

Synthesis, characterisation and chemical reactivity of some new dioxouranium(VI) complexes of 2-aminobenzoylhydrazone of butane-2,3-dione

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MS received 11 June 1986; revised 13 October 1986

Abstract. A new series of dioxouranium(VI) complexes of a potential ONNO tetradentate donor 2-aminobenzoylhydrazone of butane-2,3-dione (L_1H_2) have been synthesized. At pH 2.5–4.0, the donor (L_1H_2) reacts in the keto form and complexes of the type $[UO_2(L_1H_2)(X)_2]$ ($X = Cl^-, Br^-, NO_3^-, NCS^-, ClO_4^-, CH_3COO^-, \frac{1}{2}SO_4^{2-}$) are obtained. At higher pH (6.5–7), the complex of the enol form having the formula $[UO_2(L_1)(H_2O)]$ has been isolated. On reaction with a monodentate lewis base (B), both types of complexes yield adducts of the type $[UO_2(L_1)(B)]$. All these complexes have been characterised adequately by elemental analyses and other standard physicochemical techniques. Location of the bonding sites of the donor molecule around the uranyl ion, status of the uranium-oxygen bond and the probable structure of the complexes have also been discussed.

Keywords. Synthesis; chemical reactivity; dioxouranium(VI) complexes; 2-aminobenzoylhydrazone of butane-2,3-dione.

1. Introduction

Ligational behaviour of acid hydrazones of alpha-ketooximes towards several first row transition metal ions have been studied in detail (Mostafa *et al* 1980, 1983; Ghosh *et al* 1984, 1985; Ghosh and Maiti 1987). But the coordination ability of the acid hydrazones of alpha-diketones acting as tetradentate donors towards oxometal cations have not been adequately explored. The present work reports the synthesis of a tetradentate ONNO donor from *o*-aminobenzoylhydrazide and diacetyl and its ligational behaviour towards the dioxouranium(VI) cation. A series of dioxouranium(VI) complexes of both keto and enol forms of the donor have been isolated and characterised. These complexes have also been prepared by reacting diacetyl with the corresponding uranyl complexes of *o*-aminobenzoyl hydrazide. Reactivity of these complexes towards some monodentate lewis bases (like pyridine, methylamine etc.) have been explored. The status of the uranium-oxygen multiple bond have also been discussed.

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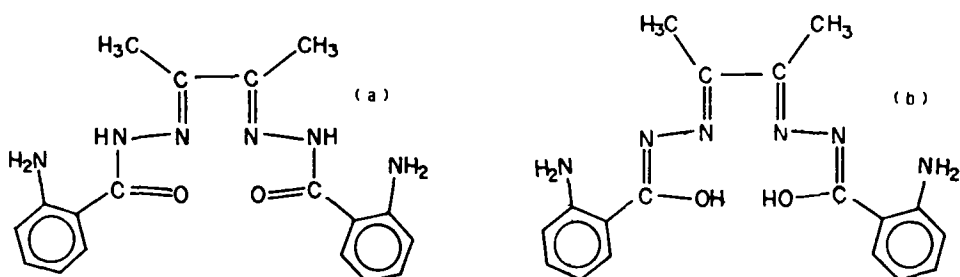


Figure 1. Keto (a) and enol (b) forms of the donor.

2. Experimental

2.1 Preparation of the Schiff base (L_1H_2)

o-Aminobenzoyl hydrazide was prepared by refluxing methyl anthranilate (0.01 mol) with hydrazine hydrate (99.9%, 0.0125 mol) in the presence of a few ml of dry ethanol. The Schiff base (L_1H_2) was obtained by the reaction of diacetyl on *o*-aminobenzoylhydrazide in 1:2 molar ratio in ethanol medium at room temperature in the presence of 2–3 drops of conc. HCl. The desired compound was isolated as a yellow powder. It is sparingly soluble in methanol and ethanol and highly soluble in DMF and DMSO. The melting point of this compound is 276°C. Carbon, hydrogen and nitrogen analysis of this compound corresponds very well with the molecular formula $C_{18}H_{20}N_6O_2$. The donor (L_1H_2) can exist both in the keto and the enol forms as shown in figures 1a and b, respectively.

