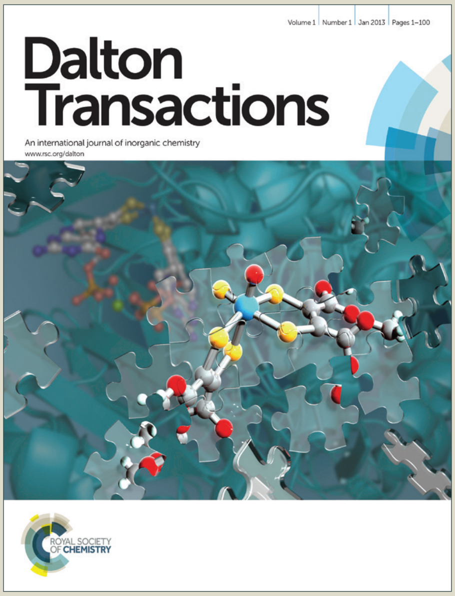
Dalton Transactions

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

Journal Name

ARTICLE

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Alkali - Metal Ion Coordination in Uranyl(VI) Poly-Peroxo Complexes in Solution, Inorganic Analogues to Crown-Ethers. Part 2. Complex Formation in the Tetramethyl Ammonium-, Li^+ -, Na^+ - and K^+ – Uranyl(VI) – Peroxide – Carbonate Systems.*

Pier Luigi Zanonato,[i] Zoltán Szabó,[iii] Valerie Vallet,[ii] Plinio Di Bernardo,[i] and Ingmar Grenthe.[iii*]

The constitution and equilibrium constants of ternary uranyl(VI) peroxide carbonate complexes $[(UO_2)_p(O_2)_q(CO_3)_r]^{2(p-q-r)}$ have been determined at 0 °C in 0.50 M MNO_3, M = Li, K, and TMA (tetramethyl ammonium), ionic media using potentiometric and spectrophotometric data; ^{17}O NMR data were used to determine the number of complexes present. The formation of cyclic oligomers, “$[(UO_2)(O_2)(CO_3)]_n$”, n = 4, 5, 6 , with different stoichiometry depending on the ionic medium used suggests that Li^+, Na^+, K^+ and TMA ions act as templates for the formation of uranyl peroxide rings where the uranyl-units are linked by μ-η^2-η^2 bridged peroxide-ions. The templating effect is due to coordination of the M^+-ions to the uranyl oxygen atoms, where the coordination of Li^+ results in the formation of $Li[(UO_2)(O_2)(CO_3)]_4{}^{7-}$, Na^+ and K^+ in formation of $Na/K[(UO_2)(O_2)(CO_3)]_5{}^{9-}$ complexes, while the large tetrametyl ammonium ion promotes the formation of two oligomers, $TMA[(UO_2)(O_2)(CO_3)]_5{}^{9-}$ and $TMA[(UO_2)(O_2)(CO_3)]_6{}^{11-}$. The NMR spectra demonstrate that the coordination of Na^+ in the five- and six-membered oligomers is significantly stronger than that of TMA^+; these observations suggest that the templating effect is similar to the one observed in the synthesis of crown-ethers. The NMR experiments also demonstrate that the exchange between $TMA[(UO_2)(O_2)(CO_3)]_5{}^{9-}$ and $TMA[(UO_2)(O_2)(CO_3)]_6{}^{11-}$ is slow on the ^{17}O chemical shift time-scale, while the exchange between $TMA[(UO_2)(O_2)(CO_3)]_6{}^{11-}$ and $Na[(UO_2)(O_2)(CO_3)]_6{}^{11-}$ is fast. There was no indication of the presence of large clusters of the type identified by Burns and Nyman (M. Nyman and P. C. Burns, *Chem. Soc. Rev.* 2012, **41**, 7314-7367) and possible reasons for this and the implications for the synthesis of large clusters are briefly discussed.

Dalton Transactions Accepted Manuscript

---

[i]Dipartimento di Scienze Chimiche, Università di Padova, Via Marzolo, 1 35131 Padova, Italy.
[ii]Université de Lille 1, Laboratoire PhLAM, CNRS UMR 8523, Bât P5, F-59655 Villeneuve d'Ascq Cedex, France .
[iii]School of Chemical Science and Engineering, Department of Chemistry, Royal Institute of Technology (KTH), S-10044 Stockholm, Sweden. E-mail: ingmarg@kth.se

---

∗Electronic Supplementary Information (ESI) available: Tables S1a-S4a and S1b-S4b composition of test solutions used in the potentiometric study and details of model testing. Table S5 Chemical shifts used in Eqn. (7). Tables S6-S8 and S6b – S8b, composition of test solutions used in the spectrophotometric titrations and details of model testing. Figures S1-S4, comparison of experimental data from potentiometry with those calculated using the selected equilibrium constants. Figure S5, ^{17}O-NMR spectra from the TMA^+, Li^+ and K^+ uranyl(VI) – peroxide-carbonate systems. Figures S6-S8, are comparisons of experimental and calculated absorbance using the selected equilibrium constants and molar absorptivities. Figure S9, absorption spectra of the $M[(UO_2)(O_2)(CO_3)_2]^{3-}$ and $M[(UO_2)_2(O_2)(CO_3)_4]^{5-}$ complexes. Figure S10, comparison of experimental absorptivities in the Li- and K-systems.

This journal is © The Royal Society of Chemistry 20xx

Journal Name

ARTICLE

Introduction

X-ray structure investigations of uranyl(VI)- peroxide clusters[1] reveal the presence of structure elements that bear a striking resemblance to crown-ethers,[2] Figure 1. A typical feature of these uranyl(VI) – peroxide frameworks, as those of many poly-oxometallates, is their high negative charge, which in the solid phases are compensated by cations, often alkali and ammonium / tetraalkyl ammonium ions. Most studies of peroxide and poly-oxymetallate clusters are focused on preparative methods, solid state structures and chemical properties, such as catalysis, and not on their mechanism of formation[3], an exception is the extensive studies by Pettersson *et al.* on anion condensation in aqueous vanadium and molybdenum systems.[4] We have suggested[5] that clusters of the Burns type are formed in the nucleation/crystallization process by the assembly of larger precursors present in solution, but there is to our knowledge no clear evidence on how this process takes place. The assembly of cyclic oligomers to larger clusters requires the presence of bridging groups; one example is the U_{50} and U_{120} clusters studied by Burns *et al.*[6] where five coordinated oxalate ions acts as bridges between "$[(UO_2)(O_2)]_5$" units; a second example[5b] is the structure of the U-24 clusters $[Na_6(OH_2)_8]@[(UO_2)(O_2)(OH)/(F)]_{24}{}^{18-}$, that contains "$[(UO_2)(O_2)]_4$" rings linked by hydroxide or fluoride bridges. In solution hydroxide bridging is well established, but fluoride bridging is unknown. In previous studies[5] we have investigated the complex formation in different uranyl(VI) – peroxide systems in solution and identified both smaller complexes with a single η^2-coordinated peroxide, a single μ-η^2-η^2 bridge and cyclic oligomers $[(UO_2)(O_2)(CO_3)]_n{}^{-2n}$ with μ-η^2-η^2 bridges. As will be discussed later, the constitution of these oligomers is not compatible with clusters of the Burns type.

