DALTON
FULL PAPER

# Synthesis, structure and reactivity of *trans*-$UO_2^{2+}$ complexes of OH-containing ligands †

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*trans*-Dioxouranium dinuclear complexes of a few OH-containing ligands possessing N-, O-binding sites were synthesized and characterised. Seven of these were also structurally characterised by single crystal X-ray diffraction. All these complexes exhibit symmetric $U_2O_2$ core structures in addition to having a seven-co-ordinated environment about each uranium centre. Even when the ligand possessed more than one $CH_2OH$ group, only one such group was found to be involved both in chelation as well as in bridging. These complexes exhibited facile transmetallation reactions with vanadium and molybdenum precursors. Though their core structures are alike, the complexes differ in their lattice arrangement by exhibiting novel types of structures such as channel, herringbone and corrugated sheets owing to the presence of a number of extended weak interactions.

## Introduction

Hydroxy-containing molecules possessing N-, O-donor groups, where N is present as imine, are of interest in developing the co-ordination chemistry in general and biomimetic chemistry in particular of a number of metal ions including that of vanadium.[1] Also the literature is rich with OH bound oxo-vanadium complexes with or without N-binding.[2] However, in the recent past, our group has systematically developed the co-ordination chemistry of such ligands using oxo-centres of $V^V$.[3] The studies demonstrated the structure and reactivity of a number of complexes of $VO^{3+}$ and $VO_2^+$ motifs having different geometries. While all the $VO_2^+$ complexes were found to be mononuclear, a few of $VO^{3+}$ were dinuclear. The nuclearity exhibited by these complexes has bearing on the number of available $CH_2OH$ groups as well as on the reaction conditions. In all these cases only a *cis*-oxo geometry has been observed as expected. Some of the *cis*-$VO_2^+$ complexes of these ligands have exhibited bromination activity under acidic $H_2O_2$ conditions on substrates such as xylene cyanol, phenol red, monochlorodimedone (2-chloro-5,5-dimethylcyclohexane-1,3-dione) or 1,3,5-trimethoxybenzene.[4,5] However, the *cis*-$MoO_2^{2+}$ core has resulted only in mononuclear complexes of octahedral geometry with one of the axial sites being co-ordinated by a solvent molecule and did not show any dinuclear ones even when there were additional unbound $CH_2OH$ functions available.[5a] These molecules have also shown interesting co-ordination properties with a non-oxo metal centre, titanium(IV).[6] Transmetallation reactions have been observed among a number of different complexes containing these ligands.[7] While the oxovanadium(V) complexes of these ligands have shown interesting lattice interactions, the corresponding *cis*-$MoO_2^{2+}$ complexes have exhibited no such lattice interactions. These studies inspired us to look into the influence of the geometry of the oxometal centre. Therefore, the present paper deals with the studies performed on the influence of the *trans*-dioxouranium centre on co-ordination chemistry aspects of hydroxy-containing ligands possessing N-, O-ligating centres.

## Experimental

The complex $[UO_2(O_2CMe)_2]·2H_2O$ was obtained from BDH Limited (UK). All the other chemicals and solvents were procured and used as mentioned earlier.[5a] UV-Vis absorption spectra of solutions were measured using a Shimadzu UVPC-2101 Spectrophotometer and FTIR spectra of solids in the 4000–400 $cm^{-1}$ region in KBr matrix using an Impact 400 Nicolet FTIR Spectrometer. The $^1H$ and $^{13}C$ NMR spectra of all the complexes were measured using JEOL JNM GSX-270 FT, Varian XL-300 or Bruker DRX500 spectrometers in $(CD_3)_2SO$ and of the ligands in $CDCl_3$. Elemental analyses were performed using a Carlo-Erba 1106 elemental analyser. All the ligands prepared and the complexes synthesized and their abbreviations are shown in Chart 1. The ligands were synthesized and confirmed as reported earlier.[3c–e]

### Schiff base complexes of uranium

Complexes **1**–**9** were synthesized and purified using the same procedure and a representative procedure for **1** is given here. To naph-$H_4L^3$ (0.275 g, 1 mmol) in 10 mL MeOH was added $[UO_2(O_2CMe)_2]·2H_2O$ (0.424 g, 1 mmol) and the reaction mixture was stirred at reflux for 4 h. A yellow precipitate was formed, filtered off and washed by stirring in MeOH for 1 h in order to purify the crude product. This purification procedure was repeated thrice before drying the sample *in vacuo* to give $[UO_2(naph\text{-}H_2L^3)(H_2O)]_2·2H_2O$ **1** (0.480 g) in 83% yield. All the synthetic reactions (**1** to **11**) were carried out on a 1 mmol scale, however a few were repeated on a 2 mmol scale.

**$[UO_2(naph\text{-}H_2L^3)(H_2O)]_2·2H_2O$ 1.** Yield: 0.478 g (83%). Calc. for $C_{15}H_{19}NO_8U$: C, 31.10; H, 3.31; N, 2.42. Found: C, 30.84; H, 3.32; N, 2.25%. $^1H$ NMR (in dmso-$d_6$): $\delta$ 10.39 (s, 1 H, imine); 8.16 (t, 2 H, aromatic); 7.86 (d, 1 H, aromatic); 7.57 (t, 1 H, aromatic); 7.46 (d, 1 H, aromatic); 7.28 (t, 1 H, aromatic); 6.20 (s, 2 H, $CH_2O$); 5.15 (s, 2 H, free $CH_2O$*H*) and 4.35 (m, 4 H, free C*$H_2$*OH). $^{13}C$ NMR (in dmso-$d_6$;): $\delta$ 161.95 (imine); 169.01, 134.82, 134.62, 128.60, 127.12, 126.74, 124.22, 121.76, 120.06, 113.56 (aromatic); 77.41 (bound $CH_2O$); 75.57 (tert C) and 62.31 ($CH_2OH$). FTIR (KBr matrix, in $cm^{-1}$): $\nu$(OH) 3370; $\nu$(C=N) 1610; $\nu(UO_2)$ 897. UV-Vis (dmso), $\lambda$/nm

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† This paper is dedicated to Professor Richard H. Holm on his 65th birthday.

