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# Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry

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Metal Chelates of Cerium(III), Thorium(IV), and Dioxouranium(VI); Complexes with Some Derivatives of Aryl Schiff Bases

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#### SYNTHESIS AND REACTIVITY IN INORGANIC AND METAL-ORGANIC CHEMISTRY Vol. 33, No. 3, pp. 453–468, 2003

## Metal Chelates of Cerium(III), Thorium(IV), and Dioxouranium(VI); Complexes with Some Derivatives of Aryl Schiff Bases

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#### ABSTRACT

New Ce(III), Th(IV) and U(VI) complexes with the aryl Schiff bases 2hydroxybenzylamine-2'-hydroxybenzylidene (HL<sup>1</sup>), -2'-hydroxynaphthylidene (HL<sup>2</sup>), -2'-hydroxy-5'-bromobenzylidene (HL<sup>3</sup>), -2'hydroxy-5'-chlorobenzylidene (HL<sup>4</sup>), 2'-hydroxy-3',5'-dichlorobenzylidene (HL<sup>5</sup>) and 2'-hydroxy-3-methoxybenzylidene (HL<sup>6</sup>) have been synthesized and characterized by elemental and thermal analyses, molar conductance, magnetic susceptibility, IR, <sup>1</sup>H NMR and electronic spectra. Elemental analyses along with conductometric titrations showed the formation of 1:1 and 1:2 (M:L) complexes while IR, molar conductance and <sup>1</sup>H NMR data proved that these ligands act as monobasic, tridentates for the 1:1 and monobasic, bidentates for the 1:2 complexes with a coordination number of eight in both.

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#### **INTRODUCTION**

Although o,o'-dihydroxyaryl Schiff bases have been recognized as forming stable complexes with transition metal ions<sup>[1-3]</sup> and found to have wide applications in coordination chemistry,<sup>[4,5]</sup> little work has appeared on their complex formation with rare earth metal ions.<sup>[6]</sup> The present paper deals with the preparation and characterization of Ce(III), Th(IV) and U(VI) complexes with some arylidene Schiff bases based of 2-hydroxybenzylamine (shown in Figure 1). The new complexes were investigated by various physico-chemical techniques.

#### **EXPERIMENTAL**

#### **Preparation of the Schiff Bases**

The Schiff bases included in this study were prepared according to our previous work<sup>[7]</sup> by refluxing a mixture of *o*-hydroxybenzylamine and salicy-laldehyde derivatives (1:1 molar ratio) in ethanol in the presence of piperidene.

#### o-Hydroxybenzylamine

o-Hydroxybenzylamine was prepared by dissolving 20 g (0.146 mol) salicylaldoxime in 300 mL of 50% ethanol and reduced by 2.5% sodium amalgam ( $\sim 2.0$  g). The temperature was kept below 55 °C and excess of alkali was continuously neutralized by the addition of dilute HCl. The reaction mixture must be slightly alkaline until the reaction has been completed. The solution was then made slightly acidic, separated from the mercury and evaporated under reduced pressure until sodium chloride began to crystallize. The remaining solution was diluted with water to  $\sim 300$  mL and then transferred to an Erlenmeyer flask containing  $\sim 25$  mL



 $X = H (HL^{1}), 5, C_{6}H_{4} (HL^{2}), 5-Br (HL^{3}), 5-Cl (HL^{4}), 3, 5-Cl_{2} (HL^{5}) and 3-OCH_{3} (HL^{6})$ 

Figure 1. Structure of the Schiff bases.

#### Cerium(III), Thorium(IV), and Dioxouranium(VI)

of diethyl ether. Ammonium hydroxide was added in small portions until a slight excess was present. The mixture was vigorously shaken after each addition for a few minutes whereby the amine began to crystallize on the walls of the flask. The product was removed by filtration and recrystallized from absolute alcohol-petroleum ether (60% v/v ethanol), m.p. 129 °C; yield, 12.23 g (68%).

#### Salicylaldoxime

Salicylaldoxime was prepared by dissolving 20 g (0.164 mol) of salicylaldehyde in 30 mL of ethanol, then added to a solution of 15 g (0.216 mol) of hydroxylamine hydrochloride in 10% Na<sub>2</sub>CO<sub>3</sub> solution (100 ml) whilst cooling in ice. After standing overnight, the solution was acidified with acetic acid, the alcohol was diluted off under reduced pressure using a rotary evaporator. The distillate (salicylaldoxime) was distilled with twice its volume of water and extracted with 50 mL of diethyl ether. The product was crystallized from chloroform-light petroleum (60% v/v chloroform); yield, 15.95 g (71%).

