THE INTERACTION OF 2,2'-BISBENZOXAZOLINE WITH URANYL ION

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Abstract—The synthesis and characterization of a number of complexes of uranyl (VI) ion containing the anionic residue of bis-benzoxazoline rearranged to its Schiff base tautomeric form (H₂B) and a neutral ligand are reported and discussed together with kinetic data on the reaction between UO_2^{2+} and the organic ligand H₂B in ethanol solution at different temperatures.

INTRODUCTION

URANYL complexes containing as anionic chelate the residue L^{2-} of a deprotonated Schiff base H_2L have been known for many years[1–3]. The structures of various of these complexes have been determined by X-ray investigations[4–6].

We started recently the study of the interactions between 2,2'-bisbenzoxazoline, H₂B, and uranyl salts. The molecule H₂B is known[8] to have the structure in Fig. 1(a) and it is also known that it can be rearranged by transition metal ions to give complexes derived from the tautomeric tetradentate Schiff base[7, 8] (Fig. 1b). Thus, on allowing H₂B to react in ethanol with hydrated uranyl salts (chloride or nitrate), the complex [UO₂(B) (H₂O)] is formed and its structure corresponds to that of a Schiff-base derivative[9].

We now report the preparation and characterization of complexes of the type [UO₂(B) (A)] and some information on the mechanism of reaction between uranyl (VI) ion and 2,2'-bisbenzoxazoline.

EXPERIMENTAL

Materials. $UO_2Cl_2 \cdot 3H_2O$ and $UO_2(NO_3)_2 \cdot 6H_2O$ and the solvents were reagent grade. 2,2'-Bisbenzoxazoline was prepared according to the method of Bayer[10].

The complex [UO₂(B) (H₂O)] was prepared in three different ways:

(i) by refluxing in ethanol for 3 hr equimolar amounts of a uranyl salt (chloride or nitrate) and 2,2'-bisbenzoxazoline. The blue precipitate was filtered, washed with ethanol, dried in vacuum.

(ii) by adding to a solution of 1 mM of a uranyl salt in 50 ml ethanol, first 1 mM (58 mg) of glyoxal and then 2 mM (218 mg) of o-aminophenol. A blue product precipitates, after 12 hr.

(iii) by adding to a solution of 1 mM of a uranyl salt in 50 ml

ethanol first 2 mM of o-aminophenol and then, after the yellow solution turned to dark red, 1 mM of glyoxal. Again a blue precipitate is formed after 12 hr.

Analytical figures are reported in Table 1.

The complexes [UO₂(B) (py)] and [UO₂(B) (Me₂SO)] were obtained by dissolving 200 mg of [UO₂(B) (H₂O)] in 10 ml of pure pyridine or 5 ml of dimethylsulphoxide, respectively. The products precipitated on addition of n-pentane (80 ml), were isolated by filtration and washed with n-pentane.

The complex [UO₂(B) (Ph₃PO)] was prepared by adding a 10-fold excess of Ph₃PO to a solution of 200 mg of [UO₂(B) (H₂O)] in 50 ml of chloroform. The solution was clarified by filtration, partially evaporated and the product precipitated by adding diethylether. It was filtered, washed with CHCl₃/ether (1:10) and vacuum dried.

I.R. spectra were recorded for Nujol mulls or KBr pellets with a Perkin-Elmer 621 spectrophotometer, ¹H NMR spectra were recorded with a Varian T 60 instrument, using TMS as internal standard and CDCl₃ (or py-d₅ or DMSO-d₆ wherever possible) as solvent.

Kinetic measurements. The changes with time of the optical density of an ethanolic solution originally containing a uranyl salt (chloride or nitrate) and 2,2'-bisbenzoxazoline was followed, at various wavelengths in the range 300–450 nm, using an Optica CF4R double beam recording spectrophotometer. Known volumes of ethanolic solutions of the uranyl salt and reagent were brought separately to the desired temperature and then mixed in the thermostated cell of the spectrophotometer. All the species involved in the reaction, including 2,2'-bisbenzoxazoline, follow closely Beer's law in ethanol. The kinetic experiments were carried out in the presence of an excess of the organic reagent in order to achieve pseudo-first-order conditions.

RESULTS AND DISCUSSION

It is known[8] that the condensation product between glyoxal and o-aminophenol is not the corresponding Schiff-base (Fig. 1b) but has the formula shown in Fig. 1(a). Such a structure is confirmed by absence in the i.r. spectrum of $\nu_{(C=N)}$ in the range 1700–1500 cm⁻¹ and by the presence of the N–H stretching band at 3370 cm⁻¹ (see Table 2). The ¹H NMR spectrum is also consistent with this formulation, showing peaks at $5·32\delta$ and $5·39\delta$ which can be attributed to the H_a protons and two peaks at $7·27\delta$ and $7·34\delta$ attributed to the H_b protons in Fig. 1(a).

