Reaction of Some Ambident Nucleophiles, Thiourea, Substituted Thioureas, Biuret & Oxamide with Uranyl Nitrate & Chloride & Isolation of Some Novel Adducts

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The ambident nucleophiles, viz. thiourea (Tu), monobenzoylthiourea (MBTu), oxalylthiourea (OxTu), biuret (BuH$_2$) and oxamide (OxamH$_2$) react with $UO_2(NO_3)_2.6H_2O$ in acetonitrile medium via base hydrolysis affording hydroxo complexes of the types $UO_2(OH)_2Tu$, $UO_2(OH)_2MBTu$, $UO_2(OH)_2OxTu$, $UO_2(OH)_2 3BuH_2$ and $UO_2(OH)_2(OxamH_2)_2$. However UO_2Cl_2 reacts with Tu and BuH_2 forming adducts $UO_2Cl_2.2Tu$ and $UO_2Cl_2.BuH_2$ respectively. The IR spectra reveal that thiourea is S-bonded to uranium and in the chloro complex biuret behaves as oxygen donor chelate while in the other case it is probably acting as a unidentate ligand. Oxamide behaves as an oxygen donor neutral chelating ligand.

FROM the consideration of the electronic structure of UO_2^{2+} it has been inferred[1] that the isolation of any stable adduct of thiourea (Tu) with UO_2^{2+} ion would be very difficult. However, the Russian authors[2] described the preparation of the complexes of the type $UO_2X_2.2Tu(X=NO_3$ or Cl and $X_2=SO_4$), but they neither thoroughly characterized the complexes nor indicated the coordination site of thiourea. We have now observed that $UO_2(NO_3)_2.6H_2O$ in acetonitrile solution reacts with some highly basic ambident nucleophiles, viz. thiourea (Tu), monobenzoylthiourea (MBTu), oxalylthiourea (OxTu) and biuret (BuH$_2$) via base hydrolysis of the uranyl(VI) salt affording hydroxo compounds, $UO_2(OH)_2L$ (L=Tu, MBTu or OxTu) and $UO_2(OH)_2.L_3$ (L=BuH$_2$). On the other hand, freshly prepared UO_2Cl_2 reacts with Tu and BuH_2 furnishing adducts $UO_2Cl_2.2Tu$ and $UO_2Cl_2.BuH_2$ respectively. Oxamide (OxamH$_2$) also afforded the hydroxo compound $UO_2(OH)_2(OxamH_2)_2$.

Results and Discussion

The composition of the complexes with their physical properties and analytical data are shown in Table 1. The IR spectra* of all the hydroxo complexes exhibited νOH in the region 3660-3500 either as a strong, broad band as in the case of $UO_2(OH)_2.Tu$ (3566-3500) or as a strong band as in the case of $UO_2(OH)_2.3BuH$ (3500) or as shoulders as in the case of $UO_2(OH)_2.MBTu$ (3660), $UO_2(OH)_2.OxTu$ (3600) and $UO_2(OH)_2(OxamH_2)_2$ (3515). This is expected for hydroxo ligands[3]. The νNH of NH$_2$ and NH groups and δNH_2 of free thiourea and its derivatives[4-9] did not undergo any significant shift in the complexes precluding the possibility of coordination of thiourea and its derivatives through nitrogen atoms. However, a slight shifting of νNH in the complexes can be ascribed to the variation in the extent and nature of the hydrogen bonding in the complexes as compared with free ligands[10]. The strong band of thiourea at 725 which is primarily due to $\nu C=S$ (refs.

