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STEREOCHEMISTRY OF URANYL ACETYLACETONATE MONOHYDRATE

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1. INTRODUCTION

The configuration of the uranyl ion has been under discussion for a long time, as indicated by the following structure studies. Fankuchen[1] found the UO_2 group linear in $NaUO_2(acetate)_3$, on the basis of the geometry of the space group. Although the exact localization of the oxygen atoms could not be obtained by X-ray diffraction methods, the U–O distance was assumed to be 2.2 Å. Samson and Sillén[2] determined the structure of $BaUO_2O_2$ but they too were unable to locate the oxygen atoms on the Fourier maps; the linear shape of the uranyl group was a consequence of uranium being at an inversion centre; the U–O distance was assumed to be 1.7 Å. Hoard and Stroupe[3] confirmed the above conclusions and estimated that the length of the U–O bond in $RbUO_2(NO_3)_3$ was 1.58 Å. The linear shape[4] of the uranyl group in $CaUO_2O_2$ follows from space group symmetry; the oxygen atoms were located on the basis of intensity measurements and the U–O distances were found to be 1.91 Å. The uranyl group was also found to be linear[5,6] in $K_3UO_2F_5$ and $MgUO_2O_2$. In this case the linearity of the uranyl group is not required by space group symmetry. The U–O distances are respectively 1.92 and 1.76 Å.

On the other hand, infrared and Raman spectra are in favour of a bent structure of the uranyl group. Such conclusions follow from Raman spectra of the nitrate, chlorate and sulphate of UO_2 obtained by Conn and Wu[7] and from the infra-red spectra of about twenty uranyl salts recorded by Lecompte and Freymann[8].

The Raman spectra of some uranyl complexes examined by Satyanarayana[9] are also in favour of a bent configuration for the uranyl ion. As far as uranyl acetylacetonate monohydrate is concerned, studies by Sacconi *et al.*[10,11,12] on infrared spectra, and on the thermodynamic properties of solutions showed that "the attraction between uranium and water molecules should be considered as coordinative forces" and that the coordination of uranium should be greater than six. Comyns, Gatehouse and Wait[13] also studied three allotropic forms (1, 2 and 3) of this complex: Crystallographic data for the three forms have been given by the Authors.

