

## Synthesis and X-Ray Crystal Structure of $[\text{H}_5\text{O}_2^+\cdot 21\text{-Crown-7}][\text{WOCl}_5^-]$ , a Complex in which the 21-Crown-7 Molecule adopts a Rigid, Bowl-like Conformation

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The reaction of  $\text{W}(\text{CO})_6$  with 21-crown-7 in the presence of  $\text{H}_2\text{O}$  and  $\text{HCl}_{(\text{g})}$  in toluene has yielded  $[\text{H}_5\text{O}_2^+\cdot 21\text{-crown-7}][\text{WOCl}_5^-]$ , a complex exhibiting a bowl-like conformation for the 21-crown-7 molecule which is bound to an  $\text{H}_5\text{O}_2^+$  ion in the unusual, high energy *cis* conformation.

Crown ethers and other macrocyclic compounds have received much attention since the pioneering work of Pedersen in 1967.<sup>1,2</sup> Considerable effort has focussed on the ion-selective properties of the macrocyclic ethers, and structural studies of such complexes have aided the elucidation of the interactions between the ions and the cyclic host.<sup>3</sup> The structural properties of 18-crown-6 have been explored widely, and to a lesser extent 15-crown-5, 12-crown-4 and dibenzo-30-crown-10.<sup>3-5</sup> On the other hand, only one structure of an unsubstituted 21-crown-7 has been reported.<sup>6</sup> Other structural studies are limited to those in which the 21-crown-7 is substituted with benzo, pyrido or methyl groups, making the crown more rigid.<sup>7-15</sup> Recently, our group<sup>16-22</sup> and others<sup>24-28</sup> have reported the interaction of oxonium ions with crown ethers. In such complexes the selectivity of 18-crown-6 for  $\text{H}_3\text{O}^+$  has been established.<sup>16-18</sup>

As part of a general study of liquid clathrate systems,<sup>29-31</sup> we now report the synthesis and first X-ray crystal structure of an unsubstituted 21-crown-7 in a bowl-like conformation. The complex exhibits an  $\text{H}_5\text{O}_2^+$  cation bound within the macrocycle in a *cis* conformation, in which the terminal protons of  $\text{H}_5\text{O}_2^+$  are in an eclipsed arrangement.

The complex studied herein,  $[\text{H}_5\text{O}_2^+\cdot 21\text{-crown-7}][\text{WOCl}_5^-]$ , was prepared in moderate yield according to Scheme 1.<sup>†</sup> Almost immediately after  $\text{HCl}_{(\text{g})}$  was commenced bubbling through the reaction mixture, a yellow liquid clathrate separated from the toluene layer. The yellow colouration is most likely due to the presence of other tungsten species in the liquid clathrate layer, in particular  $[\text{W}^{\text{IV}}(\text{CO})_4\text{Cl}_3^-]$ , which we have previously observed in these types of reactions.<sup>21</sup> Subsequently, deep blue crystals of the  $\text{W}^{\text{VI}}$  complex  $[\text{H}_5\text{O}_2^+\cdot 21\text{-crown-7}][\text{WOCl}_5^-]$  deposited from the liquid clathrate layer and were analysed by X-ray crystallographic techniques.<sup>‡</sup> We have established previously that oxidation of the metal centre from [0] to [+6] is due to the presence of atmospheric oxygen.<sup>21</sup>

The structure of the  $[\text{H}_5\text{O}_2^+\cdot 21\text{-crown-7}]$  cation is shown in Fig. 1. The  $\text{H}_5\text{O}_2^+$  ion fits snugly within the cavity of the macrocycle [Fig. 1(a)] and adopts the *cis* arrangement [Fig. 1(b)] to bind through hydrogen bonds to O(4), O(19), O(7) and O(13) of the crown. These distances of 2.63(2)–2.70(3) Å are significantly shorter than the O(A)⋯O(10) and O(B)⋯O(1) distances of 2.85(4) and 2.97(3) Å, respectively, and even though the protons on the  $\text{H}_5\text{O}_2^+$  ion were not located, the hydrogen bonding pattern is evident. The  $\text{H}_5\text{O}_2^+$  ion has no other intermolecular contacts less than 3.0 Å,<sup>§</sup> and the O(A)⋯O(B) distance of 2.41(3) Å is typical of this ion.<sup>32,33</sup> The 21-crown-7 adopts a shallow bowl-like conformation [Fig. 1(b)], in order to bind the higher energy<sup>34</sup> *cis* conformation of the  $\text{H}_5\text{O}_2^+$  ion. The conformation of the 21-crown-7 molecule is significantly different from the only previous structure determination of an unsubstituted 21-crown-7, where the macrocycle adopted a much flattened form.<sup>6</sup>

