

Synthesis and reactivity of some octacoordinated dioxouranium(VI) complexes of diacetyl bis(benzoylhydrazone) and benzil bis(benzoylhydrazone)

Amalendu Maiti† & Saktiprosad Ghosh*

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032

Received 3 October 1988; revised and accepted 16 January 1989

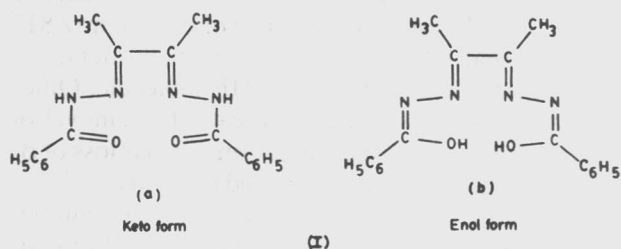
Octacoordinated dioxouranium(VI) complexes of the tetradentate ONNO donors diacetyl bis(benzoylhydrazone) (H_2L) and benzil bis(benzoylhydrazone) (H_2L') are reported. At low pH (1.5-2.5) complexes of the formula $[UO_2(H_2L/H_2L')X_2]$ ($X^- = Cl^-, Br^-, NO_3^-, NCS^-, ClO_4^-, OAc^-$ or $0.5SO_4^{2-}$) containing the keto form of the ligands are isolated. At higher pH (6-7), the complexes $[UO_2(L/L')(H_2O)_2]$ are obtained in which the ligand is present in its deprotonated enolate form (L^{2-} or L'^{2-}). Reactions of $[UO_2(H_2L/H_2L')X_2]/[UO_2(L/L')(H_2O)_2]$ with neutral monodentate (B) and bidentate lewis bases (AA) lead to the formation of mixed-ligand complexes of the type $[UO_2(L/L')(B)_2]$ and $[UO_2(L/L')(AA)]$ respectively. Results of elemental analyses, magnetic susceptibility and conductivity measurements, spectroscopic (IR, electronic etc.) and thermal decomposition studies have been utilised to characterise the complexes. (1889)

Reports on the coordination complexes of acid hydrazones of diketones with oxometal cations in general and the dioxouranium(VI) cation in particular are scanty^{1,2}. As a part of our programme of exploring the coordination behaviour of multidentate mixed N-O donors towards oxometal cations³, we report here the synthesis and characterisation of the octa-coordinated dioxouranium(VI) complexes of the tetradentate ONNO donors diacetyl bis(benzoylhydrazone) (H_2L) and benzil bis(benzoylhydrazone) (H_2L'). In the case of the UO_2^{2+} cation, in which the two oxo oxygens occupy axial positions, these two ligands can occupy only the four adjacent equatorial positions. Hence, the other two adjacent positions of the hexagonal equatorial plane of the complexes may be occupied by two monodentate donors, anionic or neutral. They may also be occupied by a neutral bidentate or a biantionic bidentate donor. Thus, a variety of coordination environments may be created around the UO_2^{2+} acceptor centre. The influence of the monodentate or bidentate donors will be shown by the change in the position of $\nu_{as}(UO_2)$ mode in the resultant complexes.

Materials and Methods

Preparation of the schiff bases and the complexes

Benzoylhydrazide was prepared by the standard method. To a well-stirred dry ethanolic solution of benzoylhydrazide (0.06 mol), diacetyl/benzil (0.03 mol) was added followed by the addition of 2-3 drops of conc. HCl. The mixture was stirred for 1 h and the desired compound was isolated as a white solid. The



ligands can exist both in the keto and the enol forms (Ja, Ib).

The complexes of the types $[UO_2(H_2L)X_2]$ ($X^- = Cl^-, Br^-, NO_3^-, NCS^-, ClO_4^-, OAc^-$ or $0.5SO_4^{2-}$) and $[UO_2(H_2L')X_2]$ ($X^- = Cl^-, NO_3^-, OAc^-$ or $0.5SO_4^{2-}$) were obtained by adding an ethanolic/methanolic solution of the hydrated metal salt to a well-stirred ethanolic suspension of the ligand in 1.25:1 molar ratio. pH of the solution was adjusted to 1-2 by adding an ethanolic solution of the corresponding acid. The mixture was stirred for 1-2 h, the yellow to orange-red compound was filtered, washed with ethanol and finally dried over fused $CaCl_2$.

