

excess free energy the electrostatic term is rather uncertain. It should be emphasized that the choice of the Bjerrum q -value is rather arbitrary although it seems to be a useful compromise giving a self-consistent description of the systems studied so far. It is quite possible that some other choice (choices) for the distance of closest approach may emerge in the future.

A detailed account of this work will be published elsewhere.

Acknowledgements. The author is indebted to the Department of Chemistry, SUNYAB for an invitation to spend a semester at the University. The present work is also supported financially by the Swedish Natural Science Research Council.

1. Högfeldt, E. *Chemica Scripta*. In print.
2. Stokes, R. H. and Robinson, R. A. *J. Amer. Chem. Soc.* 20 (1948) 1820.
3. Pitzer, K. S. *J. Chem. Soc. Faraday Trans. 2* (1968) 101.
4. Robinson, R. A. and Stokes, R. H. *Electrolyte Solutions*, 2nd. Ed., Butterworth, London 1959, Appendix 8.
5. *International Critical Tables*, Washburn, E. W., Ed., McGraw, New York 1928, Vol. III, pp. 54–95.

Received September 10, 1974.

Dinuclear Hydrolysis Complexes of Uranium(IV)

STEVAN POCEV*

Department of Inorganic Chemistry, The Royal Institute of Technology, S-100 44 Stockholm 70, Sweden

X-Ray scattering measurements on acid and hydrolyzed uranium(IV) perchlorate solutions¹ have shown that polynuclear complexes are formed in the hydrolyzed solutions. The U–U distance within the complexes was found to be 4.00 Å. This distance is similar to the Th–Th distance found in hydrolyzed thorium(IV) nitrate solutions² and in the dinuclear complex $\text{Th}_2(\text{OH})_2(\text{NO}_3)_6(\text{H}_2\text{O})_6$ in which the Th atoms are joined by double hydroxo bridges.³ It seems likely, therefore, that in the hydrolysis com-

* Present address: University of "Kiril and Methodi", Faculty of Technology and Metallurgy, Skopje, Yugoslavia.

Table 1. Results of the chemical analysis.

	Observed value	Calculated value for $\text{U}_2(\text{OH})_2(\text{ClO}_4)_z(\text{H}_2\text{O})_{13}$
% UO_2	41.4	40.27
% Cl_2O_7	38.3	40.92
% H_2O	20.0	18.81
Density	3.1 ₃	3.091 ($z = 4$)

plexes in the uranium(IV) perchlorate solutions the uranium atoms are bound together by the sharing of two hydroxo groups.

In an attempt to obtain more information on the structures of the uranium(IV) hydrolysis complexes, two different basic perchlorates, obtained from the solutions used for the X-ray scattering measurements, have been investigated. For one of these a preliminary crystal structure determination has shown that it contains discrete dinuclear hydrolysis complexes.

The crystals, which can be obtained from solutions with a $\text{OH}^-/\text{U}^{4+}$ ratio between about 0.2 and 0.5, are very soluble in water and are unstable outside the mother liquor, which makes their separation from the mother liquor difficult. The analysis, which is given in Table 1 leads to the formula $(\text{UO}_2)_2(\text{Cl}_2\text{O}_7)_3(\text{H}_2\text{O})_x$ ($x \sim 13$).

From Weissenberg and precession photographs the unit cell was found to be monoclinic. The derived values for the unit cell dimensions were refined by a least squares procedure with the use of a Guinier powder photograph, taken with $\text{CuK}\alpha$ radiation ($\lambda = 1.5405$ Å) with Si as internal standard ($a = 5.4301$ Å). The values found were $a = 26.084(4)$ Å, $b = 9.493(1)$ Å, $c = 16.945(3)$ Å, and $\beta = 136.63(1)$ Å. Systematically absent reflections were hkl for $h + k = 2n + 1$ and $h0l$ for $l = 2n + 1$. This is characteristic for the space groups No. 15, $C2/c$ and No. 9; Cc .

Difficulties were encountered in getting good intensity data since the crystals seemed to be unstable under X-ray exposure and, therefore, absorption corrections could not be done. From intensities estimated visually by comparison with an intensity scale and corrected for Lorentz and polarization factors the Patterson projections along the three axes of the unit cell were calculated. An apparently unique interpretation of all the possible U–U peaks could be obtained by assuming the eight uranium atoms in the unit cell to occupy the position 8(f) in the centrosymmetric space group $C2/c$. Electron density projections along the three axes of the unit cell confirmed the correctness of the derived positions. A least squares refinement of the uranium positions with the use of the 180 observed $h0l$ and $hk0$ reflections lead to an R value of 0.24 and the final parameter values were $x = 0.095$; $y = 0.075$; $z = -0.079$.