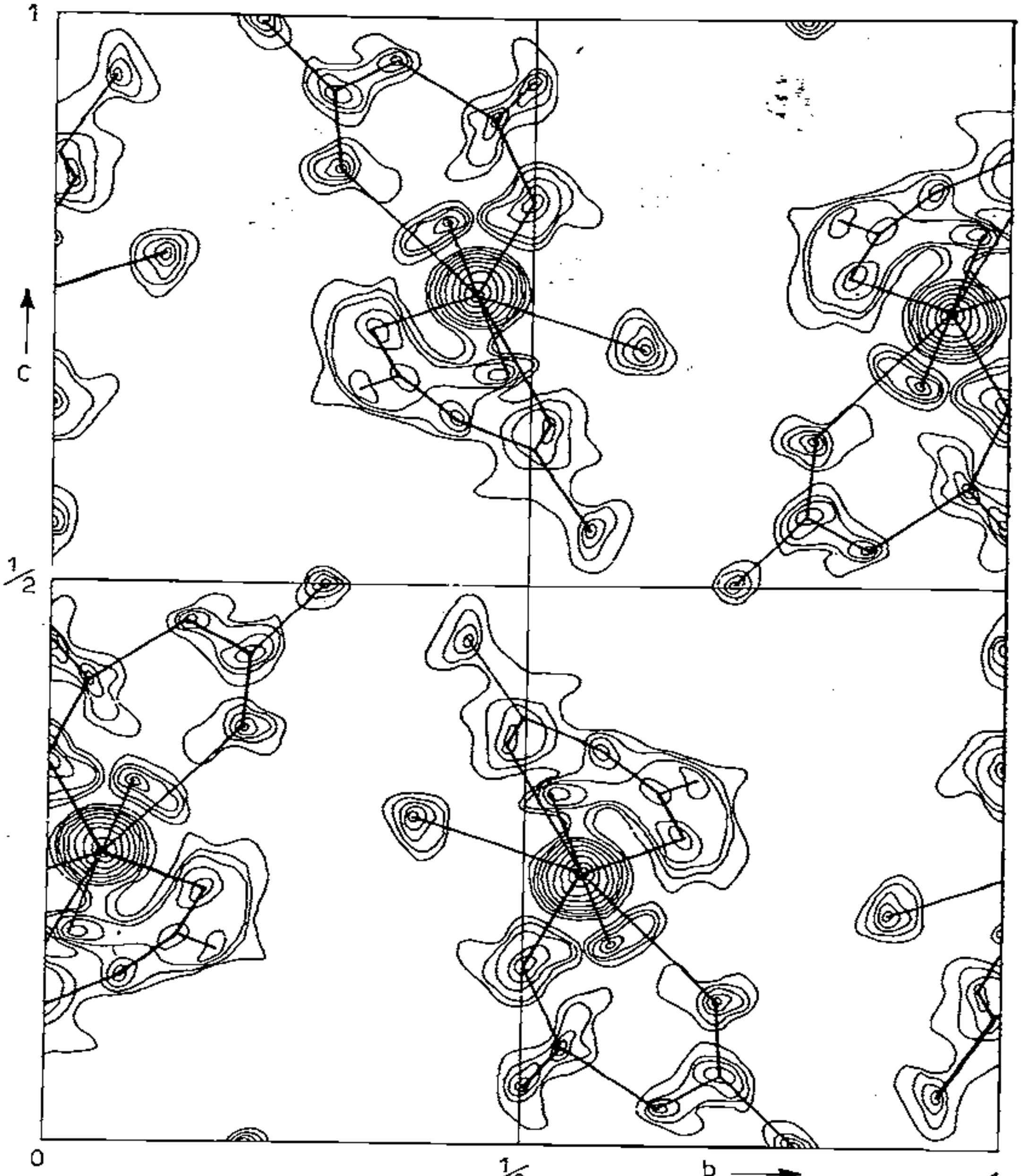

Fig. 1. Electron density projection on (100) for uranyl acetylacetonate monohydrate. Contours at 0, 2, 4, etc. $e\ \text{Å}^{-2}$.

Comyns *et al.* interpreted I.R., U.V. and visible spectra, as well as the physical properties of the same compound as evidence of the existence of a dimeric molecule in benzene solution formed through one or two intermolecular bonds between the oxygen atoms of the rings and uranium. Therefore a coordination of seven or eight was postulated for uranium. These authors believe that the uranyl ion has the same structure in all three forms, that it is not bent and no other atoms are attached to the uranyl oxygen except uranium. Owing to the great interest in a conclusive structural determination of this complex, we planned an X-ray and neutron diffraction investigation of this series of compounds.

This communication discusses the structure of form 2.

2. EXPERIMENTAL

Single crystals of the compound were prepared according to the method of Comyns *et al.*[13]. Very small crystals were enclosed in Lindemann capillary tubes; the diffraction of Mo-Kα X-rays was recorded by Weissenberg and precession cameras, and the intensities were read with a photometer fitted with a potentiometric recorder. The use of crystals of regular section and very small dimensions (less than 0.1 mm) as well as the use of Mo-Kα radiation reduced the absorption errors to a minimum. The crystal data of Comyns *et al.* were confirmed as follows: $a = 7.83$ Å; $b = 11.99$ Å; $c = 15.64$ Å; $\beta = 103.7°$, and space group $P2_{1/c}$ with four molecules per unit cell. Patterson projections were calculated on (001) and (100).

Electron density projections were first obtained using the heavy atom method. Afterwards, the light atoms were introduced in the calculated structure factors. A series of trial hypotheses on the disposition of the chelate rings were made following the usual conception that the chelate rings are in a transplanar configuration with respect to uranium. During this series of trial hypotheses, the reliability index remained relatively high (greater than 0.20).

The electron-density projections (Fig. 1) were then interpreted in terms of a "bent" configuration of the chelate rings with respect to the uranium atom. The reliability index fell to acceptable values (under 0.15). The Cochran method of differential synthesis[14] was used to refine the atomic co-ordinates, and we obtained the following reliability factors: *hk*0 reflexions R = 0.13; 0*kl* reflexions R = 0.08. Using the Cruickshank method[15], we calculated that the actual coordinates have the following standard errors:

Oxygen: $\delta_x = \pm 0.05$ Å; $\delta_y = \pm 0.03$ Å; $\delta_z = \pm 0.02$ Å;
Carbon: $\delta_x = \pm 0.09$ Å; $\delta_y = \pm 0.07$ Å; $\delta_z = \pm 0.07$ Å.

3. RESULTS AND DISCUSSION

The uranium atom in this compound exhibits a co-ordination number of seven. A perspective view of the structure of a molecule of uranyl acetylacetonate, is given in Fig. 2.

