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RESEARCH GROUP**
Department of Chemistry
Rand Afrikaans University

REPORT NO. 1856
A STUDY OF MODEL SYSTEMS IN
ANIONIC EXCHANGE

**Head of Department
of Chemistry** R.R. Arndt

Research Group Leader J.C.A. Boeyens

Director of Division M.J. Nicol

Investigators R. Haegele
J.C.A. Boeyens

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**NATIONAL
INSTITUTE
for
METALLURGY**
200 Hans Strydom Avenue
RANDBURG
2194 South Africa



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SYNOPSIS

Preliminary experiments are reported on the preparation and characterization of anionic sulphate and chloride complexes of UO_2^{2+} and iron(III), benzyl-trimethylammonium cation being used as a model substance for the simulation of positive sites in an anionic-exchange resin.

The structure of $(\text{BTMA})_2[\text{UO}_2\text{Cl}_3-\text{O}_2-\text{Cl}_3\text{UO}_2]$, a binuclear uranyl-peroxocomplex that has not been reported in the literature, was elucidated by single-crystal X-ray examination, and is described and discussed.

SAMEVATTING

Daar word verslag gedoen oor voorlopige eksperimente in verband met die bereiding en karakterisering van anioniese sulfaat- en chloriedkomplekse van UO_2^{2+} en yster(III) met bensieltrimetielammoniumkation as 'n modelstof vir die simulering van positiewe terreine in 'n anioonuitruilhars.

Die struktuur van $(\text{BTMA})_2[\text{UO}_2\text{Cl}_3-\text{O}_2-\text{Cl}_3\text{UO}_2]$, 'n tweekernuranielperoksokompleks waaroor daar nog nie in die literatuur verslag gedoen is nie, is toegelig deur 'n enkelkristal-X-straalondersoek en word beskryf en bespreek.

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1. SULPHATOCOMPLEXES AND CHLOROCOMPLEXES OF UO_2^{2+} AND IRON(III)

A sound understanding of ion-exchange processes requires a detailed knowledge of the ions involved and of the mechanism by which these are bound on the matrix of the exchange resin. For instance, the anionic uranyl species that feature in the concentration of uranium by strong-base resins have never been positively identified, and neither have the anionic complexes of iron(III), which compete with uranium for resin sites and are thus detrimental to the efficient and economically important recovery of the latter by this technique. There is good reason for the assumption that the complexes formed between anionic uranyl and related species and suitably selected compounds, which are similar to the functional groups of the resin, should correspond closely to the products that form on a resin during ion exchange.

Uranium-containing ores or residues are leached with sulphuric acid. The leach liquor, which has a pH value of about 1.5 and contains 3 g of UO_2 or less per litre, is passed through an anionic-exchange resin having functional groups mainly of the quaternary ammonium type. In this way, uranium is retained selectively in the form of its uranyl-sulphatocomplexes, the only other interfering metal species – besides real poisons, e.g., the $[\text{Co}(\text{CN})_6]^{3-}$ complex – being the corresponding iron(III)-sulphatocomplexes. However, since these species are less tightly bound to the resin, they are displaced by the uranium complexes in the course of the loading process, thus playing a hampering role only if they are present in high concentration. As previously reported¹⁻³, the uranium is finally eluted by a mixture of NH_4NO_3 and HNO_3 .

The retention of uranium species on the resin is favoured by an increase in pH value, which reduces the competition of HSO_4^- . However, in practice, the pH value should be kept below 3.5 since, otherwise, precipitation of accompanying metals occurs. The most favourable SO_4^{2-} concentration is two parts of SO_4 to one of uranium, since higher ratios prevent a uranium loading of 100 per cent owing to the competition from SO_4^{2-} for the resin sites. Temperature has no effect on the equilibrium loading⁴.

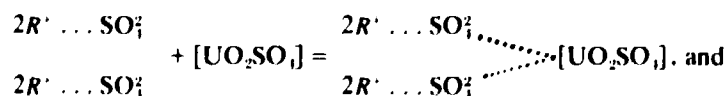
The uranium-sulphatocomplexes are of the type $[\text{UO}_2(\text{SO}_4)_n]^{2-2n}$, with $n=1, 2$, or 3, in equilibrium with one another and with both UO_2^{2+} and SO_4^{2-} . In aqueous solutions having a pH value of less than 3, the neutral UO_2SO_4 predominates⁵⁻⁷, only a minor proportion of $[\text{UO}_2(\text{SO}_4)_2]^{2-}$ being present, which gradually increases with increasing pH value⁸. In spite of the fact that only these two species are present, there is general agreement that the particle finally bound to the positive resin sites is $[\text{UO}_2(\text{SO}_4)_3]^-$, although the possibility that this is the bisulphatocomplex is not totally discarded⁹.