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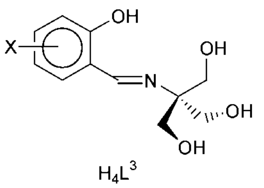
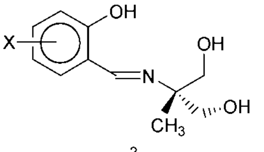


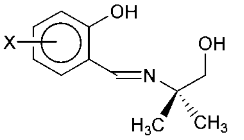
$H_4L^3$

| X | Complexes | Formulae |
|---|---|---|
| 5,6-Benzo | **1** | $[UO_2(naph\text{-}H_2L^3)(H_2O)]_2{\bullet}2H_2O$ |
| | **1a**•$H_2O$* | $[UO_2(naph\text{-}H_2L^3)(dmso)]_2{\bullet}H_2O$ |
| 5,6-Benzo | **1a**•bipy* | $[UO_2(naph\text{-}H_2L^3)(dmso)]_2{\bullet}bipy$ |
| H | **2** | $[UO_2(H_2L^3)(H_2O)]_2$ |
| | **2a**•$2H_2O$* | $[UO_2(H_2L^3)(dmso)]_2{\bullet}2H_2O$ |
| 5-Br | **3** | $[UO_2(5\text{-}Br\text{-}H_2L^3)(H_2O)]_2$ |
| | **3a*** | $[UO_2(5\text{-}Br\text{-}H_2L^3)(dmf)]_2$ |
| 3-OMe | **4** | $[UO_2(3\text{-}OMe\text{-}H_2L^3)(H_2O)]_2{\bullet}H_2O$ |



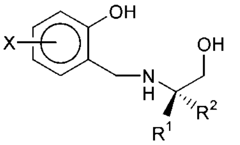
$H_3L^2$

| X | Complexes | Formulae |
|---|---|---|
| 3-OMe | **5** | $[UO_2(3\text{-}OMe\text{-}HL^2)(H_2O)]_2$ |
| | **5a*** | $[UO_2(3\text{-}OMe\text{-}HL^2)(dmso)]_2$ |
| 5-Br | **6** | $[UO_2(5\text{-}Br\text{-}HL^2)(H_2O)]_2{\bullet}2CH_3OH$ |
| | **6a**•dmf* | $[UO_2(5\text{-}Br\text{-}HL^2)(dmf)]_2{\bullet}dmf$ |
| 5,6-Benzo | **7** | $[UO_2(naph\text{-}HL^2)(H_2O)]_2{\bullet}2H_2O$ |



$H_2L^1$

| X | Complexes | Formulae |
|---|---|---|
| 5,6-Benzo | **8** | $[UO_2(naph\text{-}L^1)(H_2O)]_2{\bullet}2H_2O$ |
| 5-Br | **9** | $[UO_2(5\text{-}Br\text{-}L^1)(H_2O)]_2$ |



$H_2L^{rn}$ ($n$ = 1 or 2)

| $R^1$ | $R^2$ | Ligands | Complexes | Formulae |
|---|---|---|---|---|
| $CH_3$ | $CH_3$ | $H_2L^{r1}$ | **10** | $[UO_2(L^{r1})(H_2O)]_2$ |
| | | | **10a*** | $[UO_2(L^{r1})(dmso)]_2$ |
| $CH_3$ | $CH_2OH$ | $H_2L^{r2}$ | **11** | $[UO_2(HL^{r2})(CH_3OH)]_2$ |

**Chart 1** Representation of the ligands used and the composition of the complexes synthesized: '*', single crystal structure determination; subscript '**r**', presence of amine ($CH_2NH$) in place of imine (CH=N); bipy, bipyridyl molecule in the crystal lattice.

($\varepsilon$/$M^{-1}$ $cm^{-1}$): 252 (51531), 273 (10070), 345 (4200), 391 (2220) and 463 (126).

**$[UO_2(H_2L^3)(H_2O)]_2$ 2** Yield: 0.400 g (78%). Calc. for $C_{11}H_{15}NO_7U$: C, 25.84; H, 2.96; N, 2.74. Found: C, 26.36; H, 3.17; N, 2.13%. $^1H$ NMR (in dmso-$d_6$): $\delta$ 9.41 (s, 1 H, imine); 7.58 (m, 2 H, aromatic); 7.07 (d, 1 H, aromatic); 6.72 (d, 1 H, aromatic); 6.18 (s, 2 H, $CH_2O$); 4.97 (t, 2 H, free $CH_2OH$) and 4.26 (m, 4 H, free $CH_2OH$); $^{13}C$ NMR (in dmso-$d_6$): $\delta$ 167.19 (imine); 168.56, 135.42–115.58 (aromatic); 77.25 (bound $CH_2O$); 75.36 (tert C) and 61.87 ($CH_2OH$). FTIR (KBr matrix, in $cm^{-1}$): $\nu$(OH) 3421, 3370; $\nu$(C=N) 1617; $\nu(UO_2)$ 899. UV-Vis (dmso), $\lambda$/nm ($\varepsilon$/$M^{-1}$ $cm^{-1}$): 250 (34707), 273 (9480), 336 (4640) and 390 (1820).

**$[UO_2(5\text{-}Br\text{-}H_2L^3)(H_2O)]_2$ 3** Yield: 0.480 g (81%). Calc. for $C_{11}H_{14}BrNO_7U$: C, 22.39; H, 2.39; N, 2.37. Found: C, 22.14; H, 2.62; N, 1.80%. $^1H$ NMR (in dmso-$d_6$): $\delta$ 9.33 (s, 1 H, imine); 7.82 (d, 1 H, aromatic); 7.67 (dd, 1 H, aromatic); 7.05 (d, 1 H, aromatic); 6.20 (s, 2 H, $CH_2O$); 4.96 (t, 2 H, free $CH_2OH$) and 4.25 (m, 4 H, free $CH_2OH$); $^{13}C$ NMR (in dmso-$d_6$): $\delta$ 166.23 (imine); 167.67, 136.87, 136.25, 126.55, 122.45, 105.44 (aromatic); 77.19 (bound $CH_2O$); 75.79 (tert C) and 61.72 ($CH_2OH$). FTIR (KBr matrix in $cm^{-1}$): $\nu$(OH) 3506, 3359; $\nu$(C=N) 1616; $\nu(UO_2)$ 906. UV-Vis (dmso), $\lambda$/nm ($\varepsilon$/$M^{-1}$ $cm^{-1}$): 249 (26718), 273 (14730), 366 (4350), 397 (3960) and 451 (157).

