

Schiff Base Complexes of the Lanthanoids and Actinoids. Part 3^a. Lanthanoid(III), Cerium(IV), Thorium(IV), and Uranium(IV) Complexes with NN'-Ethylenebis(5-t-butylsalicylideneimine); ¹H N.M.R. and other Spectroscopic Properties

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The Schiff base, *H*₂busalen, forms polymeric *M*₂-(busalen)₃ (*M* = Pr, Nd, Sm, Eu, Gd, and Ho) and monomeric *M*(busalen)₂ (*M* = Ce, Th, and U) complexes which are readily soluble in CDCl₃, a property conferred by the presence of the *t*-butyl groups. The ¹H n.m.r. spectra are reported. Very large shifts to low and high field were observed for the paramagnetic complexes and the U^{IV} spectrum was well-resolved with very little broadening. The lanthanoid(III) complexes (*M* = Pr, Nd, and Sm) are probably eight-coordinate both in solution and the solid state.

Introduction

Although Schiff bases complexes [1, 2] of the lanthanoids(III) and actinoids(IV) have been known for some years investigations of their spectroscopic properties are often hampered by low solubility in

low dielectric organic solvents. When polar organic solvents are used there is usually the possibility of solvent molecules acting as ligands particularly in complexes of the type *M*₂*L*₃, where *M* = a trivalent lanthanoid element and *L* = a doubly-charged anionic ligand such as NN'-ethylenebis(salicylideneiminato), salen, because such complexes which probably contain bridging ligands and are polymeric, are likely to dissolve by reaction with the solvent. The introduction of bulky organic substituents into the phenyl rings of such ligands should increase the solubility of the metal complexes as was found [3] for some manganese(III) complexes. In the present work it was hoped that the introduction of *t*-butyl groups would allow the study of the ¹H n.m.r. spectra of the complexes in non-coordinating solvents.

Results and Discussion

Satisfactory analytical results were obtained (Table I) for the stoichiometries *M*(busalen)₂ and

^aFor Part 2, see previous paper.

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TABLE I. Analytical Data (%).^a

Complex	Found				Calc.			
	C	H	N	M	C	H	N	M
UL ₂	57.8	6.1	5.6	—	58.0	6.0	5.6	—
CeL ₂	64.2	6.8	6.3	15.8	64.3	6.7	6.3	15.6
ThL ₂	58.2	6.1	5.7	23.5	58.3	6.1	5.7	23.5
Pr ₂ L ₃	60.8	6.4	5.9	20.4	61.0	6.4	5.9	19.9
Nd ₂ L ₃	59.9	6.3	5.5	20.0	60.8	6.3	5.9	20.3
Sm ₂ L ₃	58.8	6.2	5.8	20.6	60.2	6.3	5.8	21.0
Eu ₂ L ₃	60.0	6.3	5.8	20.9	60.1	6.3	5.8	21.1
Gd ₂ L ₃	58.7	6.3	6.0	21.0	59.7	6.2	5.8	21.7
Ho ₂ L ₃	58.9	6.2	5.8	22.1	59.0	6.1	5.7	22.5

^aL = NN'-ethylenebis(5-*t*-butylsalicylideneiminato).

TABLE II. ¹H N.m.r. Results for the Tetravalent Metal Ion Complexes.

Complex	Coupling Constant ^a (Hz)		Chemical Shift, δ (ppm) ^b						
	J ₁₂	J ₂₃			Ring Protons			t-Butyl	-OH
			-(CH ₂) ₂ -	-CH=N-	H(1)	H(2)	H(3)		
H ₂ busalen	8.78	2.63	3.90 s ^c	8.33 s	6.87 d	7.33 q	7.18 d	1.27 s	12.97
Ce(busalen) ₂	9.36	2.63	4.46 s	8.46 s	5.97 d	7.08 q	7.06 d	1.17 s	-
Th(busalen) ₂	8.48	2.34	4.20 s	8.25 s	6.26 d	7.15 q	7.04 d	1.19 s	-
U(busalen) ₂	8.82	2.90	-37.47 s	11.15 s	15.76 d	14.44 d	12.04 d	3.74 s	-

^aJ₁₃ is unobserved. ^bChemical shifts are in units of ppm related to TMS as internal standard on the δ scale (*i.e.* low field shifts are taken to be positive). ^cs = singlet, d = doublet, q = quartet.

