of NH among other reactions as sources of instability of ligand L and its homodinuclear complexes.

= L'
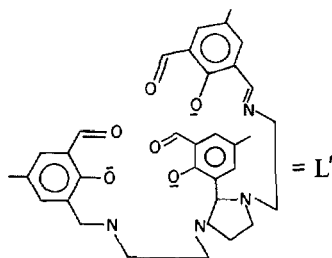
Experimental

Partial Hydrolysis of L and Subsequent Carbonyl–NH Condensation

(a) The orange Pr$_2$L(NO$_4$)$_4$ complex

To a solution of 1 mmol PrCl$_3$·nH$_2$O and 1 mmol Pr(NO$_3$)$_3$·nH$_2$O in 10 ml ethanol, 3 drops of concentrated hydrochloric acid were added followed by 3 mmol of (Bu$_4$N)ClO$_4$. To the solution obtained, 1 mmol of orange Pr$_2$L(NO$_3$)$_4$ [1] was added followed by stepwise additions of solid NaCH$_3$COO·3H$_2$O until the orange complex dissolved. The mixture was filtered and the filtrate allowed to stand at ambient temperature in an open flask. Yellow crystals later found to be those of the complex [Pr(H$_3$L')-(NO$_3$)(OH)]$_2$(ClO$_4$)$_2$·NaNO$_3$·2H$_2$O were deposited within 7 h along with those of a less colored but unidentified compound. After 6 days the mixture was filtered and a single crystal of the yellow complex was picked for single crystal X-ray crystallographic studies.

(b) The off-white Nd$_2$L(NO$_3$)$_4$·2H$_2$O complex

To 0.5 mmol of the off-white homodinuclear complex Nd$_2$L(NO$_3$)$_4$·2H$_2$O [1] in 22 ml of methanol, 1.8 mmol of 2,6-diformyl-p-cresol was added. The flask containing the reaction mixture was covered with paraffin film to avoid evaporation. The mixture was then kept at ambient temperature and

shaken 2–3 times daily for two months when most of the off-white complex dissolved. The mixture was then filtered and the filtrate was allowed to evaporate slowly at ambient temperature from a small flask. Within two days crystallization began and was allowed to proceed until the crystals were large enough for a single crystal X-ray diffraction study. Several products were obtained some of which were very sensitive to solvent loss. After several trials a single crystal which was stable to the atmosphere was picked and studied by single crystal X-ray crystallography. The crystal was found to be that of the complex [Nd(H$_3$L')(NO$_3$)(OH$_2$)](NO$_3$)$_2$. The orange complexes did not dissolve in ethanolic 2,6-diformyl-p-cresol.

Preparation of [Nd(H$_4$L')(NO$_3$)(OH$_2$)]Cl$_3$ from 2,6-Diformyl-p-cresol and Triethylenetetramine

The title complex was prepared by template condensation of 2,6-diformyl-p-cresol and triethylenetetramine, in the presence of Nd^{3+} in a mole ratio of 3:1:1, respectively, as follows. To 8 ml of methanol containing 1.3 mmol of Nd(NO$_3$)$_3$, 0.7 mmol of NdCl$_3$, 2.9 mmol of [Bu$_4$N]ClO$_4$ and 5 mmol NaAc·3H$_2$O, 6 mmol of 2,6-diformyl-p-cresol was added followed by 2 mmol of triethylenetetramine in 2 ml of methanol. The resulting solution was allowed to sit at ambient temperature. After 2 days, 2 drops of concentrated hydrochloric acid and 2 drops of water were added to the deep orange solution. Within 6 h large crystals of the complex of L were deposited. After one day the mixture was filtered and the crude crystalline compound was recrystallized from hot ethanol (20% yield). *Anal.* Calc. for [Nd(H$_4$L')(NO$_3$)-(OH$_2$)]Cl$_3$: C, 40.4; H, 4.0; N, 7.1; Cl, 10.8. Found: C, 40.41; H, 4.33; N, 7.05; Cl, 10.45%.