**$[UO_2(3\text{-}OMe\text{-}H_2L^3)(H_2O)]_2{\cdot}2H_2O$ 4.** Yield: 0.35 g (63%). Calc. for $C_{12}H_{19}NO_9U$: C, 25.77; H, 3.42; N, 2.50. Found: C, 25.94; H, 3.28; N, 2.37%. $^1H$ NMR (in dmso-$d_6$): $\delta$ 9.39 (s, 1 H, imine); 7.22 (m, 2 H, aromatic), 6.65 (t, 1 H, aromatic); 6.17 (s, 2 H, $CH_2O$); 4.93 (t, 2 H, free $CH_2OH$); 4.25 (m, 2 H, free $CH_2OH$) and 4.00 (s, 3 H, $OCH_3$). $^{13}C$ NMR (in dmso-$d_6$): $\delta$ 166.06 (imine); 158.97, 151.25, 126.81, 124.42, 115.15, 114.64 (aromatic); 77.43 (bound $CH_2O$); 75.21 (tert C); 62.01 ($CH_2OH$) and 55.42 ($OCH_3$). FTIR (KBr matrix, in $cm^{-1}$): $\nu$(OH) 3383; $\nu$(C=N) 1617; $\nu(UO_2)$ 904. UV-Vis (dmso), $\lambda$/nm ($\varepsilon$/$M^{-1}$ $cm^{-1}$): 250 (30151), 274 (10590), 348 (3740), 396 (2240) and 447 (227).

**$[UO_2(3\text{-}OMe\text{-}HL^2)(H_2O)]_2$ 5.** Yield: 0.37 g (71%). Calc. for $C_{17}H_{17}NO_7U$: C, 27.44; H, 3.26; N, 2.67. Found: C, 27.39; H, 3.58; N, 2.30%. $^1H$ NMR (in dmso-$d_6$): $\delta$ 9.35 (d, 1 H, imine); 7.27 (m, 2 H, aromatic); 6.65 (t, 1 H, aromatic); 6.35, 5.65 (dd, 2 H, $CH_2O$); 5.05 (q, 1 H, free $CH_2OH$); 4.16 (m, 2 H, free $CH_2OH$); 4.00 (s, 3 H, $OCH_3$) and 1.7 (d, 3 H, $CH_3$). $^{13}C$ NMR (in dmso-$d_6$): $\delta$ 166.05 (imine); 159.02, 151.24, 126.69, 124.27, 115.21, 114.69 (aromatic); 80.17 (bound $CH_2O$); 72.51 (tert C); 65.68 ($CH_2OH$); 55.40 ($OCH_3$) and 18.59 ($CH_3$). FTIR (KBr matrix, in $cm^{-1}$): $\nu$(OH) 3299; $\nu$(C=N) 1622; $\nu(UO_2)$ 906. UV-Vis (dmso), $\lambda$/nm ($\varepsilon$/$M^{-1}$ $cm^{-1}$): 249 (20590), 270 (12510), 353 (3690), 406 (1890) and 460 (70).

**$[UO_2(5\text{-}Br\text{-}HL^2)(H_2O)]_2{\cdot}2CH_3OH$ 6.** Yield: 0.46 g (80%). Calc. for $C_{12}H_{18}BrNO_7U$: C, 23.78; H, 2.99; N, 2.31. Found: C, 23.57; H, 2.86; N, 2.26%. $^1H$ NMR (in dmso-$d_6$): $\delta$ 9.32 (d, 1 H, imine); 7.91 (t, 1 H, aromatic); 7.67 (dd, 1 H, aromatic); 7.05 (d, 1 H, aromatic); 6.39, 5.64 (d, 1 H each, $CH_2O$); 5.10 (q, 1 H, free $CH_2OH$); 4.23 (m, 2 H, free $CH_2OH$) and 1.7 (d, 3 H, $CH_3$). FTIR (KBr matrix, in $cm^{-1}$): $\nu$(OH) 3447; $\nu$(C=N) 1622; $\nu(UO_2)$ 909. UV-Vis (dmso), $\lambda$/nm ($\varepsilon$/$M^{-1}$ $cm^{-1}$): 249 (23870), 271 (14190), 345 (4700), 390 (2490) and 456 (61).

**$[UO_2(naph\text{-}HL^2)(H_2O)]_2{\cdot}2H_2O$ 7.** Yield: 0.38 g (69%). Calc. for $C_{15}H_{19}NO_7U$: C, 31.98; H, 3.40; N, 2.49. Found: C, 32.31; H, 3.47; N, 2.27%. $^1H$ NMR (in dmso-$d_6$): $\delta$ 10.26 (s, 1 H, imine); 8.24 (d, 1 H, aromatic); 8.14 (d, 1 H, aromatic); 7.87 (d, 1 H, aromatic); 7.58 (t, 1 H, aromatic); 7.47 (d, 1 H, aromatic); 7.29 (t, 1 H, aromatic); 6.38 (dd, 1 H, $CH_2O$); 5.76 (t, 1 H, $CH_2O$); 5.25 (m, 1 H, free $CH_2OH$); 4.30 (m, 2 H, free $CH_2OH$) and 1.82 (d, 3 H, $CH_3$). FTIR (KBr matrix, in $cm^{-1}$): $\nu$(OH) 3481; $\nu$(C=N) 1612; $\nu(UO_2)$ 905. UV-Vis (dmso), $\lambda$/nm ($\varepsilon$/$M^{-1}$ $cm^{-1}$): 251 (42000), 302 (11810), 365 (5530), 401 (4110) and 460 (91).

**$[UO_2(naph\text{-}L^1)(H_2O)]_2{\cdot}2H_2O$ 8.** Yield: 0.43 g (79%). Calc. for $C_{15}H_{19}NO_6U$: C, 32.92; H, 3.50; N, 2.56. Found: C, 32.56; H, 3.54; N, 2.43%. FTIR (KBr matrix, in $cm^{-1}$): $\nu$(OH) 3485; $\nu$(C=N) 1613; $\nu(UO_2)$ 900. UV-Vis (dmso), $\lambda$/nm ($\varepsilon$/$M^{-1}$ $cm^{-1}$): 250 (33320), 305 (9440), 367 (4510), 394 (3980) and 463 (73).