In Ref. 5c, the formation and constitution of the precursors were identified by a combination of ^{17}O and ^{13}C NMR spectroscopy and potentiometric titrations, but the nuclearity, *n*, could not be determined in this way and had to be based on the five- and six-membered "$[(UO_2)(O_2)]_n$" units identified in solid state structures.[5c]

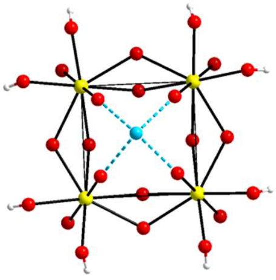
The structural similarity between the $[(UO_2)(O_2)(CO_3)]_n{}^{-2n}$ oligomers and crown-ethers suggests that alkali-ions are coordinated to the uranyl oxygen atoms and may acts as templates for the formation of oligomers, as observed in the synthesis of crown ethers in organic solvents,[2] but there is to our knowledge, no information of a similar mechanism in aqueous solution. Understanding of the role of precursors might be of importance for the rational synthesis of cluster compounds, an approach that does not seem to have been followed in the synthesis of uranyl clusters.

Complex formation between crown-ethers and alkali ions depends on the relative size of the alkali-ion and the crown-ether cavity and one may ask if this similarity also extends to the $[(UO_2)(O_2)(CO_3)]_n{}^{-2n}$ oligomers. There is, however, one important difference between the two systems, complex formation between metal ions and crown-ethers can be studied directly by determining the equilibrium constant for reaction (1), but this is not possible in the uranyl(VI) – peroxide systems as there is no experimental evidence for the presence of a non-coordinated ligand $[(UO_2)(O_2)(CO_3)]_n{}^{-2n}$, reaction (2). The relative stabilities of different $M[(UO_2)(O_2)(CO_3)]_n{}^{1-2n}$ complexes in the form of *conditional* equilibrium constants must instead be determined studying reaction (3) in different ionic media (0.5 M $LiNO_3$, KNO_3, and $TMANO_3$ and 0.1 M $NaNO_3$ /0.40 M $TMANO_3$.

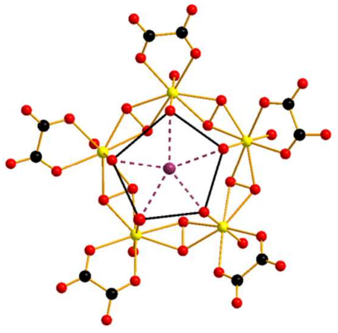
$$M^+ + 15\text{-crown-5} \rightarrow M[15\text{-crown-5}]^+; \qquad (1)$$

$$M^+ + [(UO_2)(O_2)(CO_3)]_n{}^{-2n} \rightarrow M[(UO_2)(O_2)(CO_3)]_n{}^{1-2n}; \qquad (2)$$

$$p[UO_2(CO_3)_3]^{4-} + qH_2O_2 \rightarrow [(UO_2)_p(O_2)_q(CO_3)_r]^{2(p-q-r)} + (3p-r)CO_3{}^{2-} + 2qH^+; \qquad (3)$$

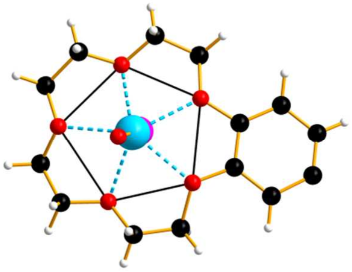


(a)



(b)

Dalton Transactions Accepted Manuscript



(c)

Figure 1. (a) Four-membered "$Na[(UO_2)(O_2)(OH)_2]_4$" present in U-24 clusters such as $[Na_6(OH_2)_8]@[(UO_2)(O_2)(OH)]_{24}^{18-}$; hydroxide can be replaced by fluoride In the isostructural fluoride compound.[5b] (b) five-membered ring "$[UO_2(O_2)(oxalate)]_5$" in $K_{10}[(UO_2)(O_2)(oxalate)]_5{\cdot}(H_2O)_{13}$.[7] (c) The X-ray structure of aqua-(benzo-15-crown-5)-sodium iodide from Bush and Truter.[8]

We are particularly interested in the role of the large TMA^+ ion for the formation of uranyl peroxide rings, because we noticed[5b,e] that $M[(UO_2)(O_2)(F/OH)_4^{3-}$ with a 4-membered ring, was only formed in $LiNO_3$, $NaNO_3$ and KNO_3 ionic media and not in the $TMANO_3$ one, suggesting that the former may act as templates for ring formation, but not the latter.

Experimental

Chemicals used.

Analytical grade $LiNO_3$, Li_2CO_3, KNO_3 and K_2CO_3 (Aldrich) were used as purchased. $TMANO_3$ was prepared as in ref. 5. $(TMA)_2CO_3$ was obtained by reaction of stoichiometric amounts of NH_4HCO_3 and TMAOH in methanol. The solvent was removed by means of a rotary evaporator. Successively, fresh dry methanol was added and evaporated three times. The final product was then obtained by cooling a dry methanol/ether solution. MilliQ© grade water was used in preparation of all solutions. KOH, LiOH and TMAOH stock solutions were obtained from Aldrich and diluted to the final concentrations. Preparation of H_2O_2 and uranyl nitrate stock solutions and the procedures of standardization are described in previous studies.[5]

Experimental methods and analyses of data.

The experimental methods used to determine the stoichiometry and equilibrium constants in uranyl(VI) – peroxide systems have been discussed in previous publications.[5] Potentiometric, spectrophotometric and NMR titrations started from test solutions where all uranium was present as $UO_2(CO_3)_3^{4-}$ and the complex formation with peroxide was then followed by adding hydrogen peroxide and measuring the resulting changes in $-\log[H^+]$, UV/VIS absorptivity and in the ^{17}O NMR spectra, according to reaction (3).