The $[UO_2(H_2L)X_2]/[UO_2(H_2L')X_2]$ -type of complexes (except $[UO_2(H_2L)(NCS)_2]$) were also obtained by stirring a suspension of the compounds $[UO_2(L)(H_2O)_2]/[UO_2(L')(H_2O)_2]$ in dry ethanol for 2 h in the presence of the corresponding acid at pH 1-2. They were also prepared by stirring an ethanolic suspension of the corresponding uranyl complexes of benzoylhydrazide with diacetyl/benzil in 1:1.25 molar ratio for 1-2 h at room temperature.

The yellow solids $[UO_2(L/L')(H_2O)_2]$ were prepared by raising the pH of the suspension of the $[UO_2(H_2L/H_2L')X_2]$ -type complexes in rectified spir-

† Present address: Department of Chemistry, Ramnagar College, P.O. Depal, Dist. Midnapore, West Bengal, India.

Table 1—Analytical and other physical data of the compounds

Compound	Found (Calc.), %				λ_{max} (μ)	$\nu_{\text{as}}(\text{UO}_2)$ (cm^{-1})	Other selected IR bands
	M	N	C	H			
H_2L		17.1(17.4)	67.6(67.1)	5.5(5.6)			
$[\text{UO}_2(\text{H}_2\text{L})(\text{NO}_3)_2]$	33.5(33.2)	11.6(11.7)	30.4(30.2)	2.2(2.5)	420	930s	$\nu(\text{NO}_3)$: 1485s, 1272s
$[\text{UO}_2(\text{H}_2\text{L})(\text{OAc})_2]$	33.4(33.5)	8.2 (7.9)	37.8(37.2)	3.1(3.4)	420	920a	$\nu(\text{CH}_3\text{COO})$: 1545s, 1330s
$[\text{UO}_2(\text{H}_2\text{L})(\text{SO}_4)]$	33.9(34.6)	8.5 (8.1)	31.6(31.4)	2.6(2.6)	430	918s	SO_4 bands: ν_3 : 1200-1185 s,t 1130-1110 s, br, 1065-1045 s, br; ν_1 : 990 s, ν_4 : 650 s
$[\text{UO}_2(\text{H}_2\text{L})\text{Cl}_2]$	35.2(35.9)	8.7 (8.4)	32.9(32.5)	2.6(2.7)	420	920 s	
$[\text{UO}_2(\text{H}_2\text{L})\text{Br}_2]$	31.2(31.6)	7.7 (7.4)	28.2(28.7)	2.5(2.4)	418	925 s	
$[\text{UO}_2(\text{H}_2\text{L})(\text{NCS})_2]$	33.2(33.6)	11.6(11.9)	34.2(33.9)	2.3(2.5)	417	908 vs	$\nu(\text{CN})$: 2020 vs, 2000 s; $\delta(\text{CNS})$: 49
$[\text{UO}_2(\text{H}_2\text{L})(\text{ClO}_4)_2]$	30.3(30.1)	7.4 (7.1)	26.9(27.3)	2.3(2.3)	418	928 vs	$\nu(\text{ClO}_4)$: 1170 s, 1145 s, 1060s
$[\text{UO}_2(\text{L})(\text{H}_2\text{O})_2]$	37.6(38.0)	8.5 (8.9)	34.0(34.5)	2.9(3.2)	420	918 s	$\nu(\text{O}-\text{H})$: 3580-3320 s,br
$[\text{UO}_2(\text{L})(\text{py})_2]$	31.5(31.8)	11.4(11.2)	44.6(44.9)	3.4(3.5)	419	906 s	630 s, 470 s
$[\text{UO}_2(\text{L})(4\text{-pic})_2]$	30.3(30.7)	10.9(10.8)	46.1(46.4)	3.8(3.9)	418	906 s	610 s, 480 s
$[\text{UO}_2(\text{L})(\text{Anilin})_2]$	30.8(30.7)	10.4(10.8)	46.7(46.4)	3.7(3.9)	418	906 s	$\nu(\text{N}-\text{H})$: 3240 s, 3060 s
$[\text{UO}_2(\text{L})(\text{MeNH}_2)_2]$	36.2(36.5)	12.5(12.9)	36.7(36.8)	4.1(4.0)	420	905 s	$\nu(\text{N}-\text{H})$: 3520 s, 3425 s
$[\text{UO}_2(\text{L})(o\text{-phen})]$	30.7(30.9)	10.6(10.9)	46.8(46.7)	3.2(3.1)	420	895 s	1428 s
$[\text{UO}_2(\text{L})(2,2'\text{-dipy})]$	31.6(31.9)	11.5(11.3)	45.3(45.0)	3.0(3.2)	420	900 s	1430 s
$[\text{UO}_2(\text{L})(\text{en})]$	36.4(36.6)	12.5(12.9)	36.8(36.9)	3.8(3.7)	418	902 s	$\nu(\text{N}-\text{H})$: 3340 s, 3280 s
$\text{H}_2\text{L}'$		12.7(12.5)	75.1(75.3)	4.8(4.9)			
$[\text{UO}_2(\text{H}_2\text{L}')(\text{NO}_3)_2]^*$	28.5(28.3)	9.8(10.0)	40.3(40.0)	2.5(2.6)	435	935 s	$\nu(\text{NO}_3)$: 1432 s, 1275 s
$[\text{UO}_2(\text{H}_2\text{L}')(\text{OAc})_2]^*$	28.3(28.5)	6.9 (6.7)	45.7(46.0)	3.3(3.5)	435	930 s	$\nu(\text{CH}_3\text{COO})$: 1570 s, 1380 s
$[\text{UO}_2(\text{H}_2\text{L}')(\text{SO}_4)]$	29.6(29.3)	6.3 (6.9)	41.1(41.4)	2.8(2.7)	438	925 s	SO_4 bands: ν_3 : 1265 s, 1140 s, 1110 s; ν_1 : 990 s, ν_4 : 595
$[\text{UO}_2(\text{H}_2\text{L}')\text{Cl}_2]^*$	30.1(30.2)	7.4 (7.1)	42.6(42.7)	2.5(2.8)	435	929 s	
$[\text{UO}_2(\text{L}')(\text{H}_2\text{O})_2]$	31.1(31.7)	7.2 (7.5)	44.3(44.8)	3.1(3.2)	436	925 s	$\nu(\text{O}-\text{H})$: 3640-3140 s, br
$[\text{UO}_2(\text{L}')(\text{py})_2]^*$	27.5(27.3)	9.7 (9.6)	52.1(52.3)	3.9(3.7)	440	915 s	620 s, 450 s
$[\text{UO}_2(\text{L}')(\text{o-phen})]^*$	26.8(26.6)	9.1 (9.4)	53.9(53.7)	3.2(3.1)	445	912 s	1425 s