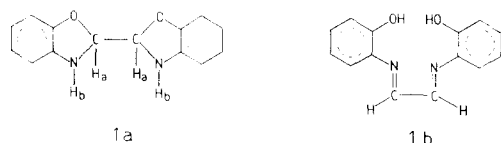

Fig. 1.

Table 1. Elemental analyses and physical properties of the uranyl complexes†

Compound	C		H		M		
	Calcd.	Found	Calcd.	Found	Calcd.	Found	M.p. (°C)
[UO₂(B) (H₂O)]*	31·82	32·00	2·65	2·48	5·30	5·49	>270
[UO₂(B) (py)]	38·71	39·00	2·83	2·84	7·13	7·37	>270
[UO₂(B) (Ph₃PO)]	48·73	49·12	3·43	3·21	3·55	3·44	>270
[UO₂(B) (Me₂SO)]	32·65	32·84	3·06	3·01	4·76	4·66	>270

*The percentage of H₂O was determined by Karl-Fischer method and is in good agreement with the above formulation.
†All products were blue.

(J$_{ab}$ = 7·0 cps is consistent with the values obtained for vicinal hydrogens).

The blue color of [UO₂(B) H₂O] is probably due to the planarity of the system of conjugated double bonds present in the molecule and this is the major difference from other Schiff base complexes of the uranyl ion.

If we compare for instance (Fig. 2) the complex with ligand B with that derived from the Schiff-base *o* - phenylen - N,N' - bis(salicyladimine), for both of which the structure is known [4, 9], it appears that only in the first one is the structure planar in the equatorial plane of the UO₂²⁺ ion. This could be due to the fact that in the case of ligand B three 5-membered rings are formed in the chelation, whereas in the second case there are two 6-membered rings and one 5-membered ring, which, if coplanar could give rise to some strain. If it is true, this is a difference between the behaviour of uranyl ion and that of transition metal ions of the *d*-block, where a 6-5-6 combination of chelating ring is less strained than the 5-5-5 combination [11, 12].

It seems reasonable to assume also that the complexes of the type [UO₂(B) (A)], derived from [UO₂(B) (H₂O)] by substitution of the water molecule with the neutral ligand A, have the same basic structure. Thus all these species are uranyl complexes with equatorial coordination number five, containing ligand B in the form of the deprotonated Schiff bases. In fact, this point can be easily seen (Table 2) by comparing the main features of the i.r. absorption spectra of the complexes [UO₂(B) (A)] and of the analogous uranyl complexes derived from the

Schiff-base *o* - phenylen - N,N' - bis(salicylaldimine) [3].

The kinetic data reported in Table 3 can be reasonably attributed to the reaction:

$$[(UO_2)(S)_n]^{2+} + H_2B \rightarrow [UO_2(B)(S)] + 2H^+ \quad (1)$$

where S indicates ethanol or water (the water is present in the system since the uranyl salts are hydrated), H₂B is the 2,2'-bisbenzoxazoline and B is the anionic residue of the Schiff base corresponding to 2,2'-bisbenzoxazoline in its tautometric form. In fact, the u.v. spectrum at the end of the reaction is that of [UO₂(B)(H₂O)] in acid ethanol, whereas the spectrum obtained by extrapolation to time zero of the kinetic data is that expected for the mixture of the reacting species. The reaction is completed in only one detectable kinetic stage.

An alternative reaction scheme, also in agreement with the experimental data, is the slow isomerization of the molecule H₂B to the tautomeric Schiff base form, followed by fast coordination with uranyl ion. Our experimental technique is such that we cannot study the dependence of the rate constant upon the uranyl ion concentration. However, we have evidence that the rate is not independent of |UO₂²⁺| and therefore we prefer the hypothesis of a direct bimolecular reaction. Some hypothesis on the mechanistic meaning of these data and the associated activation parameters, ΔH* = 21·9 kcal/mole and ΔS* = 12·1 e.u./mole can be made. The

Table 2. I.R. spectra of the ligand H₂B, the derived complexes |UO₂(B)(A)| and those of the type |UO₂(B₄)(A)| (cm⁻¹).