As the equilibrium constant for the formation of $UO_2(CO_3)_3^{4-}$ is known, the stoichiometry and equilibrium constants for the formation of $[(UO_2)_p(O_2)_q(CO_3)_r]^{2(p-q-r)}$, in the following denoted ($-2q$, p, q, r), using the reactants in reaction (3) as components, was obtained as described in Ref. 5, where we also discussed the difficulty to obtain a unique model for systems that contain several protolytic ligands. ^{17}O and ^{13}C NMR spectroscopy[5c], turned out to be important tools in the analysis of these data, because they provide information on the number of different species present in solution and the ratio, *p/r*, between the stoichiometric coefficients for uranyl and carbonate. The large molar absorptivity of the complexes $[(UO_2)_p(O_2)_q(CO_3)_r]^{2(p-q-r)}$ makes spectrophotometry a useful tool to explore the composition of test solutions with low total concentration of uranium, down to 0.05 mM in the present study; this is important because the relative amount of "$[(UO_2)(O_2)(CO_3)]_n$" oligomers are strongly dependent on the total concentration of uranium. The potentiometric and NMR studies were made at 0 ^{o}C, but for technical reasons the spectrophotometric experiments had to be made at 25 ^{o}C. The composition of the test solutions used in the potentiometric titrations are given in the Electronic Supporting Information, ESI, Tables S1a – S4a, and the corresponding data for the spectrophotometric titrations In ESI, Tables S5 – S7. Experiments using ^{17}O enriched UO_2^{2+} were used to confirm that the model used in Ref. 5c was applicable also in the present study (Figures 2 and 3 and ESI Figure S5).

A least-squares method (Hyperquad[9]) was used to test the agreement in $-\log[H^+]$ between experimental values and those calculated using the total concentration of the different test solutions and the equilibrium constants from the different chemical models described in ESI (Tables S1b – S4b). The agreement between experimental and calculated values of $-\log[H^+]$ is shown in Figures S1 – S4 using the selected set of constants reported in Table 1. As noted in Ref. 5c, it was not possible to determine the size of the "$[(UO_2)(O_2)(CO_3)]_n$" rings, values of *n* equal to 4, 5, 6, and larger gave equally good agreement between the experimental and calculated quantities (the model with $n = 5$ in Ref 5c, was based on solid state structures).

The experimental data from the spectrophotometric titrations were analyzed using the Hyperquad program by comparing measured and calculated absorptivity for different models with the same major complexes as in the potentiometric study (ESI, Tables S6b – S8b) and the selected equilibrium model/constants in Table 2 are in good agreement with those in the potentiometric study, considering the difference in temperature, 25 *vs.* 0 ^{o}C.

^{17}O-NMR spectroscopy. The test solutions were prepared using ^{17}O enriched uranyl nitrate, hydrogen peroxide and M_2CO_3, M = TMA^+, Li^+ and K^+. The spectra were recorded using a Bruker DRX-400 spectrometer operating at 0 ^{o}C in order to avoid decomposition of the peroxide. Additional experimental details are given in Ref. 5c, p. 11637.

Four sets of titrations were made, in the first three we studied reaction (3) by titrating 4.00 mL of a test solution with the initial composition, U(VI) = 20.0 mM, M_2CO_3 = 70.0 mM, M = TMA, Li, K, with a 274.4 mM solution of H_2O_2 and recorded the O-17 spectra after each addition (ESI, Figure S5). The analysis of the spectra is described in Results.

Dalton Transactions Accepted Manuscript

Results

Potentiometry.

The equilibrium constants for the different models tested are reported ESI, Tables S1b – S4b, where the ones for the oligomers "$[(UO_2)(O_2)(CO_3)]_n$" vary with the value of *n*, while the equilibrium constants for the other complex remain nearly unchanged. An important point is that the "goodness-of-fit" quantity, σ, which corresponds to the *R*-factor in the refinement of X-ray data, does not change significantly between the different oligomer models; hence it is not possible to determine the value of *n*.

The chemical model for the KNO_3 system turned out to be the same as in the previously studied[5c] $NaNO_3$ medium. The NMR data in the $TMANO_3$ medium showed that two $[(UO_2)(O_2)(CO_3)]_n$ oligomers were formed, but no equilibrium constants for these are reported in Table 1, because all oligomer models result in the same value of σ (ESI, Table 3b).

The conditional equilibrium constants for formation of "$Na_x[(UO_2)(O_2)(CO_3)]_5$" in 0.10 M $NaNO_3$ / 0.40 M $TMANO_3$ and 0.50 M $NaNO_3$ differ by log $K = 0.78 \pm 0.09$ ($K = 6 \pm 1$). This difference is within the estimated uncertainty equal to the ratio of the Na^+ concentrations in the two ionic media, that is $x = 1$, demonstrating that a single Na^+-ion is coordinated.

Dalton Transactions Accepted Manuscript

Please do not adjust margins

Journal Name

ARTICLE

Table 1. Selected equilibrium constants at 0 °C in the uranyl(VI) – peroxide – carbonate systems in 0.5 M MNO_3 ionic media, M = Li, Na, K and TMA, based on the potentiometric data. Different models have been tested as described in ESI, Table S1b – S3b. The experimental data in 0.50 M $NaNO_3$ from Ref. 5c have been reanalyzed and the result is reported in ESI, Table S4b. The equilibrium constants for the complexes -10, 5, 5, 5 and -12, 6, 6, 6 cannot be optimized simultaneously for reasons given in the main text.

-2*q*, *p*, *q*, *r*	0.5 M $TMANO_3$	0.5 M $NaNO_3$	0.1M $NaNO_3$ / 0.4 M $TMANO_3$	0.5 M $LiNO_3$	0.5 M KNO_3
-2, 2, 1, 4	29.09 ± 0.09	28.11 ± 0.07	27.69 ± 0.14	27.25 ± 0.11	27.96 ± 0.05
-2, 1, 1, 2	4.45 ±0.04	4.58 ± 0.03	4.37 ± 0.07	4.30 ± 0.02	4.40 ± 0.03
-2, 2, 1, 2	-	18.76 ± 0.08	18.31 ± 0.16	20.26 ± 0.03	20.44 ± 0.10
-2, 2, 1, 3	25.36 ± 0.09	-	-	-	-
-10, 5, 5, 5	-	20.47 ± 0.08	19.69 ± 0.10	-	21.26 ± 0.15

Dalton Transactions Accepted Manuscript

This journal is © The Royal Society of Chemistry 20xx

Please do not adjust margins

Dalton Transactions Accepted Manuscript

In the TMA$^+$ system it was necessary to replace the complex -2, 2, 1, 2 by -2, 2, 1, 3 in order to obtain a good agreement between the experimental data and the model (Table S3b). The presence of the latter complex was confirmed by the NMR data.