M₂(busalen)₃. There was no evidence for the presence of water. As we hoped the introduction of the t-butyl substituents rendered the complexes soluble in many low dielectric organic solvents but attempts to recrystallise the lanthanoid(III) complexes resulted in gums which may indicate some decomposition on dissolution (see below).

Polymeric Nature of the Lanthanoid(III) Complexes

For the Pr^{III} complex, molecular weights of 1460, 1740, 2320, 2720, and 3060 were obtained at concentrations 7.75×10^{-4} , 8.13×10^{-4} , 1.15×10^{-3} , 1.50×10^{-3} , and 1.83×10^{-3} M respectively (1 mol = 1416 g based on the empirical formula Pr₂(busalen)₃) in chloroform solution. The conductance (solvent CHCl₃, 1.00×10^{-3} M) was greater than that of the pure solvent. In the same solvent Ce(busalen)₂ gave molecular weights 750 ± 40 in the concentration range 1.10 to 3.72×10^{-3} M (Ce(busalen)₂ requires 900).

X-ray Powder Diffraction Studies

The complexes M₂(busalen)₃ (M = Nd, Pr, Sm) were isomorphous as were the Gd and Ho complexes but the diffraction pattern for Eu₂(busalen)₃ was different from the rest. The thorium and uranium complexes were isomorphous but not with Ce(busalen)₂.

Infrared Spectra

Both types of complex had essentially the same i.r. spectra with the frequency of the C=N stretching vibration (at 1635 cm⁻¹ in the free ligand) falling by *ca.* 15 cm⁻¹ and the C-O stretching vibration (at 1290 cm⁻¹ in the free ligand) increasing by *ca.* 10–20 cm⁻¹ on complex formation. Similar results [4] have been found for metal complexes which are known from crystallographic evidence to contain co-ordinated phenolic oxygen and azomethine nitrogen atoms. A medium band in the spectra of the complexes at 520–530 cm⁻¹, which was absent in the

free ligand spectrum may be assigned to a M–N stretching vibration [5]. There has been a suggestion [6] that mono- and dimeric iron Schiff base complexes may be distinguished by means of i.r. spectroscopy. Monomers had [6] one band (*ca.* 865 cm⁻¹) in the 850–900 cm⁻¹ region whereas dimers showed three (*ca.* 890, 865, and 855 cm⁻¹). All of our complexes have the same spectra with three weak bands (*ca.* 800, 860, and 880 cm⁻¹) and two medium-strong bands (*ca.* 825 and 835 cm⁻¹) in this region except for ML₂ (M = Th and U) for which the weak absorption at 880 cm⁻¹ is split (875 and 890 cm⁻¹).

Coordination Numbers

It would be surprising if the complexes M(busalen)₂ were other than eight coordinate. Dodecahedral stereochemistry has been found [7] for U(salen)Cl₂·2thf (thf = tetrahydrofuran). There is strong evidence that Nd₂(busalen)₃ and hence the Pr and Sm compounds contain eight-coordinate metal ions both in the solution and solid phases. The hypersensitive [8] transition for Nd^{III}, ⁴I_{9/2} → ⁴G_{5/2}, ²G_{7/2}, near 17400 cm⁻¹ is particularly useful. Here, the band shape for solid Nd₂(busalen)₃ was almost identical to that of Nd₂(SO₄)₃·8H₂O which is known [9] to be eight-coordinate and a solution of Nd₂(busalen)₃ in CHCl₃ had a spectrum very similar to that [10] of the ion [Nd(CH₃COCHCOCF₃)₄]⁻ in ethanolic solution.

For Ho^{III}, a band near 21750 cm⁻² is [10] characteristic of seven- or eight-coordination. This was absent in our spectra which may indicate a lower co-ordination number but the tail of a strong charge-transfer absorption is present in this region.

¹H NMR Spectroscopy

All spectra were recorded in CDCl₃ solution; chemical shifts are in units of ppm related to TMS as internal standard on the delta (δ) scale; low field shifts are taken to be positive. The solvent impurity CHCl₃ resonates near 7.3 ppm (variable position).