The mechanism proposed to account for this fact consists of the following four steps^{9,10} in which the functional group of the resin is designated by R^+ :

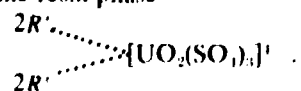
- (1) saturation of the positive resin sites with the excess sulphate

$$2R^+ + \text{SO}_4^{2-} = 2R^+ \dots \text{SO}_4^{2-}$$
- (2) formation of the neutral uranium complex in solution

$$\text{UO}_2^{2+} + \text{SO}_4^{2-} = [\text{UO}_2\text{SO}_4]$$
- (3) easy passage of the neutral uranium complex into the resin phase without the hindrance of a Donnan potential and subsequent association of this complex with the bound SO_4^{2-} in a topochemical reaction,



- (4) formation of the ionic pair consisting of the resin site and the uranium-sulphatocomplex in the resin phase



If this mechanism is correct, it requires the accommodation of four positive resin sites. These sites must be suitably positioned to fulfil the steric requirements for complex formation and to afford a balanced charge distribution after the ion pair has formed. Because of the random crosslinking, the ion-exchange resin, e.g., of the type shown in Figure 1, primarily has a disordered structure. However, owing to the flexibility of the chains, some short-range order can certainly be imposed by the presence of the uranium sulphatocomplex, though under loss of entropy.

So that the uranium-complex species involved and the kind of arrangement of the resin in relation to this species can be elucidated, it seems appropriate to synthesize suitable model substances and to study their crystalline state, e.g., by single-crystal determination of the structure. This method is justified, even if the arrangement in the crystal is influenced by packing effects: the short-range order in the real resin should account for similar effects. The anionic uranyl-sulphatocomplexes so far reported in the literature for which the crystal structure has been determined (e.g., by Ross and Evans¹¹) contain mainly small inorganic cations. Thus, although the formulae for these compounds may provide some hint about the possible composition of the complexes, their arrangement in space is certainly different from that expected for larger, organic cations. On the other hand, the only results that have been published for those compounds are the results of spectroscopic methods on solutions (e.g., Lipovskii and Kuzina¹²). These findings did not seem to be complete enough to account for what actually happens on the site of an exchange resin. The same argument holds good for purely spectroscopic studies on resin-bound UO_2^{2+} species¹³.

Therefore, it was decided to start experiments in the system $\text{R}^+-\text{UO}_2^{2+}-\text{SO}_4^{2-}-\text{H}_2\text{O}$, use being made of benzyl-trimethylammonium (BTMA), which is readily available in the form of its chloride salt. This cation constitutes a close analogue of the functional group of strong-base polystyrene resins (see Figure 2).

Parallel experiments were carried out with iron(III). In this system, no bisulphate complexes are formed in the region considered below a pH value of 3, the only non-positive species being monovalent anions¹⁴. These might be $[\text{Fe}(\text{SO}_4)_2]^-$, or, as claimed in a study on adsorption equilibria by anion-exchange resins¹⁵, a mixed hydroxo-sulphatocomplex of the form $[\text{Fe}(\text{OH})_2\text{SO}_4]^-$.

1.1. Experiments on Uranium Compounds

The general procedure for the preparation of compounds in the system mentioned involved the mixing of aqueous solutions of $\text{UO}_2\text{SO}_4 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ and $(\text{BTMA})\text{Cl}$ or $(\text{BTMA})_2\text{SO}_4$ in molar ratios of 1 to 2 or 1 to 4, and evaporation of the solutions — on some occasions by gentle heating initially — until some solid formed. In some instances, methanol was used as a solvent for the (BTMA) salt to facilitate the crystallization of a product. In all the experiments, the pH value was kept below 3.5. For the attainment of very low pH values, small amounts of sulphuric acid were added, which simultaneously offered additional SO_4^{2-} ions to form complexes with UO_2^{2+} , for which latter purpose Na_2SO_4 was also used. The possible interference from chloride was excluded, either by addition of SO_4^{2-} ions in the form of Ag_2SO_4 , after which precipitation of AgCl took place, or by the initial use of $(\text{BTMA})_2\text{SO}_4$, instead of $(\text{BTMA})\text{Cl}$. The former compound was prepared by addition of Ag_2SO_4 to a solution of the latter, and filtration and evaporation to dryness or precipitation with acetone. Commercially available chemicals of reagent grade were used throughout.