Spectrophotometric data.

The spectrophotometric data are analyzed in ESI, Tables S6b – S8b using the Hyperquad least-squares program to obtain equilibrium constants and absorption spectra of the different complexes. The resulting equilibrium constants at 25 ^oC are reported in Table 2 and result in an excellent agreement between experimental and calculated absorptivity (ESI, Figures S6 – S8); the agreement with the equilibrium constants determined by potentiometry is satisfactory, considering the difference in temperature. Also in this case models with different nuclearity, *n*, of the oligomers, resulted in the same value of the overall goodness-of-fit, σ. It should be noted that a change of *n* does not result in a change in the shape of the absorption spectra of the complexes, *cf.* Rossotti and Rossotti, pp 274 – 280).[10]

The molar absorptivity depends on the number of "$(UO_2)(O_2)$" chromophors and to a smaller extent on the different coordinated M$^+$-ions. The absorption spectra and equilibrium constants for $[(UO_2)(O_2)(CO_3)_2]^{4-}$ and $[(UO_2)_2(O_2)(CO_3)_4]^{6-}$, respectively, are very similar in $LiNO_3$, KNO_3 and $TMANO_3$ (ESI, Figure S9), suggesting similar structures. The large difference in molar absorptivity between the spectrum of the Li-oligomer and the corresponding K$^+$ and TMA$^+$ spectra (Figure 2) is a result of formation of a complex with a smaller number of chromophors in the case of Li and we suggest that this is $Li[(UO_2)(O_2)(CO_3)]_4{}^{7-}$, a similar four-membered complex, $Li[(UO_2)(O_2)(OH)]_4{}^{3-}$, has been identified in Ref. 5e.

Table 2. Conditional equilibrium constants, log *K*, at 25 ^oC for the formation of the major complexes at 25 ^oC in 0.50 M MNO_3 ionic media, M = TMA$^+$, Li$^+$ and K$^+$ using spectrophotometric titrations. The constants refer to reaction (3) $pUO_2{}^{2+} + qH_2O_2 + rCO_3{}^{2-} \rightarrow [(UO_2)_p(O_2)_q(CO_3)_r]^{2(p-q-r)} + 2qH^+$; the notation is the same as in Table 1. The other models tested are reported in ESI, Table S9. The estimated uncertainty is reported at the 3σ level and the goodness-of-fit factor σ between measured and calculated absorptivity varies between 0.002 and 0.005 absorption units.

-2*q*, *p*, *q*, *r*	0.5 M $TMANO_3$	0.5 M $LiNO_3$	0.5 M KNO_3
-2, 2, 1, 4	27.58 ± 0.02	26.65 ± 0.03	27.43 ± 0.03
-2, 1, 1, 2	4.20 ± 0.01	3.50 ± 0.02	4.09 ± 0.03
-10, 5, 5, 5	-	-	21.23 ± 0.13
-8, 4, 4, 4	-	16.76 ± 0.18	-

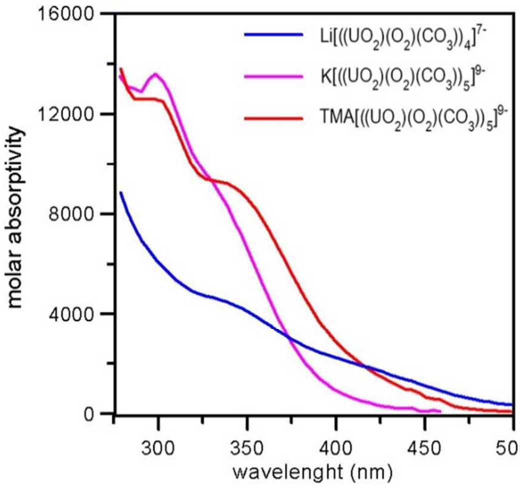


Figure 2. Absorption spectra of $K[(UO_2)(O_2)(CO_3)]_5{}^{9-}$, $TMA[(UO_2)(O_2)(CO_3)]_5{}^{9-}$ and $Li[(UO_2)(O_2)(CO_3)]_4{}^{7-}$.

NMR data.

A detailed study of the uranyl(VI) peroxide – carbonate system using ^{17}O and ^{13}C NMR data is reported in Ref. 5c and this information allowed us to determine the ratio between the stoichiometric coefficients *p* and *r* in the different complexes $[(UO_2)_p(O_2)_q(CO_3)_r]^{2(p-q-r)}$, this information was essential also in the analysis of the present systems where we only had access to ^{17}O NMR data reported in Figures 3, 4 and ESI, Figure S5a-c. Four series of experiments were made, in the first three, test solutions of uranyl(VI) in M_2CO_3, M = Li, K and TMA were titrated with H_2O_2 and in the fourth a solution containing only the TMA-complexes (bottom spectrum in Figure 4) was titrated with $NaNO_3$. The spectra in Li and K carbonate systems (Figures S5b and c) from the first series of experiments are very similar to the ones in Na-carbonate, Ref. 5c, while those in the TMA-carbonate system differ significantly (Figure 3).

Please do not adjust margins

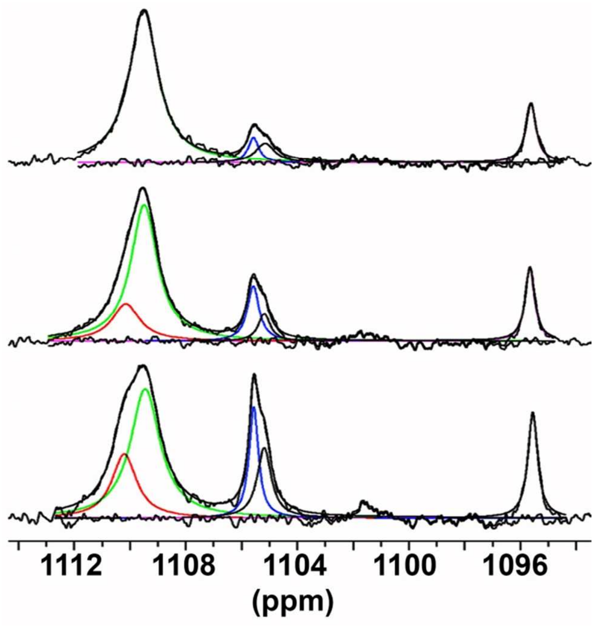


Figure 3. Deconvoluted ^{17}O NMR signals in the TMA-carbonate system, measured in test solutions at different H_2O_2 concentrations (from bottom to top these are 38.3, 48.0 and 61.2 mM); the spectra from the complete titration are shown in Figure S5a. The signals around 1110 ppm can be deconvoluted into two peaks that refer to $TMA[(UO_2)(O_2)(CO_3)]_5^{9-}$ (red curve) and $TMA[(UO_2)(O_2)(CO_3)]_6^{11-}$ (green curve) and the one around 1105 ppm into peaks referring to $[(UO_2)_2(O_2)(CO_3)_3]^{4-}$ (cyan curve) and $[(UO_2)_2(O_2)(CO_3)_4]^{6-}$ (blue curve). The integrals of the deconvoluted peaks are very uncertain due to their small chemical shift difference. The peak at 1095.5 ppm is from $[(UO_2)(O_2)(CO_3)_2]^{4-}$.