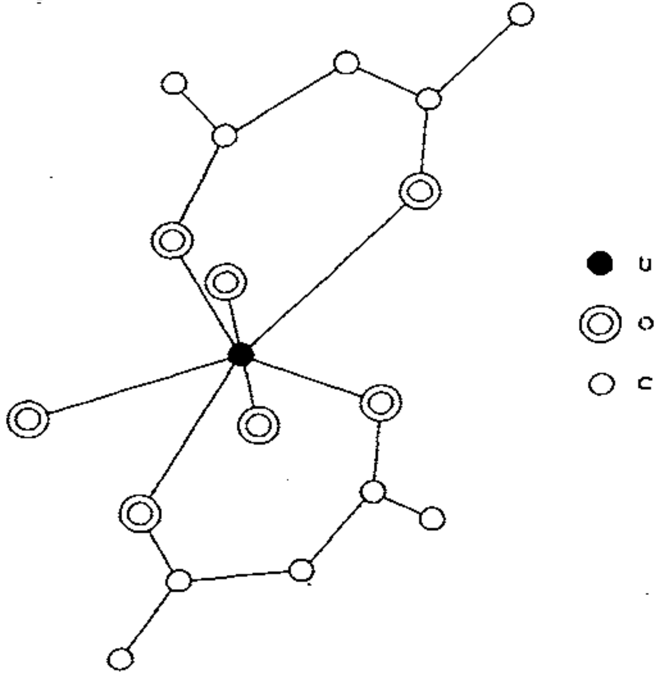

Fig. 2. A perspective view of the molecule of uranyl acetylacetonate monohydrate.

The geometry of co-ordination is that of a pentagonal bipyramid, with seven oxygen atoms localized at the corners. The pentagonal basis of the bipyramid is formed by the four oxygens belonging to the chelate rings, and the water molecule.

The uranyl group is linear within the limits of experimental error and is normal to the plane of the other oxygen atoms. The U–O bond-lengths are 2.51 ± 0.07 Å for the oxygen atoms in the rings, 2.48 ± 0.07 Å for water oxygen and 1.60 ± 0.07 Å for the oxygen atoms in the uranyl group.

Coordination number seven is rather uncommon; Fig. 3 shows a perspective view of the three geometrical configurations which are predicted for coordination number seven; a face-centred trigonal prism in a); a pentagonal bipyramid in b) and a face-centred octahedron in c). The face-centred trigonal prism structure is reported[16] for the ions $[NbF_7]^{2-}$ and[17] $[TaF_7]^{2-}$ and also for the polymeric structure found by Nardelli and Fava[18] in bis-thiourea lead chloride. The face-centred octahedron was originally considered[19] to be the structural characteristic

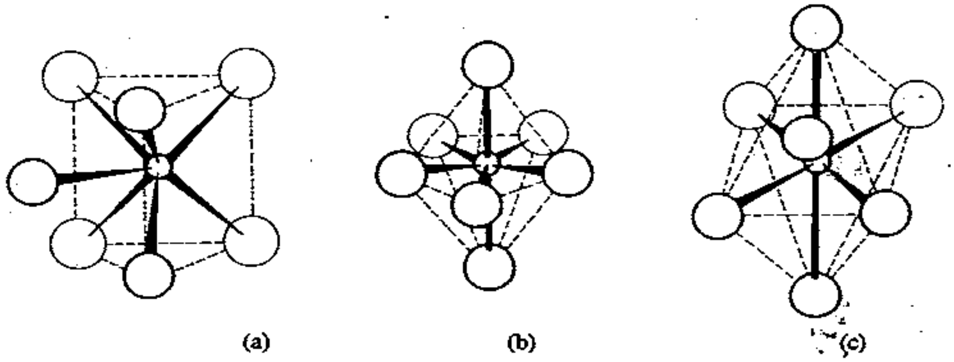

Fig. 3. Geometry of seven-coordination.

of the $[ZrF_7]^{3-}$ ion, but recent investigations indicate that this ion is a pentagonal bipyramid. The face-centred octahedron was found in the MO_7 groups in some rare-earth oxides of formula M_2O_3.

The pentagonal bipyramidal coordination is more frequently represented.

This arrangement of bonds was found[20] in the compounds IF_7 by La Villa and Bauer using electron diffraction methods. Zachariasen[5,21] showed that the ions $[UF_7]^{3-}$ and $[UO_2F_5]^{3-}$ were pentagonal bipyramidal. This configuration was also recently found by Arutyunyan and Porai-Koshits[22] in the caesium salt of $[UO_2(NCS)_5]^{3-}$; uranium is linked to five thiocyanato groups through the nitrogen atoms. The caesium salt of uranyl oxychloride was examined by Allpress and Wadsley[23].

In this polymeric structure, uranium exhibits the bipyramidal pentagonal coordination number seven.

To this series of pentagonal bipyramidal complexes we add uranyl acetylacetonate monohydrate; on the other hand we point out that this is the first example of a chelate compound showing this unusual configuration.

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