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# The Preparation and Characterization of some Uranium(VI) Complexes of *N*,*N*′-Bis(*o*-hydroxyaryl) Aldimino Schiff Bases

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## Abstract

Some of the stable chelate complexes of uranium(VI) were prepared with alkyl or aryl (R) bridged *o*,*o*′-dihydroxyaryl Schiff bases of $HO{-}C_6H_4{-}CH{=}N{-}R{-}N{=}CH{-}C_6H_4{-}OH$ and $HO{-}C_{10}H_6{-}CH{=}N{-}R{-}N{=}CH{-}C_{10}H_6{-}OH$ (R: $(CH_2)_n$; $(C_2H_4NH)_n$-$(C_2H_4)$; $(C_6H_4CH_2C_6H_4$; *o*, *m*, *p*-$C_6H_4$). Their structures were determined by UV, IR and elemental analyses. It is evident that strong ligand–ion interaction usually caused the polymeric structure. This is supported by the high decomposition point and low solubilities of the complexes.

## Introduction

Very little work has appeared on the complex formation phenomena of actinides with the *o*,*o*′-dihydroxyaryl Schiff bases although these ligands have already been recognized as forming stable complexes with transition elements [1–4].

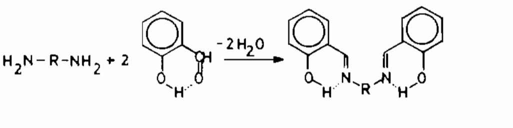
In this study, *N*,*N*′-bis(*o*-hydroxyaryl) aldimines and *N*,*N*′-bis(2-hydroxy-1-naphthyl) aldimines were synthesized [5a–d], as given in eqns. (1) and (2).

Compounds **1d**, **2c**, **d** were obtained by the condensation of $UO_2^{2+}$ and *N*,*N*′-bis(salicylaldehyde) polymethylenediimine and *N*,*N*′-bis(2-hydroxy-1-naphthaldehyde) polymethylenediimine (R: $(CH_2)_n$, (*n*: 3,6) eqn. (3), Table 1.

The uranyl complexes of *o*-, *m*-, *p*-phenylenedisalicylaldimine and *m*-, *p*-phenylene bis(2-hydroxy-1-naphthaldimine) were also prepared as stated above: compounds **3c**; **4c**, **d**; **5c**, **d**; eqn. (3), Table 1.

Compounds **6c**, **d**; **7d**; **8c**; **9c** were obtained by the condensation of $UO_2^{2+}$ with *N*,*N*′-bis(salicylaldehyde) polyethyleneaminediimines and *N*,*N*′-bis(2-hydroxy-1-naphthaldehyde) polyethyleneaminediimines (R: $(C_2H_4NH)_nC_2H_4$ (*n*: 1,2,3,4)) eqn. (3), Table 1.

The strained type of $UO_2^{2+}$ complexes with *N*,*N*′-bridged Schiff bases such as 4,4′-bis(*o*-hydroxybenzaldimino) diphenylmethane derivatives were also obtained: compounds **10c**, **d**; eqn. (3), Table 1.



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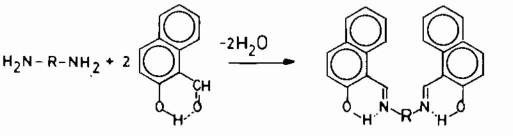
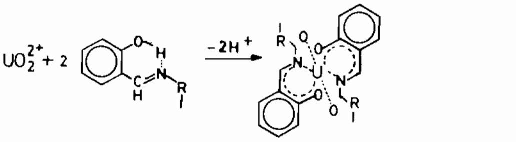