As shown in Figure 3, the signal around 1105 ppm in the TMA-system can be deconvoluted into two peaks, which refer to $[(UO_2)_2(O_2)(CO_3)_3]^{4-}$ and $[(UO_2)_2(O_2)(CO_3)_4]^{6-}$, both of which have been identified in the potentiometric experiments. The corresponding peak in the Li- and K-carbonate media has a Lorentzian line shape, suggesting that only one complex, $[(UO_2)_2(O_2)(CO_3)_4]$ is present, as was also found by analysis of the potentiometric data. Also the broad signal at around 1110ppm in the TMA^+ system at intermediate concentrations of H_2O_2 can be deconvoluted into two peaks (Figure 3). At higher peroxide concentrations this signal appears as a single peak with Lorentzian line shape (top spectrum in Figure 3). This change can be explained by reaction (4) that involves equilibrium between complexes with 5- and 6-membered rings, where the latter is predominant at the highest concentration of H_2O_2.

$2(TMA)[(UO_2)(O_2)(CO_3)]_5^{9-} + [(UO_2)_2(O_2)(CO_3)_4]^{6-} + H_2O_2 \rightarrow 2(TMA)[(UO_2)(O_2)(CO_3)]_6^{11-} + 2HCO_3^-$; (4)

In the Na-, Li- and K- carbonate systems the corresponding broad signals around 1107 and 1104 ppm have Lorentzian line shapes that do not change with increasing concentration of H_2O_2 (Figure S5b-c and Ref. 7b) indicating that these arise from a single predominant complex. Based on the discussion of the potentiometric and spectrophotometric data (*vide infra),* we suggest that the signals around 1107 ppm refer to $Li[(UO_2)(O_2)(CO_3)]_4^{7-}$ and $K/Na[(UO_2)(O_2)(CO_3)]_5^{9-}$, respectively. The signals at around 1104 ppm refer to $[(UO_2)_2(O_2)(CO_3)_4]^{6-}$ in all three systems.

The deconvoluted peaks for the signals around 1105 and 1110 ppm in the TMA system demonstrate that the exchange between $[(UO_2)_2(O_2)(CO_3)_3]^{4-}$ and $[(UO_2)_2(O_2)(CO_3)_4]^{6-}$, and between the 5- and 6-membered rings, respectively, is slow on the ^{17}O chemical shift time scale.

In a new titration, we added $NaNO_3$, to a solution that originally contained only the TMA-complexes, and this resulted in two characteristic changes in the spectra (Figure 4). One is that the chemical shift of the single peak (red) at 1109.2 ppm (the first spectrum of Figure 4 assigned to $(TMA)[(UO_2)(O_2)(CO_3)]_6^{11-}$) is decreasing gradually by adding $NaNO_3$. At the same time a new peak (green) appears around 1107.2 ppm. This observation can be described by reactions (5) and (6):

$(TMA)[(UO_2)(O_2)(CO_3)]_6^{11-} + Na^+ \rightarrow Na[(UO_2)(O_2)(CO_3)]_6^{11-} + TMA^+$; (5)

$(TMA)[(UO_2)(O_2)(CO_3)]_6^{11-} + Na^+ \rightarrow Na[(UO_2)(O_2)(CO_3)]_5^{9-} + [(UO_2)(O_2)(CO_3)]^{2-} + TMA^+$; (6)

The gradual chemical shift change of the red signal is the result of fast exchange In reaction (5) between the two six-membered complexes. The appearance of two NMR signals for the complexes with six- and five-membered rings (red and green signals in Figure 4) demonstrates that the exchange between them in reaction (6) is slow on the NMR time-scale, as was also the case in the pure TMA-system. It should be pointed that the exchange reaction (6) is more complex than suggested by the stoichiometry, as it also includes reaction (4).

Under the fast exchange condition for reaction (5), the mol fractions, X, and (1 – X) of the exchanging complexes can be calculated from the shift of exchange averaged signal, δ_{av}, and the chemical shifts of $(TMA)[(UO_2)(O_2)(CO_3)]_6^{11-}$ and $Na[(UO_2)(O_2)(CO_3)]_6^{11-}$, $\delta_{TMA} = 1109.2$ and $\delta_{Na} = 1106.6$, respectively, using Eqn. (7)[11]

$\delta_{av} = X\,\delta_{TMA} + (1 - X)\,\delta_{Na}$; (7)

The chemical shift, δ_{av} is decreasing gradually and is, at the highest Na^+ concentration, very close to the chemical shift of $Na[(UO_2)(O_2)(CO_3)]_5^{9-}$, 1106.6 ppm. Therefore, we assumed that the shifts of the two Na^+-complexes are identical and used the latter value in Eqn. (7), the data used are reported in ESI, Table S5. And result in the equilibrium constant $K(5) = (4 \pm 2)$.

The two uranyl oxygens in the cyclic oligomers have different chemical surrounding, despite this a single peak ^{17}O peak is observed; this is most likely a result of rapid exchange between coordinated and non-coordinated M^+.