2.2 Syntheses of the complexes

The $[UO_2(L_1H_2)(X)_2]$ -type complexes ($X^- = Cl^-, Br^-, NO_3^-, NCS^-, ClO_4^-, CH_3COO^-, \frac{1}{2}SO_4^{2-}$) having the keto form of the donor were obtained by adding an ethanolic solution of the hydrated uranyl salt to a well-stirred alcoholic suspension of the ligand in 1.25:1 molar ratio. An orange-yellow to red coloured compound gradually separated out (pH \approx 2.5–4.0). It was filtered, washed with alcohol and finally dried over fused $CaCl_2$.

The above keto compounds were also obtained by stirring an ethanolic suspension of the corresponding uranyl complexes of *o*-aminobenzoylhydrazide with diacetyl in 1:1.25 molar ratio for 1–2 hr at room temperature.

The complex $[UO_2(L_1)(H_2O)]$ containing the bianionic enolate ligand was prepared by raising the pH of a suspension of any of the $[UO_2(L_1H_2)(X)_2]$ -type complexes to \approx 7–7.5 in rectified spirit by the careful addition of alcoholic NaOH solution and stirring the mixture for \approx 8–10 hr. The resulting orange-red compound was filtered, washed with a little ethanol and then thoroughly with water. It was dried over fused $CaCl_2$.

Preparation of $[UO_2(L_1)(B)]$ -type complexes ($B = Py, CH_3NH_2$ etc.): The pyridine adduct $[UO_2(L_1)(Py)]$ was obtained by heating under reflux (or simply stirring at room temperature) an ethanolic suspension of either the enol or a keto compound with a little excess of pyridine for \approx 2 hr and evaporating the orange-red solution to a small volume at room temperature. An orange-red

Table 1. Analytical and physical data for the uranyl complexes.

Compound	Colour	Found (calcd.)%	C	H	Anion	Λ_{ur} ($\Omega\text{hm}^{-1}\text{cm}^{-2}$ mol ⁻¹)	$R_{U-O}(n)$ (\AA^2)	$F_{U-O}(n)$ (milli- dynes/ \AA^2)
		M	N					
$[UO_2(L_1H_2)(SO_4)]H_2O$	Orange-red	32.22 (32.34)	11.20 (11.41)	28.32 (29.35)	3.20 (2.99)	10	1.773	6.163
$[UO_2(L_1H_2)(NO_3)_2]$	Red	31.68 (31.90)	14.60 (15.01)	28.05 (28.95)	2.80 (2.68)	35	1.750	6.215
$[UO_2(L_1H_2)(CH_3COO)_2]$	Orange-yellow	32.00 (32.16)	11.17 (11.35)	35.04 (35.67)	3.69 (3.51)	10	1.764	5.98
$[UO_2(L_1H_2)(ClO_4)_2]$	Orange	28.82 (28.99)	10.06 (10.23)	25.55 (26.31)	2.24 (2.44)	36	1.747	6.267
$[UO_2(L_1H_2)Cl_2]$	Orange-red	34.04 (34.34)	12.30 (12.12)	30.25 (31.17)	3.00 (2.88)	34	1.759	6.063
$[UO_2(L_1H_2)Br_2]$	Red	30.33 (30.43)	10.47 (10.74)	26.57 (27.62)	2.78 (2.55)	33	1.756	6.113
$[UO_2(L_1H_2)(NCS)_2]$	Reddish brown	32.42 (32.25)	14.87 (15.17)	33.10 (32.52)	2.90 (2.71)	34	1.763	5.996
$[UO_2(L_1)(H_2O)]$	Orange-red	37.20 (37.30)	13.00 (13.16)	32.80 (33.85)	2.97 (3.13)	6	1.764	5.980
$[UO_2(L_1)(Py)]$	Orange-red	34.01 (34.05)	14.18 (14.02)	38.55 (39.48)	3.48 (3.29)	8	1.767	5.931
$[UO_2(L_1)(MeNH_2)]$	Yellow	36.28 (36.56)	14.80 (15.05)	34.40 (35.02)	3.37 (3.53)	9	1.769	5.899
L_1H_2	Light yellow	—	23.75 (23.86)	61.45 (61.36)	5.28 (5.68)	—	—	—

Table 2. Some characteristic IR spectral bands of the uranyl complexes* (cm^{-1}).