**$[UO_2(5\text{-Br-}L^1)(H_2O)]_2$ 9.** Yield: 0.31 g (56%). Calc. for $C_{11}H_{14}BrNO_5U$: C, 23.67; H, 2.53; N, 2.51. Found: C, 23.48; H, 2.86; N, 2.38%. FTIR (KBr matrix, in $cm^{-1}$): ν(OH) 3484; ν(C=N) 1629; ν($UO_2$) 912. UV-Vis (dmso), λ/nm (ε/$M^{-1}$ $cm^{-1}$): 249 (21160), 270 (11560), 346 (3610), 393 (980) and 459 (58).

### Mannich base complexes of uranium

Uranium(VI) complexes of Mannich bases, **10** and **11**, were synthesized by adopting the procedure given for **1**, except that in the present case the reaction mixture was refluxed for 6 h. An orange-yellow precipitate formed was filtered off and washed by stirring in MeOH for 1 h in order to purify the crude product. This purification procedure was repeated thrice before drying the sample *in vacuo* to give **10** in 50% yield. Both the complexes were recrystallised from dmso solution by diffusing methanol in order to obtain the single crystals. However good crystals of X-ray quality were obtained only in the case of **10**, to result in **10a**.

**$[UO_2(L_r^1)(H_2O)]_2$ 10.** Reaction scale: 2 mmol, yield: 0.46 g (50%). Calc. for $C_{11}H_{17}NO_6U$: C, 27.45; H, 3.56; N, 2.91. Found: C, 28.21; H, 3.39; N, 3.50%. $^1H$ NMR (in dmso-$d_6$): δ 7.39 (t, 1 H, aromatic); 7.31 (d, 1 H, aromatic); 7.01 (d, 1 H, aromatic); 6.55 (d, 1 H, aromatic); 6.18, 5.47 (t, 1H each, $CH_2O$); 4.44 (d, 1 H, $CH_2$NH); 4.66 (m, 2 H, $CH_2NH$); 1.66, 1.76 (d, 3H each, $CH_3$); $^{13}C$ NMR (in dmso-$d_6$): δ 171.28, 131.04, 130.41, 129.91, 120.00, 116.72 (aromatic); 85.24 (bound $CH_2O$); 63.89 (tert C); 49.63 ($CH_2NH$) and 22.87 ($CH_3$). FTIR (KBr matrix, in $cm^{-1}$): ν(OH) 3422; ν(NH) 3256; ν($UO_2$) 910. UV-Vis (dmso), λ/nm (ε/$M^{-1}$ $cm^{-1}$): 250 (6615), 284 (3475), 385 (734) and 465 (270).

**$[UO_2(HL_r^2)(CH_3OH)]_2$ 11.** Yield: 0.20 g (42%). Calc. for $C_{12}H_{19}NO_6U$: C, 28.20; H, 3.75; N, 2.74. Found: C, 28.38; H, 3.72; N, 3.26%. $^1H$ NMR (in dmso-$d_6$): δ 7.37 (m, 1 H, aromatic); 7.31 (t, 1 H, aromatic); 7.05 (t, 1 H, aromatic); 6.56 (t, 1 H, aromatic); 6.12, 5.65 (d, 1H each, $CH_2O$); 5.30 (br, 1 H, free $CH_2OH$); 4.67 (m, 2 H, $CH_2NH$); 4.41 (d, 1 H, $CH_2$NH); 4.13 (d, 1 H, free $CH_2$OH); 3.85 (t, 1 H, free $CH_2$OH) and 1.72 (d, 3 H, $CH_3$). $^{13}C$ NMR (in dmso-$d_6$): δ 169.71, 129.54, 129.06, 128.08, 118.58, 115.38 (aromatic); 80.76 (bound $CH_2O$); 65.48 (free $CH_2OH$); 61.38 (tert C); 47.34 ($CH_2NH$) and 16.57 ($CH_3$). FTIR (KBr matrix, in $cm^{-1}$): ν(OH) 3427; ν(NH) 3136; ν($UO_2$) 910. UV-Vis (dmso), λ/nm (ε/$M^{-1}$ $cm^{-1}$): 250 (8302), 285 (5486), 375 (998) and 477 (392).

### Crystallisation

The crude products were recrystallised from dmso solution by diffusing methanol at room temperature in order to obtain single crystals. Good crystals of X-ray quality were obtained only in case of **1**(**1a**·$H_2O$), **2**(**2a**·$2H_2O$), **5a** and **10a**. All these complexes possess dmso in their co-ordination spheres in place of $H_2O$. Further, the crystals of **1a** and **2a** have $H_2O$ in their lattices. On the other hand, single crystals of **3** and **6** have been grown from dmf solution by diffusing methanol to result in good crystals of X-ray quality of **3a** and **6a**·dmf. In both these complexes, dmf was present in the co-ordination sphere in place of $H_2O$. Complex **6a** has dmf present in the lattice. However, no single crystals could be obtained with the other complexes. When complex **1** was dissolved in dmso and recrystallised by diffusing a methanolic solution of bipyridyl (bipy), single crystals of X-ray quality of **1a**·bipy were obtained.

### X-Ray crystallography

Standard procedures were adopted for mounting the crystals, collecting the data and for solving the structures as reported by us earlier.[3a,5a] The diffraction data were collected on a Nonius CAD4 diffractometer in the $\omega$–$2\theta$ scan mode using Mo-Kα radiation. The data reduction process incorporated all the preliminary corrections. The structures were solved using SHELXS 86 and the model was refined using SHELXL 93 program packages.[8,9] The diagrams were generated using ORTEP 3.[10] The hydrogen atoms were fixed through the SHELXL program. Empirical absorption corrections were performed for all the data. Full matrix least squares refinement with anisotropic thermal parameters for all non-hydrogen atoms was used. The hydrogen atoms were treated as riding atoms with a fixed thermal parameter. Details of the collection and refinement are provided in Table 1.

In the complex **5a** the position of the sulfur atom of dmso and that of O3 (of the free $CH_2OH$ group) were disordered and were modelled with two positions having occupancies of 0.57 and 0.43 respectively in both cases. Disorder was also found with the oxygen atom (O6) of the free $CH_2OH$ group in the case of **6a**·dmf and was modelled with two positions having occupancies of 0.80 and 0.20 respectively.

