Nature of Bonding in Mixed Chelate Complexes of Dioxouranium(VI) with Benzhydroxamic Acid

PHATIK CHANDRA KUNDU* & SADANANDA BHATTACHERJYA
Inorganic Chemistry Laboratories, University College of Science, Calcutta University, 92, A.P.C. Road, Calcutta 700 009

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Several anions and coordinating amines have been successfully employed along with benzhydroxamic acid (BH) for chelation and subsequent expansion of coordination number of dioxouranium(VI) in the established bis complex of dioxouranium(VI) with BH. DTA and TG data of the mixed chelate complexes indicate the following order of relative stabilities: acetato = iodo = bipyridyl < carboxato < chloro = phenanthroline < urea < nitrito < sulphato. Far infrared data of the complexes have been utilised to predict geometry of the complexes. The lowering in symmetry of the anions as revealed by the IR data indicates their coordination. The broad and split νs (O-U-O) in phenanthroline and bipyridyl complexes favours bridged structures. The linearity of UO2+ moiety in the complexes has been suggested.

The bidentate benzhydroxamic acid (BH) has been reported1 to form a complex of the type, \( \text{UO}_4(\text{C}_4\text{H}_4\text{CONHO})_2\cdot\text{H}_2\text{O} \) with dioxouranium(VI). The use of BH in the analysis of \( \text{UO}_4^{2+} \) is also reported2,3. Except for these isolated reports no attempt has been made so far to study the mixed chelate complexes of dioxouranium(VI) involving BH and other ligands. The present study of the mixed chelate complexes of dioxouranium(VI) with BH and the anionic ligands like \( \text{SO}_4^{2-}, \text{Cl}^- \) and 1,10-coordinating amines like 1,10-phenanthroline (phen), 2,2'-bipyridyl (bipy) or urea is a step to fill the void. As a result of detailed characterisation of the mixed chelate complexes based on far IR and DTA, it is observed that the overall coordination of uranium changes and expands with the formation of mixed chelate complexes based on far IR and DTA, it is observed that the overall coordination of uranium changes and expands with the formation of mixed chelate complexes of the types: (i) \((\text{NH}_4)_x[\text{UO}_4(\text{B})_2(L_x)]_X \cdot x\text{H}_2\text{O} \) where \( L = 4\text{CO}_2^-; \text{CH}_3\text{COO}^-, \text{SO}_4^{2-}, \text{Cl}^- \) and \( x = 0.5 \) to 2; (ii) \( \text{NH}_4[\text{UO}_4(\text{B})_2\text{L}_2\text{H}_2\text{O}] \cdot x\text{H}_2\text{O} \) where \( L = \text{Br}^-; \text{I}^- \); and (iii) \((\text{UO}_4)_2(\text{B})_x \) where \( L = \text{phen}, \text{bipy} \). Complexes like \( \text{NH}_4[\text{UO}_4(\text{B})_2\text{NO}_3] \cdot x\text{H}_2\text{O} \) and \( \text{UO}_4(\text{B})_2\cdot2\text{CO}(\text{NH}_3)_2 \) have been obtained.

Materials and Methods

All the reagents used were of AR grade. Benzhydroxamic acid (BH) was prepared according to the reported method4.

Preparation of the mixed chelate complexes: Ammonium carbonato bis(benzhydroxamato)dioxouranium(VI) dihydrate \((\text{NH}_4)_x[\text{UO}_4(\text{B})_2\text{CO}_2] \cdot x\text{H}_2\text{O} \) — To an aqueous uranyl nitrate solution (6%, 15 ml) was added solid ammonium carbonate (0.5 g) in small portions till a greenish white precipitate appeared first and then dissolved on stirring into a clear solution. To this clear solution was added a solution (6%, 15 ml) of benzhydroxamic acid in acetone-water (2:1). The mixture became a clear red solution. In case of any turbidity, minimum amount of water was added to dissolve it, otherwise filtered to get a clear red solution, which was heated on a boiling water-bath for 10-15 min., when an orange-brown precipitate separated. The precipitate was allowed to settle for 45 min, filtered, washed with hot water and finally dried in a vacuum desiccator for 72 hr, yield > 60%.