X-ray Data

Intensity data were collected on an Enraf-Nonius CAD4 diffractometer equipped with Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. The ω–2θ scans were made at variable rates, designed to yield measurements of equal relative precision for all significant data, subject to a maximum scan time for each reflection. Crystal data and specifics for each dataset are given in Table I. One hemisphere of data was measured for the triclinic crystal, one quadrant for the monoclinic one, within the specified angular limits. Data reduction included corrections for background, Lorentz, polarization, decay (for the Nd complex), and absorption effects. The latter corrections were based on psi scans of reflections near χ = 90°. Reflections having $I > 3\sigma(I)$ were considered observed and were used in the refinements. Structures were solved by heavy atom methods and refined by full-matrix least-squares based on F with weights w = $\sigma^{-2}(F_o)$, using the Enraf-Nonius SDP programs [17]. The higher quality of the crystals of the Pr complex

TABLE I. Crystal Data

Compound	Pr complex	Nd complex
Formula	$Na[Pr(C_{33}H_{36}N_4O_6)(NO_3)(OH)]_2(NO_3)(ClO_4)_2 \cdot 2H_2O$	$[Nd(C_{33}H_{36}N_4O_6)(NO_3)(OH_2)](NO_3)_2$
Formula weight	1929.1	932.9
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$ (#2)	$P2_1/m$ (#11)
a (Å)	10.443(4)	10.198(3)
b (Å)	13.334(3)	17.876(9)
c (Å)	16.441(9)	11.951(3)
α (deg)	83.07(3)	
β (deg)	84.78(4)	110.65(2)
γ (deg)	65.48(3)	
Cell volume (Å^3)	2066(2)	2039(2)
Z	1	2
D_c (g cm^{-3})	1.551	1.520
μ (cm^{-1})	13.2	13.5
Crystal dimensions (mm)	0.14 × 0.32 × 0.36	0.10 × 0.30 × 0.45
θ limits (deg)	$1 < \theta < 25$	$1 < \theta < 25$
Scan speeds (deg min^{-1})	1.0–4.0	1.7–4.0
Max. scan time (s)	60	60
Min. relative transmission (%)	91.1	80.2
Decay (%)	–	4.3
T (°C)	23	23
Unique data	7267	3705
Observed data	4869	2615
Variables	501	133
R	0.059	0.081
R_w	0.084	0.100
Max. residual density (e Å^{-3})	0.85	0.94

as contrasted with those of the Nd complex led to differences in the two refinements. Specifics for each are specified below.

Pr complex. With the exception of those of the uncoordinated nitrate ion and water molecule, non-hydrogen atoms were refined anisotropically. Where possible, hydrogen atoms were fixed in calculated positions. The H atoms on N1, N2, and N4 were visible in difference maps, and form intramolecular hydrogen bonding interactions. The H atom of the coordinated hydroxy ligand was not located. The oxygen atom of the solvent water molecule was refined isotropically, and its H atoms were not located. The uncoordinated nitrate ion is disordered about a center of symmetry. It was modelled by one isotropically-refined N atom half populated in a general position, and six oxygen sites with population 1/4, adjusted by difference maps. Thus, the nitrate ion takes on four orientations.

Nd complex. Due to the low quality of the crystals, complete anisotropic refinement was not possible. Only the Nd atom was refined anisotropically, while other non-hydrogen atoms were refined isotropically, and H atoms were ignored. By analogy to the Pr complex, in which protonated N was directly observed, it is assumed that three of the N atoms

here are protonated, and by charge balance requirements, that the third ligand is water. The possibility that the hexadentate ligand is tetraprotonated and the third ligand is OH$^-$ cannot be ruled out.

