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Confirmation of the Structure of $(UO_2)_3(CO_3)_6{}^{6-}$ by ^{17}O NMR

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The aqueous chemistry of the uranyl ion continues to draw the attention of chemists. Recently, several papers on this subject have appeared (e.g. refs. 1–5). Carbonate complexes of the $UO_2{}^{2+}$ ion play an important role in studying the migration of uranium which may be released from nuclear waste repositories. These complexes have been previously studied in this laboratory using a potentiometric method and the data were explained by assuming the equilibrium [6]:

$$3UO_2(CO_3)_3{}^{4-} + 6H^+ \rightleftharpoons (UO_2)_3(CO_3)_6{}^{6-} + 3CO_2(g) + 3H_2O \qquad (1)$$

The structure of the mononuclear complex is well known from crystal structures [7–9] and it is probable that the structure in solution is not very different. The structure of the trinuclear complex $(UO_2)_3(CO_3)_6{}^{6-}$ is not known in the solid state. In solution, we have performed a combined X-ray diffraction and ^{13}C NMR study and have suggested a model for this complex (Fig. 1) [10].

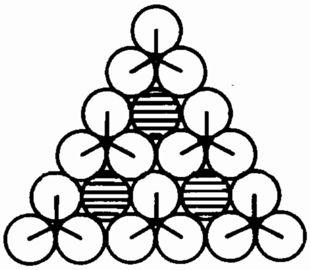

Fig. 1. Suggested model for the trinuclear complex $(UO_2)_3(CO_3)_6{}^{6-}$: filled circles = uranyl groups; open circles = carbonate oxygens.

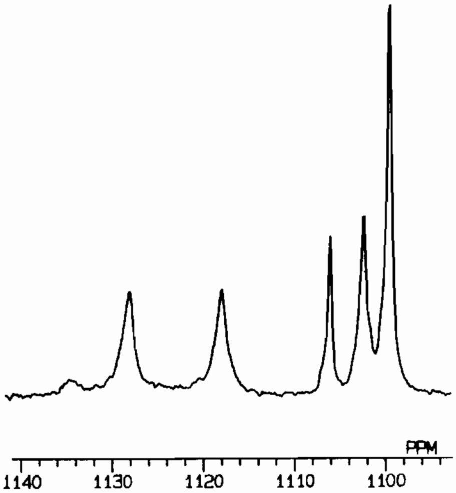

Fig. 2. ^{17}O NMR spectrum (54.1 MHz) of ~0.5 M aqueous solution of uranyl(VI) containing mostly the trinuclear complex $(UO_2)_3(CO_3)_6{}^{6-}$. The peak area ratio is ~2:2:1:1:2. The chemical shift reference is internal H_2O.

Here we present an independent confirmation of this structure obtained by ^{17}O NMR. To about 2 ml of a solution (solution B2, ref. 10) containing uranyl ion almost only in the form of the trinuclear complex [10], 0.3 ml of 18% $H_2{}^{17}O$ was added† and the spectrum shown in Fig. 2 was recorded on a JEOL GX400 NMR spectrometer at about 25 °C§. The suggested structure would require five ^{17}O NMR peaks with the area ratio 6:6:3:3:6. The actual spectrum (Fig. 2) is in excellent agreement with this prediction and thus confirms the structure of the complex. The peak at about 1099 ppm represents the uranyl oxygens. The small peak at ~1135 ppm originates from some minor species. Unfortunately, the solubility of the mononuclear complex $UO_2(CO_3)_3{}^{4-}$ is very low and, accordingly, no ^{17}O spectra have been obtained for this complex.

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†$H_2{}^{17}O$ was purchased from Yeda Research and Development Co. Ltd., Rehovot, Israel.

§Some NMR parameters: spectrometer frequency ~54.1 MHz; ~45° pulse (11.5 μs); pulse repetition time ~1 s; preaquisition delay time = 12 μs; chemical shift reference = internal water signal.

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