(2)

| No. | R | *n* |
|---|---|---|
| **1a**, **b** | $(CH_2)_n$ | 3 |
| **2a**, **b** | $(CH_2)_n$ | 6 |
| **3a**, **b** | $C_6H_4$ | *o* |
| **4a**, **b** | $C_6H_4$ | *m* |
| **5a**, **b** | $C_6H_4$ | *p* |
| **6a**, **b** | $(C_2H_4NH)_nC_2H_4$ | 1 |
| **7a**, **b** | $(C_2H_4NH)_nC_2H_4$ | 2 |
| **8a** | $(C_2H_4NH)_nC_2H_4$ | 3 |
| **9a** | $(C_2H_4NH)_nC_2H_4$ | 4 |
| **10a**, **b** | $(C_6H_4)_nCH_2$ | 2 |
| **11a**, **b** | $C_6H_4N(CH_3)_2$ | |

a,c. phenyl; b, d. naphthyl.



(3)

| No. | R | *n* |
|---|---|---|
| **1d** | $(CH_2)_n$ | 3 |
| **2c**, **d** | $(CH_2)_n$ | 6 |
| **3c** | $C_6H_4$ | *o* |
| **4c**, **d** | $C_6H_4$ | *m* |
| **5c**, **d** | $C_6H_4$ | *p* |
| **6c**, **d** | $(C_2H_4NH)_nC_2H_4$ | 1 |
| **7d** | $(C_2H_4NH)_nC_2H_4$ | 2 |
| **8c** | $(C_2H_4NH)_nC_2H_4$ | 3 |
| **9c** | $(C_2H_4NH)_nC_2H_4$ | 4 |
| **10c**, **d** | $(C_6H_4)_nCH_2$ | 2 |
| **11d** | $C_6H_4N(CH_3)_2$ | |

a,c. phenyl; b, d. naphthyl.

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TABLE 1. The chemical nature of the uranyl(VI) complexes of the Schiff bases

