

## Thorium[IV], Uranium[VI] and Ce[III] Complexes With Bidentate and Tridentate *Schiff* Bases

Mohamed R. Mahmoud\*, Issa M. Issa†, Mahmoud S. El-Melliigy, and S. A. El-Gyar

Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt

(Received 22 July 1977. Accepted 6 September 1977)

Thorium(IV), Uranium(VI) and Cerium(III) complexes with some bidentate and tridentate *Schiff* bases—derived from salicylaldehyde—have been prepared. The effect of the molecular structure of the *Schiff* base molecule on its tendency towards complex formation has been studied. The structures of the complexes have been investigated by elemental analysis, molar ratio and continuous variation spectrophotometric methods, infrared spectra and conductometric titrations; the apparent formation constants have been determined as well.

*Thorium(IV)-, Uran(VI)- und Cer(III)-Komplexe mit zwei- und dreizähligen Schiff-Basen*

Es wurden Thorium(IV)-, Uran(VI)- und Cer(III)-Komplexe einiger zwei- und dreizähliger *Schiff*-Basen (hergeleitet vom Salicylaldehyd) dargestellt, um den Einfluß der Molekülstruktur der *Schiff*-Base auf das Komplexierungsvermögen zu studieren. Die Struktur der Komplexe wurde mittels Elementaranalyse, elektronenspektrometrischer Methoden, IR-Spektrometrie und Leitfähigkeitsmessungen untersucht. Die Komplexbildungskonstanten wurden gleichfalls bestimmt.

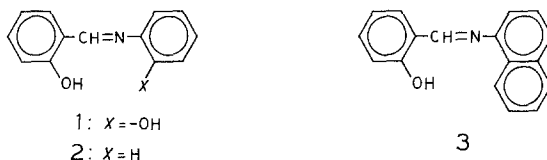
### Introduction

*Schiff* bases derived from salicylaldehyde are well known as polydentate ligands<sup>1, 2</sup>, coordinating in diprotonated or neutral forms. Several papers on the uranium(VI) complexes of monobasic bidentate<sup>3–6</sup> as well as bibasic tridentate<sup>7–9</sup> *Schiff* bases have been reported. On the other hand very scanty references are available regarding the Thorium(IV)<sup>10</sup>—and no work was published on Ce(III) complexes with *Schiff* bases. In the present paper we report the preparation, properties

† Deceased December 1977.

and structures of U(VI), Th(IV) and Ce(III) complexes with some bi- and tri-dentate monobasic *Schiff* bases.

The following ligands have been used for the preparation of the complexes.



## Experimental

### Materials

The chemicals used in this investigation were of reagent grade. Salicylaldehyde was distilled before use.

The *Schiff* bases were prepared by refluxing the amine with salicylaldehyde in 1:1 molar ratio in an alcoholic medium. The *Schiff* bases thus separated were filtered and recrystallized from ethanol.

### Preparation of the Complexes

The different metal complexes were prepared by treating the *Schiff* base dissolved in the least amount of ethanol with the appropriate amount of the metal salt [ $\text{UO}_2(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ ,  $\text{Th}(\text{NO}_3)_4 \cdot 5 \text{H}_2\text{O}$ ,  $\text{CeCl}_3 \cdot 7 \text{H}_2\text{O}$ ] in molar ratios 1:1 and 1:2. The reaction mixture was refluxed for about 0.5-1 h. The solution

Table 1. *Elemental analysis of the Schiff base complexes*

Compound	Formula	%C		%N	
		Found	Calc.	Found	Calc.
1 Th(IV)	$\text{Th}(\text{C}_{13}\text{H}_9\text{NO}_2)_2$	47.20	47.56	4.40	4.26
1 $\text{UO}_2$ (II)	$\text{UO}_2(\text{C}_{13}\text{H}_9\text{NO}_2)_2$	44.58	44.45	3.92	4.03
1 Ce(III)	$\text{H}[\text{Ce}(\text{C}_{13}\text{H}_9\text{NO}_2)_2]$	54.80	55.22	5.08	4.96
2 Th(IV)	$[\text{Th}(\text{C}_{13}\text{H}_{11}\text{NO}_2)_2] (\text{NO}_3)_4$	34.05	34.40	9.15	9.30
2 $\text{UO}_2$ (II)	$\text{UO}_2(\text{C}_{13}\text{H}_{10}\text{NO}_2)_2$	45.13	44.96	4.10	4.00
3 Th(IV)	$[\text{Th}(\text{C}_{17}\text{H}_{13}\text{NO}_2)] (\text{NO}_3)_4$	41.50	41.99	8.75	8.62
3 $\text{UO}_2$ (II)	$[\text{UO}_2(\text{C}_{17}\text{H}_{13}\text{NO})] (\text{NO}_3)_2$	31.60	31.83	6.45	6.55
	$[\text{UO}_2(\text{C}_{17}\text{H}_{13}\text{NO})_2] (\text{NO}_3)_2$	45.35	45.49	6.38	6.31