Compound	$\nu(\text{NH}_2)$ (<i>asym</i> and <i>sym</i>)	$\nu(\text{C}=\text{O})$ <i>amide I</i>	$\nu(\text{C}=\text{N})$ <i>azomethine</i>	$\nu(\text{CN}) + \delta(\text{NH})$ <i>amide II</i>	$\nu_3(\text{UO}_2)$ (<i>asym</i>)
L_1H_2	3480 <i>s</i> 3380 <i>s</i>	1640 <i>s</i>	1608 <i>s</i>	1550 <i>s</i>	
$[\text{UO}_2(\text{L}_1\text{H}_2)(\text{SO}_4)]\text{H}_2\text{O}$	3480–3420 <i>s</i> , <i>br</i> 3380–3330 <i>s</i> , <i>br</i>	1620 <i>s</i>	1585 <i>s</i>	1545 <i>s</i>	920 <i>s</i>
$[\text{UO}_2(\text{L}_1\text{H}_2)(\text{NO}_3)_2]$	3480 <i>s</i> 3380 <i>s</i>	1615 <i>s</i>	1580 <i>s</i>	1540 <i>s</i>	925 <i>s</i>
$[\text{UO}_2(\text{L}_1\text{H}_2)(\text{CH}_3\text{COO})_2]$	3480 <i>s</i> 3375 <i>s</i>	1620 <i>s</i>	1580 <i>s</i>	1535 <i>m</i>	903 <i>s</i>
$[\text{UO}_2(\text{L}_1\text{H}_2)(\text{ClO}_4)_2]$	3480 <i>s</i> 3380 <i>s</i>	1612 <i>s</i>	1580 <i>s</i>	1540 <i>s</i>	930 <i>s</i> , <i>br</i>
$[\text{UO}_2(\text{L}_1\text{H}_2)\text{Cl}_2]$	3480 <i>s</i> 3375 <i>s</i>	1610 <i>s</i>	1580 <i>s</i>	1535 <i>s</i>	910 <i>s</i>
$[\text{UO}_2(\text{L}_1\text{H}_2)\text{Br}_2]$	3480 <i>s</i> 3380 <i>s</i>	1610 <i>s</i>	1585 <i>s</i>	1540 <i>m</i>	915 <i>s</i>
$[\text{UO}_2(\text{L}_1\text{H}_2)(\text{NCS})_2]$	3480 <i>s</i> 3380 <i>s</i>	1615 <i>s</i>	1585 <i>s</i>	1540 <i>m</i>	905 <i>s</i>
$[\text{UO}_2(\text{L}_1)(\text{H}_2\text{O})]$	3475 <i>s</i> 3375 <i>s</i>	—	1585 <i>s</i>	—	903 <i>s</i>
$[\text{UO}_2(\text{L}_1)(\text{Py})]$	3480 <i>s</i> 3380 <i>s</i>	—	1585 <i>s</i>	—	898 <i>s</i>
$[\text{UO}_2(\text{L}_1)(\text{MeNH}_2)]$	3465 <i>s</i> 3300 <i>s</i>	—	1580 <i>s</i>	—	895 <i>s</i>

* *s* = strong, *m* = medium, *br* = broad

compound slowly separated out. It was filtered and washed with ethanol and dried over fused CaCl_2 . The methyl amine compound was obtained by the above method, the pH of the mixture being adjusted to $\approx 7-7.5$ by the addition of dry alcoholic methyl amine solution. It is to be noted that we could not isolate eight coordinated complexes of the formula $[\text{UO}_2(\text{L}_1)(\text{B})_2]$ and $[\text{UO}_2(\text{L}_1)(\text{B}-\text{B})]$, where $\text{B}-\text{B}$ = a bidentate lewis base like α , α' -dipyridyl or *o*-phenanthroline.