* Conductivity and electronic spectra of these complexes were recorded in methanol. For other complexes DMSO was used as the solvent.

it to 6-7 by the careful addition of an ethanolic NaOH solution and stirring the mixture for 1-2 h.

Preparation of the mixed ligand complexes

The $[\text{UO}_2(\text{L}/\text{L}')(\text{B})_2]/[\text{UO}_2(\text{L}/\text{L}')(\text{AA})]$ -types of complexes (where B = a monodentate lewis base like pyridine, picoline or aniline, etc. and AA = a bidentate lewis base like *o*-phenanthroline, 2,2'-bipyridyl or ethylenediamine) were prepared by refluxing the compounds $[\text{UO}_2(\text{H}_2\text{L}/\text{H}_2\text{L}')\text{X}_2]$ or $[\text{UO}_2(\text{L}/\text{L}')(\text{H}_2\text{O})_2]$ in ethanol with a slight excess of the base B or AA for 30 min (pH of the solution 6-7). The compounds $[\text{UO}_2(\text{L}/\text{L}')(\text{AA})]$ were also prepared by refluxing $[\text{UO}_2(\text{L}/\text{L}')(\text{B})_2]$ (0.001 mol) with AA (0.002 mol) for 1-2 h.

Details of the physicochemical methods utilised for the characterisation of the complexes are reported elsewhere³. Analytical results together with the electronic spectral data (λ_{max}) and important infrared stretching frequencies are presented in Table 1.

Results and Discussion

Colours of the dioxouranium(VI) complexes vary from yellow to reddish brown. All these complexes are diamagnetic indicating the presence of d^0 system. All the UO_2^{2+} complexes are non-electrolytes in DMSO or methanol (Λ_M 8-15 $\text{ohm}^{-1}\text{cm}^2/\text{mol}$).

Infrared spectra

The $\nu(\text{C}=\text{O})$ mode (amide-I band) observed at 1655 and 1645 cm^{-1} for the free ligands H_2L and $\text{H}_2\text{L}'$, respectively, is shifted to lower wavenumbers ($\Delta\nu = 25\text{-}35\text{ cm}^{-1}$) in the $[\text{UO}_2(\text{H}_2\text{L}/\text{H}_2\text{L}')\text{X}_2]$ -type of complexes indicating the participation of the carbonyl oxygen in complexation. Similarly, a negative shift of the $\nu(\text{C}=\text{N})$ band of the ligands H_2L and $\text{H}_2\text{L}'$ observed at 1642 and 1605 cm^{-1} , respectively, by 10-30 cm^{-1} points to the coordination of the azomethine nitrogen to the metal ion⁴⁻⁶. In all the complexes obtained at higher pH (6-7), disappearance of the amide-I band clearly demonstrates the enolisation of