The purity and structures of the prepared Schiff bases were confirmed by the melting point constancy, elemental analyses and various spectroscopic techniques.

#### **Preparation of Complexes**

The solid complexes of the stoichiometric ratios 1:1 and 1:2 (M:L) were prepared by mixing a hot ethanolic solution (50 mL) of the metal salt (0.01 mol) [Ce(NO<sub>3</sub>)<sub>3</sub>, ThCl<sub>4</sub> or UO<sub>2</sub>(OAc)<sub>2</sub>] with 0.01 or 0.02 mol of an ethanolic ligand solution (50 mL). The mixture was refluxed for ~6 h and then allowed to cool when the solid chelates separated. The complexes were crystallized from pure ethanol (96%), dried and stored over dried silica gel. Analyses of the solid complexes for C, H and N were performed at the Microanalytical Centre, Cairo University, Giza, Egypt. The water content was determined by the dehydration method while the metal contents were determined as metal oxides<sup>[8]</sup> after ignition of the solid complexes at ~750 °C.

#### Instrumentation

IR spectra of the Schiff bases and their metal complexes were recorded using a Beckman IR 4220 double-beam spectrophotometer within the range 4000–200 cm<sup>-1</sup> using KBr discs. <sup>1</sup>H NMR spectra of some selected metal complexes and their free ligands were recorded on a Varian EM 390–90



MHz NMR spectrometer using TMS as internal standard and DMSO-d<sub>6</sub> as solvent. Electronic absorption spectra in the UV/Visible region of the free ligands and their chelates were recorded both in DMF solution and in the solid state by the Nujol mull technique using a Perkin–Elemer  $\lambda_{3B}$  spectrophotometer with 1 cm matched silica cells. Magnetic susceptibilities of some selected solid complexes were measured applying Gouy's method using HgCo(SCN)<sub>4</sub> as calibrant. The experimental susceptibilities were corrected for diamagnetism.

#### **RESULTS AND DISCUSSION**

The Schiff bases included in this study were prepared according to the following scheme in Figure 2.

The general scheme for preparing the solid complexes is as shown in Figure 3.



Figure 2. Synthesis of the ligands.



Figure 3. Synthesis of the complexes.

#### **Elemental Analyses**

Conductometric titration along with elemental analysis data for all the newly prepared metal complexes, listed in Table 1, indicate that they have 1:1 or 1:2 (M:L) stoichiometric ratios. All the complexes are hygroscopic, soluble in DMF but insoluble in other common organic solvents. The insolubility of the solid complexes in common organic solvents indicates either their non-electrolytic or polymeric nature. Molar conductance values of the solubilized chelates in DMF lie within the range 76.6–189.2 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> indicating the presence of both 1:1 and 1:2 electrolytes. The presence of Cl<sup>-</sup> outside the coordination sphere in case of the Th(IV) complexes was confirmed by the precipitation of AgCl when AgNO<sub>3</sub> was added to the solubilized chelates in DMF.

#### **Thermal Analyses**

Thermogravimetric (TG) and differential thermogravimetric (DTA) analyses of some chelates were measured up to 500  $^{\circ}$ C at a heating rate of 10  $^{\circ}$ C/min in air. From the TG curves, the weight loss corresponding to each endo or exothermic peak on the DTA curve was calculated from which the number of water molecules and the percent of metal ion content