2.3 Analyses of the complexes

Uranium was estimated by the oxime method (Vogel 1961). Carbon, hydrogen and nitrogen were determined by the Perkin Elmer 240C Elemental Analyser. The anions were analysed by standard analytical procedures (Vogel 1961).

2.4 Physical measurements

Magnetic susceptibilities of the compounds were recorded by a EG & G PAR Vibrating Sample Magnetometer (model 155). UV spectra was recorded in DMSO solvent using a Pye-Unicam SP8-150 UV-VIS spectrophotometer. IR spectra were taken in KBr on a Perkin Elmer 783 IR spectrophotometer. Conductance measurements were performed in DMSO with the help of a Philips conductivity

bridge (PR 9500). The chemical formulae of the complexes together with their analytical data, colour, molar conductance value (Λ_M), uranium-oxygen multiple bond length $R_{U-O(1)}$, and force constant $F_{U-O(1)}$, are included in table 1. Important infrared spectral bands are presented in table 2.

3. Results and discussion

The colour of the dioxouranium(VI) complexes varied from yellow to red. The compounds of the type $[UO_2(L_1H_2)(X)_2]$ are moderately soluble (except the sulphate and the acetate compound) in methanol, ethanol, acetone and sparingly soluble in benzene, chloroform and carbon tetrachloride. All of them are highly soluble in DMSO and DMF.

As is expected for d^0 systems, all the dioxouranium(VI) complexes are diamagnetic.

All the uranyl complexes behave as non-electrolytes in solution. The non-ionic nature of the keto compounds $[UO_2(L_1H_2)(X)_2]$ indicates the existence of coordinated anions in all these complexes which is corroborated by the relevant IR data.

3.1 Infrared spectra

Presence of the $\nu(NH_2)$ modes of the aromatic ring $-NH_2$ group at $3480\text{ cm}^{-1}(\nu_{as})$ and $3380\text{ cm}^{-1}(\nu_s)$ (Bellamy 1975) and disappearance of the $\nu(NH_2)$ modes of the hydrazinic $-NH_2$ group in the IR spectrum of the free donor (L_1H_2) clearly indicates that the Schiff base formation has taken place exclusively from the hydrazinic $-NH_2$ group of *o*-aminobenzoyl hydrazide leaving the aromatic ring $-NH_2$ group free. In all the complexes the position of $\nu(NH_2)$ of the free donor remains almost unaltered (table 2) indicating the non-participation of the ring $-NH_2$ group in coordination to the metal ion. The presence of a free aromatic $-NH_2$ group in the L_1H_2 molecule is confirmed through the diazo reaction. The amide I band ($\nu_{C=O}$) located at 1640 cm^{-1} (Bellamy 1975) and the $\nu(C=N)$ at 1608 cm^{-1} in the IR spectrum of the free donor are shifted to lower frequencies in all the complexes having the keto form of the donor. This clearly indicates that the donor L_1H_2 coordinates to the UO_2^{2+} acceptor centre through its amide carbonyl oxygen and the azomethine nitrogen (Percy and Thornton 1971), respectively.

In the complexes obtained at higher pH in solution, the amide I band disappears completely. This clearly demonstrates that at higher pH, the donor enolises and binds the metal ion subsequently via two deprotonated enolate oxygens and two azomethine nitrogens. A new band is found to appear at $\sim 1615\text{ cm}^{-1}$ indicating the generation of a new $>C=N$ bond due to the enolisation of the $-NH-C=O$ group.

Characteristic IR bands of the complexes containing nitrate, perchlorate, acetate, indicate the presence of these anions in the monocoordinated fashion (Nakamoto 1978). Relevant IR spectra also indicate that the CNS^- ion is coordinated to the metal ion through the nitrogen atom. The presence of coordinated Cl^- and Br^- ions are substantiated by the nonelectrolyte nature of the corresponding complexes. The characteristic features of the IR spectrum of the

compound $[\text{UO}_2(\text{L}_1\text{H}_2)(\text{SO}_4)]\text{H}_2\text{O}$ clearly show that the SO_4^{2-} ion is coordinated in a bidentate manner. In the spectrum of the pyridine adduct, the in-plane ring deformation mode of pyridine (at 604 cm^{-1}) is shifted to a higher frequency (640 cm^{-1}), implying coordination from the pyridine nitrogen (Gill *et al* 1961). Specific bands of the coordinated water molecule are also observed in the complex $[\text{UO}_2(\text{L}_1)(\text{H}_2\text{O})]$ which contains H_2O in the inner sphere.