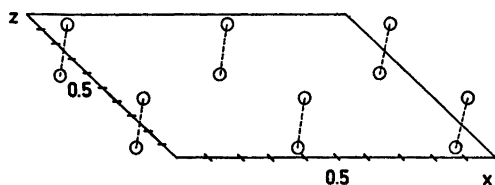


Fig. 1. The positions of the U atoms as seen in a projection along the b axis of the unit cell. Uranium atoms belonging to the same hydrolysis complex are joined by dashed lines.

The positions of the uranium atoms as seen in a projection along the b axis are shown in Fig. 1. The uranium atoms occur in pairs with a U—U distance of 4.03 Å. The shortest distance between atoms belonging to different pairs is 7.22 Å. The structure, therefore, seems to be built up from discrete dinuclear complexes.

In the $\text{Th}_2(\text{OH})_2(\text{NO}_3)_6(\text{H}_2\text{O})_6$ complexes found in crystals of $\text{Th}_2(\text{OH})_2(\text{NO}_3)_6(\text{H}_2\text{O})_6$, the distance between the Th atoms is 3.99 Å.³ This indicates that the dinuclear U(IV) hydrolysis complexes are very similar to those formed by thorium and the formula for the compound investigated should be written $\text{U}_2(\text{OH})_2(\text{ClO}_4)_6(\text{H}_2\text{O})_x$ ($x \approx 13$).

Acknowledgements. I wish to express my thanks to Dr. Georg Johansson for his inspiring interest during the course of this work. Thanks are also due to all colleagues at the X-ray group for the cooperation. The work has been supported by Statens Naturvetenskapliga Forskningsråd (Swedish Natural Science Research Council). This work has also been supported by grants (scholarship) from the Scientific and Research Council, Skopje, Yugoslavia.

1. Pocev, S. and Johansson, G. *Acta Chem. Scand.* 27 (1973) 2146.
2. Johansson, G. *Acta Chem. Scand.* 22 (1968) 379.
3. Johansson, G. *Acta Chem. Scand.* 22 (1968) 389.

Received August 29, 1974.

Normal Coordinate Analysis of Hexafluoroacetone

MATTI PERTTILÄ

Department of Physical Chemistry, University of Helsinki, Meritullinkatu 1C, Helsinki 17, Finland

The infrared and Raman spectra of hexafluoroacetone were first reported by Berney.¹ As pointed out by Miller and Kiviat,² his original assignment of the band at 194 cm^{-1} (gas spectrum) as being due to CCC bending is possibly in error. In the present work a harmonic force field was developed for hexafluoroacetone and an alternative assignment of the bands is proposed. This work is part of a larger study on polyfluoro compounds.^{3,4}

Berney¹ concludes that the actual point group of hexafluoroacetone should be C_s , instead of C_{2v} , basing his argument mainly on the depolarization ratios of a CF bending and the assumed CO bending vibrations. As Miller and Kiviat point out, however, the intensity of the Raman band at 716 cm^{-1} is too weak to give decisive information on its polarization. They also give evidence indicating that the 320 cm^{-1} band, assigned by Berney to a CO wag, is in fact due to the CCC scissoring mode. This result is in good agreement with the experimental studies of Murto *et al.*,⁵ on hexafluoro alcohols. Obviously the full C_{2v} symmetry can be used.

According to Berney, the 194 cm^{-1} band clearly represents a totally symmetric fundamental. Accepting this as a CF_3 rocking band, we are left with one rocking band too many. In our opinion the band at 233 cm^{-1} in the vapour spectrum, the weakest of the rocking bands proposed by Berney, is not a fundamental band; rather, the band at 265 cm^{-1} is the B_1 rocking vibration. This also is a weak band and its depolarization ratio has not been reported. The B_1 CO bending band is probably in the region 450 cm^{-1} –500 cm^{-1} ,^{7,8} being obviously superimposed by other bands. In the present work it is assumed to be at 470 cm^{-1} .

The distribution of the normal modes among the symmetry species is $10A_1 + 4A_2 + 8B_1 + 5B_2$, including two redundancies in the A_1 species and one redundancy in the B_1 species.

The G matrix was calculated by the modified programme written by Schachtschneider⁹ for the Wilson s-vector method. The normal coordinate calculations were carried out on a Univac 1108 computer using a programme written by the author. In the course of the calculations the diagonal and largest off-diagonal elements of the F matrix were first perturbed on order to get the best possible F matrix with a minimum number of parameters. Using the obtained L matrix, a full harmonic force field was developed for each species to fit exactly