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| Table 1. Elen                         | nental analysi | s data of the lig        | ands and thei | r complexes  | s with UO <sub>2</sub> ( | VI), Th(IV), | and Ce(III) i | ons.              |
|---------------------------------------|----------------|--------------------------|---------------|--------------|--------------------------|--------------|---------------|-------------------|
| Tentative formula                     | Vield          | Der                      | Aı            | nalyses, % o | calcd. (found            | (p           |               |                   |
| (empirical formula)                   | (%)            | point <sup>a</sup> ,(°C) | C%            | %Н           | %N                       | M%           | FW            | $\Lambda^{\rm a}$ |
| HL <sup>1</sup>                       | I              |                          | 74.02         | 5.72         | 6.16                     | I            | 227.14        | I                 |
| $(C_{14}H_{13}NO_2)$                  |                |                          | (74.35)       | (5.60)       | (5.99)                   |              |               |                   |
| $[UO_{2}(L^{1})(H_{2}O)_{4}]OAc$      | 76.1           | 345                      | 30.59         | 2.87         | 2.23                     | 37.89        | 628.19        | 33.50             |
| $(C_{16}H_{23}NO_{10}U)$              |                |                          | (31.08)       | (2.91)       | (2.47)                   | (37.33)      |               |                   |
| $[Ce(L^{1})(H_{2}O)_{5}](NO_{3})_{2}$ | 73.3           | 350                      | 28.90         | 3.79         | 7.23                     | 27.04        | 581.26        | 74.66             |
| $(C_{14}H_{22}CeN_{3}O_{13})$         |                |                          | (29.81)       | (3.66)       | (1.66)                   | (26.84)      |               |                   |
| $[Th(L^{1})(H_{2}O)_{3}]Cl_{3}$       | 66.4           | 330                      | 25.69         | 3.36         | 2.14                     | 35.45        | 654.53        | 140.44            |
| $(C_{14}H_{22}C_{13}NO_{7}Th)$        |                |                          | (25.09)       | (3.66)       | (2.33)                   | (35.39)      |               |                   |
| $[UO_2(L^1)_2(H_2O)_2]$               | 72.1           | 345                      | 44.36         | 3.69         | 3.69                     | 31.39        | 758.31        | 12.65             |
| $(C_{28}H_{28}N_2O_8U)$               |                |                          | (44.68)       | (3.85)       | (3.77)                   | (31.44)      |               |                   |
| $[Ce(L^1)_2(H_2O)_4]NO_3$             | 77.2           | 350                      | 46.29         | 4.41         | 5.78                     | 19.29        | 726.40        | 69.55             |
| $(C_{28}H_{32}CeN_3O_{11})$           |                |                          | (46.95)       | (4.22)       | (5.39)                   | (19.63)      |               |                   |
| $[Th(L^{1})_{2}(H_{2}O)_{4}]Cl_{2}$   | 67.5           | 345                      | 40.65         | 3.87         | 3.38                     | 28.05        | 827.22        | 101.30            |
| $(C_{28}H_{32}Cl_2N_2O_8Th)$          |                |                          | (41.05)       | (4.13)       | (3.71)                   | (27.94)      |               |                   |
| $HL^{2}$ ( $C_{18}H_{16}NO_{2}$ )     | I              |                          | 77.68         | 5.79         | 5.03                     | I            | 278.33        | I                 |
|                                       |                |                          | (17.66)       | (5.38)       | (4.51)                   |              |               |                   |
| $[UO_2(L^2)(H_2O)_4]OAc$              | 73.4           | 370                      | 35.41         | 3.86         | 2.06                     | 35.08        | 678.46        | 45.67             |
| $(C_{20}H_{26}NO_{10}U)$              |                |                          | (35.77)       | (4.02)       | (2.06)                   | (35.37)      |               |                   |
| $[Ce(L^{2})(H_{2}O)_{5}](NO_{3})_{2}$ | 69.2           | 370                      | 34.23         | 3.99         | 6.65                     | 22.19        | 631.53        | 89.94             |
| $(C_{18}H_{25}CeN_3O_{13})$           |                |                          | (34.12)       | (3.32)       | (6.62)                   | (22.43)      |               |                   |
| $[Th(L^{2})(H_{2}O)_{5}]Cl_{3}$       | 70.2           | 350                      | 30.63         | 3.57         | 1.98                     | 32.88        | 705.79        | 180.20            |
| $(C_{18}H_{25}Cl_3NO_7Th)$            |                |                          | (30.38)       | (3.03)       | (2.13)                   | (33.02)      |               |                   |