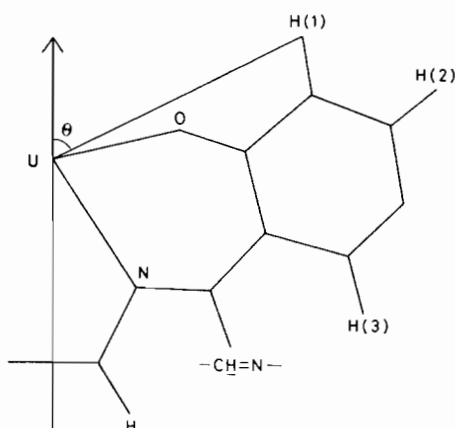


Fig. 1. Model for the co-ordination of uranium(IV) and the Schiff base.

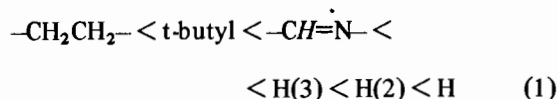
The spectral assignments for H_2 busalen and $M(\text{busalen})_2$, ($M = \text{Ce}$ and Th), were straightforward (Table II). The ring protons (H(1), H(2), and H(3), Fig. 1) gave the expected eight-line spectrum with para-coupling between H(1) and H(3) unobserved in each case. High field shifts were observed for the diamagnetic metal complexes. The coupling constants were as expected. The integrated intensities showed that the single resonance at 3.90 ppm (low field shifts for the complexes) was derived from protons in the ethylene linkage which are equivalent under the prevailing conditions. The remaining resonances (from magnetically equivalent protons of t-butyl, the azomethine protons, and internally-hydrogen bonded protons in $-\text{OH}$ groups) were readily assigned as shown in Table II.

The spectrum of the paramagnetic $\text{U}(\text{busalen})_2$ was greatly shifted with respect to those of the Ce^{IV} and Th^{IV} complexes but with little loss of resolution and insignificant broadening (Table II). As has been suggested previously [11], uranium(IV) offers distinct possibilities as a shift reagent in the resolution of ^1H NMR spectra. The assignment of the spectrum rested partly on integration differences. The integrated intensity of the resonance at -37.47 ppm was exactly twice that of each of the four resonances (three of which were doublets) found between 11.15 and 15.76 ppm and is assigned to the protons in the ethylene linkage. The resonance at 3.74 ppm was clearly derived from equivalent t-butyl protons because of the integrated intensity. Of the remaining resonances three (15.81 and 15.72, 14.49 and 14.39, and 12.06 and 12.02 ppm) were doublets and the fourth (11.15 ppm) a singlet. We assign these to H(1), H(2), H(3), and $-\text{CH}=\text{N}-$ respectively since $J_{12} = J_{21} = 8.8244$ Hz exactly ($\text{Th}(\text{busalen})_2$, $|J_{12}| = 8.4993$ Hz) so that ortho-coupling is confirmed. No sign of meta-coupling was apparent for H(2) but $|J_{23}|$

TABLE III. Relative Shifts for Protons in $\text{U}(\text{busalen})_2$.

	r	θ	Shift Relative to H(3)	
			Found	Calculated
H(1)	4.6	64	1.90	2.11
H(2)	6.5	80	1.46	1.61
H(3)	5.7	117	1.00	1.00
$-\text{CH}=\text{N}-$	4.3	136	0.58	-4.37

= 2.9414 Hz ($\text{Th}(\text{busalen})_2$, $|J_{23}| = 2.3419$ Hz) based on the doublet near 12 ppm. The order in terms of low field shift relative to TMS was:



which is not the same as for H_2 busalen or $\text{Th}(\text{busalen})_2$ (Table II). Clearly the paramagnetic ion gives low and high field shifts which may be caused by magnetic anisotropy within the complex and by changes in the relative angular and radial dependences of individual protons derived from the molecular stereochemistry.