CCDC reference number 186/1840.

See http://www.rsc.org/suppdata/dt/b0/b000142m/ for crystallographic files in .cif format.

## Results and discussion

Reactions between the ligands reported in Chart 1 and $[UO_2(O_2CMe)_2]\cdot 2H_2O$ in MeOH resulted in the synthesis of *trans*-dioxouranium(VI) dimeric complexes, independent of the number of $CH_2OH$ groups present in the ligand (one in $H_2L^1$, two in $H_3L^2$ and three in $H_4L^3$ series), as per reaction (1) where

$$2H_mL^n + 2[UO_2(O_2CMe)_2]\cdot 2H_2O \longrightarrow [UO_2(H_{m-2}L^n)(\text{solv})]_2 + 4CH_3CO_2H \quad (1)$$

$m = 2$, 3 or 4, $n = 1$, 2 or 3 and solv = $H_2O$ or $CH_3OH$. All the products have been isolated with $H_2O$ as co-ordinated solvent before recrystallisation except in the case of **11** where one $CH_3OH$ was co-ordinated. Complexes, **1**, **4**, **7** and **8** also possess additional lattice water molecules. Complex **6** possesses MeOH as lattice solvent. When these crude products were recrystallised in dmso or dmf correspondingly the co-ordinated water was replaced by dmso or dmf. In the case of **6** additional dmf is incorporated into the lattice. While the formulae given in Chart 1 are from the initial products obtained from the reactions directly, the crystal structures correspond to those recrystallised either from dmso or dmf. Thus the crystallographic structures of **1a**·$H_2O$, **1a**·bipy, **2a**·$2H_2O$, **5a** and **10a** contain a dmso molecule in the co-ordination sphere and **3a** and **6a**·dmf contain a co-ordinated dmf molecule.

### Molecular structures

Structures **1a**·$H_2O$, **2a**·$2H_2O$, **3a**, **5a**, **6a**·dmf and **10a** exhibit the presence of dimeric *trans*-dioxouranium(VI) units giving rise to a centrosymmetric $U_2O_2$ core. Each uranium(VI) is bound to phenoxo, an imine nitrogen, an alkoxo and a solvent oxygen (dmso/dmf) in addition to the *trans* dioxo moiety. The alkoxo moiety that is bound to the metal centre is also involved in bridging the two uranium centres to result in a centrosymmetric dimer, giving rise to seven-co-ordination at each uranium centre as seen in Fig. 1. In all the complexes only one $CH_2OH$ group was involved in binding as well as bridging the uranium centers through deprotonation ($CH_2O^-$), even when there were more than one $CH_2OH$ group available, as in the case of $H_3L^2$ (two groups) and $H_4L^3$ (three groups). However, the *cis*-dioxo centres of $V^V$ and $Mo^{VI}$ could not yield dinuclear complexes, keeping the *cis*-dioxo core intact in case of the alkoxo rich ligands. In the crystals of **1a**·bipy the geometry of the $U_2O_2$ core of **1a** was unperturbed and the bipyridyl moieties were

**Table 1** Summary of crystallographic data and parameters for complexes **1a**·$H_2O$, **1a**·bipy, **2a**·$2H_2O$, **3a**, **5a**, **6a**·dmf and **10a**

| | **1a**·$H_2O$ | **1a**·bipy | **2a**·$2H_2O$ | **3a** | **5a** | **6a**·dmf | **10a** |
|---|---|---|---|---|---|---|---|
| Formula | $C_{36}H_{48}N_2O_{15}S_3U_2$ | $C_{44}H_{50}N_4O_{14}$-$S_2U_2$ | $C_{26}H_{46}N_2O_{18}$-$S_2U_2$ | $C_{28}H_{38}Br_2N_5$-$O_{14}U_2$ | $C_{28}H_{38}N_2O_{14}$-$S_2U_2$ | $C_{34}H_{50}Br_2N_6$-$O_{14}U_2$ | $C_{26}H_{42}N_2O_{10}$-$S_2U_2$ |
| $M$ | 1321.00 | 1399.06 | 1214.82 | 1290.50 | 1166.78 | 1402.68 | 1082.80 |
| $T$/K | 293(2) | 173(2) | 180(2) | 293(2) | 180(2) | 293(2) | 180(2) |
| Crystal system | Orthorhombic | Monoclinic | Orthorhombic | Monoclinic | Orthorhombic | Monoclinic | Monoclinic |
| Space group | *Pbca* | *P*2$_1$/*c* | *Pbca* | *P*2$_1$/*c* | *Pbca* | *P*2$_1$/*c* | *P*2$_1$/*c* |
| $a$/Å | 7.682(2) | 16.775 | 20.106(3) | 11.562(2) | 12.010(3) | 8.142(2) | 13.069(4) |
| $b$/Å | 17.995(3) | 7.762 | 17.502(3) | 18.277(2) | 16.968(2) | 25.595(5) | 17.011(7) |
| $c$/Å | 32.276(4) | 17.891 | 10.3781(14) | 9.097(2) | 17.342(3) | 10.927(2) | 7.534(2) |
| $\beta$/° | — | 101.07 | — | 109.01(2) | — | 107.86(2) | 97.11(2) |
| $V$/Å$^3$ | 4462.0(13) | 2286.2 | 3661.8(9) | 1817.5(5) | 3534.1(11) | 2167.5(8) | 1662.1(9) |
| $Z$ | 4 | 2 | 4 | 2 | 4 | 2 | 2 |
| $D_c$/g cm$^{-3}$ | 1.966 | 2.032 | 2.204 | 2.358 | 2.193 | 2.149 | 2.164 |
| Total reflections | 4063 | 4137 | 3401 | 7254 | 3315 | 4093 | 3158 |
| Unique reflections | 3914 | 3991 | 3209 | 3698 | 3097 | 3812 | 2917 |
| Parameters | 258 | 300 | 228 | 234 | 210 | 269 | 194 |
| Final $R$ | 0.0503 | 0.0307 | 0.0338 | 0.0294 | 0.0376 | 0.0486 | 0.0566 |
| $R_w$ | 0.1482 | 0.0599 | 0.0865 | 0.0698 | 0.0983 | 0.1253 | 0.1534 |

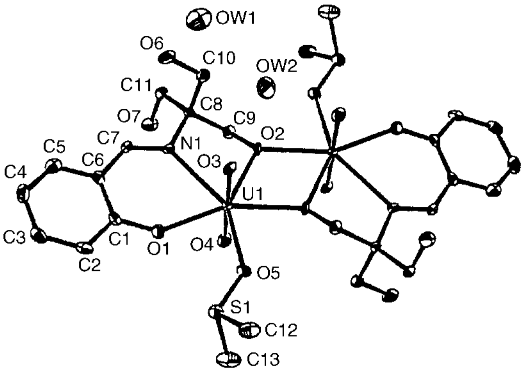


**Fig. 1** Molecular structure of complex **2a**·$2H_2O$ showing 50% probability thermal ellipsoids using ORTEP.

introduced into the host crystal lattice formed by molecules of **1a** in an interesting fashion.