1.1.1. The Sulphatocomplex

In all of the seven experiments carried out, the first substance to be formed out of solution was a light-yellow compound soluble only in water but not in any of the organic solvents more generally used, except dimethyl-sulphoxide, which, however, was disregarded as a suitable medium for recrystallization since it is a strongly complexing agent. This first substance formed very thin, hair-like crystals that showed a strong tendency towards intergrowth (see Plate I). These crystals were not suitable for single-crystal X-ray diffraction, and subsequent attempts to grow larger specimens, either by slow evaporation of aqueous solutions or by slow diffusion into acetone, were not successful, although the latter method seems to be promising (see Plate I). However, the recrystallized products have not been conclusively identified with the original.

From the appearance and behaviour of this product, it is obvious that the same compound formed in all the experiments. Analyses of three samples yielded slightly different results, that of the possibly purest substance being in accordance with the formula $(\text{BTMA})_2 [(\text{UO}_2)_2(\text{SO}_4)_3(\text{H}_2\text{O})_5]$, and displaying a ratio of sulphur to uranium of 1.5 (uranium found 39.8 per cent, uranium calculated 39.08 per cent, sulphur found 7.54 per cent, sulphur calculated 7.88 per cent, carbon found 19.2 per

cent. carbon calculated 19.70 per cent). Compounds of this composition are known from the respective NH_4^+ and K^+ salts¹¹, but a binuclear arrangement of the UO_2 groups is not necessarily implied. The water of crystallization showed up clearly in the infrared spectra (broad strong bands at 3400 and 1640 cm^{-1}), as well as in the differential-thermal-analysis (DTA) diagram, where it was recorded at temperatures somewhat higher than 100°C. The diagram also revealed that no melting occurs before decomposition at about 370°C.

In the infrared spectra (see Figure 3), a group of very strong peaks was observed at wavenumbers between 1260 and 1020 cm^{-1} , which were assigned to sulphate ligands. This result accords qualitatively with what was observed for UO_2SO_4 , and what is reported in the literature¹². Compared with $(\text{BTMA})_2\text{SO}_4$ (strong band centred at 1130 cm^{-1}), a shift to lower wavenumbers has taken place, as well as splitting, certainly due to bonding between SO_4 -oxygen and uranium. Sharp peaks at 850 and 930 cm^{-1} were assigned to the symmetrical and asymmetrical vibrations of the UO_2^{2+} in accordance with those described in the literature^{12,15}.

In the solutions, which contained SO_4^{2-} as the only anionic species, a yellow compound formed as an amorphous, glassy solid. Short-range order was shown to exist by rings on a Laue photograph, as well as by partial birefringence. Attempts to cause crystallization by heating, cooling, or seeding with crystals were unsuccessful. The influence of the chloride ions upon the crystallization of this compound is not yet understood.

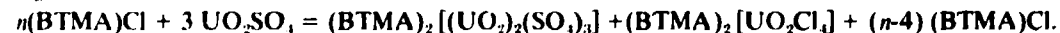
1.1.2. The Chlorocomplex

For the experiments in which $(\text{BTMA})\text{Cl}$ was used, a second compound formed after the yellow sulphate complex as light-green, well-shaped crystals that were soluble in water, less readily soluble in methanol, and melted at 190°C. Single-crystal X-ray photographs showed them to be monoclinic with $a = 10.37 \text{ \AA}$, $b = 8.97 \text{ \AA}$, $c = 15.32 \text{ \AA}$, and $\beta = 97.5^\circ$, the probable space group being Cc or C2/c . Although the composition of this compound is not yet fully known, the absence of SO_4^{2-} in qualitative and quantitative analysis and also in the infrared spectra, and the qualitative presence of chloride indicated that it is likely to be a chloride complex of uranyl, probably of the kind



with ambiguity regarding the water content. This formulation is in accordance with the uranium analysis of one of the samples (uranium found 32.0 per cent, calculated 32.6 per cent for $n = 1$). Uranyl-chloride complexes of this kind are reported in the literature¹⁵⁻¹⁷.