was then reduced to a small volume on a water bath and left to cool whereby the complexes separated as fine crystals. The solids were filtered off, washed with ethanol, dried and preserved in a desiccator over silica gel. The solid complexes obtained were analysed for their carbon and nitrogen contents. The results of elemental analysis are recorded in Table 1. It is worthy to mention that several attempts have been made to isolate the solid Ce(III) complex with ligands **2** and **3** but without success.

### *Preparation of Solutions*

$10^{-2} M$  solutions of the ligands were prepared by dissolving the accurately weighed amount of each reagent in the appropriate volume of ethanol.  $0.01 M$  solutions of each of U(VI), Th(IV) and Ce(III) were obtained by dissolving the *A. R.*  $UO_2(NO_3)_2 \cdot 6 H_2O$ ,  $Th(NO_3)_4 \cdot 5 H_2O$ ,  $CeCl_3 \cdot 7 H_2O$ , resp., in pure absolute ethanol. These solutions were standardized using the recommended procedures<sup>11</sup>. Solutions of low molarity were prepared by accurate dilution of the stock solutions by pure absolute ethanol.

### *Physical Measurements*

The electronic absorption spectra in the visible and ultraviolet regions were recorded with a Unicam SP 800 spectrophotometer using 1 cm matched glass stoppered silica cells.

The infrared spectra of the ligands and their complexes were recorded on a Beckman infrared spectrophotometer as KBr disc.

Conductivity measurements were carried out using a PYE conductance bridge at 25°C.

## Results

The absorption spectra of ligands **1**, **2** and **3** and their solutions with the metal ions under investigation have been recorded. The ir-spectra of the ligands and their complexes are summarized in Table 2. The stoichiometry of the complexes was studied by applying the molar ratio and continuous variation method. The results proved that ligand **1** and **2** form complexes of the types 1:2 only (metal:ligand) whereas ligand **3** forms complexes of the type 1:1 and 1:2. Representative results are given in Figs. 2 and 3. The formation of 1:1 and 1:2 complexes is supported by the results of conductometric titrations. The titration of 25 ml  $10^{-3} M$  of the metal ion solutions with  $10^{-2} M$  of the ligand solution yields curves with one break at the molar ratio 1:2 in case of ligands **1** and **2**, and two breaks at molar ratios 1:1 and 1:2 in case of ligand **3** (Fig. 4).

## Discussion

### *Electronic Spectra*

The lack of resemblance between the spectra of ligand **1** and its mixtures with Th(IV),  $UO_2(II)$  and Ce(III) in 2:1 ratio (Fig. 1) may be taken as an evidence for complex formation. Generally the longer wavelength band of the ligand which was assigned to a transition of intramolecular charge transfer type within the whole molecule<sup>12</sup> exhibit a red shift upon complexation. This red shift can be explained by an easier intramolecular charge transfer in the complex ligand, hence the  $M^{x+}$ —ligand bonding is more ionic in comparison to the  $H^+$ —ligand bond.