4, 5, 9, 10) disappeared in the complex $UO_2(OH)_2Tu$, and in $UO_2Cl_2.2Tu$ the same was red shifted and appeared at 696. It may be inferred that in both these complexes thiourea coordinates as usual[11] through its sulphur atom[4,5,9,10]. In pure monobenzoylthiourea and oxalylthiourea two bands appeared at 782 and 860 respectively which underwent red shift and appeared at 740 and 788 respectively in $UO_2(OH)_2MBTu$ and $UO_2(OH)_2OxTu$. Sulphur coordination in these two cases may be inferred but it is not possible, at present, to make any firm assignment from the above frequency shift since these bands in thiourea derivatives may appear due to mixed vibrations[10]. The $\nu C=O$ band[5,8] of pure monobenzoylthiourea (1680) and oxalylthiourea [1740 (sh), 1720 (s)] (qualitatively assigned by us by comparing with analogous carbonyl compounds) underwent splitting in their complexes and did not undergo clear red shift. Apparently, the coordination through carbonyl oxygen in these two cases cannot be inferred. However, an examination of molecular model indicates that maximum coordination number that can be satisfied by oxalylthiourea is three and it can do so only when one C=O group and both the C=S groups are involved in coordination. Therefore, it might also be possible that in the complex $UO_2(OH)_2OxTu$, the $\nu(C=O)$ of one of the two C=O groups is lowered and marked by δNH_2. This may be the reason for splitting of $\nu(C=O)$ [shoulders at 1740, 1720 and 1705] and the appearance of $\delta(NH_2)$ as strong and broad band at 1660-1600. Unfortunately, the hygroscopic nature of the MBTu complex frustrated the unequivocal assignment of the NH$_2$ bands.

In the compound, $UO_2(OH)_2 3BuH_2$, the position and number of IR bands are not like the compounds where biuret functions as a bidentate ligand[6]. In the NH$_2$ and NH stretching region the bands are quite broad, though sharp are poorly resolved and appear ≈ 3340-3410, 3260 and 3150-3200 cm^{-1}. Again the $\nu C=O$ and δNH_2 are also characterized by broad bands (≈ 1725-1670) and the $\nu(C=O)$

*ν_{max} in cm^{-1}.

TABLE 1 — ANALYTICAL DATA OF THE COMPLEXES

Compound	Colour and m.p. (°C)	Decomp. temp. (°C)	M (%)	N (%)	S (%)	Cl (%)
$UO_2(OH)_2Tu$	Yellowish brown	80	62·4 *(62·6)	7·00 (7·37)	8·30 (8·42)	—
$UO_2Cl_2 2Tu$	Yellow 210	150	48·1 (48·4)	10·9 (11·4)	12·5 (13·0)	13·7 (14·4)
$UO_2(OH)_2MBTu$	Yellowish brown	75	49·1 (49·0)	5·40 (5·79)	6·20 (6·60)	—
$UO_2(OH)_2OxTu$	Yellow	215	49·5 (50·0)	6·79 (6·90)	12·2 (12·5)	—
$UO_2(OH)_2 3BuH_2$	Yellow 209	200	38·7 (38·8)	20·6 (20·6)	—	—
$UO_2Cl_2BuH_2$	Greenish yellow	150	53·7 (53·6)	8·90 (9·46)	—	16·1 (16·0)
$UO_2(OH)_2(OxamH_2)_2$	Yellow	140	49·5 (49·6)	12·4 (11·6)	—	—

*Calculated percentages are given in parentheses.

actually starts from a region where uncoordinated C=O group absorbs[5-8]. All those observations point to (i) occurrence of both coordinated and free (but intramolecularly H-bonded) C=O group and (ii) extensive intramolecular H-bonding even in the coordinated biuret molecule. So, biuret may function here as unidentate oxygen donor ligand as in the case of Cd complex[7] in which case the structure has been confirmed by X-ray crystallography[12]. On the other hand the IR spectrum ($\nu C=O$, 1670-1650) of $UO_2Cl_2BuH_2$ suggests that the biuret molecule coordinates through two oxygen atoms[6,7]. In the oxamide complex the $\nu(C=O)$ is drastically lowered (1608-1596) and overlapped with the δNH_2 band. A close comparison of the literature data [on the basis of normal coordinate analysis of a Ni(II) complex[7-13]] with our observed results suggests that the protons of both the NH_2 groups of the oxamide molecule are intact and in the complex $[UO_2(OH)_2(OxamH_2)_2]$ the oxamide ligands are linked to the uranium atom through the two oxygen atoms thereby acting as a bidentate chelate ligand. This uranium complex is probably the only known complex where the oxamide molecule is acting as a neutral ligand, since literature[7,13] shows that it always coordinates as an oxamido anion.

