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On the structure and relative stability of uranyl(VI) sulfate complexes in solution

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Received 14 August 2006; accepted after revision 8 March 2007

Available online 2 May 2007

Abstract

The mode of coordination, mono-, bidentate, sulfate in $\text{UO}_2(\text{SO}_4)$ and $\text{UO}_2(\text{SO}_4)_2^{2-}$, and the relative energy of the various isomers have been studied at the DFT and MP2 levels using DFT-optimized geometry in a CPCM solvent model. The U–S distances in the mono- and bidentate coordination, 3.63 and 3.08 Å, respectively, agree very well with experimental observations from solutions. The U–O_{sulfate} distance is significantly different in complexes with mono- and bidentate coordination, 2.23, vs. 2.37 Å, an observation difficult to deduce from the experimental studies. The experimental distance between uranium and the equatorial oxygen atoms, U–O_{eq}, is very close to the calculated average distance in a five-coordination model, but significantly longer in a six-coordination model, indicating a preference for the former; this finding is supported by energy calculations, where the five-coordinated isomers for the $\text{UO}_2(\text{SO}_4)$ have the lowest Gibbs energy. For $\text{UO}_2(\text{SO}_4)_2^{2-}$, the calculated Gibbs energy of reaction indicates that the six-coordinated isomer is slightly more stable than the five-coordinated one; however, the difference is small and less than the expected uncertainty in calculations of this type. Bidentate coordination of the sulfate group is always preferred over monodentate coordination. However, all differences in Gibbs energy between the different isomers is small, indicating that the mode of coordination may change with the composition of test solutions used, as observed experimentally. The U–O–S_{mono} angle is close to 143° in complexes with a monodentate sulfate group; this is traced to steric effects, which overcome the electronic preference for a linear U–O–S bond. This study demonstrates the significant increase in chemical information that may be obtained by combining experimental data on structures and thermodynamics with quantum chemical methods. **To cite this article: V. Vallet, I. Grenthe, C. R. Chimie 10 (2007).**

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Résumé

Le mode de coordination, monodentate ou bidentate, de l'ion sulfate dans $\text{UO}_2(\text{SO}_4)$ et $\text{UO}_2(\text{SO}_4)_2^{2-}$ et la stabilité relative des différents isomères conformationnels en phase aqueuse ont été étudiés par des calculs de chimie quantique au niveau DFT et MP2, utilisant des géométries optimisées au niveau DFT avec le modèle de solvant CPCM. Les distances U–S sont de 3,63 Å et 3,08 Å pour une coordination monodentate et bidentate, respectivement, et sont en très bon accord avec les mesures expérimentales en solution. La distance U–O_{sulfate} est sensiblement plus courte dans les complexes monodentés, 2,22 Å, que dans les complexes bidentés, 2,37 Å, une disparité qu'il est difficile de déduire des données expérimentales. La distance expérimentale entre l'uranium et

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les oxygènes coordonnés dans le plan équatorial, $U-O_{\text{eq}}$, est très proche de la valeur calculée dans les isomères pentacoordinés, alors que cette distance est plus longue dans les modèles hexacoordinés, indiquant une préférence pour une coordination 5. Cette observation est corroborée par les valeurs calculées des énergies libre relatives, qui indiquent que les isomères pentacoordinés ont l'énergie libre la plus basse pour le complexe $UO_2(SO_4)$. Pour $UO_2(SO_4)_2^{2-}$, l'énergie libre de réaction indique que l'isomère hexacoordiné est légèrement plus stable que celui pentacoordiné; cependant, la différence est, très faible et plus petite que l'incertitude des calculs de ce type. Nous observons aussi une préférence pour la coordination bidentate des ions sulfate dans les deux composés mono- et bisulfate. Or, l'énergie libre de réaction entre les différents isomères structuraux est faible, indiquant que le mode de coordination de l'ion sulfate peut changer avec la composition chimique de la solution ionique utilisée. Dans les complexes monodentés, l'angle $U-O-S_{\text{mono}}$ est proche de 143° ; ceci est attribué aux effets stériques qui dominent les effets d'interaction électronique tendant à rendre la liaison linéaire. Cette étude illustre comment l'analyse des données expérimentales concernant les structures et la thermodynamique, couplée aux calculs de chimie quantique, permet d'accroître la compréhension de la chimie des actinides en solution. *Pour citer cet article* : V. Vallet, I. Grenthe, C. R. Chimie 10 (2007).

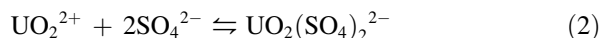
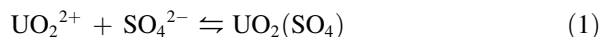
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Keywords: Structure; Bonding; Equilibria; Uranyl; Sulfate; Complexes; Quantum chemistry

Mots-clés : Structure ; Liaison ; Équilibres chimiques ; Uranyl ; Sulfate ; Complexes ; Chimie quantique

1. Introduction

Quantitative information on chemical equilibria and the thermodynamics of actinide complex formation in aqueous solution is, in addition to its pure scientific interest, also important in many applications, such as separation technology and speciation in ground and surface water systems. Solution thermodynamic data provide information on the stoichiometry of the complexes formed, but little or no information on the structure of the first coordination sphere, i.e. the mode of coordination of ligands and the possible formation of isomers of various types. There is extensive information [1] on the chemical thermodynamics of actinide complex formation reactions, including the following uranyl(VI) sulfate reactions that will be discussed in this communication:



We will use experimental and quantum chemical data to provide information on the mode of coordination of the sulfate ion and the number of coordinated water molecules in the uranyl(VI) sulfate complexes formed in reactions (1) and (2).

Single-crystal X-ray structures of a number of uranyl(VI) sulfate compounds reveal that the sulfate ion can be coordinated both in bidentate [2] and monodentate [3] fashion, but with predominance of the latter type. A characteristic feature of the bond distances in solid compounds that contain both mono- and bidentate

sulfate coordination is that the $U-O_{\text{sulfate}}$ bond distance is about 0.15 \AA shorter in the former than in the latter. Structure studies of uranyl(VI) sulfate complexes in solution have been made by Moll et al. using EXAFS [4] and by Neufeind et al. using large-angle X-ray diffraction (LAXS) [5]. Both methods provide accurate information on bond distances, but much less precise information on coordination numbers. These two studies demonstrate that the sulfate ion also in solution can be coordinated both in a monodentate [5] and bidentate fashion [4]. The solution structure determinations are complicated by the fact that the test solutions may contain a mixture of different uranyl species, as will be discussed in the following.

The equilibrium constants for the formation of uranyl(VI) sulfate complexes are moderately large at zero ionic strength, $\log \beta_1^0 = 3.15$ and $\log \beta_2^0 = 4.14$, respectively [1] for the reactions (1) and (2). These equilibrium constants decrease substantially with increasing ionic strength [1], cf. Appendix, and from their magnitude it is not possible to make a reliable prediction of the mode of coordination of sulfate and the number of donor atoms in the equatorial plane of the UO_2^{2+} ion. We have therefore used quantum chemical methods to determine the structure and bond distances in various isomers of $UO_2(SO_4)$ and $UO_2(SO_4)_2^{2-}$ and their relative electronic and Gibbs energies of formation. The bond distances can be directly compared with experimental data, while the relative energies are used to corroborate the conclusions drawn from the bond distances.

The quantum chemical calculations refer to a model where the complexes are dissolved in a model solvent

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