

Schiff Base Complexes of the Lanthanoids and Actinoids. Part 2^a. Lanthanoid(III) and Cerium(IV) Nitrate Complexes with the Zwitter-ionic Form of NN'-Ethylenebis(salicylideneimine) and Related Bases

JOSEPH I. BULLOCK and HEIDAR-ALI TAJMIR-RIAHI

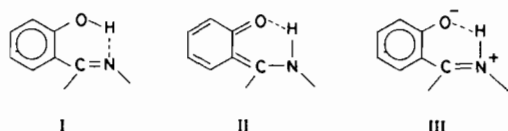
Department of Chemistry, The University of Surrey, Guildford GU2 5XH, U.K.

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The Schiff bases form complexes of the types $\text{Ln}(\text{H}_2\text{L})_2(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Gd},$ and Yb , $\text{H}_2\text{L} =$ the charge-separated (zwitter-ionic) form of the Schiff base, $n = 0, 1,$ or 2), $\text{Nd}_2(\text{H}_2\text{L})_3(\text{NO}_3)_6$, and $\text{Ce}(\text{H}_2\text{L})_2(\text{NO}_3)_4 \cdot \text{H}_2\text{O}$. Because of marked spectral similarities with $\text{Ca}(\text{H}_2\text{L})(\text{NO}_3)_2$, the Schiff bases co-ordinate through the negatively-charged oxygen and not the nitrogen atoms which carry the protons transferred from the phenolic groups on co-ordination. The nitrate groups are bidentate. The Nd^{III} and La^{III} complexes have co-ordination numbers in the range 10–12 as deduced from a hypersensitive transition for the Nd compounds and an isomorphous relationship.

Introduction

Numerous complexes of the lanthanoids, actinoids, Ti^{IV} , Zr^{IV} , Hf^{IV} , Sn^{IV} , Co^{II} , and Fe^{III} with Schiff bases containing apparently unionised phenolic groups have been prepared (see Part 1 of this series [1] and references therein). A typical example would have the analytical composition $\text{Nd}(\text{H}_2\text{L})_2\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ where $\text{H}_2\text{L} = \text{NN}'$ -ethylenebis(salicylideneimine), (H_2salen). Some authors [2] suppose that the Schiff base is co-ordinated through oxygen since an enol-imine (I) to keto-enamine (II) tautomeric conversion is possible; evidence for this came from infrared and ultraviolet spectroscopy. Others [1, 3–5] interpreted essentially identical



infrared results in terms of co-ordination through the azomethine nitrogen atoms only with the ligand

remaining in the enol-imine form in the complexes as was found [6] in the solid phase for the free base NN' -phenylenebis(salicylideneimine) from X-ray crystallography. Until recently no crystallographic work was available to resolve this problem.

The structure [7] of $\text{Ca}(\text{H}_2\text{L})(\text{NO}_3)_2$, $\text{H}_2\text{L} = \text{NN}'$ -propane-1,3-diylbis(salicylideneimine), ($\text{H}_2\text{sal-1,3pn}$), has been determined recently in which the Schiff base is best described by the third tautomer (III), namely, the charge-separated (zwitter-ionic) form. Co-ordination takes place through charged phenolic oxygen atoms (and not the nitrogen atoms) and bidentate nitrate groups. The changes observed on comparing the i.r. spectra of this compound and the free Schiff base in the C=N stretching region are the same as for the other [1–5] compounds (see below).

Results and Discussion

This paper describes 22 nitrate complexes of the trivalent lanthanoids and Ce^{IV} with the bases $\text{H}_2\text{-salen}$, ($\text{H}_2\text{sl-1,3pn}$, NN' -propylenebis(salicylideneimine)), ($\text{H}_2\text{sal-1,2pn}$), and NN' -hexane-1,6-diylbis(salicylideneimine), ($\text{H}_2\text{sal-1,6hex}$). The ligand $\text{H}_2\text{sal-1,3pn}$ has been used previously [2] in the preparation of $\text{Ln}(\text{H}_2\text{L})_2(\text{NO}_3)_3$, ($\text{Ln} = \text{La-Sm}$) and $\text{Ln}_2(\text{H}_2\text{L})_3(\text{NO}_3)_6$, ($\text{Ln} = \text{Eu-Lu}$) – see experimental section.