For $\text{U}(\text{busalen})_2$ a model was constructed (Fig. 1) using the U-O and U-N distances and appropriate angles found [7] for $\text{U}(\text{salen})\text{Cl}_2 \cdot 2\text{thf}$ in which the co-ordinated atoms from salen and uranium form an approximate plane, along with mean distances and angles found [12, 13] within co-ordinated salen for iron and cobalt complexes; it was assumed that all atoms (except those in the ethylene linkage) were coplanar and the t-butyl groups ignored. In general, the fit between the metal ion and ligand data was poor. Only one half of a co-ordinated ligand was considered and a symmetry axis passing through the uranium atom and the mid-point between the nitrogen atoms was constructed. The relevant distances (r , Å) and angles (θ , degrees) with respect to the axis are shown in Table III. This crude model shows that the relative shifts in resonance frequency are likely to be strongly angular and distance dependent. By using the relationship [14] $(3\text{Cos}^2\theta - 1) r^{-3}$ a relative order of shifts was calculated (Table III). Changing the bond lengths or angles by $\pm 10\%$ preserved the relative order which was the same as that observed except that the experimental shifts were all to low field. The model shows an opposite field shift for $-\text{CH}=\text{N}-$ because $(3\text{Cos}^2\theta - 1)$ changes sign at $\theta \approx 125^\circ$. To obtain $(3\text{Cos}^2\theta - 1) = 0$, the azomethine carbon atom would only need to be shifted by ca. 0.35 Å from the position shown in Fig. 1. Should $(3\text{Cos}^2\theta - 1) \neq 0$ then the relative shift of $-\text{CH}=\text{N}-$ becomes strongly dependent on r^{-3} as this proton is close to the metal atom.

The ligand and metal atom are rarely strictly coplanar in salen complexes so that a more complex geometric relationship [15] involving all polar quantities (r , θ , ϕ) should be used in rigorous work if bond lengths and angles are accurately known. The ethylene protons were observed as a singlet which may mean that on the n.m.r. time-scale the flexibility of the chain was sufficient to render the protons magnetically equivalent so that their mean positions would be in the plane described in Fig. 1. Such a position is approximately 4.3 Å from U^{IV} and has a θ value ($\approx 165^\circ$) such that $(3\cos^2\theta - 1)$ is large and positive giving rise to large shifts in the opposite sense to those observed for the ring protons. It is interesting to note that H(1), $-CH=N-$, and ethylene hydrogen atoms are almost equidistant from U^{IV} .

Of the trivalent lanthanoid ions studied, Ho should give [14] the largest shifts; if Ho = 100% then the relative shifting powers of the other metal ions are approximately: Pr = 20; Nd = 10; Sm = 2 to 3; Eu = -5 to -10%. For 1H spectra, the broadening effects are [14] typically $Gd \gg Ho \gg Pr \approx Nd \approx Sm \approx Eu$. For $Gd_2(busalen)_3$, very broad absorptions barely discernible above background were observed near 7, 4, and 1 ppm other than a sharp, intense resonance from t-butyl groups (1.2777 ppm; $H_2busalen$ 1.2730 ppm). All of the other spectra had a t-butyl resonance very close to that found for the ligand (Ho 1.2579; Pr 1.2914; Nd 1.2777; Sm 1.2777; Eu 1.2743 ppm) which was the sharpest and most intense absorption in all cases. This could indicate a ligand acting as an end-group or in a dissociated form. Each of the spectra A-E (Fig. 2) had 7 or 8 other narrow, strong absorptions. By inspection and from the resonance frequencies for $H_2busalen$, we assign these to t-butyl protons with non-equivalence derived from the polymeric nature of the complexes. Approximately the same number of lines was found in each case and the relative shifts, which occurred to both low and high field, bear favourable comparison to the order given above. For Ho the lines were much the broadest; typically, near 4 ppm band widths at half height were Ho 40 Hz and Eu or Nd 5 to 10 Hz. For any structure, the t-butyl protons would be furthest from the metal ion.