From this formulation it is likely that, in the presence of Cl^- , the following scheme of reaction is true:



From the mother liquid of this chloride complex, a uranium-peroxocompound could be obtained that is described in full detail in Section 2.

1.2. EXPERIMENTS ON IRON(III) COMPOUNDS

The general procedure for synthesis of iron(III)-sulphatocomplexes was similar to that described for uranium. $\text{Fe}_2(\text{SO}_4)_3$ and 2 $(\text{BTMA})\text{Cl}$ or $(\text{BTMA})_2\text{SO}_4$ were mixed in aqueous-methanolic solutions, and some concentrated sulphuric acid was added. The results of three experiments can be summed up as follows:

In the presence of Cl^- , large yellow crystals, which were very easily soluble in water and methanol, formed as the first product. In the infrared spectra, only the peaks of the organic cation were visible. Qualitative analysis showed no sulphate, but chloride was determined, which was proved by quantitative analysis. However, the analyses (iron 3.75 per cent, chloride 37.9 per cent, and carbon 13.2 per cent) do not comply with any possible formula for a chlorocomplex, giving the atomic ratio of Fe to Cl to BTMA as 1 to 16 to 1.6. Single-crystal X-ray examination showed that these crystals were triclinic with $a = 14.75 \text{ \AA}$, $b = 8.87 \text{ \AA}$, $c = 7.15 \text{ \AA}$, and $\alpha = 92.3^\circ$, $\beta = 90.6^\circ$, and $\gamma = 119.4^\circ$.

From the mother liquid of the chlorocomplex, a second product could be obtained that was the only product when Cl^- was excluded initially. It formed nearly white, small, flat crystals that were readily soluble in water (forming a yellow solution), but not in methanol. The infrared spectrum showed broad water bands and bonded sulphate, but no sign of the organic cation. The quantitative analysis of the obviously impure substance (carbon found 0.31 per cent, iron 17.1 per cent, sulphur 18.5 per cent) closely approximates the formula $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ (calculated iron 19.9 per cent,

sulphur 17.1 per cent), which is a known simple hydrate. Therefore, it seems that it is difficult to prepare the kind of model substance required from the system $(\text{BTMA})^+ - \text{Fe(III)} - \text{SO}_4^{2-} - \text{H}_2\text{O}$.

1.3. Discussion

No great progress was made in the achievement of the original aim of the project, but some insight was gained on how model systems like the one chosen should be approached. The following factors should influence any future work.

- Any interference of ions other than those belonging to the system under study should be avoided.
- Greater attention should be given to the technique of growing crystals. Unless the crystals are well developed, X-ray determination of the structure, which is the procedure adopted in this project, is impossible.
- Where the growth of suitable crystals becomes too difficult or even impossible, other cations R^+ should be chosen that might be more favourable in this respect, for instance, a more polar species like 4-nitro-benzyl-trimethylammonium might be considered.
- In general, cations R^+ that simulate the actual resin site more realistically should be introduced into the model system. So, while the adopted positive group (BTMA) is retained, the reverse side of the cation should be made as bulky and as inaccessible to the anionic complex as possible (see Figure 4).

2. THE STRUCTURE OF $(\text{BTMA})^+$, $[\text{UO}_2\text{Cl}_3 \cdot \text{O}_2 - \text{Cl}_3\text{UO}_2]$

It is known that the peroxy-anion, O_2^{2-} , can act as a ligand in coordination compounds¹⁸. All O-O distances in complex and simple ionic peroxides, as well as in H_2O_2 seem to be the same¹⁹⁻²¹, i.e., approximately 1.49 Å. Coordinated O_2^{2-} can behave as a monodentate²¹ and as a bidentate²² ligand, and might also form bridges between two cations, thus forming binuclear entities^{23, 25}.

Many coordination compounds of uranium(VI) prepared in aqueous solutions are known. Their main characteristics consist of a linear uranyl group, $(\text{O}-\text{U}-\text{O})^{2+}$, that is vertical to a plane in which the other ligands are arranged. Therefore, the configuration round uranium is a tetragonal, pentagonal, or hexagonal bipyramid, depending on the number of ligands in the plane^{15, 27}.