Analytical results are given in Table I. Only bis-complexes (2:1) were identified, $\text{Ln}(\text{H}_2\text{L})_2(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ and $\text{Ce}(\text{H}_2\text{L})_2(\text{NO}_3)_4 \cdot \text{H}_2\text{O}$, except for Nd^{III} where 3:2 complexes, $\text{Nd}_2(\text{H}_2\text{L})_3(\text{NO}_3)_6$, were prepared in addition in marked contrast [1] to the halide results where 1:1, 3:2, 2:1, and 3:1 compounds were reported (see also experimental section). The experimental method is the same as that used to prepare $\text{Ca}(\text{H}_2\text{L})(\text{NO}_3)_2$.

Infrared Spectroscopy

2500–650 cm^{-1}

The C=N stretching vibration for the complexes of $\text{H}_2\text{sal-1,3pn}$ are compared in Table II. The other

^aFor Part 1 see ref. 1.

TABLE I. Analytical Data (%).^a

| No. | Compound | M | C | H | N |
|---------|--|------------|------------|----------|------------|
| (i) | La(H ₂ salen) ₂ (NO ₃) ₃ ·2H ₂ O | 15.7(15.5) | 42.3(42.8) | 3.6(4.0) | 10.9(10.9) |
| (ii) | La(H ₂ sal-1,2pn) ₂ (NO ₃) ₃ ·H ₂ O | 15.5(15.3) | 45.0(45.0) | 4.2(4.2) | 10.8(10.8) |
| (iii) | La(H ₂ sal-1,3pn) ₂ (NO ₃) ₃ ·2H ₂ O | 15.4(15.0) | 43.3(44.1) | 4.1(4.4) | 10.2(10.6) |
| (iv) | La(H ₂ sal-1,6hex) ₂ (NO ₃) ₃ ·H ₂ O | 14.2(14.0) | 47.5(48.4) | 5.0(5.1) | 9.8(9.9) |
| (v) | Pr(H ₂ salen) ₂ (NO ₃) ₃ | 16.2(16.3) | 44.3(44.5) | 3.7(3.7) | 11.0(11.4) |
| (vi) | Pr(H ₂ sal-1,2pn) ₂ (NO ₃) ₃ ·H ₂ O | 15.3(15.5) | 44.5(44.9) | 3.8(4.2) | 10.6(10.8) |
| (vii) | Pr(H ₂ sal-1,3pn) ₂ (NO ₃) ₃ ·H ₂ O | 15.4(15.5) | 45.1(44.9) | 3.8(4.2) | 10.4(10.8) |
| (viii) | Pr(H ₂ sal-1,6hex) ₂ (NO ₃) ₃ | 14.2(14.4) | 49.5(49.2) | 4.8(4.9) | 9.5(10.0) |
| (ix) | Nd ₂ (H ₂ salen) ₃ (NO ₃) ₆ | 19.4(19.7) | 39.0(39.3) | 3.3(3.3) | 11.3(11.5) |
| (x) | Nd(H ₂ salen) ₂ (NO ₃) ₃ ·2H ₂ O | 16.1(16.0) | 41.9(42.6) | 3.7(4.0) | 10.6(10.8) |
| (xi) | Nd ₂ (H ₂ sal-1,2pn) ₃ (NO ₃) ₆ | 18.9(19.1) | 40.4(40.7) | 3.6(3.6) | 11.0(11.1) |
| (xii) | Nd(H ₂ sal-1,3pn) ₂ (NO ₃) ₃ ·2H ₂ O | 15.4(15.5) | 43.2(43.9) | 4.0(4.3) | 10.4(10.5) |
| (xiii) | Nd(H ₂ sal-1,6hex) ₂ (NO ₃) ₃ | 14.5(14.7) | 49.5(49.1) | 5.1(4.9) | 9.7(10.0) |
| (xiv) | Gd(H ₂ salen) ₂ (NO ₃) ₃ | 17.7(17.9) | 44.3(43.7) | 3.7(3.7) | 11.2(11.1) |
| (xv) | Gd(H ₂ sal-1,2pn) ₂ (NO ₃) ₃ ·H ₂ O | 16.8(17.0) | 43.9(44.1) | 3.8(4.1) | 10.4(10.6) |
| (xvi) | Gd(H ₂ sal-1,3pn) ₂ (NO ₃) ₃ ·H ₂ O | 16.8(17.0) | 44.3(44.1) | 3.7(4.1) | 10.3(10.6) |
| (xvii) | Yb(H ₂ salen) ₂ (NO ₃) ₃ | 19.2(19.3) | 43.1(42.9) | 3.6(3.6) | 10.3(10.9) |
| (xviii) | Yb(H ₂ sal-1,6hex) ₂ (NO ₃) ₃ | 17.0(17.2) | 47.5(47.7) | 4.9(4.8) | 9.5(9.7) |
| (xix) | Ce(H ₂ salen) ₂ (NO ₃) ₄ ·H ₂ O | 14.7(14.9) | 40.9(40.8) | 3.8(3.6) | 11.3(11.9) |
| (xx) | Ce(H ₂ sal-1,2pn) ₂ (NO ₃) ₄ ·H ₂ O | 14.5(14.4) | 41.8(42.1) | 4.0(3.9) | 11.5(11.5) |
| (xxi) | Ce(H ₂ sal-1,3pn) ₂ (NO ₃) ₄ ·H ₂ O | 14.6(14.4) | 42.5(42.1) | 4.0(3.9) | 11.5(11.5) |
| (xxii) | Ce(H ₂ sal-1,6hex) ₂ (NO ₃) ₄ ·H ₂ O | 13.4(13.3) | 45.5(45.5) | 4.7(4.8) | 10.3(10.6) |