On the other hand complex formation of U(VI) and Ce(III) with ligands **2** and **3** is observed only at higher concentrations of these ligands relative to ligand **1** ( $> 7.0 \cdot 10^{-4} M$  in case of ligand **2** and  $> 3 \cdot 10^{-3} M$  in case of ligand **3**). This was concluded from the appearance of absorption bands for the complexed solutions, the blank being a solution of the ligand of the same concentration as in the solution of the complexes. This behaviour can be explained by the fact that Schiff bases derived from salicylaldehyde form metal complexes through the azomethine-N and the *ortho* OH. Thus the difference in tendency of the

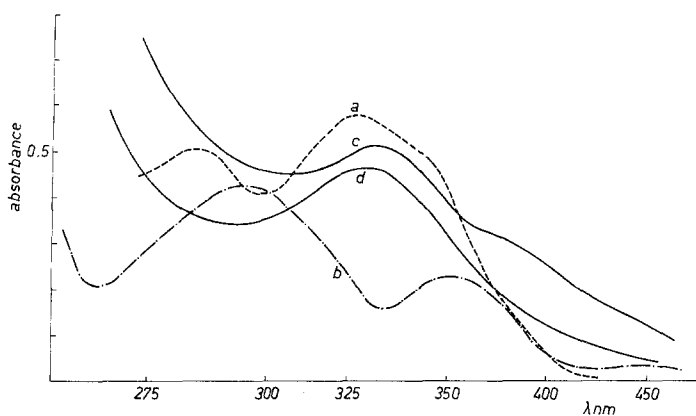


Fig. 1. Absorption spectra of  $1 \cdot 10^{-4} M$  solutions of ligand **1** plus Th(VI)-, U(VI)- and Ce(III)-solutions in 2:1 ratio. *a* Ligand **1**; *b* Ligand **1** Th(VI); *c* Ligand **1**  $UO_2(II)$ ; *d* Ligand **1** Ce(III)

ligands under investigation towards complex formation can be expected to be due to the difference in the strength of the intra molecular hydrogen bond established in the ligand molecule. In ligand **1** the interaction between the two *ortho* OH groups or between each of them and the azomethine nitrogen will weaken the strength of the H-bond between the basic nitrogen atom and the (aldehydic) OH group. This results in an increase of the tendency of this ligand towards complex formation. The absence of an absorption band at  $3,200-3,600 \text{ cm}^{-1}$  in the ir-spectrum of the free ligand **1** can be considered as a strong evidence for this behaviour. The high donor character of the *p*-OH group of the amine residue of the ligand **2** moiety or the greater bulk of the naphthalene moiety of ligand **3** will increase the charge density at the  $C=N$  group. This leads to a stronger H-bonding between the nitrogen atom and the *o*-OH group attached to

the aldehyde moiety which reflects itself in a weak tendency of ligands **2** and **3** towards complex formation.

Furthermore, it was found that Th(IV) does not form complexes easily with ligands **2** and **3** at room temperature even on using higher concentrations of these ligands. This is presumably due to the weak

Table 2. *Some infrared frequencies (in  $\text{cm}^{-1}$ ) of the Schiff bases and their complexes*

Ligand 1	Th(IV)	Complexes		Ligand 2	Complexes	
		UO <sub>2</sub> (II)	Ce(III)		Th(IV)	UO <sub>2</sub> (II)
—	—	3400	—	3320	3400	—
3010	3070	3045	3050	3060	3000	3200
2540	—	—	—	2560	—	—
1605	1615	1612	1612	1618	1650	1608
1290	1320	1305	1310	1288	1290	1290

Ligand 3	Th(IV)	Complexes		Assignment
		UO <sub>2</sub> (II) 1:1	1:2	
—	3400	3460 w	3460 w	OH-stretching
3050	3080	3060	3030	aromatic CH and CH stretching
2620	—	—	—	intramolecular H-bonded OH
1596	1620	1640	1632	C=N stretching vibration
1284	1284	1290	1292	phenolic C—O stretching

tendency of both ligands **2** and **3** towards complex formation and the fact that in Th(IV) the energy of the  $5f$  orbitals is not comparable with those of  $6d$ ,  $7s$  and  $7p$  orbitals<sup>13</sup>. This will cause the inability of the  $5f$  orbitals to form hybrid orbitals which might have led to covalent bonds with appreciable strengths. This is in accordance with the results of microanalysis of Th(IV) solid complexes with ligands **2** and **3** (cf. Table 1) as well as the ir-spectra (Table 2), from which it was proved that the ligand molecules and not its anions coordinate to the central thorium metal ion.