Results

The yellow–orange crystals grown from an ethanolic sodium acetate solution of yellow Pr_2L-$(NO_3)_4$ in the presence of ClO_4^-, Cl^- and Bu_4N^+ ions and in the slow reaction of methanolic 2,6-diformyl-p-cresol with solid off-white $Nd_2L(NO_3)_4 \cdot 2H_2O$ are those of mononuclear acyclic complexes of the zwitterionic 3:1 Schiff base/aldehyde ligand $H_nL'^{(n-3)+}$, $n = 3$, 4. In the case of praseodymium the complex crystallizes as $[Pr(H_3L')(NO_3)(OH)]_2$-$[ClO_4]_2 \cdot NaNO_3 \cdot 2H_2O$, with three of the four nitrogen sites likely protonated and coordination to Pr^{3+} afforded by the three phenolic and three aldehyde sites of L', a bidentate nitrate anion and an hydroxyl group as shown in Fig. 1 which also shows the numbering scheme. The coordination polyhedron of Pr^{3+} is in this case best described as a distorted mono-capped dodecahedron in which the perpendicularly intersecting planes are made up of: (a) O6, O1, O1W and O8 (b) O2, O5, O3 and O4, with capping from O7. As shown in Fig. 1, L' is constituted by three
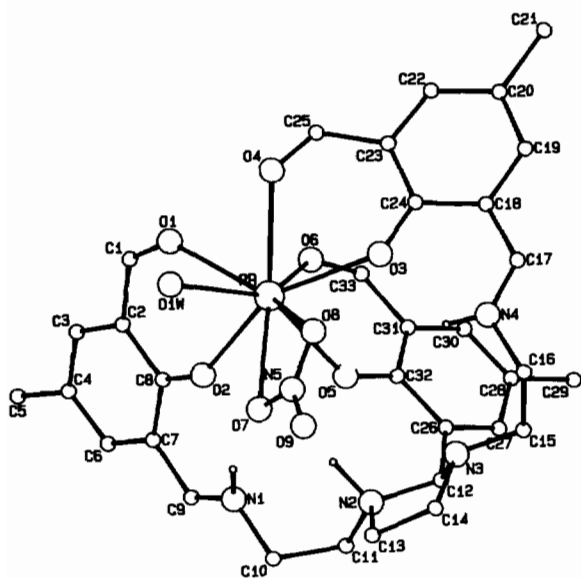
Fig. 1. Molecular structure of $[Pr(H_3L')(NO_3)(OH)_2]_2$-$[ClO_4]_2$.

Fig. 2. Molecular structure of $[Nd(H_3L')(NO_3)(OH_2)]$-$(NO_3)_2$.

molecules of 2,6-diformyl-*p*-cresol and one molecule of triethylenetetramine which utilizes two primary and a pair of adjacent secondary amino groups for condensation with the carbonyls.

In the case of neodymium, the complex appears to crystallize as $[Nd(H_3L')(NO_3)(OH_2)][NO_3]_2$, with three of the four nitrogen sites of L' likely protonated and the Nd^{3+} coordination polyhedron made up of the three phenolate and three aldehyde sites of L' as well as a bidentate nitrate anion and a water molecule as shown in Fig. 2 which also shows the numbering scheme. The Nd^{3+} coordination polyhedron may also be thought of as a distorted monocapped dodecahedron but one of the perpendicularly intersecting planes is constituted by O1, O1W, O1A and O3 and the other by O2, O4, O2 and O1A; capping is afforded by O1'. The unnumbered atoms are related to those appearing in the numbered half of L' by a crystallographic mirror plane which passes between C12 and C12', the two O3 and O2 atoms. The atomic positions are given in Tables II and III. The coordination polyhedron of Nd^{3+} has a crystal-

lographic mirror plane along the plane defined by O1W, O3 and O4 and a less perfect mirror plane is defined by O1W, O2 and O3 for the praseodymium complex.

Interatomic distances Pr—O1W (Table IV) and Nd—O1W (Table V) were not conclusive on whether O1W is an OH^- or H_2O site since there is generally no significant difference between Ln—OH and Ln—OH_2 distances [18–20]. The basis of the above molecular formulations is thus charge balance. Steric hindrance in the complexes of L' is expected to be greater than found in complexes of a 1:1 cyclic Schiff base of 2,6-diformyl-*p*-cresol and triethylenetetramine (L'') reported earlier [2]. This is reflected in longer Ln—O-(phenolate) distances, 2.338, 2.409 and 2.434 Å for Ln = Pr (Table III) and 2.365 and 2.408 Å for Ln = Nd^{3+} (Table IV) compared to the Pr—O(phenolate) = 2.263 Å found in the 1:1 cyclic Schiff base (L'') [2]. The Ln—O(nitrate) [2] and Ln—O(hydroxyl/