Sound structural information on uranyl-peroxocompounds is scarce. Most such compounds were prepared in alkaline solution and contain only oxygen as ligands^{28, 29}. The structure of the simplest compound, i.e., the hydrated uranium-peroxide $\text{UO}_2 \cdot x \text{H}_2\text{O}$, is still unknown, its determination obviously being prevented by the difficulties experienced in the growing of suitable crystals. As far as is known, the only structure already elucidated by single-crystal work²² is that of $\text{Na}_4[\text{UO}_2(\text{O}_2)_3]$.

In view of the theoretical interest in uranium-ligand bonding, the presentation of these results concerning the crystal structure of $(\text{BTMA})^+$, $[\text{UO}_2\text{Cl}_3 \cdot \text{O}_2 - \text{Cl}_3\text{UO}_2]$ is justified.

2.1. Experiments

While the preparation of uranyl-sulphatocomplexes of the (BTMA) cation was being attempted, the title compound was formed accidentally. Fairly concentrated solutions of $(\text{BTMA})\text{Cl}$ (in methanol) and $\text{UO}_2\text{SO}_4 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ (in water) were mixed in a ratio of 2. Both substances were commercial products of reagent grade, and were used without further purification. About 2 per cent by volume of concentrated H_2SO_4 was added, and the clear mixture was heated for about one hour. After several days, during which the mixture stood open to the air, a sulphate complex had formed, which was then filtered off. Again, after some days, platelike, green crystals, probably consisting of a uranyl-chloride complex, formed and were filtered off. Finally, in the remaining mother liquid (which had a pH value of 0.5), orange-yellow crystals grew, which were then recrystallized from methanol. Although these crystals were stable in air when dry, they slowly became green and changed their habit after being kept in methanol for several months.

The described preparation of the orange-coloured product was repeated. Its composition was not revealed until the X-ray analysis of the crystal structure, but a subsequent chemical analysis confirmed the given title formula (uranium found 34.0 per cent, calculated 34.37 per cent, chlorine found 15.1 per cent, calculated 15.38 per cent). The melting-point of the substance, which is fairly soluble in water, was found to be about 190°C. In addition to the peaks due to the organic cation and to the asymmetric uranyl vibration²⁶ at about 930 cm^{-1} , the infrared spectrum showed a strong absorption at about 905 cm^{-1} , which might be assigned¹⁸ to the stretching frequency of the peroxy-group O-O (890 cm^{-1} for H_2O_2).

An orange-yellow crystal from the original preparation was chosen for structural determination by X-rays. The crystal had the form of a parallelepiped having dimensions of approximately 0.11 by 0.17 by 0.27 mm ($\bar{\mu} = 103.5 \text{ cm}^{-1}$ for Mo K α). Precession and Weissenberg photographs showed that the crystal was monoclinic, with systematic absences leading to the centrosymmetrical space-group $P2_1/c$. The lattice constants, which were determined precisely on a two-circle automatic diffractometer having Weissenberg equi-inclination geometry (STADI 2 from Stoë, Darmstadt), were $a = 8.869 \pm 0.005 \text{ \AA}$, $b = 11.013 \pm 0.005 \text{ \AA}$, $c = 25.60 \pm 0.01 \text{ \AA}$, and $\beta = 103.66 \pm 0.10^\circ$ (cell volume = 2430 \AA^3).

The diffractometer was then used to measure 5362 reflections (graphite monochromatized Mo-K α_1 radiation, ω -scan, θ -dependent scan width, counting time for 0.02° step 1 second, either background 20 seconds, seven layers $0kl \dots 6kl$, $\theta_{\text{max}} = 30^\circ$ for the first two, and $\theta = 20^\circ$ for the rest of the layer lines). The data reduction³⁰ consisted of Lp- and an approximate spherical-absorption correction ($\bar{\mu}R = 1.13$) (also see the Appendix), omission of systematic absent, zero-intensity and $F \leq 2\sigma$ reflections, and a merging of symmetry-related reflections. Calculations were done with 2442 unique reflections, and the least-squares refinement was based on F . The necessary computations were done with the crystallographic computer-programme SHELX³¹ and the atomic-scattering factors of Cromer and Mann³² for the lighter atoms. For uranium, the respective values of Doyle and Turner³³ were used, together with the real and imaginary correction factors for anomalous dispersion of Cromer and Liberman³¹. Neutral atoms were assumed throughout.