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| (continued) |        |         |        |        |         |     |      |                                  |
|-------------|--------|---------|--------|--------|---------|-----|------|----------------------------------|
|             |        | (23.11) | (6.37) | (3.71) | (27.13) |     |      | $(C_{14}H_{21}CICeN_3O_{13})$    |
| 120.45      | 614.71 | 22.79   | 6.83   | 3.42   | 27.35   | 335 | 69.4 | $[Ce(L^4)(H_2O)_5](NO_3)_2$      |
|             |        | (35.62) | (2.60) | (3.46) | (28.65) |     |      | $(C_{16}H_{22}CINO_{10}U)$       |
| 51.90       | 662.64 | 35.92   | 2.11   | 3.32   | 29.00   | 382 | 70.3 | $[UO_{2}(L^{4})(H_{2}O)_{4}]OAc$ |
|             |        |         | (5.55) | (4.70) | (64.02) |     |      | $(C_{14}H_{12}CINO_2)$           |
| I           | 261.59 | I       | 5.35   | 4.59   | 64.28   |     | I    | HL <sup>4</sup>                  |
|             |        | (23.73) | (2.48) | (3.24) | (34.55) |     |      | $(C_{28}H_{30}Br_2Cl_2N_2O_8Th)$ |
| 147.45      | 985.02 | 23.56   | 2.84   | 3.05   | 34.14   | 345 | 70.4 | $[Th(L^3)_2(H_2O)_4]Cl_2$        |
|             |        | (16.12) | (4.66) | (3.34) | (38.62) |     |      | $(C_{28}H_{30}Br_2CeN_3O_{11})$  |
| 101.67      | 884.50 | 15.84   | 4.75   | 3.42   | 38.02   | 360 | 68.6 | $[Ce(L^3)_2(H_2O)_4]NO_3$        |
|             |        | (26.14) | (3.25) | (2.99) | (36.21) |     |      | $(C_{28}H_{26}Br_2N_2O_8U)$      |
| 16.50       | 916.11 | 25.98   | 3.06   | 2.84   | 36.71   | 403 | 68.3 | $[UO_2(L^3)_2(H_2O)_2]$          |
|             |        | (31.83) | (2.03) | (2.41) | (23.15) |     |      | $(C_{14}H_{21}BrCl_3NO_7Th)$     |
| 180.65      | 733.43 | 31.64   | 1.91   | 2.86   | 22.93   | 335 | 66.3 | $[Th(L^3)(H_2O)_5]Cl_3$          |
|             |        | (21.60) | (6.71) | (3.57) | (25.13) |     |      | $(C_{14}H_{21}BrCeN_3O_{13})$    |
| 110.32      | 659.16 | 21.26   | 6.37   | 3.34   | 25.51   | 385 | 70.1 | $[Ce(L^3)(H_2O)_5](NO_3)_2$      |
|             |        | (33.58) | (2.13) | (2.99) | (27.61) |     |      | $(C_{16}H_{22}BrNO_{10}U)$       |
| 44.78       | 707.09 | 33.66   | 1.98   | 2.83   | 27.18   | 415 | 73.4 | $[UO_2(L^3)(H_2O)_4]OAc$         |
|             |        |         | (4.71) | (4.05) | (55.21) |     |      | $(C_{14}H_{12}BrNO_2)$           |
| Ι           | 306.64 | I       | 4.57   | 3.92   | 54.94   |     | I    | HL <sup>3</sup>                  |
|             |        | (25.21) | (2.92) | (4.35) | (46.63) |     |      | $(C_{36}H_{38}Cl_2N_2O_8Th)$     |
| 139.50      | 929.65 | 24.96   | 3.01   | 4.12   | 46.51   | 360 | 72.2 | $[Th(L^2)_2(H_2O)_4]Cl_2$        |
|             |        | (17.11) | (4.91) | (4.77) | (52.23) |     |      | $(C_{36}H_{38}CeN_{3}O_{11})$    |
| 76.40       | 828.83 | 16.91   | 5.07   | 4.62   | 52.17   | 385 | 70.1 | $[Ce(L^2)_2(H_2O)_4]NO_3$        |
|             |        | (27.88) | (3.32) | (4.39) | (50.07) |     |      | $(C_{36}H_{34}N_2O_8U)$          |
| 14.56       | 860.70 | 27.66   | 3.25   | 3.98   | 50.24   | 405 | 69.8 | $[UO_2(L^2)_2(H_2O)_2]$          |