^aCalculated % in parentheses.

TABLE II. Infrared Spectroscopy (cm⁻¹).^a

| Compound Number | C=N Stretching ^a | Nitrate Vibrations ^b | | | |
|-----------------|-----------------------------|---------------------------------|---------|---------|---------|
| | | ν_1 | ν_2 | ν_4 | ν_6 |
| (iii) | 1645 | 1482 | 1030 | 1282 | 820 |
| (vii) | 1645 | 1480 | 1025 | 1280 | 820 |
| (xii) | 1650 | 1475 | 1030 | 1285 | 820 |
| (xvi) | 1645 | 1480 | 1025 | 1282 | 812 |
| (xxi) | 1645 | 1480 | 1025 | 1282 | 812 |

^aH₂sal-1,3pn as example, 1633 cm⁻¹; Ca(H₂sal-1,3pn)(NO₃)₂, 1645 cm⁻¹. ^b ν_1 , strong and broad; ν_2 , medium-strong; ν_4 , strong and broad; ν_6 , medium-weak.

compounds had very similar spectra in this region. As before [1–5, 7], the C=N vibration increased in frequency (by 5–20 cm⁻¹) on complex formation. It has been predicted and demonstrated by experiment [8] that C=N⁺ groups have in general higher frequencies than the parent C=N groups. Thus the results are consistent with the presence of charge-separated forms and these and the other complexes [1–5, 7] are likely to be structurally related in that the negatively charged phenolic oxygen atoms rather

than the positively charged nitrogen atoms are co-ordinated.

There was no evidence for ionic nitrate [9] as shown by the absence of broad, strong absorption near 1385 cm⁻¹. The organic ligands had sharp, medium-strong absorption at much the same frequencies as those expected for co-ordinated nitrate in C_{2v} symmetry (except ν_3 , ν_5 , and ν_6 using the labelling in ref. 9). However, on comparing the spectra of the free ligands and the halide complexes with those of the nitrate complexes, the nitrate spectra were dominated by broad, strong absorption from ν_1 , ν_2 , and ν_4 of the nitrate group in low symmetry such that the underlying ligand absorption was obscured. The nitrate vibrations (Table II) are thus listed with confidence. Since these spectra were essentially the same as that [7] of Ca(H₂sal-1,3pn)(NO₃)₂ and monodentate nitrate has never been observed crystallographically for a lanthanoid complex, the nitrate groups are bidentate. The weak fundamentals ν_3 and ν_5 were not observed because of strong ligand absorption (700–800 cm⁻¹).

Because of strong absorption from nitrate near 1280 cm⁻¹ it was not possible to assign the C–O stretching vibration. This changed only slightly, if at all, for the halide and other spectra [1–5].