Dalton Transactions Accepted Manuscript

Please do not adjust margins

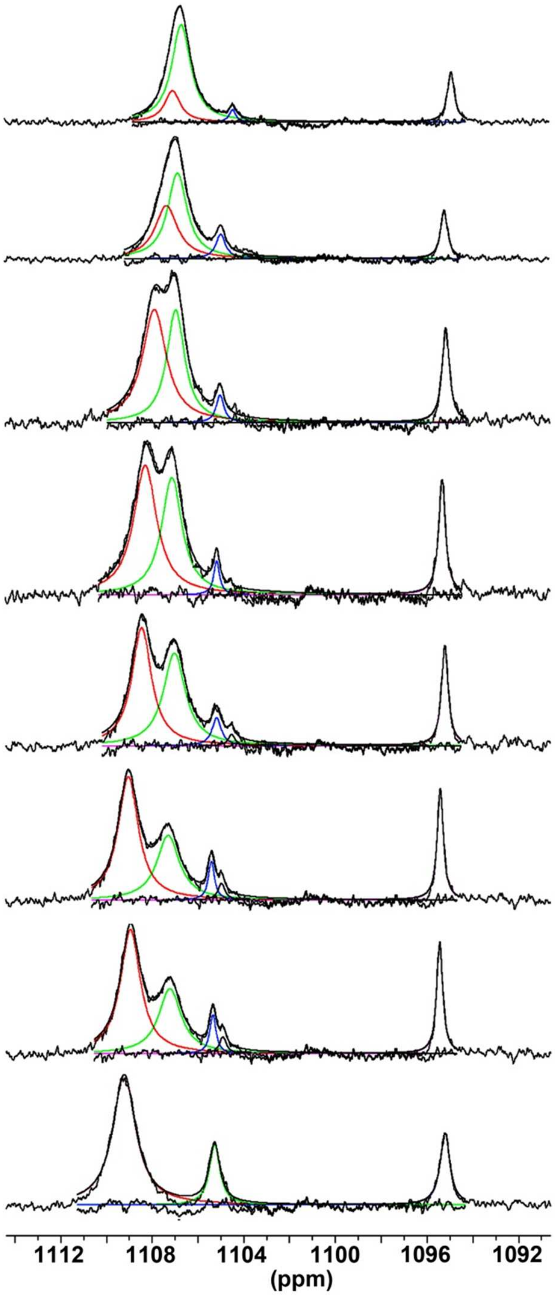


Figure 4. [Na^+]-ion concentration dependence of the ^{17}O NMR spectra measured in TMA-carbonate-peroxide- solutions. The total concentrations of U(VI) and $(TMA)_2CO_3$ are equal to 21.3 mM and 70 mM, respectively and for H_2O_2, 65.8 mM. The total Na^+-ion concentration from bottom to top are 0, 9.5, 19.0, 28.4, 37.6, 48.4, 111.8 and 146.7 mM. The green curve corresponds to $Na[(UO_2)(O_2)(CO_3)]_5^{9-}$ and the red to the TMA-complex.

Discussion

The complex formation results in a change in the hydrogen ion concentration in the test solutions and the deduction of the chemical model and the corresponding equilibrium constants is based on this. However, as a change in the stoichiometry of the hypothetical reaction $n[(UO_2)(O_2)(CO_3)]^{2-} \rightarrow [(UO_2)(O_2)(CO_3)]_n^{-2n}$ does not result in any change in [H^+], the value of n has a small influence on the goodness of fit, σ, and the agreement between experimental and calculated –log[H^+] values. The situation is different in the spectrophotometric experiments where the change in absorptivity is directly related to the stoichiometry and concentration of the different complexes. The difference in molar absorptivity is particularly large between the cyclic oligomers in the Li-, K- and TMA-systems that differ by the number of "$[(UO_2)(O_2)]$" chromophors (Figure 2).

Stoichiometry of the oligomers and the relative stability of TMA^+, Li^+, Na^+ and K^+ complexes. The potentiometric data demonstrate that one Na^+-ion is coordinated to the oligomer in the $NaNO_3$ ionic medium, the NMR titrations described by reactions (5) and (6) demonstrate that Na^+ is stronger bonded than TMA^+, finally the spectrophotometric data in $LiNO_3$ demonstrate that the structure/composition of the oligomer is significantly different from the ones in the other MNO_3 media. These observations are strong evidence of a size-dependent templating effect on the formation of the oligomers. The size of M^+ which provides a restriction on the size of the oligomer ring – the larger the ring the smaller the templating effect; in this respect it is of interest to note that no oligomers with ring-size larger than six has been observed in the solid state.

The conditional equilibrium constants, log K, for reaction (3) in Table 1, vary from 20.47 ± 0.08 in $NaNO_3$ to 21.26 ± 0.15 in KNO_3 and this difference is much larger than observed in corresponding crown-ether systems studied by Høland *et al.* (Table 3),[12] which presumably is a result of the large difference in charge between the complexes.

Table 3. Equilibrium constants in aqueous solution, K, for the reaction M^+ + crown-ether → $M[\text{crown-ether}]^+$, where M^+ is an alkali-ion, data from Ref. 12.

Cation	K (M^{-1})	K (M^{-1})
	12-crown-4	15-crown-5
Li^+	No complex formation detected	Not studied
Na^+	"	4.7
K^+	"	5.8
Rb^+	"	No detection
Cs^+	"	6.7

The large equilibrium constants for reactions (3) for the formation of peroxide complexes are a result of the formation of strong peroxide bridges and not by strong coordination of M^+-ions.

Possible structures of $[(UO_2)_2(O_2)(CO_3)_4]^{6-}$ and $M[UO_2(O_2)(OH_2)_2]_n$; n = 4, 5, 6.

There are two solid phases with stoichiometry that relates to the complex $[(UO_2)_2(O_2)(CO_3)_4]^{6-}$, one is found in the solid $K_6(OH_2)_4[(UO_2)_2(O_2)(\text{oxalate})_4]$,[7] the other in $[(UO_2)_2(O_2)(\text{pyridine})_4]\cdot(NO_3)_2^{9-}$.[13] Both complexes contain two uranyl ions linked by μ - η^2 - η^2 bridged peroxide and to four

This journal is © The Royal Society of Chemistry 20xx

Dalton Transactions Accepted Manuscript

Please do not adjust margins

additional ligands, in the first one to bidentate oxalate and in the second to four N-coordinated pyridine ligands. The X-ray structures of a large number of other uranyl(VI) – peroxide phases, demonstrate the presence of planar, or close to planar, 4-, 5- and 6-membered "$[(UO_2)(O_2)]_n$"-rings, examples relevant for the present study are the structures of $K_{10}[(UO_2)(O_2)(oxalate)]_5\cdot(H_2O)_{13}$ and $Na_{12}[(UO_2)(O_2)(oxalate)]_6\cdot(H_2O)_{29}$, which contain five- and six-membered rings with K^+ and Na^+ coordinated to yl-oxygen.[7] In these and other uranyl peroxide rings, uranium and uranyl oxygen atoms are located in separate parallel planes where the linear uranyl-ions are tilted with respect to the planes, resulting in two sets of $O_{yl} – O_{yl}$ distances in the planes, one at a distance of about 3.2 Å and in the other at about 5.5 Å from the $[U_n]$-plane; coordination of alkali-ions can only take place to the first set, consistent with the experimental observation in solution in the present study. There are examples of preferential coordination sites in other solid state structures. In $Na_{12}[(UO_2)(O_2)(oxalate)]_6\cdot 29H_2O$,[7] the peroxide bridged uranyl peroxide units form a 6-membered ring in boat conformation where the size of the ring is too large to allow $[Na\text{-}O_{yl}]_6$ coordination; Na^+-ions are instead coordinated to three O_{yl} on the concave side of the ring and to three O_{yl} atoms on the convex side, as shown in Figure 5 a.