## Cerium(III), Thorium(IV), and Dioxouranium(VI)



|                                       |       |                          | Table 1. Cor | nannu.      |                |         |
|---------------------------------------|-------|--------------------------|--------------|-------------|----------------|---------|
| Tentative formula                     | Vield | Der                      | 7            | Analyses, % | calcd. (found) |         |
| (empirical formula)                   | (%)   | point <sup>a</sup> ,(°C) | C%           | %Н          | N%             | M%      |
| $[Th(L^4)(H_2O)_5]Cl_3$               | 75.2  | 362                      | 24.40        | 3.05        | 2.03           | 33.68   |
| $(C_{14}H_{21}Cl_4NO_7Th)$            |       |                          | (24.11)      | (3.23)      | (2.24)         | (33.42) |
| $[UO_2(L^4)_2(H_2O)_2]$               | 71.6  | 403                      | 40.64        | 3.17        | 3.39           | 28.77   |
| $(C_{28}H_{26}Cl_2N_2O_8U)$           |       |                          | (40.33)      | (3.51)      | (3.67)         | (28.39) |
| $[Ce(L^4)_2(H_2O)_4]NO_3$             | 70.8  | 330                      | 42.28        | 2.26        | 5.28           | 17.62   |
| $(C_{28}H_{30}Cl_2CeN_3O_{11})$       |       |                          | (42.52)      | (2.33)      | (5.27)         | (17.86) |
| $[Th(L^4)_2(H_2O)_4]Cl_2$             | 69.4  | 370                      | 37.53        | 3.35        | 3.13           | 25.89   |
| $(C_{28}H_{30}Cl_4N_2O_8Th)$          |       |                          | (37.13)      | (3.62)      | (3.41)         | (25.69) |
| $\mathrm{HL}^{5}$                     | Ι     | I                        | 56.80        | 3.72        | 4.73           | Ι       |
| $(C_{14}H_{11}CINO_2)$                |       |                          | (56.91)      | (3.85)      | (4.50)         |         |
| $[UO_{2}(L^{5})(H_{2}O)_{4}]OAc$      | 70.4  | 395                      | 27.57        | 3.01        | 2.01           | 34.15   |
| $(C_{16}H_{21}C_{12}NO_{10}U)$        |       |                          | (27.61)      | (3.40)      | (2.22)         | (34.62) |
| $[Ce(L^{5})(H_{2}O)_{5}](NO_{3})_{2}$ | 76.1  | 365                      | 25.90        | 3.08        | 6.47           | 21.59   |
| $(C_{14}H_{20}Cl_2CeN_3O_{13})$       |       |                          | (25.67)      | (3.35)      | (6.71)         | (21.42) |
| $[Th(L^{5})(H_{2}O)_{5}]Cl_{3}$       | 74.2  | 340                      | 23.24        | 4.15        | 1.94           | 32.07   |
| $(C_{14}H_{20}CI_5NO_7Th)$            |       |                          | (23.33)      | (4.02)      | (2.11)         | (31.88) |

187.16

723.43

130.51

649.16

49.45

60.769

Ι

296.04

140.45

896.12

185.92

688.98

 $\Lambda^{a}$ 

FW

14.14

827.45

77.49

795.30

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| $[UO_2(L^5)_2(H_2O)_2]$             | 76.3 | 385 | 37.53   | 2.68   | 3.13   | 26.56   | 896.11 | 17.98  |
|-------------------------------------|------|-----|---------|--------|--------|---------|--------|--------|
| $(C_{28}H_{24}Cl_4N_2O_8U)$         |      |     | (37.36) | (2.61) | (3.51) | (26.70) |        |        |
| $[Ce(L^5)_2(H_2O)_4]NO_3$           | 76.3 | 340 | 38.91   | 1.97   | 4.86   | 16.21   | 864.20 | 81.61  |
| $(C_{28}H_{28}Cl_4CeN_3O_{11})$     |      |     | (38.61) | (2.13) | (4.77) | (16.14) |        |        |
| $[Th(L^5)_2(H_2O)_4]Cl_2$           | 70.2 | 355 | 34.85   | 2.90   | 2.90   | 24.05   | 965.02 | 130.43 |
| $(C_{28}H_{28}Cl_6N_2O_8Th)$        |      |     | (34.65) | (2.75) | (3.01) | (23.88) |        |        |
| HL <sup>6</sup>                     | I    |     | 70.06   | 5.83   | 5.45   | I       | 257.14 | I      |
| $(C_{15}H_{15}NO_3)$                |      |     | (70.01) | (5.34) | (5.32) |         |        |        |
| $[UO_{2}(L^{6})(H_{2}O)_{4}]OAc$    | 73.1 | 390 | 31.02   | 3.80   | 2.13   | 36.16   | 658.19 | 54.81  |
| $(C_{17}H_{25}NO_{11}U)$            |      |     | (31.33) | (4.00) | (2.27) | (36.52) |        |        |
| $[Ce(L^6)(H_2O)_5](NO_3)_2$         | 69.3 | 335 | 29.51   | 3.96   | 6.88   | 22.95   | 610.48 | 110.54 |
| $(C_{15}H_{24}CeN_{3}O_{14})$       |      |     | (29.05) | (4.24) | (6.64) | (23.23) |        |        |
| $[Th(L^{6})(H_{2}O)_{5}]Cl_{3}$     | 68.8 | 320 | 26.32   | 3.51   | 2.05   | 33.90   | 684.53 | 178.76 |
| $(C_{15}H_{24}Cl_3NO_8Th)$          |      |     | (26.11) | (3.33) | (2.23) | (34.21) |        |        |
| $[UO_2(L^6)_2(H_2O)_2]$             | 73.0 | 385 | 44.03   | 3.91   | 3.42   | 29.09   | 818.31 | 19.01  |
| $(C_{30}H_{32}N_{20}10U)$           |      |     | (44.88) | (3.55) | (3.24) | (28.87) |        |        |
| $[Ce(L^{6})_{2}(H_{2}O)_{4}]NO_{3}$ | 75.3 | 330 | 45.82   | 2.67   | 5.34   | 17.82   | 786.40 | 78.65  |
| $(C_{30}H_{36}CeN_{3}O_{13})$       |      |     | (45.61) | (2.84) | (5.22) | (18.06) |        |        |
| $[Th(L^{6})_{2}(H_{2}O)_{4}]Cl_{2}$ | 72.6 | 340 | 40.61   | 4.06   | 2.71   | 26.15   | 887.22 | 140.65 |
| $(C_{30}H_{36}Cl_2N_2O_{10}Th)$     |      |     | (40.80) | (3.99) | (2.55) | (26.37) |        |        |
| $^{a}Ohm^{-1} cm^{2} mole^{-1}$ .   |      |     |         |        |        |         |        |        |