The asymmetric stretching frequency (ν_3) of the UO_2^{2+} group in all the complexes appears at 902-932 except in $UO_2(OH)_2Tu$ where it is found at 852. Considering the empirical formula of the said compound and its extreme insolubility, it may be suggested that the compound is polymeric involving probably the oxobridging, lowering the uranium-oxygen bond order[15]. Some other hydroxo compounds, viz. $UO_2(OH)_2MBTu$ and $UO_2(OH)_2OxTu$ are also very moderately soluble in methanol, ethanol and acetonitrile and in these cases polymerization may also occur through hydroxo bridging. Infact, only the complexes $UO_2Cl_2 2Tu$ and $UO_2(OH)_2 3BuH_2$ have characteristic melting points and show quite high solubility in polar organic solvents.

As usual, due to involvement of 5f orbitals in forming the dioxouranium(VI) ion and consequent generation of large orbital contribution[16] the χ_A of UO_2^{2+} ion in all the complexes are positive and the

values range from quite a low value in the case of $UO_2(OH)_2MBTu$ (48×10^{-6} e.m.u. mole^{-1}) to a pretty high value of 750×10^{-6} e.m.u. mole^{-1} in the case of $UO_2(OH)_2(OxamH_2)_2$. The values in such higher region have never been reported earlier. The reason for such high values is, at present, obscure.

The molar conductances of the complexes which are at least moderately soluble in acetonitrile [$UO_2(OH)_2MBTu$, $UO_2(OH)_2(BuH_2)_3$, $UO_2Cl_2 2Tu$ and $UO_2Cl_2BuH_2$] show that the compounds $UO_2(OH)_2MBTu$ and $UO_2Cl_2BuH_2$ are practically non-electrolytes. But the compounds $UO_2Cl_2 2Tu$ and $UO_2(OH)_2(BuH_2)_3$ though behave as very weak electrolytes, a progressive change in Λ_M values with dilution (6-25 ohm^{-1} cm^2 in the case of Tu and 8-22 ohm^{-1} cm^2 in the case of the BuH_2 complex) if adjudged in the light of our previous work[17,18] suggests that probably some amount of acid-solvolysis occurs in these two cases in acetonitrile. Whatever may be the case, it is sure, that in all these cases anions are quite strongly ligated to central metal ion.

From the electronic spectra of the above four complexes in acetonitrile in the range 350-550 nm it is clear that the numbers, intensity and the structured features of the T←S transition[19] (O→U electron transfer in the UO_2^{2+} ion) are very much dependent on the equatorial ligands as we have observed previously in other sets of complexes[20,21]. However, an interesting feature of the electronic spectra of all the uranyl complexes studied here is the absence of a peak below 20000 cm^{-1}. This would suggest[22] that in all the cases uranium has equatorial coordination number more than four (i.e. total coordination number more than six). It has already been argued that most of the compounds are polymeric and thereby the uranium atom extends its coordination number. So, the compound $UO_2Cl_2 2Tu$, though freely soluble in many polar organic solvents and melts at 208°, may even be polymeric presumably through chlorine bridging. Unfortunately, it is insoluble in non-interacting organic solvents making its molecular weight determination impossible and because of the lack of instrumental facilities far IR spectra (νU-Cl) could not be recorded.

Thermogravimetric analyses show that all the complexes except $UO_2Cl_2BuH_2$ decompose slowly

into the oxide, U_3O_8, without giving any intermediate product. But, a horizontal region in the temperature range 380-430° in TGA curve of the complex $UO_2Cl_2BuH_2$ corresponds to the formation of UO_2Cl_2 as obtained from the weight loss data.

Materials and Methods

The IR spectra in nujol mull were recorded on a Perkin-Elmer model 337 recording spectrophotometer equipped with rock salt optics. Ethanol was lime-distilled and the middle fraction was used for synthetic purposes. Description of all other instruments and solvent purifications were reported earlier[21,23].