The metric parameters of the co-ordination spheres in all the complexes were consistent with a distorted pentagonal bipyramidal geometry about each uranium (Table 2). The C–N bond length that was observed in the range, 1.282–1.296 Å, in the case of Schiff base complexes **1a**·$H_2O$, **1a**·bipy, **2a**·$2H_2O$, **3a**, **5a** and **6a**·dmf and that observed in the Mannich base complex **10a** (1.500 Å) confirms the bond order in these two types of complexes, on going from the Schiff base to the Mannich base upon $NaBH_4$ reduction. In all these structures, U=O distances were found to be in the range 1.77–1.80 Å and these agree well with those reported in the literature.[11] The U–$O_{phe}$ and U–$N_{imi}$ bond distances were found to be in the ranges 2.21–2.29 and 2.52–2.65 Å respectively and well in agreement with those found in Schiff base complexes of uranium bound to phenoxo and imine nitrogen ligands. The U–$O_{alk}$ distances observed in the range 2.34–2.39 Å were indicative of the symmetric nature of the $U_2O_2$ rhomb. The bond distance of the solvent (dmso or dmf) oxygen to the uranium centre in these complexes (**1a**, **2a**, **3a**, **5a**, **6a** and **10a**) was found to be in the range 2.38–2.43 Å. The U···U distance, 3.86–3.97 Å, is indicative of the absence of any bond between the two uranium centres.

## Crystal structures

While the core molecular structure of these *trans*-dioxo uranium complexes is similar in all the cases studied, their crystal structures differ significantly owing to the presence of a number of weak intermolecular hydrogen bond interactions. Among the structures reported in this paper, the O–H···O interactions were found in the range 2.68–3.39 Å, 145.3–168.2°; and the O–H···N interaction that was found in **1a**·bipy exhibited metric parameters of 2.82 Å and 169.8°.

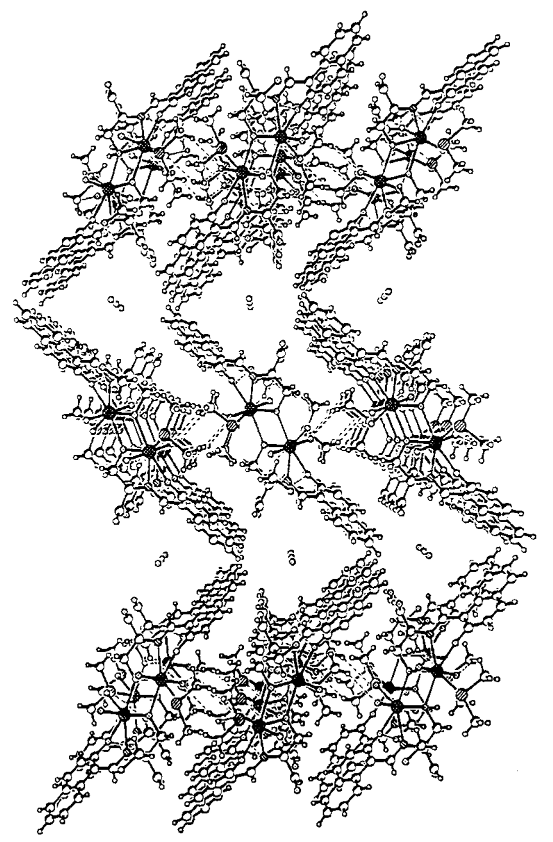


**Fig. 2** Lattice structure of corrugated sheet type with channels possessing water molecules in complex **1a**·$H_2O$.

In the crystal lattice of **1a**·$H_2O$ the neighbouring molecules in each column interact through weak hydrogen bonds leading to a corrugated sheet structure possessing channels filled with $H_2O$ molecules as shown in Fig. 2. Comparison of this structure with that of **1a**·bipy (Fig. 3) reveals that the entry of bipy molecules into the host lattice of **1a** results in collapse of the original corrugated channel structure and aligns the uranium complex molecules into a layered form. Further, the 2,2′-bipy molecules were found in their *trans* configuration sandwiched between the naphthyl units of adjacent molecules.

However, in the case of **2a**·$2H_2O$, the $H_2O$ molecules showed hydrogen bond interactions with the main complex unit by