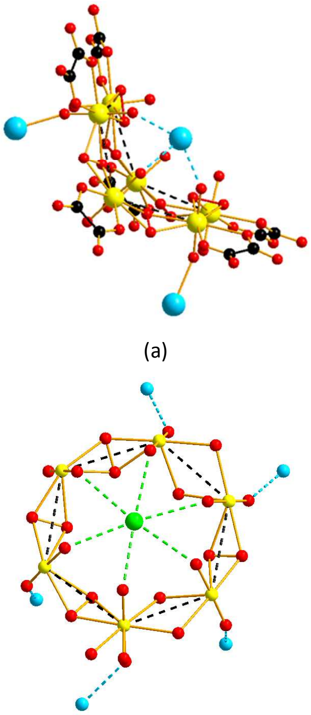


Figure 5. (a) Structure of the six-membered ring in $Na_{12}[(UO_2)(O_2)(oxalate)]_6\cdot 29H_2O$.[7] Coordinated Na^+ denoted in blue, is coordinated to three O_{yl} atoms on the concave side of the ring with additional Na^+-coordination on the "outside". (b) Cs^+ (green) and Na^+ (blue) coordination in the 6-membered uranyl(VI) peroxide ring in the bowl-shaped U-16 cluster $[(UO_2)_{16}(O_2)_{24}(OH)_8]^{24-}$ discussed in Ref. 14, the uranyl units are linked by four peroxide and two hydroxide bridges.

Other examples are the bowl-shaped U-16 structure of $[(UO_2)_{16}(O_2)_{24}(OH)_8]^{24-}$ and the cylindrical structure of $[(UO_2)_{24}(O_2)_{36}(OH)_{12}]^{36-}$ studied by Sigmon *et al.*[14] and prepared by crystallization from solutions with an 8:1 excess of Na^+ over Cs^+. Despite the large excess of Na^+, Cs^+ is preferentially coordinated to six O_{yl}-atoms in a close to planar six-membered ring, while Na^+ is coordinated on the "outside" (Figure 5 b), demonstrating a site preference similar to the ones found among the crown-ethers.

The implications of speciation in solution for the synthesis and mechanism of cluster formation.

Burns *et al.*[15] report the preparation and X-ray structures of $K_6(OH_2)_4[(UO_2)_2(O_2)(oxalate)_4]$, $K_{10}[(UO_2)(O_2)(oxalate)]_5\cdot(H2O)_{13}$ and $Na_{12}[(UO_2)(O_2)(oxalate)]_6\cdot(H_2O)_{29}$, which contain complexes with the same stoichiometry as those identified in the present study. The solutions from which these compounds where obtained had an approximately ten-fold excess of oxalate over uranium, similar to the conditions were the corresponding uranyl peroxide carbonate complexes are formed. On the other hand the large U-50 and U-120 clusters in another study by Burns *et al.*[15] were obtained under conditions where the ratio between uranium and oxalate was close to one, where one can expect formation of precursors with a different stoichiometry and one may ask if this will allow linking by oxalate and the formation of large clusters. Cyclic "$[(UO_2)(O_2)(L)]_n$" oligomers, where L is a bidentate ligand like oxalate and carbonate, cannot assemble to clusters of the Burns type by using L as linker, because this would result in a cluster stoichiometry of "$[(UO_2)(O_2)(L)_{0.5}]_n$". One possibility for the assembly in solution would be if $[(UO_2)_5(O_2)_5(L)_5]$ and $[(UO_2)_5(O_2)_5(OH_2)_5]$ are present in comparable concentrations. However, this is very unlikely to occur because coordination of L in solution always takes place in a step-wise fashion where the concentration of $[(UO_2)_5(O_2)_5(OH_2)_5]$ decreases as the number of coordinated ligands increases, suggesting that assembly takes place during the nucleation/crystallization process. It might, however, be possible to use solutions where "$[(UO_2)(O_2)(L)]_n$" is the predominant complex and assemble new clusters by adding ligands that coordinate stronger than L, phosphate and hydrogen phosphate are two possibilities because they form complexes that are much stronger than oxalate, the log *K*-values for formation of $[UO_2(PO_4)]^-$, $[UO_2(HPO_4)](aq)$ and $[UO_2(oxalate)]$ are (13.23 ± 0.15)[16], (7.24 ± 0.26)[16] and (7.13 ± 0.16),[17] respectively; these phosphate ligands can be used over a broad pH range from about 7 to 12. Another possible ligand system might be based on "$O_3P\text{-}O\text{-}(R)_n\text{-}OPO_3$", where the chain length can be varied.

In the complex $[(UO_2)(O_2)(OH)]^-$ that is a predominant complex in solution, it is more easy to envisage the assembly to large cluster such as the U-24 one, discussed in Ref. 5a, b, but this complex was not identified in solution. There are a number of different linkers discussed by Burns et al. in Ref. 1, but there is no information on the solution chemistry in these systems. The examples above illustrate how the understanding of the coordination chemistry in solution might offer guidance for optimization of the conditions for preparations of solid compounds like peroxide/oxide clusters.

Dalton Transactions Accepted Manuscript

Please do not adjust margins

Acknowledgements

This study has been supported by a grant from the Swedish Nuclear Waste Management Co (contracts 11217 and 14066). V. V. acknowledges support from PhLAM (Unité Mixte de Recherche de l'Université de Lille 1 et du CNRS) and from the CaPPA project (Chemical and Physical Properties of the Atmosphere) which is funded by the French National Research Agency (ANR) through the PIA (Programme d'Investissement d'Avenir) under contract "ANR-11-LABX-0005-01" and by the Regional Council "Nord-Pas de 664 Calais" and the "European Funds for Regional Economic 665 Development" (FEDER).