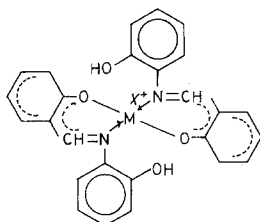
#### *Infrared Spectra*

In Table 2 frequencies and their assignments are listed. Some interesting features of the ir-spectra should be emphasized:

The broad band in the region  $2,540$ - $2,620 \text{ cm}^{-1}$  appearing in the ir-

spectra of the free ligands is attributed to the intramolecular hydrogen bonded OH established between the aldehydic *o*-OH group and the basic nitrogen atom. This assignment is in line with that made by other investigators<sup>14-17</sup>. This broad band of the ligands disappears in the complexes leaving only a fine structure which is due mainly to the CH modes.

The strong band found around  $1,284\text{ cm}^{-1}$  in the ligands is assigned to the phenolic C—O stretching vibration<sup>18, 19</sup>. This is shifted towards higher frequency on complexation. The red shift observed of the phenolic C—O bond in going from a hydrogen bonded structure to a covalent metal bonded structure may be due to the higher mesomeric interaction in the complex, which is activated by the presence of the metal ion. This mesomeric interaction can be represented schematically as follows.



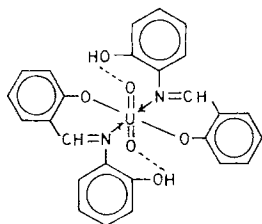
A comparison of the C=N stretching vibration of the free *Schiff* base with that found in the complexes shows a consistent shift towards higher frequency, suggesting coordination of the *Schiff* base through the nitrogen of the azomethine group.

#### *Structure of Complexes*

Our study reveals that ligand **1** coordinates to Th(IV) and Ce(III) as tridentate ligand ( $L^{--}$ ) but with  $\text{UO}_2(\text{II})$  as bidentate ligand ( $\text{HL}^-$ ). This was achieved from the following:

- (i) Microanalysis of the solid metal complexes (Table 1).
- (ii) The absence of an absorption band in the  $3,200\text{--}3,600\text{ cm}^{-1}$  region in the infrared spectra of Th(IV) and Ce(III) complexes which is due either to the stretching frequency of the free or complexed OH group. This is an indication that the oxygen atoms of the two OH groups must be coordinated to these central metal ions. On the other hand the appearance of a broad band at  $3,400\text{ cm}^{-1}$  in the infrared spectrum of the  $\text{UO}_2(\text{II})$  complex (Table 2) may be ascribed to the stretching frequency of the free OH group attached to the aniline residue of the ligand moiety. The broadening and weakening of this

band is due to the existence of an intramolecular hydrogen bond between this OH group and the oxygen atom of the complexed uranyl ion. This can be represented as follows:



However, the inactivity of this OH group towards complex formation with  $\text{UO}_2(\text{II})$  has been reported previously also<sup>20</sup>.

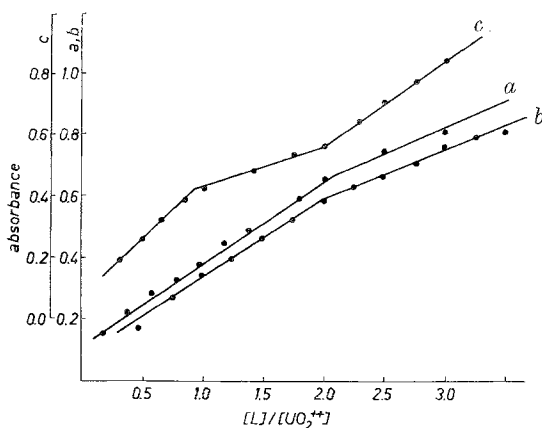


Fig. 2. Molar ratio method for  $\text{UO}_2(\text{II})$ -ligand complexes. *a* Ligand **1** ( $\lambda = 400 \text{ nm}$ ,  $[\text{UO}_2^{++}] = 5 \cdot 10^{-4} \text{ M}$ ); *b* Ligand **2** ( $\lambda = 415 \text{ nm}$ ,  $[\text{UO}_2^{++}] = 2 \cdot 10^{-3} \text{ M}$ ); *c* Ligand **3** ( $\lambda = 430 \text{ nm}$ ,  $[\text{UO}_2^{++}] = 1.5 \cdot 10^{-3} \text{ M}$ )

(iii) The increase in conductance upon titrating metal ion solutions by the ligand is probably due to the liberation of hydrogen ions during complex formation.