**Table 2** Selected bond distances (Å) and angles (°) for the primary co-ordination spheres of the complexes

| | **1a**·$H_2O$ | **1a**·bipy | **2a**·$2H_2O$ | **3a** | **5a** | **6a**·dmf | **10a** |
|---|---|---|---|---|---|---|---|
| U=O | 1.778(9) | 1.781(5) | 1.791(5) | 1.773(4) | 1.779(6) | 1.776(8) | 1.769(8) |
| | 1.802(9) | 1.788(5) | 1.795(4) | 1.775(4) | 1.783(6) | 1.787(7) | 1.781(9) |
| U–$O_{phe}$ | 2.298(9) | 2.289(5) | 2.213(5) | 2.227(4) | 2.255(6) | 2.260(8) | 2.233(6) |
| U–$O_{alk}$ | 2.341(9) | 2.336(5) | 2.347(4) | 2.333(4) | 2.347(6) | 2.343(7) | 2.387(8) |
| | 2.358(9) | 2.351(4) | 2.348(4) | 2.373(4) | 2.350(6) | 2.365(7) | 2.387(8) |
| U–$O_{sol}$ | 2.383(9) | 2.416(5) | 2.400(4) | 2.428(4) | 2.386(7) | 2.429(7) | 2.412(8) |
| U–N | 2.522(12) | 2.553(5) | 2.593(5) | 2.608(4) | 2.588(7) | 2.597(8) | 2.656(10) |
| U···U′ | 3.914(1) | 3.972(1) | 3.897(1) | 3.863(1) | 3.920(7) | 3.899(1) | 3.908(1) |
| O=U=O | 177.2(4) | 177.0(2) | 179.1(2) | 178.6(2) | 178.6(3) | 178.0(4) | 178.0(4) |
| O=U–$O_{phe}$ | 84.2(4) | 83.9(2) | 88.0(2) | 89.2(2) | 87.0(3) | 86.1(4) | 88.8(4) |
| | 93.7(4) | 93.5(2) | 92.5(2) | 90.7(2) | 92.0(3) | 92.7(4) | 89.8(4) |
| O=U–$O_{alk}$ | 86.9(4) | 85.9(2) | 88.0(2) | 87.3(2) | 86.6(3) | 87.5(3) | 89.8(3) |
| | 95.8(4) | 97.0(2) | 91.1(2) | 91.8(2) | 94.8(3) | 92.3(3) | 90.0(3) |
| | 93.4(4) | 88.2(2) | 89.5(2) | 88.7(2) | 90.0(3) | 90.5(4) | 92.1(3) |
| | 87.9(4) | 93.7(2) | 90.4(2) | 92.0(2) | 90.6(3) | 91.3(3) | 90.7(4) |
| O=U–$O_{sol}$ | 86.9(4) | 86.7(2) | 93.3(2) | 87.0(2) | 88.3(3) | 90.2(3) | 88.5(3) |
| | 90.9(4) | 91.4(2) | 87.6(2) | 94.3(2) | 90.6(3) | 91.1(3) | 89.8(3) |
| O=U–N | 85.2(4) | 83.9(2) | 84.8(2) | 87.6(2) | 85.2(13) | 88.0(3) | 80.6(3) |
| | 95.7(4) | 96.6(2) | 94.6(2) | 91.1(2) | 95.2(3) | 90.1(3) | 100.3(4) |
| $O_{phe}$–U–$O_{alk}$ | 132.6(3) | 132.8(2) | 137.3(2) | 137.1(1) | 135.0(2) | 136.9(3) | 136.5(3) |
| | 159.7(3) | 159.4(2) | 154.7(2) | 153.2(1) | 157.6(2) | 154.5(3) | 156.4(3) |
| $O_{phe}$–U–$O_{sol}$ | 79.1(3) | 80.1(2) | 77.7(2) | 76.4(1) | 80.7(2) | 76.8(3) | 77.4(3) |
| $O_{phe}$–U–N | 69.2(3) | 69.8(2) | 70.8(2) | 70.6(1) | 70.0(2) | 70.2(3) | 72.1(3) |
| $O_{alk}$–U–$O_{sol}$ | 80.7(3) | 79.5(2) | 77.2(2) | 76.9(1) | 77.0(2) | 77.8(2) | 79.0(3) |
| | 147.6(3) | 146.2(2) | 145.1(2) | 145.8(1) | 143.8(2) | 145.9(3) | 146.1(3) |
| $O_{alk}$–U–N | 65.4(3) | 65.8(2) | 67.2(2) | 66.6(1) | 66.3(2) | 67.3(2) | 65.4(3) |
| | 131.1(3) | 130.7(2) | 134.5(2) | 136.2(1) | 132.4(2) | 135.3(2) | 131.0(3) |
| $O_{sol}$–U–N | 146.8(3) | 147.8(2) | 147.1(2) | 146.6(1) | 149.7(2) | 146.8(2) | 147.6(3) |
| $O_{alk}$–U–$O'_{alk}$ | 67.2 | 67.1(3) | 67.8(2) | 69.7(1) | 67.0(2) | 68.2(3) | 67.0(2) |
| U–O–U′ | 112.8(4) | 112.9(3) | 112.2(2) | 110.3(1) | 113.0(2) | 111.8(3) | 113.0(2) |

phe = phenoxo; alk = alkoxo; sol = solvent; N = nitrogen of $CH_2NH$ or CH=N.

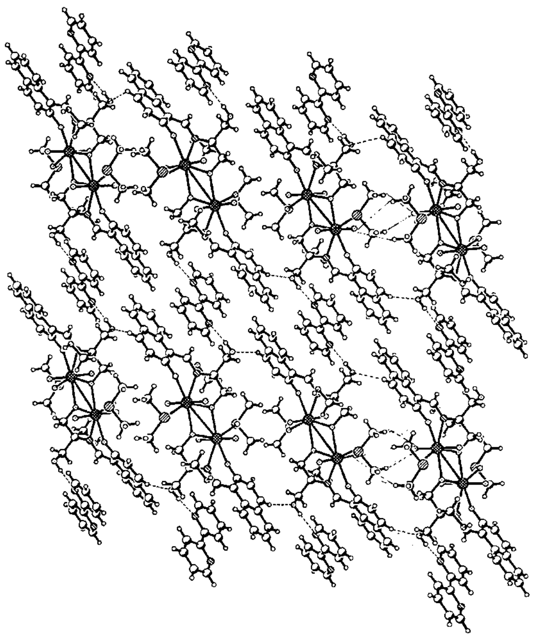


**Fig. 3** Lattice structure of the intercalation of bipy resulting in a layered structure in complex **1a**·bipy.

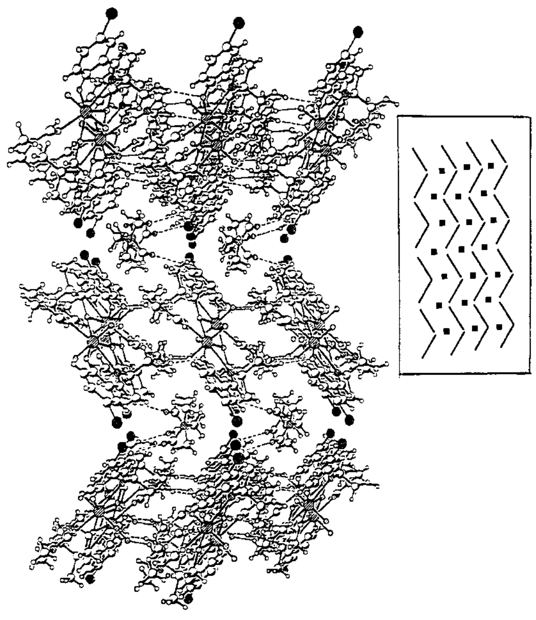


**Fig. 4** Lattice structures showing the channels filled with dmf molecules in complex **6a**·dmf. Inset: the herringbone pattern.