Cerium(III), Thorium(IV), and Dioxouranium(VI)



in each chelate molecule were determined (cf. Table 2). Inspection of these curves shows that the weight loss below 100 °C is attributed to the loss of moisture and hygroscopic water while that within the range 130–180 °C is due to dehydration of coordinated water molecules. The number of the latter amounts to 5 or 4 per chelate molecule for the 1:1 and 1:2 (M:L) complexes respectively, which are coordinated to the metal ion to fulfill the coordination number of eight. The final residue is considered to be Ce<sub>2</sub>O<sub>3</sub>, ThO<sub>2</sub> or UO<sub>3</sub> from which the metal contents may be calculated. The results

|  |       | Weight lo  | ss (%) | Temn       |  |
|--|-------|------------|--------|------------|--|
| Complex  | Ratio | Calculated | Found  | range (°C) | Assignment                                       |
| [Th(L1)(H2O)5]Cl3  | 1:1   | 13.75      | 13.91  | 120-175    | 5H <sub>2</sub> O<br>(coordinated)               |
|  |       | 16.71      | 17.01  | 300-375    | 3HCl   |
|  |       | 40.35      | 41.66  | 480        | Metal oxide<br>(ThO <sub>2</sub> )               |
| $[\operatorname{Ce}(\operatorname{L}^1)_2(\operatorname{H}_2\operatorname{O})_4]\operatorname{NO}_3$ | 1:2   | 9.91       | 10.48  | 125-180    | 4H <sub>2</sub> O<br>(coordinated)               |
|  |       | 8.67       | 9.78   | 255-320    | HNO <sub>3</sub>                                 |
|  |       | 45.19      | 46.20  | 465        | Metal oxide<br>(Ce <sub>2</sub> O <sub>3</sub> ) |
| $[\mathrm{UO}_2(\mathrm{L}^2)(\mathrm{H}_2\mathrm{O})_4]\mathrm{OAc}$                                | 1:1   | 10.22      | 11.34  | 130-180    | 4H <sub>2</sub> O<br>(coordinated)               |
|  |       | 8.38       | 9.21   | 215 - 245  | CH <sub>3</sub> COOH                             |
|  |       | 40.62      | 42.01  | 445        | Metal Oxide<br>(UO <sub>3</sub> )                |
| $[Th(L^3)(H_2O)_5]Cl_3$  | 1:1   | 12.27      | 14.10  | 140.200    | 5H <sub>2</sub> O<br>(coordinated)               |
|  |       | 14.91      | 15.03  | 320-350    | 3HCl   |
|  |       | 36.00      | 36.81  | 480        | Metal oxide<br>(ThO <sub>2</sub> )               |
| $[UO_2(L^4)_2(H_2O)_2]$  | 1:2   | 4.53       | 5.07   | 120-160    | 2H <sub>2</sub> O<br>(coordinated)               |
|  |       | 35.97      | 36.66  | 495        | Metal oxide<br>(UO <sub>3</sub> )                |
| $[Th(L^5)_2(H_2O)_4]Cl_2$  | 1:2   | 9.95       | 11.00  | 130-150    | 4H <sub>2</sub> O<br>(coordinated)               |
|  |       | 10.08      | 11.64  | 235-265    | 2HCl   |
|  |       | 36.5       | 37.24  | 435        | Metal oxide<br>(ThO <sub>2</sub> )               |

Table 2. TGA results of some Ce(III), Th(IV), and UO<sub>2</sub>(VI) complexes.

obtained are in good agreement with the proposed values and with those obtained from elemental analyses.