It is worthy mentioning that the tridentate character of this ligand in its reaction with vanadium(V) was previously indicated by *Biradar* and *Kulkarni*<sup>21</sup>.

With respect to ligand **2**, it was concluded that this ligand coordinates to  $\text{Th}(\text{IV})$  and  $\text{UO}_2(\text{II})$  as a bidentate ligand to yield complexes of the type 2:1. In these complexes the ligands of type  $(\text{HL}^-)$  are coordinated to  $\text{UO}_2(\text{II})$ , whereas  $(\text{H}_2\text{L})$  is coordinated to

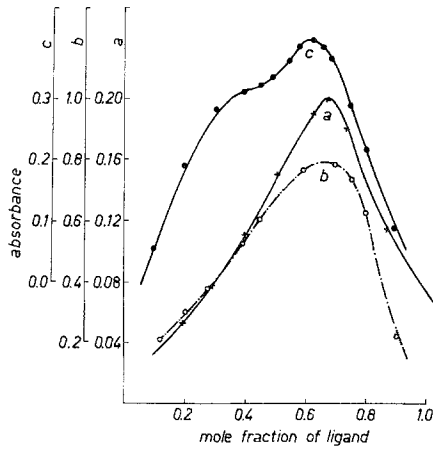


Fig. 3. Continuous variation method for  $\text{UO}_2(\text{II})$ -ligand complexes. *a* Ligand **1** ( $\lambda = 405 \text{ nm}$ , total concentration =  $2 \cdot 10^{-4} \text{ M}$ ); *b* Ligand **2** ( $\lambda = 420 \text{ nm}$ ,  $1 \cdot 10^{-3} \text{ M}$ ); *c* Ligand **3** ( $\lambda = 420 \text{ nm}$ ,  $2.5 \cdot 10^{-3} \text{ M}$ )

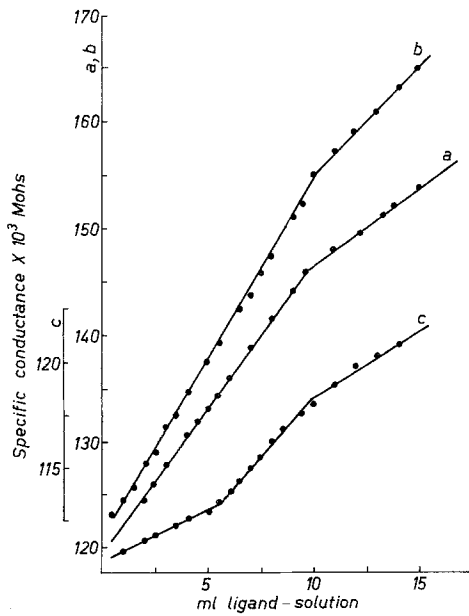


Fig. 4. Conductometric titration of  $10^{-3} \text{ M}$   $\text{UO}_2(\text{II})$  with  $10^{-2} \text{ M}$  of: *a* Ligand **1**; *b* Ligand **2**; *c* Ligand **3**



Th(IV). This conclusion was gained from the microanalysis of the solid complexes (Table 1) and the appearance of a band at  $3,400\text{cm}^{-1}$  in the ir-spectrum of Th(IV) complex (Table 2) which can be ascribed to the coordinated O—H.

Finally this investigation reveals that ligand **3** acts with Th(IV) and  $\text{UO}_2(\text{II})$  as bidentate ligand, where the ligand molecules (HL) are coordinated to these central metal ions. This is confirmed by the

Table 3. Evaluation of the apparent formation constant ( $K_f$ ) for the 1:2 (metal:ligand) complexes