| Compound |  | Yield (%) | Melting point (°C) | Found (%) |  |  | Formula | Calculated (%) |  |  | Molecular weight |
|---|---|---|---|---|---|---|---|---|---|---|---|
| No. | Name |  |  | C | H | N |  | C | H | N |  |
| 1b | Propane-1,3-di(2-hydroxy)-1-naphthaldimine uranylate(VI) | 79.5 | 276 | 45.61 | 2.92 | 5.04 | $C_{25}H_{20}N_2O_4U$ | 46.15 | 3.08 | 4.31 | 650 |
| 2a | Hexane-1,6-disalicylaldimine uranylate(VI) | 75 | 198 | 39.21 | 3.09 | 4.61 | $C_{20}H_{22}N_2O_4U$ | 40.55 | 3.72 | 4.73 | 592 |
| 2b | Hexane-1,6-di(2-hydroxy)-1-naphthaldimine uranylate(VI) | 71.5 | 253 | 43.23 | 3.67 | 4.33 | $C_{28}H_{26}N_2O_4U$ | 48.56 | 3.76 | 4.05 | 692 |
| 3a | *o*-Phenylenedisalicylaldimine uranylate(VI) | 68 | 223 | 42.09 | 2.94 | 4.76 | $C_{20}H_{14}N_2O_4U$ | 41.10 | 2.40 | 4.79 | 584 |
| 4a | *m*-Phenylenedisalicylaldimine uranylate(VI) | 76 | 305 | 40.40 | 3.31 | 5.07 | $C_{20}H_{14}N_2O_4U$ | 41.10 | 2.40 | 4.79 | 584 |
| 4b | *m*-Phenylenedi(2-hydroxy)-1-naphthaldimine uranylate(VI) | 67 | 325 | 48.57 | 2.85 | 4.85 | $C_{28}H_{18}N_2O_4U$ | 49.12 | 2.63 | 4.09 | 684 |
| 5a | *p*-Phenylenedisalicylaldimine uranylate(VI) | 71 | 320 | 41.02 | 2.81 | 4.59 | $C_{20}H_{14}N_2O_4U$ | 41.10 | 2.40 | 4.79 | 584 |
| 5b | *p*-Phenylenedi(2-hydroxy)-1-naphthaldimine uranylate(VI) | 65 | 345 | 48.90 | 2.53 | 5.05 | $C_{28}H_{18}N_2O_4U$ | 49.12 | 2.63 | 4.09 | 684 |
| 6a | *N*,*N*′-Bis(salicylidene)diethylenetriamine uranylate(VI) | 76 | 204 | 30.44 | 3.97 | 9.49 | $C_{18}H_{21}N_5O_{10}U$ | 30.64 | 2.98 | 9.93 | 705 |
| 6b | *N*,*N*′-Bis(2-hydroxy)-1-naphthalidenediethylenetriamine uranylate(VI) | 80 | 198 | 38.38 | 3.26 | 8.22 | $C_{26}H_{25}N_5O_{10}U$ | 38.76 | 3.11 | 8.70 | 805 |
| 7b | *N*,*N*′-Bis(2-hydroxy)-1-naphthalidenetriethylenetetramine uranylate(VI) | 71 | 169 | 39.21 | 2.99 | 9.30 | $C_{28}H_{30}N_6O_{10}U$ | 39.62 | 3.54 | 9.91 | 848 |
| 8a | *N*,*N*′-Bis(salicylidene)tetraethylenepentamine uranylate(VI) | 79 | 173 | 33.25 | 3.29 | 12.32 | $C_{22}H_{31}N_7O_{10}U$ | 33.38 | 3.92 | 12.39 | 791 |
| 9a | *N*,*N*′-Bis(salicylidene)pentaethylenehexamine uranylate(VI) | 83 | 180 | 34.34 | 3.88 | 12.51 | $C_{24}H_{36}N_8O_{10}U$ | 34.53 | 4.12 | 13.43 | 834 |
| 10a | 4,4′-(Disalicylaldimine)diphenylmethane uranylate(VI) | 83 | 182 | 47.52 | 3.30 | 4.80 | $C_{27}H_{20}N_2O_4U$ | 48.07 | 2.97 | 4.15 | 674 |
| 10b | 4,4′-Di(2-hydroxy)-1-naphthaldiminediphenylmethane uranylate(VI) | 78 | 193 | 51.96 | 3.51 | 4.28 | $C_{35}H_{24}N_2O_4U$ | 54.26 | 3.10 | 3.62 | 774 |
| 11b | Bis[*p*-*N*,*N*-dimethylaminophenyl(2-hydroxy)-1-naphthaldimine uranylate(VI) | 75 | 257 | 46.18 | 3.60 | 8.89 | $C_{38}H_{36}N_6O_{10}U$ | 46.82 | 3.69 | 8.62 | 974 |

Further investigation of the stereochemistry of the complexes was performed by the condensation of $UO_2^{2+}$ with 2-hydroxy-1-naphthaldehyde-*p*-(*N*,*N*′-dimethylaminophenyl) aldimine. It is interesting to see that a complex was formed in the ratio 1:2, compound **11d**, Table 1.

## Results and Discussion

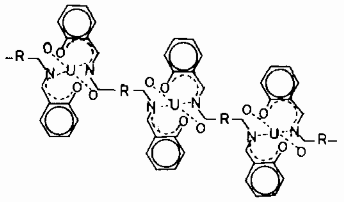
The structure of the complexes were primarily identified by IR spectroscopy. The absorption around 3600–2800 $cm^{-1}$ was due to the strong intermolecular hydrogen bonding of the Schiff bases which is lost after complete complexation. However, –O–H...N– bonding affects the stability of the metal–oxygen bonds of *o*-hydroxyaldehydediimine complexes as shown by Feedman [6]. This is the reason that the complexes were prepared in this study completely free of bound water.

The absorption around 1640–1633 $cm^{-1}$ originated from in plane stretching of –C=N– double bonds is too sensitive to environmental electronic changes and usually shifted 100 $cm^{-1}$ in conjugated systems. Such absorptions are strongly influenced by the unpaired nitrogen electrons on complexation and are mostly splitted. On the other hand the absorption peaks of the –C–O– bond observed around 1140–1105 $cm^{-1}$ in free ligands are moved to 1060–1030 $cm^{-1}$ and become less intense after metal–oxygen bond formation since the mass of a bonding site is increased by the substitution of metal with hydrogen [7, 8].