#### Magnetic Susceptibility

Magnetic data; showed the diamagnetic behaviour of the Th(IV) and UO(VI) complexes as expected, whereas the magnetic moments of the Ce(III) complexes are about 2.42 B.M. which deviates from the spin-only value for metal ions with one unpaired electron. This is simply due to the shielding of the 4f electrons in the lanthanide ions. In this case, according to vanVleck,<sup>[9]</sup> the molar susceptibility is given by

$$X_{\rm M} = N\eta_{\beta}^2/3KT + N\alpha$$

where K is the Boltzman constant, N is Avogadro's number,  $\eta_{\beta}$  is a lowfrequency part of the magnetic moment and  $\alpha$  is a combination of the highfrequency component and diamagnetic contribution. The magnitude of separation between the energy levels so formed and the term KT determine the magnitude of the spin-orbit coupling. For all tripositive lanthanide ions, except for Gd(III), Sm(III) and Eu(III), the permanent magnetic moments reflect a combination of spin and orbital effects.

It is worth to mention also that, in contrast to the first d-type transition series, complexing groups have little effect upon the magnetic moments of lanthanide ions. This is why the observed magnetic moments of the Ce(III) complexes showed nearly no variation with changing the type of ligand used.

## <sup>1</sup>H NMR Spectra

The <sup>1</sup>H NMR spectra of some  $UO_2(VI)$  complexes in DMSO-d<sub>6</sub> were measured and compared to those of the ligands in the same solvent. The various protons of the free ligands are numbered as shown in Figure 4.



Figure 4. Numbering of the various protons in the Schiff bases.



| Ligand/complex           | Ratio | $\mathrm{H}^{1}$ | $H^2$ | H <sup>3</sup> | $\mathrm{H}^4$ |
|--------------------------|-------|------------------|-------|----------------|----------------|
| HL <sup>1</sup>          | _     | 8.35             | 10.35 | 6.70           | 4.53           |
| $[UO_2(L^1)(H_2O)_4]OAc$ | 1:1   | 8.60             | _     | 6.78           | 4.51           |
| HL <sup>2</sup>          | _     | 8.35             | 10.62 | 7.07           | 4.57           |
| $[UO_2(L^2)_2(H_2O)_2]$  | 1:2   | 8.45             | _     | 6.75           | 4.54           |
| $HL^3$                   | _     | 8.40             | 10.30 | 6.70           | 4.52           |
| $[UO_2(L^3)_2(H_2O)_2]$  | 1:2   | 8.50             | _     | 6.80           | 4.54           |
| HL <sup>4</sup>          | _     | 8.25             | 10.25 | 6.65           | 4.48           |
| $[UO_2(L^4)_2(H_2O)_2]$  | 1:2   | 8.35             | _     | 6.80           | 4.5            |
| HL <sup>5</sup>          | _     | 8.35             | 10.20 | 6.60           | 4.5            |
| $[UO_2(L^5)(H_2O)_4]OAc$ | 1:1   | 8.70             | _     | 6.73           | 4.56           |
| HL <sup>6</sup>          | _     | 8.30             | 10.03 | 6.60           | 4.54           |
| $[UO_2(L^6)(H_2O)_4]OAc$ | 1:1   | 8.60             | _     | 6.80           | 4.50           |
| $[UO_2(L^6)_2(H_2O)_2]$  | 1:2   | 8.40             | _     | 6.70           | 4.54           |

*Table 3.* <sup>1</sup>H NMR signals of protons (ppm) of ligands  $HL^1-HL^6$  and their  $UO_2(VI)$  complexes.

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The <sup>1</sup>H NMR signals of the free ligands compared to those of the  $UO_2(VI)$  complexes are listed in Table 3. This comparison showed the disappearance of the signal at  $\delta 10.3 \pm 0.1$  ppm due to the proton (2) of the o-OH group of the salicylidene moiety of the ligand molecule, indicating the elimination of hydrogen ion from this group on complex formation. On the other hand, the signal at  $\delta 8.5 \pm 0.2$  ppm in the spectra of the free ligand, due to the proton (1) of the o-OH group of the arylidene moiety, is shifted downfield by  $\sim 0.50$  ppm for the 1:1 and by  $\sim 0.20$  ppm for the 1:2 (M:L) complexes. This indicates coordination of the oxygen atom of this group and the monobasic character of these ligands. The signals of the aromatic protons of the free ligands present with in the range  $\delta$  7.60–6.85 ppm are also shifted downfield with an obvious decrease and broadening in their envelopes. This is expected since the formation of M-O or M-N bonds withdraws electrons from the aromatic rings resulting in a deshielding of the proton on the carbon atom adjacent to the azomethine group. The new signal appearing at  $\delta \sim 3.4$  ppm is due to the coordinated H<sub>2</sub>O in the complexes.