I do not think we need this section

Notes and references

---

1 (a) M. Nyman and P. C. Burns, *Chem. Soc. Rev.* 2012, **41**, 7314-7367. (b) J. Qui and P. C. Burns, *Chem. Rev.* 2013, **113**, 1097-1120.
2 (a) C. J. Pedersen, Synthetic Multidentate Macrocyclic Compounds, p. 1-51, in *Synthetic Multidentate Macrocyclic Compounds* (ed. R. M. Izatt and J. J. Christiansen), Academic Press, 1978. (b) D. J. Cram and K. N. Trueblood, Concept, Structure, and Bonding, in Complexation, p 43-106, in Topics in Current Chemistry, 98, Host Guest Chemistry (ed. F. Vögtle), Springer-Verlag, 1981. (c) R. M. Izatt, K. Pawlec, J. S. Bradshaw and R. L. Bruerig, *Chem. Rev.* 1991, **91**, 1721-2085. (c) N. K. Dalley, Structural Studies of Synthetic Macrocyclic Molecules and their Cation Complexes, p. 208-243, in *Synthetic Multidentate Macrocyclic Compounds* (eds. R. M. Izatt and J. J. Christiansen), Academic Press, 1978.

3 (a) A. Müller, F. Peters, M. T. Pope and G. Gatteschi, *Chem. Rev.* 1998, **98**, 239-271 (b) M. T. Pope and A. Müller, *From Platonic Solids to Anti-retroviral Activity*, Kluwer Academic Publishers, 1994. (c) A. Müller and S. Roy in *The Chemistry of Nanomaterials, Synthesis, Properties and Application,* (Eds. C. N. R. Rao, A. Müller and A. K. Cheltham), Wiley-VCH, Weinheim, 2004. (d) D.-L. Long, R. Tsunashima and L. Cronin, *Angew. Chem. Int. Ed. Engl.*2010, **49**, 1736-1758.
4 A. Selling, I. Andersson, L. Pettersson, C. M. Schramm, S. L. Downey and J. H. Grate, *Inorg. Chem.* **1994**, *33*, 3141-3150.
5 (a) P. L. Zanonato, P. Di Bernardo and I. Grenthe, *Dalton Trans*., 2012, **41**, 3380–3386. (b) P. L. Zanonato, P. Di Bernardo, A. Fischer and I. Grenthe, *Dalton Trans*., 2013, **42**, 10129–10137. (c) P. L. Zanonato, P. Di Bernardo, Z. Szabó and I. Grenthe, *Dalton Trans*., 2012, **41**, 11635–11641. (d) P. L. Zanonato, P. Di Bernardo and I. Grenthe, *Dalton Trans*., 2014, **43**, 2378–2383. (e) P. L. Zanonato, P. Di Bernardo, V. Vallet, Z. Szabó and I. Grenthe, *Dalton Trans*., 2015, **44**, 11635–11641.

6 J. Ling, J. Qui and P. C. Burns, *Inorg. Chem.* 2012, **51,** 2403-2408.
7 G. E. Sigmon, J. Ling, D. K. Unruh, L. Moore-shay, M. Ward, B. Weaver and P. C. Burns, *J. Am. Chem. Soc.* 2009, **131**, 16648-16649.

8 M. A. Bush and M. R. Truter, *J. Chem. Soc. Perkin Trans.* 1972, 341-344.

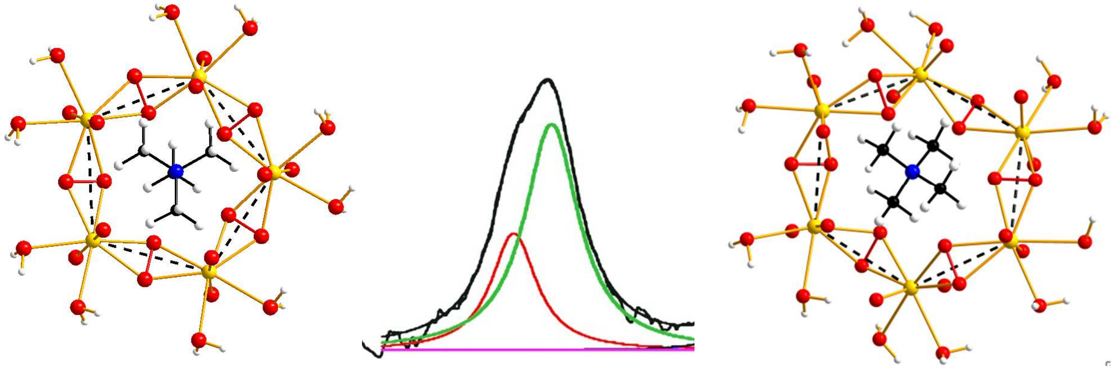
9 P. Gans, A. Sabatini and A. Vacca, *Talanta,* 1996, **43**, 1739-1753.

Dalton Transactions Accepted Manuscript

This journal is © The Royal Society of Chemistry 20xx

10 F. J. C. Rosotti and H. Rosotti, *The determination of stability constants*, McGraw-Hill, 1961.
11 J. Sandström, *Dynamic NMR Spectroscopy,* Academic Press, London, 1982, p. 90.
12 H. Høland, J. A. Ringseth and T. S. Brun, *J. Soln. Chem.*, 1979, **11**, 779-792.
13 B. T. McGrail, L. S. Pianowski and P. C. Burns, *J. AAm. Chem. Soc.* 2014, 136, 4787-4800.
14 G. E. Sigmon, B. Weaver, K.-A. Kubatko and P. C. Burns, *Inorg. Chem.* **2009**, *48*, 10907-10909.
15 J. Ling, J. Qiu and P. C. Burns, *Inorg. Chem.* **2012**, *51*, 2403-2408.
16 R. Guillaumont; T. Fanghänel, J. Fuger, I. Grenthe, V. Neck. D. A. Palmer and M. H. Rand, *Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium,* Elsevier, 2003.
17 W. Hummel, G. Anderegg, I. Puigdomènech, L. Rao and O. Tochiyama, *Chemical Thermodynamics of Compounds and Complexes of U, Np, Pu, Am, Tc, Se, Ni and Zr with Selected Organic Ligands.* Elsevier, 2005.

Dalton Transactions Accepted Manuscript



Quantum chemical models and ^{17}O NMR spectra demonstrate the formation of two uranyl(VI) peroxide rings in equilibrium
$(TMA)[(UO_2)(O_2)(CO_3)]_5^{9-} + [(UO_2)(O_2)(CO_3)]^{2-} \rightarrow (TMA)[(UO_2)(O_2)(CO_3)]_6^{11-}$

Dalton Transactions Accepted Manuscript