The magnetic susceptibility measurements carried out in our work did not exhibit paramagnetism indicating that all the electrons are paired because of strong conjugation on the chelate ring. Aromatic ring deformation bands are observed at 1450 and 1600 $cm^{-1}$.

The Schiff base derivatives of quadridentate *o*-hydroxyphenylsalicylaldimine failed to give stable complexes with $UO_2^{2+}$ which are well known to form stable inner type transition metal complexes [1, 8]. The cationic radii are small in transition metals when compared with the actinides and large radii in the actinides will force the square planar geometry to a stretched tetrahedral geometry. As a result, when ligand–metal interaction occurs, a stable complex is obtained and *N*,*N*′-alkyl bridged bisaldimines, which are compounds **1–11**, result from intramolecular ion–ligand chains. This structure resulted from the interaction of the separate end of the ligands with $UO_2^{2+}$; eqn. (4) [3a].

This observation is supported by the microanalyses results which gave low values when compared with calculated values. This observation is also discussed by Weigold and West [3b]. In a solid polymeric



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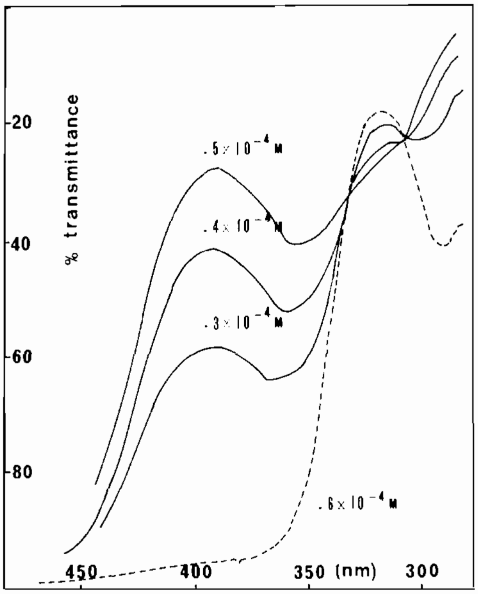

Fig. 1. The UV–Vis absorption spectra of *N,N'*-bis(salicylidene)diethylenetriamine in the presence of various amounts of uranyl nitrate in ethylacetate.

ligand–cation system the absolute 1:1 stoichiometry usually does not exist.

However, this type of polymeric complex is expected to be more stable with respect to their inner type analogous, as recently discussed by Hanack *et al.* [9].

The stability of some complexes was determined by UV–Vis spectroscopy in ethylacetate solutions on a specific wavelength of the complex spectra at which the free ligand has no appreciable absorption, Fig. 1. The dissociation constant values were estimated by JOB's method [10], Table 2.

## Experimental

A general procedure for the preparation of the *N,N'*-bis(*o*-hydroxyaryl) Schiff bases is as follows.

The diamines used in this study were from Fluka (purum) and were reacted with salicylaldehyde or 2-hydroxy-1-naphthaldehyde Fluka (purum) without further purification under the usual laboratory conditions. Solid row condensation products were successfully purified by crystallization, Table 3. The IR analyses were made on a Pye Unicam model SP1100 spectrometer and proton NMR analyses were made on Varian spectrometer model T-60. The peaks observed are given in Table 3 [5a, b]. Melting points are uncorrected. Elementary analyses were made on a Heraeus instrument.

The preparation of the $UO_2^{2+}$ complexes with *N,N'*-bis(*o*-hydroxyphenyl) aldimines were made under normal laboratory conditions. Most of the Schiff bases prepared in this work are easily soluble in ethanol or methanol so that the ligands (100 mmol) dissolved in such a solvent were allowed to react with $UO_2(NO_3)_2 \cdot 6H_2O$ at room temperature.