#### **IR** Spectra

Substantial Support for the results obtained from <sup>1</sup>H NMR spectra is gained by considering the changes in the IR spectra of the solid chelates in comparison with those of the free ligands. The absorption band at about 2900 cm<sup>-1</sup> in the spectra of the free ligands is due to the stretching



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Figure 5. Structure of 1:1 and 1:2 Th(IV) complexes ( $A = H_2O$ ).

vibration of the strongly intramolecularly hydrogen bonded o-OH (to the nitrogen atom of the azomethine group) which is lost after complexation. On the other hand, the two bands appearing at 3100-3150 and 1310-1350  $cm^{-1}$  in the IR spectra of the free ligands are due to the stretching and bending vibrations of the o-OH group, respectively. These two bands are shifted to lower frequencies on complex formation, which can be taken as another confirmation of the monobasicity of these ligands. The absorption band around 1660-1640 cm<sup>-1</sup> originating from the in-plane stretching of the -C=N-group is shifted to lower frequency by 10-30 cm<sup>-1</sup> on going from the free ligands to the solid chelate spectra. This band also is sensitive to environmental electronic changes because it is strongly influenced by delocalization of the unpaired electrons of the nitrogen atom on complexation and is mostly split. This is supported by the appearance of a new band of varying intensity in the far-IR region at 450-430 cm<sup>-1</sup> due to v(M-N) vibration. On the other hand, the absorption band of the -C-Obond observed at 1130-1105 cm<sup>-1</sup> in the free ligands is moved to 1060-1040 cm<sup>-1</sup> and becomes less intense after metal-oxygen bond formation since the mass of the bonding site is increased by substitution of metal with hydrogen.<sup>[6]</sup> Thus, a new band in the far-IR region (360-330 cm<sup>-1</sup>) has appeared due to the v(M-O) vibration.

In light of these new finding, the structure of the solid complexes may be represented by the formulas shown in Figure 5 for the Th(IV) complexes as example.

#### **Electronic Absorption Spectra**

Electronic absorption spectra of the free ligands in DMF show broad bands within the range 390–450 nm which disappear on adding a trace of

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*Figure 6.* Electronic absorption spectra of the ligand  $HL^4$  and its complexes in DMF.

an acid with the conversion of the orange colour of the solution into pale yellow. This is most probably due to protonation of the C=N linkage of the azomethine group. Therefore, the absence of this band in the spectra of the complexes (Figure 6) can be taken as evidence for the participation of the C=N group in a coordinate bond (C=N  $\rightarrow$  M).<sup>[10]</sup>

The electronic absorption spectra in the visible region of the Ce(III), Th(IV) and UO<sub>2</sub>(VI) chelates in the solid state (in Nujol mulls) exhibit alterations in the intensity or shifts in the position of the absorption bands or sometimes both. The value of Racah parameter (B) for a complex is always less than that for the free aqueous ion. This reduction of B upon complexation corresponds to a reduction of interelectronic repulsion, due to delocalization of the metal electrons onto the ligands, and is known as the nephelauxetic effect. The factor,  $\beta$ , by which B is reduced from the free-ion is the average value of  $v_{complex}/v_{equo}$  given by the equation<sup>[11]</sup> shown below.

$$\beta = \frac{1}{n} \sum (v_{complex} / v_{aquo.})$$

The wave lengths at which the various bands appear are red-shifted compared to the aquo ion, a fact which had been ascribed to a nephelauxetic effect. The extent of the red-shift is related to the covalency in the

metal-ligand bond by the  $\delta$  scale, proposed by Sinha.<sup>[12]</sup> This covalency is expressed as shown below.

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$$\delta\% = (1 - \beta)/\beta \times 100$$

The spectral data of the Ce(III) complexes were used to calculate the interelectronic repulsion parameter ( $\beta$ ) and the percentage covalency ( $\delta$ %). The values of the former lie within the range 0.9449-0.9896, while the percentage covalency values are in the range 0.6441-0.3713.

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