In view of the fact that the UO_2^{2+} moiety existing in most dioxouranium(VI) complexes is crystallographically linear (Hsieh *et al* 1975; Cattalini *et al* 1971), it is reasonable to expect the occurrence of a linear UO_2 moiety in the complexes described herein. The IR spectra of the uranyl complexes exhibit an intense absorption in the $890\text{--}930\text{ cm}^{-1}$ region attributable to the ν_3 or ν_{as} (UO_2) mode (Jones 1958). The ν_s (UO_2) expected in the region $800\text{--}900\text{ cm}^{-1}$ is generally very weak as reported earlier (Hsieh *et al* 1975). In the present study, the position of the $\nu_s(\text{UO}_2)$ could not be established unequivocally because of the presence of several ligand absorptions in the same region.

3.2 $\text{U}-\text{O}_{(1)}$ bond length and force constant

Infrared spectroscopy has been utilised for the evaluation of the $\text{U}-\text{O}$ bond lengths (Veal *et al* 1975) of the dioxouranium(VI) complexes. The two axial or uranyl oxygen atoms form the primary $\text{U}-\text{O}_{(1)}$ bonds and these $\text{U}-\text{O}$ bond lengths (R) vary as a function of the other donor atoms or groups present around the uranyl moiety. From the IR data of our compounds the primary $\text{U}-\text{O}_{(1)}$ bond distance has been calculated using a previously reported procedure (Veal *et al* 1975) and the results are presented in table 1. The force constant $F_{\text{U}-\text{O}_{(1)}}$ is also calculated by the method of McGlynn (McGlynn and Smith 1961) and are also included in table 1. Excepting the case of the sulphate compound, the shift of $\nu_{as}(\text{UO}_2)$ with the change of the coordinated anion in the equatorial plane is fairly consistent with the position of the anions in the spectrochemical series (Cotton and Wilkinson 1980). The stronger the donor character of the anion, the greater is the shift of the $\nu_{as}(\text{UO}_2)$ mode towards lower frequencies. This is also reflected in the variation of the $F_{\text{U}-\text{O}_{(1)}}$ in the reverse direction. In its enol form the donor is a stronger σ -donor than its keto counterpart because of the involvement of the two negatively charged enolate oxygens in coordination to the UO_2^{2+} moiety in place of the two neutral amide carbonyl oxygens. It is also quite expected that the $\nu_{as}(\text{UO}_2)$ band will be shifted towards lower frequency when a stronger σ -donor replaces a weaker donor in the equatorial plane. In practice, the $\nu_{as}(\text{UO}_2)$ located at 903 cm^{-1} for the compound $[\text{UO}_2(\text{L}_1)(\text{H}_2\text{O})]$ is shifted to lower wave number when the H_2O molecule is replaced by pyridine or CH_3NH_2 in accordance with the position of H_2O , Py or CH_3NH_2 in the spectrochemical series.

3.3 Electronic spectra

The UV spectra of the uranyl complexes exhibit a strong band in the $21,000\text{--}22,500\text{ cm}^{-1}$ region (Shallaby *et al* 1984). This is assigned to the uranyl absorption as ${}^3\pi_u \leftarrow {}^1E_g^+$ for the first excited state (McGlynn and Smith 1961). However, it has not been possible to assign several other bands observed beyond $25,000\text{ cm}^{-1}$ in the spectra of the complexes.