A three-dimensional Patterson synthesis revealed the positions of the uranium atoms, and subsequent Fourier syntheses, together with full-matrix least-squares refinement, the rest of the atoms, all of which occupy the general position $4e$ in $P2_1/c$.

The UO_2 group, three coordinating Cl atoms, and one (BTMA) cation were located easily, but interpretation of the electron density between the two closely approaching uranium atoms linked by a centre of symmetry was not straightforward. The best fit — also in view of normally occurring temperature parameters — was obtained by introduction of a peroxogroup across $\bar{1}$ as a bridging entity. Together with the second (BTMA) cation, which was then found by different Fourier methods, the asymmetric unit consists of $(\text{BTMA})_2[\text{UO}_2\text{Cl}_3(\text{O}_2)_1]$, four of which fit into one unit cell (calculated density 1.89 g/cm^3). Least-squares refinement, including all atoms, variation of interlayer scaling-factors, and anisotropic treatment of uranium and chlorine, finally resulted in a conventional residual index $R = 0.114$ and a simple $1/\sigma(F)^2$ weighting scheme yielded a quadratic $R_w = 0.072$, where

$$R = \frac{\sum |F_o - |F_c||}{\sum F_o}, \quad R_w = \sqrt{\frac{\sum w(F_o - |F_c|)^2}{\sum wF_o^2}}$$

The final atomic positions are given in Table 1, and some distances and angles are given in Table 2. Figure 5 shows a projection of the structure along $[010]$. A list of observed and calculated structure factors is available on request.

2.2. Discussion

The title compound that was arrived at can be described as consisting of puckered sheets of binuclear $[\text{UO}_2\text{Cl}_3\text{-O}_2\text{-Cl}_3\text{UO}_2]^+$ anions parallel to the a, b -plane, interleaved by $(\text{BTMA})^+$ cations that are arranged along the c -axis. The positive ammonium 'heads' of the two crystallographically different (BTMA) molecules point alternately to the one and to the other side in the direction of the anionic groups, while their phenyl 'tails' make up an inner uncharged section averse from them. The distances of uranium to nitrogen are in the range 5.10 to 5.93 \AA .

The average distances and angles in both (BTMA) molecules do not deviate significantly from what is expected³³: N-C (ammonium group) = 1.493 \AA and 1.498 \AA for the first and second (BTMA) respectively (expected 1.479 \AA), C-C (phenyl ring) = 1.367 \AA and 1.374 \AA (1.395 \AA), C-N-C (tetrahedral angle) = 109.47° and 109.70° (109.47°), C-C-C (hexagon angle) = 119.97° and 119.88° (120°). The N-C-phenyl angle on the methylene group is somewhat larger than the tetrahedral angle (115.0° , 115.1°), probably owing to steric repulsion. All the atoms of both benzyl groups lie in a common plane and have a maximum deviation of less than 0.04 \AA .

The binuclear anion $[\text{UO}_2\text{Cl}_3\text{-O}_2\text{-Cl}_3\text{UO}_2]^+$ can best be described as consisting of two identical (since they are linked by a centre of symmetry), irregular, pentagonal bipyramids, sharing the

peroxogroup as a common edge. The central uranium atom lies in one plane with its five equatorial ligands (the maximum deviation from the best plane through uranium, the three chlorine atoms, and the peroxy-entity is 0.14 Å) nearly vertical to the arrangement of the linear uranyl group. The linearity of the latter is not required by the space group. The O-O distance in the peroxogroup is the same as that found in other peroxides (see Section 2), and the mean U-O (peroxy) distance complies, within the limits of error, with that²² in the structure of $\text{Na}_4\text{UO}_8 \cdot 9\text{H}_2\text{O}$ (2.30 Å against 2.27 Å). The U-O (uranyl) as well as the U-Cl distances (mean 1.778 Å and 2.713 Å respectively) are in good agreement with those determined in other uranyl and uranyl-chloride compounds^{15, 36}.