On examining the spectra in more detail all (except Ho) revealed a large number of relatively weak and broad additional lines: the Eu spectrum was typical and the band heights in spectrum F, Fig. 2, are drawn to one eighth the scale used for spectrum E; the most prominent 35 are illustrated from a total of 50 or 60. These weak bands intermingle to varying extents with the intense ones and were not always well-resolved because of this. For Ho, these additional lines appeared merely as weak, broad absorptions barely discernible above background. For Sm the weak bands covered the range 13 to 0 ppm and between 13 and 3 ppm 32 additional absorptions

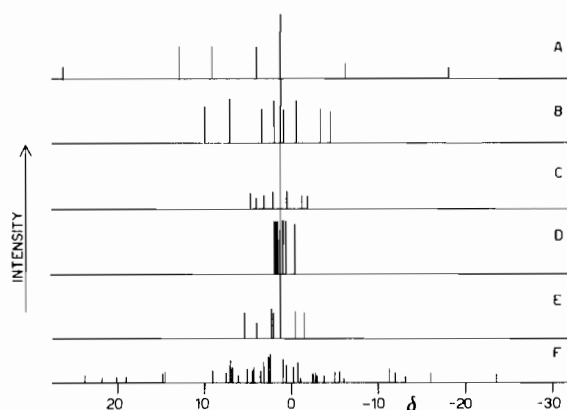


Fig. 2. Hydrogen-1 n.m.r. spectra at 90 MHz of $M_2(busalen)_3$: M = Ho, A; Pr, B; Nd, C; Sm, D; Eu, E and F. The intensity scale for spectrum F is one-eighth of that for E.

were observed with a few others poorly resolved from the strong bands (3 to -0.23 ppm). The integrated intensities in the regions 13 to 3 and 3 to -0.23 ppm were in the approximate ratio 1:2; the ligand requires 18 t-butyl protons to 10 of other types. We thus assign the weak bands to resonances derived from protons other than t-butyl protons. The spectra covered the ranges: Pr 56 to -46; Nd 17 to -3; Sm 13 to 0; Eu 30 to -23 ppm. These very large shifts are consistent with polymeric structures in which protons are likely to be under the influence of at least two paramagnetic centres and the ligands need not be magnetically or chemically equivalent. It is not possible to make further assignments of individual resonances.

For Nd, groups of weak lines near 7 ppm (8.34, 7.37, 7.19, 7.17, 6.93, 6.83 ppm ring protons) and 3.95 ppm ($-CH=N-$) were very close in position to those found for the ligand (8.34, 7.39, 7.36, 7.30, 7.20, 7.18, 6.91, 6.82, and 3.91 ppm) and some were found at identical or very similar positions in the Sm and Pr spectra. Since Sm would give smaller and Pr larger shifts than Nd we assign these to resonances derived from dissociated ligand.

Experimental

NN'-Ethylenebis(5-t-butylsalicylideneimine), $H_2busalen$, was prepared by the addition of an ethanolic solution of ethylenediamine (0.5 mol) to a boiling, ethanolic solution of 5-t-butylsalicylaldehyde (1.0 mol). The yellow solid which precipitated immediately was filtered off, recrystallized (96% ethanol) and dried ($CaCl_2$); m.p. 169-170 °C. Found: C 76.65; H 8.45; N 7.40%; $C_{24}H_{32}N_2O_2$ requires C 75.80; H 8.40; N 7.35%.

None of the metal complexes have been reported previously. Analytical results are given in Table I.

U(busalen)₂

Small portions of Cs₂UCl₆ (0.5 mmol) (prepared from uranium metal, CsCl, and hydrogen chloride) were added to a boiling, stirred solution of the ligand (1.0 mmol) in acetone (70 cm³). Gaseous ammonia was passed through the solution and a white precipitate (CsCl) removed by filtration. On storing the filtrate near 0 °C a brown precipitate was obtained which was removed and dried (CaCl₂). Dark-red Ce(busalen)₂ and pale yellow Th(busalen)₂ were prepared in a similar manner using [NH₄]₂[Ce(NO₃)₆] or Th(NO₃)₄·6H₂O in dimethylformamide solution with the ligand in absolute ethanol. Hydrated lanthanoid nitrates or chlorides in ethanol with the ligand in ethanol yielded pale yellow solids by a similar route. The lanthanum(III) complex could not be prepared by this method. X-ray powder diffraction photographs, molecular weights, conductances, diffuse reflectance and solution electronic spectra, and i.r. spectra were obtained routinely. ¹H NMR spectra were recorded on a Bruker WH-90 Fourier transform spectrometer at 90.02 MHz.

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