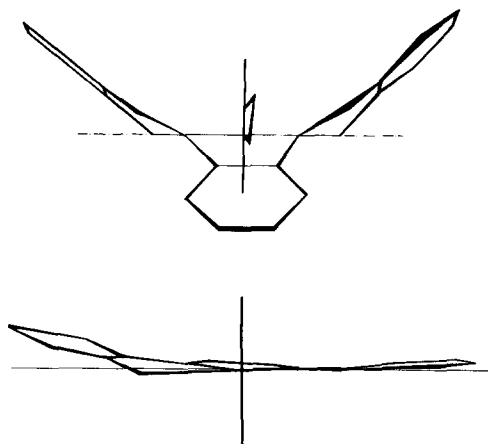| Compound	$\nu_{C=N}$	$\nu_{asO-U-O}$	Other peculiar bands
H₂B	—	—	3370 N–H
H₂B$_a^*$	1619; 1610	—	—
[UO₂(B) (H₂O)]	1585; 1578	900	—
[UO₂B₄(EtOH)]	1602; 1598	910	—
[UO₂(B) (py)]	1574	893	—
[UO₂(B₄) (py)]	1605; 1598	895	—
[UO₂(B) (Ph₃PO)]	1572	885	1135 $\nu_{(P-O)}$
[UO₂(B₄) (Ph₃PO)]	1604	895	1143 $\nu_{(P-O)}$
[UO₂(B) (Me₂SO)]	1573	890	995 $\nu_{(S-O)}$
[UO₂B₄(Me₂SO)]	1605	892	992 $\nu_{(S-O)}$

*H₂B$_a$ = *o*-phenylene-N,N'-bis(salicylaldimine).

Fig. 2.

Table 3. Pseudo-first-order rate constants (sec^{-1}) for the reaction (1).

|Substrate| $(M \times 10^4)$	|H_2B| $(M \times 10^2)$	$k_{obs} \times 10^3$	$t\,^{\circ}C$
0·5	0·25	0·62	25
0·5	0·50	1·10	25
0·5	1·00	2·46	25
0·5	1·33	3·45	25
0·5	1·66	4·30	25
0·5	0·66	4·37	32
0·5	1·00	5·48	32
0·5	1·33	7·23	32
0·5	1·66	8·59	32
0·5	0·66	23·72	40
0·5	1·00	37·07	40
0·5	1·33	47·67	40
0·5	1·66	58·26	40

Second order rate constants $(M^{-1}\,\text{sec}^{-1})$; 25°C
$0.253\,M^{-1}\,\text{sec}^{-1}$; 32°C $\,0.547\,M^{-1}\,\text{sec}^{-1}$; 40°C
$1.550\,M^{-1}\,\text{sec}^{-1}$.
Activation parameters:
$\Delta H^* \simeq 21.9\,k_{cal}/M; \Delta S^* \simeq 12.1\,\text{u.e.}/M.$

linear dependence of k_{obs} from $|H_2B|$ suggests a rate law of the type: rate $= k \,|UO_2(S)_n| \,|H_2B|$ and indicates that both the uranyl ion and organic reagent are present in the transition state. The positive value of the entropy of activation indicates that during the formation of the transition state there is a synchronous release of a number of particles, probably solvent molecules and/or proto-

nated solvent molecules. This means that the reagent H_2B rearranges to the Schiff base form during the formation of the activated complex. Parallel measurements of the rate of reaction between uranyl ion and various Schiff bases made under the same experimental conditions indicate that the processes are largely too fast to be followed by the conventional techniques.

REFERENCES

1. P. Pfeiffer, Th. Hesse, H. Pfitzner, W. Scoll and H. Thielert, *J. Fur. Pract. Chem.* **149**, 217 (1937).
2. R. H. Holm, G. W. Everett and A. Chakravorty, *Progress in Inorgamic Chemistry* (Edited by F. A. Cotton), Vol. 7, p. 23. Interscience, New York (1966).
3. L. Cattalini, S. Degetto, M. Vidali and P. A. Vigato, *Inorg. Chim. Acta,* **6**, 173 (1972).
4. G. Bandoli, D. A. Clemente, U. Croatto, M. Vidali and P. A. Vigato, *Chem. Comm.,* 1330 (1971).
5. G. Bandoli, D. A. Clemente, U. Croatto, M. Vidali and P. A. Vigato, *J. C. S. Dalton Trans.* 2331 (1973).
6. G. Bandoli, D. A. Clemente, F. Benetollo, M. Vidali, P. A. Vigato and U. Casellato, *Inorg. Nucl. Chem. Lett.* **9**, 433 (1973).
7. H. Jadamus, R. Fernando and H. Freser, *J. Am. Chem. Soc.* **86**, 3056 (1964).
8. E. Bayer and G. Schek, *Ber,* **93**, 1184 (1960).
9. G. Bandoli, L. Cattalini, D. A. Clemente, M. Vidali and P. A. Vigato, *Chem. Comm.* 344 (1972).
10. E. Bayer, *Ber.* **90**, 2324 (1957).
11. M. D. Hobday and T. D. Smith, *Coord. Chem. Rev.* **9**, 311 (1972).
12. M. Calligaris, G. Nardin and L. Randaccio, *Coord. Chem. Rev.* **7**, 385 (1972).