the carbonyl group³. In these complexes each ligand is bound to UO_2^{2+} ion through two deprotonated enolate oxygens and two azomethine nitrogens. Characteristic infrared bands present in the spectra of the complexes containing nitrate, acetate, perchlorate, thiocyanate, etc., show the attachment of these anions in the monocoordinated fashion, whereas sulphate is found to be ligated in the bidentate manner⁷ (Table 1). Relevant IR data also indicate that the thiocyanate ion is bound through its nitrogen atom⁷. Specific bands of the coordinated lewis bases (B and AA) in $[\text{UO}_2(\text{L}/\text{L}')(\text{B})_2]/[\text{UO}_2(\text{L}/\text{L}')(\text{AA})]$ and of the coordinated water molecules in $[\text{UO}_2(\text{L}/\text{L}')(\text{H}_2\text{O})_2]$ are also observed in the IR spectra of these complexes.

Each dioxouranium(VI) complex exhibits an intense absorption in the $895\text{--}935\text{ cm}^{-1}$ range which is assigned to the asymmetric stretching frequency of the uranyl moiety^{8,9}. The $\nu_{\text{as}}(\text{UO}_2)$ band is expected to shift towards lower frequency when a stronger donor replaces a weaker one in the equatorial plane. This is found to be so in the present case as $\nu_{\text{as}}(\text{UO}_2)$, located at 918 and 925 cm^{-1} in $[\text{UO}_2(\text{L})(\text{H}_2\text{O})_2]$ and $[\text{UO}_2(\text{L}')(\text{H}_2\text{O})_2]$, is lowered when water is replaced by a monodentate or a chelating bidentate lewis base like pyridine, *o*-phenanthroline etc. Hence, the relative donor strengths of the secondary ligands (B and AA) are reflected in the magnitude of the change of the $\nu_{\text{as}}(\text{UO}_2)$ mode in different complexes (Table 1).

Electroni spectra

The electronic spectra of the UO_2^{2+} complexes in DMSO or methanol exhibit a strong band in the $417\text{--}440\text{ nm}$ region. This is attributed to the uranyl absorption $^1\Sigma_g^+ \rightarrow ^3\Pi_u$ for the first excited state¹⁰.

Thermal studies

The thermal decomposition pattern of the complex $[\text{UO}_2(\text{L})(\text{H}_2\text{O})_2]$ indicates loss of one mol of water per mol of the complex in the $70\text{--}170^\circ\text{C}$ temperature range, and the product $[\text{UO}_2(\text{L})(\text{H}_2\text{O})]$ is stable upto 225°C . The second mol of water is lost in the range $225\text{--}290^\circ\text{C}$ resulting in the formation of $[\text{UO}_2(\text{L})]$ (Fig. 1). However, the anhydrous species $[\text{UO}_2(\text{L})]$, when left in contact with moist air, quickly reverts back to the octahedral species $[\text{UO}_2(\text{L})(\text{H}_2\text{O})_2]$.

Simultaneous TGA and DTA studies of the compound $[\text{UO}_2(\text{L})(\text{py})_2]$ indicate that one mol of pyridine is lost per mol of the complex in the $155\text{--}200^\circ\text{C}$ temperature range (Fig. 1). The compound $[\text{UO}_2(\text{L})(\text{py})]$ is stable from 200 to 290°C . When left in contact with pyridine, $[\text{UO}_2(\text{L})(\text{py})]$ takes up one molecule of pyridine forming again the eight-coordinated species $[\text{UO}_2(\text{L})(\text{py})_2]$. The second molecule of pyridine is lost in the range $290\text{--}315^\circ\text{C}$. The loss of the second

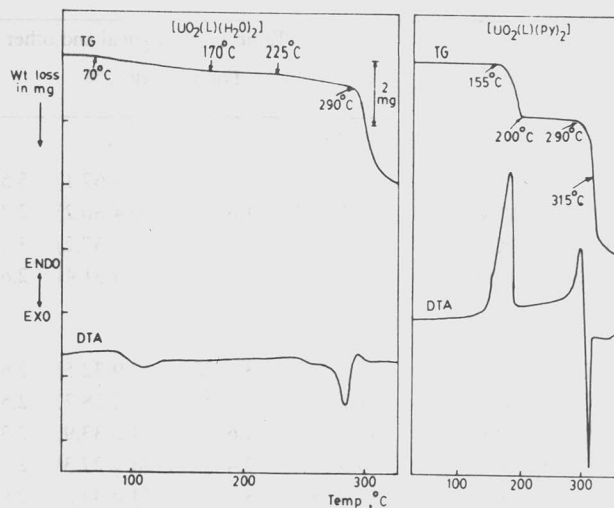
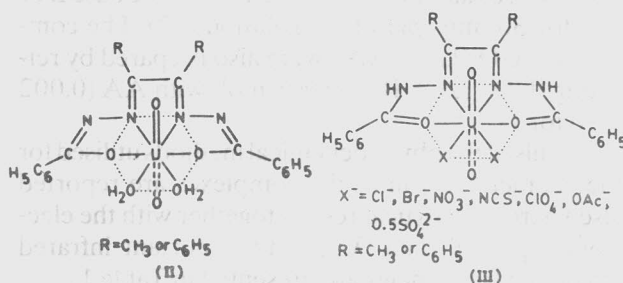