This study also reveals the first X-ray structure structure of the  $[\text{WOCl}_5^-]$  anion (Fig. 2). The tungsten(vi) centre displays a

highly distorted octahedral geometry: the axial Cl(5) ligand is bound at a distance of 2.666(5) Å, compared with an average of 2.366(7) Å for the other four chloride ligands. The significant lengthening observed for the Cl(5) ligand is typical for ligands *trans* to oxo species. The W–oxo distance is 1.67(1) Å and the Cl ligands are bent down and away from the oxo ligand at an

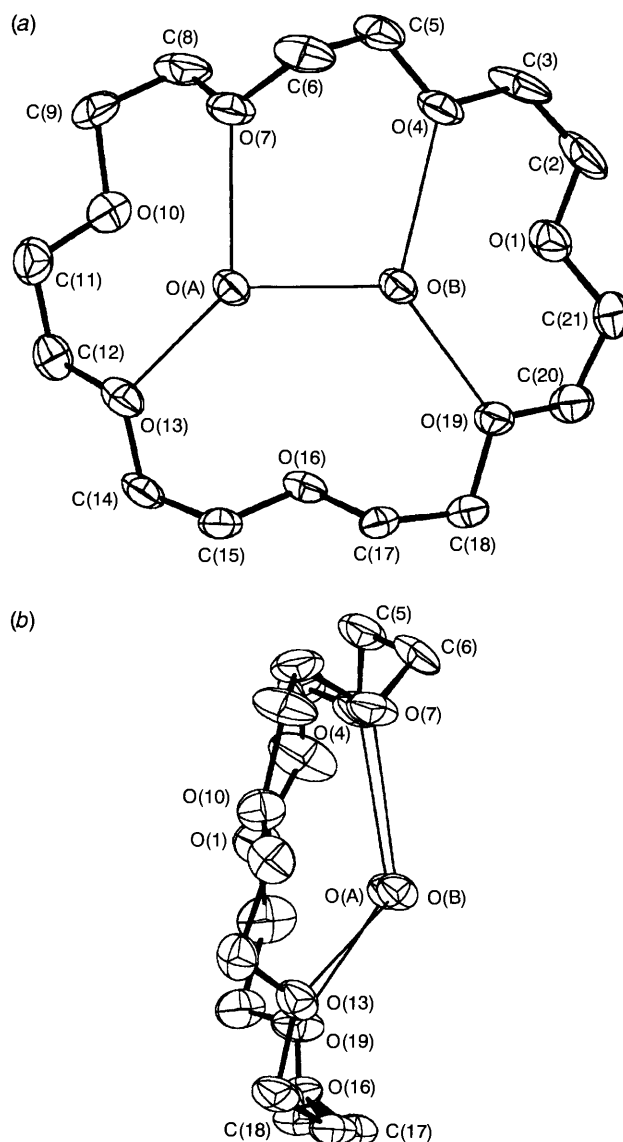
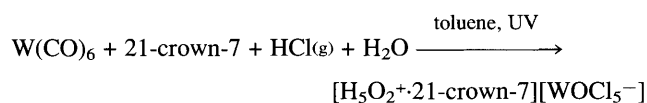
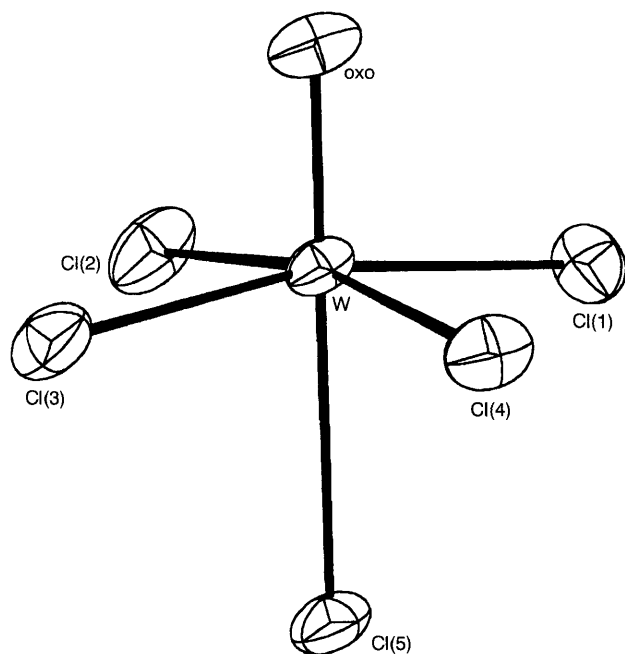