\((\text{NH}_4)_x[\text{UO}_4(\text{B})_2(L)_x] \cdot x\text{H}_2\text{O} \) where \( L = 4\text{SO}_4^{2-}, \text{CH}_3\text{COO}^-, \text{Cl}^-, \text{Br}^-; \text{I}^- \) and \( x = 0.5 \), 1, 2 etc., \( \text{NH}_4[\text{UO}_4(\text{B})_2\text{NO}_3] \cdot x\text{H}_2\text{O} \), \( \text{H}_2\text{O} \) and \( \text{UO}_4(\text{B})_2\cdot2\text{CO}(\text{NH}_3)_2 \) — To an aqueous solution (5%, 20 ml) of uranyl nitrate of \( \text{pH} \sim 1 \) was added slowly calculated amounts of solid ammonium sulphate, acetate, chloride, nitrate salts and urea respectively so that the molar ratio of uranyl nitrate and the ammonium salt or urea was nearly 1:2. The resultant solution was maintained at \( \text{pH} \sim 5 \) and the colour of the same changed to dirty yellow from fluorescent green. To this solution was added an acetone solution (6%, 15 ml) of BH at 80°C when the solution turned red. Any turbidity at this stage was removed by the addition of water (2-5 ml). Any undissolved matter was removed by filtration, the filtrate was digested over a boiling water-bath for 10 min when orange yellow or orange-brown precipitates separated out. It was filtered hot and the precipitate washed well with warm acetone-water mixture. The precipitate was dried for 72 hr, yield 70-75%.

\( \text{NH}_4[\text{UO}_4(\text{B})_2 \cdot \text{X} \cdot \text{H}_2\text{O}] \cdot x\text{H}_2\text{O} \) (X=Br and I) — To an aqueous (8%, 15 ml) of BH was added ammonium bromide or iodide (0.5 g) and this solution mixed with uranyl nitrate solution (6%, 15 ml). The final mixture was dark brown in colour. This solution yielded orange brown (in the case of X=Br) and brown precipitate (for X=I) on digestion over a boiling water bath for 10 min, allowed to settle for 15 min and filtered while hot to avoid the coprecipitation of any unreacted matter. The precipitate was washed well with hot water followed by acetone and dried for 72 hr; yield 60-65%.

\( \text{UO}_4(\text{B})_2\cdot x \) (where \( X = 2,2' \)-bipyridyl and 1,10-Phenanthroline) — 1,10-Phenanthroline (0.4 g, 0.47 ml) was dissolved in ethanol (2 ml) and added
slowly to a solution (14%, 5 ml) of uranyl nitrate in absolute ethanol. A yellow white precipitate appeared. To this suspension was added a solution (5%, 10 ml) of BH in acetone-water (1:1) and stirred to dissolve the suspension, giving finally a red coloured solution. The solution was digested over a boiling water-bath for 10-15 min when redish brown precipitate separated out, which was filtered hot, washed with aq. ethanol and dried for 72 hr; yield 50-60%.

For the preparation of 2,2'-bipyridyl mixed chelate complex, a 20% methanolic solution of 2,2'-bipyridyl was added to alcoholic uranyl nitrate solution till the greenish yellow solution changed to dirty yellowish colour (pH ~5). To this solution was added solution of BH in acetone-water when the colour of the solution turns red. The red solution on digestion over a boiling water-bath resulted in brown-yellow precipitate, which was washed and dried; yield 60-65%.

Physical measurements — Conductances of 10^{-3}M solutions in DMF were measured at 30°C using a Philips conductivity bridge model GM 4249 and a dip type cell. TG analyses were carried out in a Derivatograph-OD-103 (Hungary) at a heating rate of 7°C/min. DTA data were recorded in air in a Perkin-Elmer 577 spectrophotometer using CsI pellets in the range of (4000-200 cm^{-1}) for the visible range data were recorded in DMF on a Beckmann spectrophotometer. The IR spectra of the complexes were recorded on a Techron spectrophotometer. For the iodo and carbonate salts the visible range data were recorded in DMF and dried; yield 60-65%.

Results and Discussion

The characterisation data of the bright coloured compounds are given in Table 1. The compounds are insoluble in common organic solvents, but dissolve in DMF and DMSO. The molar conductances of the complexes (Table 1) show incomplete dissociation of the complexes. Hence the bipyr- ridyl, phenanthroline and urea derivatives are non-electrolytes. The low conductance values for 1:1 and 1:2 derivatives than those predicted theoretically indicate the covalent nature of the complexes. Moreover, the bulky groups in the surroundings prevent mobility of the heavy anion. The decomposition temperatures (Table 2) for the complexes and the mass loss occurring at the decomposition temperatures as revealed by TG data in Table 1 suggest the loss of both the organic ligand moiety at a time. The order of stabilities of the compounds is acetato = iodo = bromo = bipyridyl < carb- nato < chloro = phenanthroline < urea < nitrate < sulphato. From the loss in mass upto 120°C in TGA the number of water molecules present in the complex was calculated. The ultimate decomposition product is U_{2}O_{8} in all the cases.

It is difficult to differ lattice water from coordinated water. However, the presence of absorptions near 905 cm^{-1} and 510 cm^{-1} accounts for coordinated water but in the iodo and bromo complexes these bands are masked by the uranyl and ligand bands. DTA results have been obtained for sulphato, iodo, carbonate and bipyridyl complexes. The nature of DTA curves is similar for all the said compounds and reveals gradual removal of water molecule followed by deamination. The next step is the removal of two benzhydroxamato group and lastly the displacement of the anionic group other than BH. Above 500°C the little change is believed to be due to a complex rearrangement for the greenish black U_{2}O_{8}. The bipyridyl complex decomposes in two steps: (i) the loss of two benzhydroxamato group; (ii) removal of bipyridyl group.