TABLE II. Coordinates for Pr Schiff Base Complex

Atom	x	y	z	B (Å^2)
Pr	0.25595(6)	0.36550(5)	0.23935(4)	3.78(1)
O1	0.5069(7)	0.2685(7)	0.1750(5)	5.9(2)
O2	0.2545(7)	0.3218(6)	0.1016(4)	5.0(2)
O3	0.1636(7)	0.3626(6)	0.3806(4)	4.4(2)
O4	0.4481(7)	0.3093(7)	0.3394(5)	5.9(2)
O5	0.0600(6)	0.3177(5)	0.2368(4)	3.9(2)

(continued)

TABLE II. *(continued)*

Atom	x	y	z	B (Å^2)
O6	0.3315(7)	0.1658(6)	0.2796(5)	5.2(2)[a]
O7	0.0467(8)	0.5255(6)	0.1578(5)	5.0(2)
O8	0.0692(9)	0.5545(7)	0.2807(5)	6.1(3)
O9	−0.099(1)	0.6764(7)	0.2093(6)	7.5(3)
N1	0.0356(9)	0.3376(8)	0.0293(6)	5.0(3)
N2	−0.1868(8)	0.4120(7)	0.1702(5)	3.7(2)
N3	−0.2555(8)	0.4575(6)	0.2996(5)	3.7(2)
N4	−0.0971(8)	0.4341(6)	0.4437(5)	3.7(2)
N5	0.0040(9)	0.5866(7)	0.2154(6)	5.1(3)
C1	0.557(1)	0.220(1)	0.1141(8)	6.2(4)
C2	0.483(1)	0.2055(9)	0.0499(7)	4.7(3)
C3	0.563(1)	0.138(1)	−0.0108(7)	5.1(3)
C4	0.501(1)	0.1143(9)	−0.0730(7)	5.2(3)
C5	0.595(1)	0.038(1)	−0.1373(8)	6.5(4)
C6	0.358(1)	0.1576(9)	−0.0720(7)	5.1(3)
C7	0.271(1)	0.2283(9)	−0.0150(6)	4.4(3)
C8	0.331(1)	0.2564(9)	0.0490(7)	4.3(3)
C9	0.123(1)	0.2717(9)	−0.0197(7)	4.8(3)
C10	−0.119(1)	0.382(1)	0.0233(7)	5.7(3)
C11	−0.187(1)	0.351(1)	0.0996(7)	5.2(3)
C12	−0.2331(9)	0.3685(8)	0.2494(6)	3.8(3)
C13	−0.284(1)	0.5351(9)	0.1619(8)	5.4(3)
C14	−0.343(1)	0.5584(9)	0.2490(8)	5.3(3)
C15	−0.311(1)	0.4455(9)	0.3826(7)	4.2(3)
C16	−0.251(1)	0.4961(9)	0.4395(7)	4.5(3)
C17	−0.0390(9)	0.3767(7)	0.5100(7)	3.5(2)
C18	0.1072(9)	0.3115(8)	0.5172(6)	3.5(2)
C19	0.156(1)	0.2509(8)	0.5934(7)	4.0(3)
C20	0.295(1)	0.1878(9)	0.6068(7)	4.5(3)
C21	0.345(1)	0.123(1)	0.6909(7)	6.3(4)
C22	0.391(1)	0.1887(9)	0.5421(7)	4.7(3)
C23	0.352(1)	0.2491(9)	0.4655(7)	4.3(3)
C24	0.208(1)	0.3095(8)	0.4501(6)	3.6(2)
C25	0.461(1)	0.258(1)	0.4069(7)	5.8(4)
C26	−0.1234(9)	0.2591(8)	0.2814(6)	3.4(2)
C27	−0.165(1)	0.1798(9)	0.3197(7)	4.6(3)
C28	−0.071(1)	0.0800(9)	0.3585(8)	5.3(3)
C29	−0.124(1)	−0.005(1)	0.404(1)	8.5(5)
C30	0.068(1)	0.0626(9)	0.3526(8)	5.2(3)
C31	0.116(1)	0.1409(8)	0.3114(7)	3.9(3)
C32	0.021(1)	0.2423(8)	0.2752(6)	3.4(2)
C33	0.265(1)	0.1125(9)	0.3082(7)	4.8(3)
Na1	1/2	1/2	0	6.2(2)
N1B	−0.016(2)	0.973(1)	0.074(1)	3.8(4)[a]
Cl(1)	0.3138(4)	0.7336(3)	0.3964(3)	7.9(1)
O1A	0.366(1)	0.7945(9)	0.3393(8)	11.1(4)
O2A	0.421(2)	0.655(1)	0.440(1)	17.6(7)
O3A	0.226(2)	0.791(1)	0.4580(9)	15.8(6)
O4A	0.257(1)	0.679(1)	0.3567(9)	23.1(4)
O1W	0.3482(9)	0.5070(8)	0.1759(7)	8.8(3)
O3W	0.235(2)	0.730(2)	0.179(1)	22.9(9)
O1B	0.0292	0.9179	−0.0195	8[a]
O4B	0.0546	0.9179	0.0253	8[a]
O2B	−0.0820	1.1250	−0.0625	8[a]
O3B	0.0820	1.0410	−0.1464	8[a]
O5B	0.0290	0.9375	0.1680	8[a]
O6B	−0.1279	1.0636	0.0539	8[a]