3.4 Structure and reactivity of the complexes

IR and conductivity data indicates that in all the $[UO_2(L_1H_2)(X)_2]$ -type of complexes the anions are coordinated to the dioxouranium(VI) ion. Hence, it appears that the uranyl complexes of the keto form are 8-coordinated with the ONNO donor sites of the tetradentate donor spanning four adjacent positions while the two anions occupy the remaining two adjacent positions in the hexagonal equatorial plane. The two uranyl oxygens are bonded axially (figure 2). This is supported by the fact that the two anions (X) of the $[UO_2(L_1H_2)(X)_2]$ -type complex are replaced by one oxalate ion even at room temperature when the complex is treated with alcoholic oxalic acid solution. The product is a yellow compound of formula $[UO_2(L_1H_2)(C_2O_4)]$. Conductivity data indicate that it is a nonelectrolyte and the IR spectrum of this compound shows that the oxalate ion is attached to the dioxouranium(VI) species in a bicoordinated fashion. Therefore, from the above considerations, probable structure of the complexes of the keto form of the donor may be written as in figure 2. The complex of the enol form $[UO_2(L_1)(H_2O)]$ appears to be a seven-coordinated species. In this complex, of the five donor points present in the equatorial plane, four points are occupied by the enolised donor while one water molecule sits in the fifth position. Reactions of $[UO_2(L_1)(H_2O)]$ with excess monodentate nitrogen donors such as pyridine, picolines, methylamine etc. always led to the formation of the complex $[UO_2(L_1)(B)]$ and hence supports the seven coordinated structure (Bandoli *et al* 1972; Cattalini *et al* 1972). The complex $[UO_2(L_1)(H_2O)]$ exhibits the loss of only one water molecule at a quite high temperature range of 155–210°C. This indicates that the only water molecule present in the complex is coordinated to the uranyl moiety. The anhydrous compound thus obtained again forms $[UO_2(L_1)(B)]$ on treatment with the base (B). These two observations support the seven coordinated structure of $[UO_2(L_1)(H_2O)]$ and $[UO_2(L_1)(B)]$. Hence, the structure of the complex $[UO_2(L_1)(H_2O)]$ may be represented as in figure 3. The structure of its reaction products with (B) can easily be visualized by replacing the water molecule in figure 3 by (B).

It appears that the compound $[UO_2(L_1)(H_2O)]$ shows a strong preference towards seven-coordination. As expected from the hard acceptor UO_2^{2+} , the

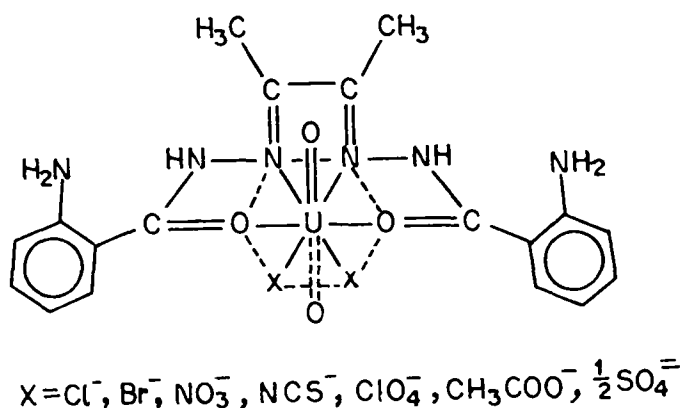


Figure 2. Donor environment around $U^{VI}O_2$ in $[UO_2(L_1H_2)(X)_2]$ -type complexes.

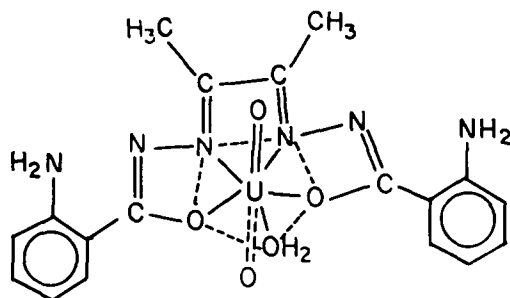


Figure 3. Donor environment around $U^{VI}O_2$ in $[UO_2(L_1)(H_2O)]$.

compound $[UO_2(L_1)(H_2O)]$ did not react with the soft donors (Cattalini *et al* 1972; Pearson 1963, 1966) like PPh_3 , thiophen, thioethers and mercaptans. Triphenyl phosphine failed to effect oxygen abstraction from the UO_2^{2+} moiety in any of the reported complexes even after prolonged heating under reflux.

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