Fig. 1 (a) Structure of the  $[\text{H}_5\text{O}_2^+\cdot 21\text{-crown-7}]$  cation viewed perpendicular to the 21-crown-7 macrocycle. Bond distances (Å) are as follows: O(A)–O(B) 2.41(3), O(A)–O(7) 2.63(3), O(A)–O(13) 2.63(2), O(B)–O(4) 2.70(3) Å, O(B)–O(19) 2.67(3) Å. The O(A)–O(10) and O(B)–O(1) distances are significantly longer at 2.85(4) and 2.97(3) Å, respectively. (b) Side-on view of the structure of the  $[\text{H}_5\text{O}_2^+\cdot 21\text{-crown-7}]$  cation, indicating the location of the  $\text{H}_5\text{O}_2^+$  ion bound to the cavity of the crown macrocycle. The *cisoid* arrangement of the  $\text{H}_5\text{O}_2^+$  ion is also evident from the hydrogen bonding pattern.



Scheme 1



**Fig. 2** Structure of the  $[\text{WOCl}_5]^-$  anion. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) are as follows: W–oxo 1.67(1), W–Cl(1) 2.366(5), W–Cl(2) 2.371(5), W–Cl(3) 2.354(6), W–Cl(4) 2.372(5), W–Cl(5) 2.666(5), oxo–W–Cl(eq) 96.5(6), oxo–W–Cl(5) 178.8(4).

average oxo–W–Cl angle of  $96.5(6)^\circ$ . The oxo–W–Cl(5) angle is  $178.8(4)^\circ$ . Other similar structures have been found, although the tungsten is in the  $[\text{+5}]$  oxidation state.<sup>35–37</sup> Indeed, the structure of the  $\text{W}^{\text{VI}}$ -containing anion, including the W–oxo distance, is very similar to the  $[\text{W}^{\text{VI}}\text{OCl}_4(\text{H}_2\text{O})]^-$  species in which the loosely bound terminal chloride ligand is replaced by a water molecule.<sup>38</sup>

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## Footnotes

† *Experimental procedure* for  $[\text{H}_5\text{O}_2\text{-21-crown-7}][\text{WOCl}_5]^-$ : To a sample of 21-crown-7 (0.25 g, 0.81 mmol) in toluene (30 ml), was added  $\text{H}_2\text{O}$  (0.015 g, 0.81 mmol) and  $\text{W}(\text{CO})_6$  (0.30 g, 0.85 mmol). The mixture was stirred vigorously for 15 min.  $\text{HCl}(\text{g})$  was then rapidly bubbled through the mixture for approx. 1 h while under UV irradiation. During this time, a yellow liquid clathrate separated from the toluene. The composition of the liquid clathrate layer was not conclusive, but the oxonium ion–crown cation : toluene ratio of 1 : 1.2 was determined by  $^1\text{H NMR}$  integration. Deep blue crystals of the title complex deposited from the liquid clathrate layer after approx. 24 h.

‡ *Crystal data* for  $[\text{H}_5\text{O}_2\text{-21-crown-7}][\text{WOCl}_5]^-$ :  $\text{C}_{14}\text{H}_{33}\text{Cl}_5\text{O}_{10}\text{W}$ , triclinic, space group  $P\bar{1}$ ,  $a = 8.328(2)$ ,  $b = 13.129(2)$ ,  $c = 13.779(1)$   $\text{\AA}$ ,  $\alpha = 103.30(1)$ ,  $\beta = 98.50(1)$ ,  $\gamma = 104.34(1)^\circ$ ,  $V = 1387$   $\text{\AA}^3$ , and  $D_c = 1.736$   $\text{g cm}^{-3}$  for  $Z = 2$ . Of 4336 data collected (CAD4,  $2\theta_{\text{max}} = 50^\circ$ ,  $\text{Mo-K}\alpha$ ), 3874 were observed at  $I > 3\sigma(I)$ . Refinement converged with  $R = 0.082$  and  $R_w = 0.097$ . Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§  $\text{O}(\text{A})$  approaches the symmetry-related  $\text{O}(\text{A}')$  at a distance of 3.07  $\text{\AA}$ , a value reminiscent of  $\text{O}\cdots\text{O}$  distances for the middle oxygen atoms in structures of the  $\text{H}_5\text{O}_4^+$  ion. However, the identity (and the charge) of the oxonium ion is clearly defined by the  $(1-)$  metal-containing anion.

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