A strong band in the region of 375-390 nm was
The characteristic N-O of hydroxamic acids appear complex such that it behaves as a bidentate ligand. According to literature, in the complexes due to protonation of one hydrogen, degenerate modes such that the point group T₆ for the degenerate vibrations v₃ and v₄ and the presence of a medium band at 440 cm⁻¹ assigned to νₛ i.e., the νU-O (carbonato) stress the bidentate nature of the carbonato group.

Carbonato complex — Activated Raman vibration v₄ at 1575 cm⁻¹ established the coordinated nature of the carbonate group. The presence of all fundamental modes of vibration indicates C₃ᵥ symmetry for the carbonate group. Though this symmetry represents both unidentate and bidentate carbonate group, the higher splitting differences of the degenerate vibrations v₂ and v₃ and the presence of a medium band at 440 cm⁻¹ assigned to νₛ i.e., the νU-O (carbonato) stress the bidentate nature of the carbonate group.

Nitrato complex — The presence of bands at 1530 (v₁), 1310 (v₄), 1010 (v₃), 745 (v₅) and 695 (v₆) indicates the coordination through nitrato group and a lowering in symmetry from D₃h for the free nitrato ion to C₃ᵥ (ref. 20-22). A medium band in the region of 815 cm⁻¹ cannot be definitely assigned to ν₆ of the nitrato group because the νN-O band of the free ligand BH prevents unambiguous assignment of the nitrato bands. The splitting difference between v₁ (symmetric stretch) and v₄ (asymmetric stretch) is large enough for a tentative assignment of bidentate nitrato group. Though splitting difference is not conclusive but still a difference of the order of 200-300 cm⁻¹ is somewhat unusual for unidentate nitrato complex.

Halocomplexes — The band in the chloro, bromo and iodo complexes in the region of 270 cm⁻¹ is assignable to (U-X) (X=Cl, Br and I) in the case of bromo and iodo complexes elemental analyses predict one halo atom and the DTA of the iodo complex suggests two water molecules. The presence of lattice water is inconclusive as the lattice water region is masked by the ligand band. Thus with a view to completing the planar hexagonal model of dioxouranium (VI) ion the formulation of NH₄[UO₂(B₈)₂X₂H₂O]H₂O where X = Br and I is suggested.

1,10-Phenanthroline and 2,2'-bipyridyl complexes — The weak bands at 620 and 404 cm⁻¹ in free phenanthroline are shifted to higher wave number with increase in intensity, occurring at around 640 and 430 cm⁻¹ in the complex. The presence of extra bands in the region of 500-600 cm⁻¹ in the phen complex compared to the free ligand accounts for the coordination of phenanthroline to uranium. The occurrence of a band at 270 cm⁻¹ assigned to ν₋₋ in spite of the heavy metal atom suggests a strong bonding.

The splitting of fundamental modes of vibration is indicative of coordination of 2,2'-bipyridyl. The presence of bands at 615 and 410 cm⁻¹ points out greater degree of probability about chelation. In the complexes phen and bipy, νₛ of UO₂⁺ group is observed in the region of 900-930 cm⁻¹ as broad and split band. This splitting indicates bridging in oxoions. Thus it is suggested that probably

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<th>Compound</th>
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<th>νₛ(UO₂⁺) cm⁻¹</th>
<th>ν₆(UO₂⁺) cm⁻¹</th>
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*SI Nos. refer to compounds listed in Table 1.
one heterocyclic amine bridges two uranyl groups, the presence of more than one ammine molecule for every dioxouranium(VI) group is restricted by the steric factor. In all the complexes studied a strong band, sometimes split, consistently appears in the region of 250-270 cm\(^{-1}\). This must correspond to bending vibration of 2\(_a\) for the dioxouranium(VI) ion.\(^4\)\(^9\)\(^1\)\(^2\) Only one IR band to the doubly degenerate deformation mode implies linearity in the dioxouranium(VI) ion. 2\(_a\) is also a measure for the prediction of stabilities of the mixed chelate complexes. The decrease of 2\(_a\) values in the order bipyrind = phenanthroline = nitrate = sulphato > chloro > carbonato = bromo = iodoo > urea > acetato. Utilising 2\(_a\) values of the (O-U-O) group, the force constant of U-O bond has been evaluated by the method of McGlynn.\(^4\)\(^4\) Putting these evaluated values in the relation \(^4\)\(^5\)\(^6\) \(R_{U-O} = 1.08 F_{1/2} + 1.17\), U-O axial bond lengths of the complexes were calculated (Table 2) and the values are in conformity with the literature.\(^4\)\(^7\)\(^8\)

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References