acting both as donor as well as acceptor of hydrogen. These interactions are responsible for the disruption of the original corrugated channel structure present in **1a**·$H_2O$ and thus **2a**·$2H_2O$ adopts a simple herringbone type structure. The lattice structure of **3a** also exhibits a simple herringbone type structure. The lattice of **6a**·dmf showed channels filled with solvent dmf molecules which interact with the lattice as shown in Fig. 4. On the other hand **5a** exhibited no special structure. Molecule **10a** exhibits a simple herringbone structure. Thus the lattice structures ranged from the simple layered type to herringbone to corrugated sheet to channel type.

## Reactivity

These dinuclear uranium complexes have shown facile transmetallation reactions in MeOH with oxovanadium-(IV) or -(V) and oxomolybdenum(VI) species resulting in the corresponding dinuclear monooxovanadium(V) complex and mononuclear *cis*-dioxo-molybdenum(VI) complexes respectively as products.[7] The transmetallation reactions proceeded only when there existed at least one unbound $CH_2OH$ group in the complex. These dinuclear uranium complexes did not show any reactivity in terms of addition or substitution of the added organic ligand either at one uranium centre or across the dimer.

### FTIR and UV-Vis spectral studies

A band observed in the range 897–912 $cm^{-1}$, in the case of complexes **1**–**11**, is assignable to asymmetric stretching of the *trans*-dioxouranyl ion.[11] The $\nu_{C=N}$ vibrations in **1**–**9** are found in the region 1610–1629 $cm^{-1}$, and are shifted by at least 10–20 $cm^{-1}$ to lower frequency as compared to those of the corresponding "free" ligands, indicating that nitrogen of azomethine is co-ordinated to the metal centre. A band corresponding to the imine stretching ($\nu_{C=N}$) of the Schiff base is absent for complexes **10** and **11**, as the imine bond is reduced from HC=N to $H_2CNH$ in these cases. The presence of OH groups arising out of free $CH_2OH$ and solvent molecules ($CH_3OH$, $H_2O$) has been observed in the $\nu_{OH}$ region of the spectra (3300–3550 $cm^{-1}$). The presence of solvent molecules has also been inferred from $^1H$ NMR data. In all the complexes the UV-Vis absorption spectral pattern observed in the solid is similar to that found in the solution state, indicating that the core structure is retained even in the solution state.

### $^1H$ NMR study

In the complexes **1**–**7** the azomethine (HC=N) proton was shifted downfield by about 1 ppm (compared to that of the corresponding "free" ligand) indicating that the nitrogen is co-ordinated to the uranium centre. Complexes **1**–**4** showed the presence of two free $CH_2OH$ groups and one bound $CH_2O^-$ group. The proton signals for bound $CH_2O^-$ were shifted downfield by about 2.5 ppm when compared with those of the corresponding "free" ligand. The methylene protons of bound $CH_2O^-$ exhibited either a singlet or a diastereotopic multiplet depending upon the symmetric or unsymmetric disposition of substituents on the neighbouring tertiary carbon centre, as for the complexes **1**, **5**, **8**, possessing $L^1$, $L^2$ and $L^3$ ligands respectively in their co-ordination spheres. Complexes **5**–**7** showed resonances corresponding to one free $CH_2OH$, one methyl and one bound $CH_2O^-$ groups (*i.e.* $H_3L^2$). However, the methylene protons of bound $CH_2O^-$ appears as 'AB' type quartet, where one of the pairs is around $\delta$ 6.38 and the other pair at around $\delta$ 5.65. A similar kind of splitting was also observed with complexes of $MoO_2^{2+}$ bound to $L^2$ ligand. For complexes of $VO_2^+$, $VO^{3+}$, $MoO_2^{2+}$ and $UO_2^{2+}$ centres with these ligands (*i.e.* $H_2L^1$, $H_3L^2$ and $H_4L^3$) there was a downfield shift of bound $CH_2O^-$ group protons in the order $UO_2^{2+}$ (2.55 ppm) > $VO^{3+}$ (1.0 ppm) > $MoO_2^{2+}$ (0.8 ppm) > $VO_2^+$ (0.45 ppm). The large downfield shift observed in the case of $UO_2^{2+}$ complexes is attributable to the *trans*-dioxo geometry. Besides this, the trend observed is also attributable to the overall positive charge present on the oxometal moiety (1+, 2+, 3+) as expected. For complexes **1**–**7** the signals of methylene and OH protons of free $CH_2OH$ groups were shifted downfield marginally. The methyl protons in the **5**–**7** have shifted downfield by 0.5–0.6 ppm in comparison with the corresponding "free" ligand positions. As these complexes are centrosymmetric dimers, the NMR spectra will show only one half of the complex dimer. If the dimer structure were to be broken, the spectra would be expected to be reflective of dissociated species. However, such dissociation was not noticed. This result when combined with the results obtained from the crystal structures as well as the UV-Vis spectra (solid and solution) revealed the robust nature of these complexes. The formation as well as the stability of complexes **10**, **11** is understood based on the disappearance of the signal in the imine region (HC=N), in the phenolic OH region and in the alkoxy OH regions, and the appearance of a benzylic $CH_2$ group in the region $\delta$ 4.44–4.67 in the proton NMR spectra.

### $^{13}C$ NMR study

Low solubility of complexes **6**–**9** has prevented their carbon-13 NMR measurements. In the case of **1**–**5** the bound $CH_2O$ carbon showed a downfield shift by about 14.9–16.6 ppm, when compared to the corresponding "free" ligand positions. Considerable downfield shifts (8.4–11.2 ppm) were also observed with the tertiary carbon indicating the binding of neighbouring alkoxo $O^-$ as well as imine nitrogen to the metal centre. Corresponding downfield shifts are also observed in the case of the azomethine carbon, by 1.7 to 6.4 ppm. Thus both the $^1H$ and $^{13}C$ NMR spectra are indicative of the presence of intact uranium complexes in solution.

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