[a] N1B half-occupied; others 1/4-occupied.

TABLE III. Coordinates for Nd Complex

Atom	x	y	z	B (Å^2)
Nd	0.3977(1)	1/4	0.1046(1)	3.02(2)
O1	0.2450(9)	0.3273(6)	0.1888(8)	4.9(2)
O2	0.4655(9)	0.3797(6)	0.1291(8)	4.8(2)
O3	0.643(1)	1/4	0.151(1)	4.7(3)
O4	0.518(1)	1/4	0.323(1)	4.5(3)
N1	0.666(1)	0.0549(7)	0.0748(9)	4.3(2)
N2	0.813(1)	0.1866(6)	0.0252(9)	3.6(2)
C1	0.262(1)	0.1141(9)	0.248(1)	4.6(3)
C2	0.367(1)	0.0585(8)	0.256(1)	3.8(3)
C3	0.462(1)	0.0630(8)	0.194(1)	3.7(3)
C4	0.558(1)	0.0036(8)	0.207(1)	3.9(3)
C5	0.561(1)	−0.0592(9)	0.283(1)	4.9(3)
C18	0.761(2)	1/4	0.358(2)	3.6(4)
C19	0.758(2)	1/4	0.241(1)	2.6(3)
C20	1.161(4)	1/4	0.536(3)	12(1)
C21	0.640(2)	1/4	0.395(2)	3.8(4)
O1W	0.162(1)	1/4	−0.055(1)	5.7(3)
O1A	0.4288(9)	0.3095(6)	−0.0801(8)	5.2(2)
O2A	0.434(1)	1/4	−0.239(1)	6.1(4)
N1A	0.431(2)	1/4	−0.137(1)	4.4(4)
N2A	0.004(2)	0.406(1)	0.778(2)	14.5(8)
O3A	0.093(2)	0.387(1)	0.875(2)	14.8(6)
O4A	−0.075(3)	0.371(2)	0.688(2)	23(1)
O5A	−0.017(3)	0.475(2)	0.755(2)	23(1)
C6	0.466(1)	−0.0623(9)	0.344(1)	5.0(3)
C7	0.367(1)	−0.0040(8)	0.328(1)	4.4(3)
C8	0.460(2)	−0.131(1)	0.423(1)	6.1(4)
C9	0.656(1)	0.0015(8)	0.148(1)	4.1(3)
C10	0.769(1)	0.0513(9)	0.013(1)	4.5(3)
C11	0.879(1)	0.1135(8)	0.060(1)	4.2(3)
C12	0.780(1)	0.2075(9)	−0.101(1)	5.1(3)
C13	0.891(2)	1/4	0.095(2)	3.7(4)
C14	0.887(2)	1/4	0.222(2)	3.5(4)
C15	1.013(2)	1/4	0.318(2)	5.2(5)
C16	1.016(3)	1/4	0.441(3)	9.3(8)
C17	0.890(2)	1/4	0.458(2)	6.5(6)

water) [18–20] given in Tables IV and V are normal. The Ln—O(aldehyde) distances are also normal when compared with those of lanthanide—carbonyl compounds with adjustments for differences in the Ln^{3+} coordination number [21]. For example calculated Pr—O(carbonyl) = 2.49 Å for nonacoordinate Pr^{3+} [20, 21] which is in agreement with the observed average in this study of 2.523 Å.