Precipitation of the complex was completed while the mixture was stirred. In fact polyethylenediamine aldimine complexes were obtained as their $HNO_3$ salt. The complexes were mostly insoluble in common solvents except DMF and DMSO and therefore the precipitates were washed with a suitable solvent before being carefully dried but were not properly crystallized. The results of the elementary analyses are displayed in Table 1. Magnetic susceptibilities were determined by a Gouy balance Type D104 and UV–Vis measurements were made on a Beckman spectrophotometer model DB-G.

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TABLE 2. The complex dissociation constants ($5.0 \times 10^{-5}$ mol/l) of some of the $UO_2^{2+}$ complexes obtained in this work. Solvent, ethylacetate at 25 °C

| No. | Name of ligand | $K_{diss} \times 10^{-6}$ | Log *k* | Δ*G* (kcal/mol) |
|---|---|---|---|---|
| 1a | 1,3-(Disalicylidene)propane | 8.200 | −11.711 | 6.465 |
| 2a | 1,6-(Disalicylidene)hexane | 1.800 | −13.227 | 7.303 |
| 6a | *N,N'*-Bis(salicylidene)diethylenetriamine | 0.655 | −14.238 | 7.861 |
| 7a | *N,N'*-Bis(salicylidene)triethylenetetramine | 0.040 | −17.034 | 9.404 |
| 9a | *N,N'*-Bis(salicylidene)pentaethylenehexamine | 0.400 | −14.732 | 8.133 |