Method	Th(IV)	$\text{UO}_2(\text{II})$	Ce(III)
<i>Complexes with ligand 1</i>			
mol. ratio	$1.1 \cdot 10^7$	$1.25 \cdot 10^{10}$	$1.80 \cdot 10^{10}$
cont. var.	$1.0 \cdot 10^7$	$1.70 \cdot 10^{10}$	$2.70 \cdot 10^{10}$
<i>Complexes with ligand 2</i>			
mol. ratio	—	$2.20 \cdot 10^9$	$1.40 \cdot 10^9$
cont. var.	—	$2.80 \cdot 10^9$	$0.95 \cdot 10^9$
<i>Complexes with ligand 3</i>			
mol. ratio	—	$1.00 \cdot 10^8$	$1.70 \cdot 10^8$
cont. var.	—	$0.95 \cdot 10^8$	$2.80 \cdot 10^8$

elemental analysis of the solid complexes (cf. Table 1) and the appearance of a weak and broad band in the region  $3,400\text{--}3,460\text{cm}^{-1}$  in the ir-spectra of the complexes which may be ascribed to absorption by the coordinated —OH. Furthermore, the very little change in conductance upon titrating  $\text{UO}_2(\text{II})$  solution with this ligand (Fig. 4) can be considered as strong evidence for the fact that the molecules of the ligand and not its anions are coordinated to the central metal ions.

#### *The Apparent Formation Constant*

The apparent formation constants ( $K_f$ ) of the complexes formed in solution are determined from the results of spectrophotometric measurement of molar ratio and continuous variation methods<sup>22</sup> (Table 3). The  $K_f$  values show that the stability of the complexes of the same metal depends largely on the molecular structure of the ligand used. The stability in decreasing order is: **1** > **2** > **3**.

## References

- <sup>1</sup> B. H. Holm, G. W. Everett, and A. Charravarty, Progress in Inorganic Chemistry (F. A. Cotton, ed.), Vol. 8. New York: Interscience. 1966.
- <sup>2</sup> M. D. Hobday and T. D. Smith, Coordin. Chem. Rev. **9**, 311 (1973).
- <sup>3</sup> V. G. Kulkarni, S. N. A. Taputre, and N. N. Sirmokadam, J. Indian Chem. Soc. **49**, 111 (1972).
- <sup>4</sup> A. K. Mukerjee and P. Ray, J. Indian Chem. Soc. **32**, 633 (1955).
- <sup>5</sup> P. Teyssie and J. J. Charette, Spectrochim. Acta **19**, 1407 (1963).
- <sup>6</sup> S. Yamada and A. Takeuchi, Bull. Chem. Soc. Jap. **42**, 2549 (1969).
- <sup>7</sup> S. N. Poddar, Z. anorg. allgem. Chem. **322**, 326 (1963).
- <sup>8</sup> A. K. Mukerjee and P. Ray, J. Indian Chem. Soc. **32**, 567 (1955).
- <sup>9</sup> R. G. Vijay and J. P. Tandon, Mh. Chem. **107**, 95 (1976).
- <sup>10</sup> N. S. Biradar and V. H. Kulkarni, Proc. Chem. Symb. **2**, 270 (1969).
- <sup>11</sup> A. I. Vogel, A Text Book of Quantitative Inorganic Analysis, 2nd ed., p. 471—473. London-New York-Toronto: Longmans, Green. 1959.
- <sup>12</sup> R. M. Issa, A. A. El-Samahy, and S. H. Etaiw, Z. Phys. Chem. **255**, 853 (1974).
- <sup>13</sup> F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, p. 1077. New York-London-Sydney-Toronto: J. Wiley. 1966.
- <sup>14</sup> L. J. Bellamy, The infrared of complex molecules, 2nd ed., pp. 64, 95, 263, 350. New York: J. Wiley. 1958.
- <sup>15</sup> K. Ueno and A. E. Martell, J. Phys. Chem. **60**, 1270 (1956).
- <sup>16</sup> A. W. Baker and A. T. Shulgin, J. Amer. Chem. Soc. **81**, 1223 (1959).
- <sup>17</sup> H. H. Freedman, J. Amer. Chem. Soc. **83**, 2900 (1962).
- <sup>18</sup> C. S. Marvel, S. A. Aspey, and A. Dudley, J. Amer. Chem. Soc. **78**, 4909 (1956).
- <sup>19</sup> J. E. Kovacic, Spectrochim. Acta **23A**, 183 (1967).
- <sup>20</sup> R. G. Vijay and J. P. Tandon, Z. Naturforsch. **31b**, 22 (1976).
- <sup>21</sup> N. S. Biradar and V. H. Kulkarni, Rev. Roum. Chim. **16**, 1203 (1971).
- <sup>22</sup> I. M. Issa, R. M. Issa, and M. K. Hassan, Egypt. J. Chem. **16**, 19 (1973).