Generally the distances within the ligand L′ and the nitrate anion (Tables III and IV) are comparable to those found earlier in the complex of Pr^{3+} and L″ [2]. However, the C=O and C—O(phenolate) distances in the complex of Nd^{3+} and L′ have comparable magnitudes 1.25–1.27 Å (average in both cases = 1.262 Å). This reflects a diminished double bond character in carbonyl bonds for which values of 1.21–1.23 Å [19, 22] are expected (as found for the Pr^{3+} complex (Fig. 1 and Table III)). The short C—O(phenolate) distances reflect an increased double

TABLE IV. Selected Bond Angles and Distances in [Pr(H₃L′)-(NO₃)(OH)]$^+$

Distances (Å)		Angles (°) (e.s.d. = 0.1–0.2)	
Pr—O1	2.583(5)	O1—Pr—O2	67.6(1)
Pr—O2	2.409(4)	O1—Pr—O3	131.5(1)
Pr—O3	2.434(4)	O1—Pr—O4	66.1(2)
Pr—O4	2.520(5)	O1—Pr—O5	128.2(2)
Pr—O5	2.388(4)	O1—Pr—O6	73.5(2)
Pr—O6	2.465(5)	O1—Pr—O7	123.0(2)
Pr—O7	2.664(5)	O1—Pr—O8	143.5(2)
Pr—O8	2.591(5)	O1—Pr—O1W	69.4(2)
Pr—O1W	2.535(6)	O2—Pr—O3	147.5(2)
O1—C1	1.211(8)	O2—Pr—O4	132.8(2)
O2—C8	1.274(8)	O2—Pr—O5	73.9(1)
O3—C24	1.285(7)	O2—Pr—O6	86.3(2)
O4—C25	1.217(9)	O2—Pr—O7	68.9(2)
O5—C32	1.308(7)	O2—Pr—O8	117.3(2)

(continued)

TABLE IV. *(continued)*

Distances (Å)		Angles (°) (e.s.d. = 0.1–02)	
O6–C33	1.216(8)	O2–Pr–O1W	86.6(2)
O7–N5	1.253(7)	O3–Pr–O4	68.5(1)
O8–N5	1.257(7)	O3–Pr–O5	74.2(1)
O9–N5	1.234(7)	O3–Pr–O6	77.6(2)
N1–C9	1.277(8)	O3–Pr–O7	104.7(1)
N1–C10	1.479(8)	O3–Pr–O8	65.5(2)
N2–C11	1.495(8)	O3–Pr–O1W	123.0(2)
N2–C12	1.484(8)	O4–Pr–O5	132.0(2)
N2–C13	1.528(9)	O4–Pr–O6	72.6(2)
N3–C12	1.454(8)	O4–Pr–O7	149.1(2)
N3–C14	1.479(8)	O4–Pr–O8	105.2(2)
N3–C15	1.448(8)	O4–Pr–O1W	85.5(2)
N4–C16	1.477(8)	O5–Pr–O6	70.7(1)
N4–C17	1.294(7)	O5–Pr–O7	69.0(1)
C1–C2	1.44(1)	O5–Pr–O8	84.9(2)
C2–C3	1.394(9)	O5–Pr–O1W	141.3(2)
C2–C8	1.448(9)	O6–Pr–O7	137.0(2)
C3–C4	1.39(1)	O6–Pr–O8	140.2(2)
C4–C5	1.54(1)	O6–Pr–O1W	142.1(2)
C4–C6	1.36(1)	O7–Pr–O8	48.4(1)
C6–C7	1.390(9)	O7–Pr–O1W	73.0(2)
C7–C8	1.427(9)	O8–Pr–O1W	74.7(2)
C7–C9	1.414(9)		
C10–C11	1.487(9)		
C12–C26	1.502(8)		
C13–C14	1.52(1)		
C15–C16	1.523(9)		
C17–C18	1.417(8)		
C18–C19	1.419(8)		
C18–C24	1.445(8)		
C19–C20	1.366(9)		
C20–C21	1.548(9)		
C20–C22	1.393(9)		
C22–C23	1.406(9)		
C23–C24	1.414(8)		
C23–C25	1.46(1)		
C26–C27	1.372(9)		
C26–C32	1.428(8)		
C27–C28	1.40(1)		
C28–C29	1.55(1)		
C28–C30	1.367(9)		
C30–C31	1.412(9)		
C31–C32	1.401(8)		
C31–C33	1.440(9)		