Thiourea, biuret and oxamide used were of GR (E. Merck) quality. Monobenzoylthiourea was prepared by the method of Pike[24]. Oxalylthiourea was prepared following the method given below:

Thiourea (15·2 g) was dissolved in ethanol (200 ml) and oxalyl chloride (12·7 g) added dropwise from a separating funnel while the solution being continuously stirred when a white solid separated out from the alcohol solution. It was filtered, washed with ethanol, dried and recrystallized from acetone. The product did not melt up to 250° (Found: C, 23·2; H, 3·10. $C_4H_6N_4O_2S_2$ requires C, 23·3 and H, 2·91%).

Dihydroxomono(thiourea)dioxouranium (VI) — $UO_2(NO_3)_26H_2O$ (5 g) and thiourea (1·52 g) were stirred with 50 ml of acetonitrile and warmed when a deep red solution was formed. The solution was then refluxed for 6 hr when yellow solid separated out and a light red solution remained. It was filtered, washed first with acetonitrile and then with dry ethanol and dried *in vacuo* (yield 500 mg).

Dichlorobis(thiourea)dioxouranium (VI) — UO_2Cl_2 (4·5 g) and thiourea (1·52 g) taken in 30 ml of CH_3CN were refluxed for 4 hr. Yellow compound separated out which was filtered, washed with dry acetonitrile and dried *in vacuo* (yield 2 g).

Dihydroxomono(1-benzoyl 2-thiourea)dioxouranium- (VI) — $UO_2(NO_3)_26H_2O$ (2·5 g) was dissolved in 20 ml of dry acetonitrile and to it was added 1·8 g of monobenzoylthiourea also dissolved in 20 ml of acetonitrile and the resulting solution refluxed for 1 hr and then concentrated and cooled. The unreacted monobenzoylthiourea separated out and filtered. The filtrate was further concentrated when a brown compound separated out which was filtered, washed with a little acetonitrile and dried *in vacuo* (yield 2·5 g).

Dihydroxotris(biuret)dioxouranium (VI) — $UO_2(NO_3)_26H_2O$ (5 g) was dissolved in 20 ml of dry acetonitrile and to it was added biuret (2 g) also dissolved in 30 ml of acetonitrile and the resulting solution was refluxed for 6 hr when a yellow compound separated out which was filtered, washed with CH_3CN and dried *in vacuo* (yield 3 g).

Dihydroxobis(oxamide)dioxouranium (VI) — $UO_2(NO_3)_26H_2O$ (2·5 g) and oxamide (0·88 g) were mixed together and taken in 50 ml of dry acetotnitrile. The mixture was refluxed for 12 hr. It was cooled, the unreacted oxamide filtered and the filtrate treated with 10% aq. NaOH in 50% excess of the theoretical amount needed to precipitate

the metal as diuranate, when a yellow compound separated out, which was filtered, washed with acetonitrile and absolute ethanol and dried *in vacuo* (yield 1·5 g).

Dihydroxobis(oxalylthiourea)dioxouranium (VI) — $UO_2(NO_3)_26H_2O$ (5 g) was dissolved in 20 ml of dry acetonitrile and to it was added 2 g of oxalylthiourea dissolved in 30 ml of the same solvent and the resulting solution was refluxed for 6 hr when a yellow derivative separated out which was filtered, washed with dry acetonitrile and dried *in vacuo* (yield 3·75 g).

Dichloromono(biuret)dioxouranium (VI) — $UO_2(NO_3)_26H_2O$ was ignited to U_3O_8 and to it was added HCl (10 ml) and 3-4 drops of conc. HNO_3 and the resulting solution evaporated to dryness. To the dry mass conc. HCl (10 ml) was added again and evaporated to dryness. The mass was immediately taken up with acetonitrile, an acetonitrile (30 ml) solution of biuret (1·2 g) added to it and the reaction mixture refluxed for 3 hr. It was concentrated and cooled when greenish yellow compound separated out which was filtered, washed with dry CH_3CN and dried *in vacuo* (yield 2·5 g).

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