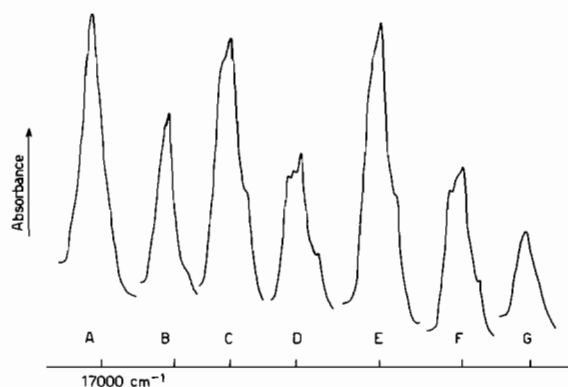


Fig. 1. The hypersensitive transition near 17000 cm^{-1} for A, $\text{Mg}_3\text{Nd}_2(\text{NO}_3)_{12}\cdot 24\text{H}_2\text{O}$; B, $\text{Nd}(\text{bipy})_2(\text{NO}_3)_3$; C, Compound no. (ix); D, (x); E, (xi); F (xii); and G, (xiii).

$4000\text{--}2500\text{ cm}^{-1}$

There was a broad absorption centred at 3000 cm^{-1} as in [7] $\text{Ca}(\text{H}_2\text{sal-1,3pn})(\text{NO}_3)_2$ presumably derived from an $[\text{N-H}]^+$ vibration with hydrogen bonding to the negatively charged phenolic oxygen atom. The free ligands have a strong, intramolecular hydrogen bond ($\text{O-H}\dots\text{N}$) which gives rise [1] to a broad absorption near 2700 cm^{-1} . The shift to 3000 cm^{-1} is presumably caused by the proposed tautomeric transition between the free and co-ordinated base. For the hydrates an additional broad band near 3400 cm^{-1} was assigned to water.

Co-ordination Numbers for Nd^{III}

The hypersensitive transition, $^4\text{I}_{9/2} \rightarrow ^4\text{G}_{5/2}$, $^2\text{G}_{7/2}$ (near 17000 cm^{-1}), shows differences in shape and intensity with variation in co-ordination number [10–12]. The band is more intense and much sharper with fewer shoulders for compounds with co-ordination number 10 or more as in the 10-co-ordinate $\text{Nd}(\text{bipy})_2(\text{NO}_3)_3$ and the 12-co-ordinate $\text{Mg}_3\text{Nd}_2(\text{NO}_3)_{12}\cdot 24\text{H}_2\text{O}$. The five Nd^{III} compounds had spectra very similar to those of the two compounds mentioned above (Fig. 1) and there was little similarity with the halide spectra [1]. Thus the nitrates have co-ordination numbers between 10 and 12. Since reflectance spectra were used band shapes but not intensities were considered.

Since the nitrate groups are bidentate, 10-, 11-, or 12-co-ordination is possible using four oxygen (phenolic), six oxygen (nitrate), and some oxygen (water) atoms as required. Co-ordinated, bidentate nitrate groups would thus account for six available positions around the metal ion so that it is hardly surprising that the range of compounds for the nitrates is smaller than for the halides [1].

The compounds $\text{La}(\text{H}_2\text{sal-1,6hex})_2(\text{NO}_3)_3$ and $\text{Nd}(\text{H}_2\text{sal-1,6hex})_2(\text{NO}_3)_3$ were isomorphous so that the La^{III} complexes also have high co-ordination numbers. The X-ray powder diffraction photograph of $\text{Yb}(\text{H}_2\text{sal-1,6hex})_2(\text{NO}_3)_3$ was quite different from the other two.

Experimental

Hydrated Ln^{III} nitrates were prepared from the oxides (99.9%); $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ was used as supplied. The complexes were prepared by the stoichiometric addition of the metal nitrate in absolute ethanol to a hot solution of the ligand in the same solvent. A yellow precipitate formed immediately and was filtered off, washed with cold ethanol, and dried (CaCl_2). There was no evidence for stoichiometries other than $\text{H}_2\text{L}:\text{M} = 2:1$ except for Nd (Table I); 1:1 and 3:1 complexes [1] could not be prepared and use of these mole ratios gave the 2:1 or 3:2 (Nd) compounds. No compound could be dissolved without decomposition. Previous work [2] with $\text{H}_2\text{sal-1,3pn}$ gave $\text{Ln}(\text{H}_2\text{L})_2(\text{NO}_3)_3$, ($\text{Ln} = \text{La-Sm}$). We found the same for La, Pr, and Nd except our compounds were hydrated. Also, we found 3:2 compounds only for Nd but with H_2salen and $\text{H}_2\text{sal-1,2pn}$ rather than $\text{H}_2\text{sal-1,3pn}$; 2:1 compounds were found also for Gd, Yb, and Ce^{IV} . We suspect [1] that there was more water in our ethanol than that used in the previous study [2]. Spectroscopic properties and X-ray powder photographs were obtained routinely.

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