bond character compared to the values of 1.302 Å found in the Pr^{3+} complex of L″ [2], 1.35 Å for [Ce(catecholate)$_4$] [23] and 1.34–1.37 Å in Sm-(salicylate)$_3$ [24] in which less or no double bond character is expected [25, 26]. Whereas increased double bond character of C–O(phenolate) in L″ was attributed to resonance with one C=N bond [2], several C=O and C=N bonds are available for L′ thus their resonance with C–O(phenolate) results in greater double bond character and thus a much shorter C–O-(phenolate) bond (Tables III and IV). The C–O-(phenolate) bonds are shorter for the Nd^{3+} complex

TABLE V. Selected Interatomic Distances and Angles in the $[Nd(H_3L')(NO_3)(OH_2)]^{2+}$ Ion

Distances (Å)		Angles (°)	
Nd–O1	2.539(5)	O1–Nd–O1′	65.9(2)
Nd–O2	2.408(6)	O1–Nd–O2	67.5(2)
Nd–O3	2.365(7)	O1–Nd–O2′	131.7(2)
Nd–O4	2.466(7)	O1–Nd–O3	130.7(2)
Nd–O1W	2.486(8)	O1–Nd–O4	74.0(2)
Nd–O1A	2.569(5)	O1–Nd–O1W	75.1(2)
O1–C1	1.243(9)	O1–Nd–O1A	113.2(2)
O2–C3	1.291(8)	O1–Nd–O1A′	147.6(2)
O3–C19	1.28(1)	O2–Nd–O2′	148.7(2)
O4–C21	1.24(1)	O2–Nd–O3	74.7(1)
N1–C9	1.319(9)	O2–Nd–O4	81.8(1)
N1–C10	1.480(9)	O2–Nd–O1W	104.6(1)
N2–C11	1.463(9)	O2–Nd–O1A	65.7(2)
N2–C12	1.476(9)	O2–Nd–O1A′	112.7(2)
N2–C13	1.464(8)	O3–Nd–O4	70.2(2)
C1–C2	1.44(1)	O3–Nd–O1W	146.8(3)
C2–C3	1.422(9)	O3–Nd–O1A	76.2(2)
C2–C7	1.41(1)	O4–Nd–O1W	143.0(3)
C3–C4	1.41(1)	O4–Nd–O1A	138.2(2)
C4–C5	1.44(1)	O1W–Nd–O1A	73.7(2)
C4–C9	1.42(1)	O1A–Nd–O1A′	49.0(3)
C5–C6	1.40(1)		
C6–C7	1.42(1)		
C6–C8	1.56(1)		
C10–C11	1.54(1)		
C12–C12′	1.52(2)		
C13–C14	1.54(1)		
C14–C15	1.38(1)		
C14–C19	1.41(1)		
C15–C16	1.45(2)		
C16–C17	1.37(2)		
C16–C20	1.52(2)		
C17–C18	1.43(2)		
C18–C19	1.39(1)		
C18–C21	1.44(1)		
N1A–O1A	1.266(7)		
N1A–O2A	1.23(1)		

(average = 1.262 Å) than those of the Pr^{3+} complex (average = 1.289 Å), the latter having a coordinated OH⁻ rather than H$_2$O. Consistent with this observation, the C–O(aldehyde) are normal C=O (average 1.215 Å) for the Pr^{3+} complex but longer for the Nd^{3+} complex (average 1.262 Å).

The bond angles in the five-membered ring are generally smaller (100.3° at C12, 103.6° at N3 and C13, 104.5° at N2 and 104.0° at C14 for the Pr^{3+} complex; 100.0° at C13, 104.8° at C12 and 105.5° at N2 for the Nd^{3+} complex) than sp^3 angles found outside this saturated five-membered ring (110–116°). This indicates strain within the five-membered ring formed by condensation of one aldehyde group and two adjacent secondary amines (Figs. 1 and 2).