TABLE 3. The chemical nature of the Schiff bases

| No. | Ligand name | Yield | Melting point[a] (°C) | Found (%) | | | Formula | Calculated (%) | | | NMR (ppm)[b] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | C | H | N | | C | H | N | |
| 1a | 1,3-Bis(salicylaldimino)propane | 75 | 59 | 68.99 | 5.82 | 10.10 | $C_{17}H_{19}N_2O_2$ | 72.34 | 6.38 | 9.93 | 2.2m; 3.6m; 7.5m; 9.1s |
| 1b | 1,3-Bis(2-hydroxy-1-naphthaldimino)propane | 67 | 212 | 78.87 | 5.25 | 7.10 | $C_{25}H_{22}N_2O_2$ | 78.87 | 5.76 | 7.33 | 2.2m; 3.6t; 7.5m; 9.0s |
| 2a | 1,6-Bis(salicylaldimino)hexane | 73 | 72 | 74.31 | 7.37 | 9.08 | $C_{20}H_{24}N_2O_2$ | 74.07 | 7.41 | 8.64 | 2.2m; 3.6m; 7.7m; 9.1s |
| 2b | 1,6-Bis(2-hydroxy-1-naphthaldimino)hexane | 65 | 173 | 75.10 | 6.40 | 6.82 | $C_{20}H_{22}N_2O_2$ | 79.20 | 6.60 | 6.60 | 2.2m; 3.6m; 7.7m; 9.1s |
| 3a | 1,2-Disalicylaldiminobenzene | 60 | 156 | 75.72 | 4.81 | 8.99 | $C_{20}H_{16}N_2O_2$ | 75.95 | 5.06 | 8.86 | 7.0–8.0m; 9.1s |
| 3b | 1,2-Bis(2-hydroxy-1-naphthaldimino)benzene | 65 | 195 | 80.47 | 4.71 | 7.33 | $C_{20}H_{20}N_2O_2$ | 80.77 | 4.80 | 6.73 | 7.0–8.0m; 9.0s |
| 4a | 1,3-Disalicylaldiminobenzene | 63 | 109 | 75.41 | 5.01 | 8.01 | $C_{20}H_{16}N_2O_2$ | 75.95 | 5.06 | 8.86 | 7.0–8.0m; 9.1s |
| 4b | 1,3-Bis(2-hydroxy-1-naphthaldimino)benzene | 60 | 222 | 80.20 | 4.90 | 5.26 | $C_{20}H_{20}N_2O_2$ | 80.77 | 4.80 | 6.73 | 7.0–8.0m; 9.0s |
| 5a | 1,4-Disalicylaldiminobenzene | 73 | 210 | 76.05 | 5.28 | 9.20 | $C_{20}H_{16}N_2O_2$ | 75.95 | 5.06 | 8.86 | 7.0–8.0m; 9.1s |
| 5b | 1,4-Bis(2-hydroxy-1-naphthaldimino)benzene | 65 | 298[d] | 81.16 | 4.32 | 9.96 | $C_{28}H_{20}N_2O_2$ | 80.77 | 4.80 | 6.73 | 7.0–8.0m; 9.0s |
| 6a | *N*,*N*,-Bis(salicylaldimino)diethylenetriamine | 62 | | 67.47 | 6.33 | 13.43 | $C_{18}H_{21}N_3O_2$ | 69.45 | 6.75 | 13.51 | 2.9–2.5m; 4.1t; 7.2m; 8.2s |
| 6b | *N*,*N*'Bis(2-hydroxy-1-naphthaldimino)diethylenetriamine | 70 | 151 | 70.06 | 6.87 | 9.59 | $C_{26}H_{25}N_3O_2$ | 75.91 | 6.08 | 10.22 | 3.0–2.5m; 4.1t; 7.3m; 8.3s |
| 7a | *N*,*N*'-Bis(salicylaldimino)triethylenetetramine | 81 | 102 | 67.70 | 6.88 | 14.42 | $C_{20}H_{26}N_4O_2$ | 67.80 | 7.34 | 15.82 | 2.9–2.5m; 4.1t; 7.2m; 8.2s |
| 7b | *N*,*N*'-Bis(2-hdroxy-1-naphthaldimino)triethylenetetraamine | 78 | 192 | 73.33 | 6.94 | 12.42 | $C_{28}H_{30}N_4O_2$ | 74.00 | 6.60 | 12.33 | 2.9–2.5m; 4.1t; 7.2m; 8.2s |
| 8a | *N*,*N*'-Bis(salicylaldimino)tetraethylenepentaamine | 69 | | 67.14 | 7.50 | 16.88 | $C_{22}H_{31}N_5O_2$ | 66.50 | 7.81 | 17.63 | 3.0–2.4m; 4.1t; 7.2m; 8.2s |
| 9a | *N*,*N*'-Bis(salicylaldimino)pentaethylenehexamine | 65 | | 65.47 | 7.95 | 18.17 | $C_{24}H_{36}N_6O_2$ | 65.49 | 8.18 | 19.10 | 3.1–2.5m; 4.1t; 7.2m; 8.1s |
| 10a | 4,4'-(Disalicylaldimino)diphenylmethane | 72 | 212 | 79.65 | 5.20 | 7.04 | $C_{27}H_{22}N_2O_2$ | 79.80 | 5.42 | 6.90 | 4.1s; 7.1–8.0m; 9.0s |
| 10b | 4,4'-(2-Hydroxy-1-napththaldimino)diphenylmethane | 68 | 198 | 82.75 | 5.84 | 6.11 | $C_{35}H_{26}N_2O_2$ | 83.00 | 5.14 | 5.53 | 4.1s; 6.9–8.2m; 9.0s |
| 11a | (*p*-*N*,*N*'-Dimethylaminophenyl)salicylaldimine | 83 | 133 | 72.18 | 6.99 | 11.74 | $C_{15}H_{16}N_2O$ | 75.00 | 6.67 | 11.67 | 3.0s; 6.9–8.0m; 9.5s |
| 11b | (*p*-*N*,*N*'-Dimethylaminophenyl)-2-hydroxy-1-naphthaldimine | 80 | 163 | 78.59 | 6.25 | 9.73 | $C_{19}H_{18}N_2O$ | 78.62 | 6.21 | 9.66 | 3.0s; 6.8–8.1m; 9.5s |

[a] d = Decomposition point. [b] m, multiplet; s, singlet; d, doublet; t, triplet.

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