Fig. 1—Thermal curves of $[\text{UO}_2(\text{L})(\text{H}_2\text{O})_2]$ (sample mass: 14.23 mg) and $[\text{UO}_2(\text{L})(\text{py})_2]$ (sample mass: 14.83 mg)

pyridine molecule is indicated in the DTA curve by a sharp exotherm which is immediately succeeded by the decomposition of the residual complex. The above observations seem to indicate that the seven-coordinated species $[\text{UO}_2(\text{L})(\text{H}_2\text{O})]$ and $[\text{UO}_2(\text{L})(\text{py})]$ have better thermal stability than the corresponding octacoordinated variety.

IR and conductivity data indicate the presence of the coordinated anions in the compounds $[\text{UO}_2(\text{H}_2\text{L}/\text{H}_2\text{L}')\text{X}_2]$. This shows the octacoordinated nature of the complexes in which the tetradentate ligand occupies four positions of the hexagonal equatorial plane. The two monodentate anions in $[\text{UO}_2(\text{H}_2\text{L}/\text{H}_2\text{L}')\text{X}_2]$ or two water molecules in $[\text{UO}_2(\text{L}/\text{L}')(\text{H}_2\text{O})_2]$ are replaced by two monodentate lewis bases (B) or a chelating bidentate donor (AA) producing mixed ligand complexes $[\text{UO}_2(\text{L}/\text{L}')(\text{B})_2]$ and $[\text{UO}_2(\text{L}/\text{L}')(\text{AA})]$. The presence of two coordinated water molecules in $[\text{UO}_2(\text{L})(\text{H}_2\text{O})_2]$ and two pyridines in $[\text{UO}_2(\text{L})(\text{py})_2]$ is substantiated by the results of their thermal decomposition studies. All the above observations point to the eight-coordinated structures (II) and (III) for $[\text{UO}_2(\text{L}/\text{L}')(\text{H}_2\text{O})_2]$ and $[\text{UO}_2(\text{H}_2\text{L}/\text{H}_2\text{L}')\text{X}_2]$ respectively. As expected for the hard acceptor UO_2^{2+} ion¹¹, the complexes $[\text{UO}_2(\text{L}/\text{L}')(\text{H}_2\text{O})_2]$ and $[\text{UO}_2(\text{H}_2\text{L}/\text{H}_2\text{L}')\text{X}_2]$ failed to react with the soft donors like thio-



phene, *p*-toluenethiol and triphenylphosphine etc. Also, PPh_3 could not effect the oxygen abstraction from the UO_2^{2+} moiety even under prolonged reflux conditions¹¹.

References

- 1 Paolucci G, Marangoni G, Bandoli G & Clemente D A, *J chem Soc, Dalton Trans.* (1980) 1304.
- 2 Marangoni G & Paolucci G, *J chem Soc, Dalton Trans.* (1981) 357.
- 3 Ghosh S & Maiti A, *Indian J Chem*, 26A (1987) 44.
- 4 Bellamy L J, *The infrared spectra of complex molecules*, 3rd Edn (Chapman and Hall, London) 1975.
- 5 Percy G C & Thornton D A, *Inorg nucl chem Lett*, 7 (1971) 599.
- 6 Kovacic J E, *Spectrochim Acta*, 23A (1967) 183.
- 7 Nakamoto K, *Infrared spectra of inorganic and coordination compounds*, 3rd Edn (Wiley Interscience, London) 1978.
- 8 Jones L H, *Spectrochim Acta*, 10 (1958) 395.
- 9 Hsieh A T T, Sheahan R M & West B O, *Aust J Chem*, 28 (1975) 885.
- 10 McGlynn S P & Smith J K, *J molec Spectrosc*, 6 (1961) 164.
- 11 Pearson R G, *J Am chem Soc*, 85 (1963) 3533; *Science*, 151 (1966) 172.