A substantial quantity of the complex of Nd^{3+} and L′, $[Nd(H_4L')(NO_3)(OH_2)]Cl_3$, was prepared by a

template procedure, and taken through hot recrystallization processes which it survived. This indicates that the complexes of L′ are stable in solution.

Discussion

The results described above provide evidence that dinuclear complexes of L are unstable in solution. Probably the complexes lose one of the two lanthanides in solution and subsequently hydrolysis occurs at C=N bonds and condensation with carbonyls occurs at adjacent secondary amine (NH) sites to yield, among other products, more stable mononuclear complexes of L′. The reactivity of the complexes of L depends very much on the manner in which L coordinates to Ln^{3+}; thus off-white complexes do not yield complexes of L′ when dissolved in alcoholic sodium acetate and solid orange/yellow complexes are not attacked by alcoholic 2,6-diformyl-*p*-cresol. The importance of the detailed coordination scheme of L to Ln^{3+} on the properties of their complexes is also shown by the magnetic, electronic absorption, ligand fluorescence and Eu^{3+} luminescence properties of complexes of L reported elsewhere [3]. The fact that the complexes of L′ were prepared and successfully taken through recrystallization processes indicates that the mere presence of a C=N bond in Schiff's base ligand does not automatically mean that ligand and its complexes must be as extremely unstable as complexes of L have turned out to be. In fact the volume of work done on many Schiff base complexes (*vide supra*) supports the view that Schiff bases are stabilized by complexation to Ln^{3+}. It thus appears that trapping a pair of Ln^{3+} ions in a macrocycle requires additional ligand features to yield solution stable species. Actually, solution instability is a major problem of most of the dinuclear complexes of multiply charged cations for which electrostatic bonding is predominant. Whereas dinuclear complexes of alkali metals are easily worked up in solutions to yield X-ray diffraction quality crystals [27, 28], dinuclear complexes of Ba^{2+} with several Schiff bases [29] and Ln^{3+} with a tricyclic cryptand [30], a pyridino alcoxide Schiff base [31], a phenolic Schiff base [1, 2] or another 2:2 Schiff base derived from 2,6-diacetylpyridine and carbohydrazide [33] have presented some difficulties. Even the mass spectra of complexes of L, show abundant Ln(HL)-$(NO_3)^+$, LnL^+ and H_3L^+ species but not those containing Ln–Ln pairs. Repulsive Ln^{3+}–Ln^{3+} interactions which are strong when the two cations are trapped in the same macrocycle are probably the major source of instability so that when one of them is leached out of the macrocycle, a series of reactions occur leading to new mononuclear complexes.

Secondary amines and alcohols generally add easily to C=N bonds to yield smaller macrocyles which offer a better fit to coordinated cations [15, 16, 29, 33, 34]. Also, secondary amines are known to condense with carbonyls in the absence of metal ions [35, 36]. However, the condensation processes involving adjacent secondary amines which lead to L′ are different and are to our knowledge the first examples of carbonyl-secondary amine condensation templated by metal ions. In fact in the absence of the metal ions, secondary amines have an extensive and complex chemistry [16] involving condensation and cyclization. It is thus worthwhile to consider coupling template condensation of secondary amines to future syntheses of new macrocyclic and macroacyclic ligands.

Conclusions

Homodinuclear lanthanide complexes of Schiff base L are unstable in solution. The complexes lose one of the trapped cations and are hydrolyzed at C=N sites to C=O; in the presence of limited amounts of water they undergo condensation with carbonyls and possibly other reactions at the secondary amine sites to yield among other products, mononuclear complexes of L′. The detailed coordination scheme of L to Ln^{3+} influences substantially the reaction mechanisms of L in solution. The fact that condensation at secondary amine sites can be templated by metal ions deserves further attention in the search for novel complexing agents.

Supplementary Material

Tables of structure factors, anisotropic thermal parameters, coordinates for H atoms, bond angles and distances not included in this report have been deposited with the British Library Document Supply Centre.

Acknowledgements

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