It is thought that the large standard deviations in the positions of the atoms, and hence in the distances between them, are mainly due to the strong scattering power of uranium in relation to that of the very much lighter atoms present, which renders the precise positioning of the latter difficult. Therefore, much depends on the scattering behaviour of uranium and thus the proper choice of its scattering factors. Besides the factors mentioned, use was made of the scattering factors of Cromer and Waber³⁷ for neutral uranium and for U^{6+} , and different factors for anomalous dispersion were also employed (e.g., those used by Roof³⁸) or omitted altogether. In all instances, no better results were obtained, and the same is true for the introduction of an extinction parameter that was subjected to least-squares refinement. In the different Fourier maps, some electron density was always found, left round uranium at a distance of less than 1 Å, which could not be accounted for by thermal motion, and probably reflects an inadequate description of the scattering by uranium atoms.

In the described preparation of the peroxocomplex without the initial addition of any peroxide, the manner of formation is not yet understood. A possible mechanism could be the addition of molecular oxygen onto a uranyl-chloride complex with subsequent reduction by the methanol present, involving an intermediate, mixed-valency uranium species. Bayer and Schretzmann³⁹ claim that similar oxygenation takes place for $[(\text{NH}_3)_5\text{Co}-\text{O}_2-\text{Co}(\text{NH}_3)_5] (\text{NO}_3)_6$, the cation of which compound displays nearly the same structural features as were found for the binuclear uranyl anion. Some older work¹⁸ reports the formation of a uranyl-peroxy-carbonatocomplex in the presence of alcohol, also without added H_2O_2 . However, any attempt to prepare the compound by bubbling of pure oxygen through an acid aqueous-methanolic solution of 4 (BTMA)Cl/ UO_2Cl_2 (also under ultraviolet radiation) proved unsuccessful (see the Appendix). Therefore, it is possible that the formation of the peroxocomplex is directly linked to the solid state, in which packing effects due to the elongated form of the (BTMA) cation play a dominating role. For further information on inorganic dioxygen carriers, which are essential in biological systems, the reader is referred to the review of Bayer and Schretzmann³⁹ and the more recent review of McLendon and Martell²⁶.

3. ACKNOWLEDGEMENT

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4. REFERENCES

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TABLE I
 Fractional atomic coordinates x, y, z , and temperature parameters U
 of the asymmetric unit

Atom	x	y	z	U_{11}/U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U	0.1690(2)	0.6365(1)	0.5366(1)	0.0466(7)	0.0364(6)	0.0567(8)	0.0020(7)	0.0044(6)	-0.0005(6)
O1	0.3181(24)	0.5424(17)	0.5224(7)	0.0378(48)					
O2	0.0226(26)	0.7306(19)	0.5515(8)	0.0479(55)					
O3	0.0116(28)	0.4695(21)	0.5267(8)	0.0576(62)					
Cl1	0.2206(11)	0.5562(8)	0.6384(3)	0.0593(25)	0.0661(52)	0.0525(45)	-0.0107(49)	0.0059(46)	0.0116(42)
Cl2	0.4012(12)	0.7952(7)	0.5802(4)	0.0648(28)	0.0338(40)	0.0958(62)	-0.0067(45)	-0.0084(57)	0.0030(45)
Cl3	0.1453(11)	0.7699(8)	0.4455(3)	0.0565(24)	0.0578(46)	0.0551(45)	-0.0016(47)	0.0031(45)	0.0178(41)
N1	0.2511(34)	0.4694(25)	0.3511(10)	0.0523(73)					
C1	0.2056(54)	0.3448(41)	0.3365(17)	0.0858(135)					
C2	0.3964(56)	0.5029(43)	0.3329(18)	0.0909(141)					
C3	0.2836(55)	0.4787(43)	0.4110(18)	0.0898(140)					
C4	0.1190(44)	0.5529(32)	0.3261(14)	0.0566(94)					
C5	0.0703(36)	0.5488(25)	0.2656(11)	0.0251(69)					
C6	-0.0415(51)	0.4663(38)	0.2395(16)	0.0762(120)					
C7	-0.0843(64)	0.4685(50)	0.1872(21)	0.1079(167)					
C8	-0.0215(60)	0.5390(47)	0.1532(19)	0.0977(152)					
C9	0.0867(53)	0.6235(40)	0.1806(17)	0.0818(125)					
C10	0.1308(47)	0.6255(36)	0.2345(15)	0.0707(110)					
N2	0.3323(35)	0.3572(27)	0.0506(11)	0.0602(79)					
Cl11	0.3135(41)	0.2224(30)	0.0440(12)	0.0499(86)					
Cl12	0.2542(49)	0.4073(37)	-0.0035(15)	0.0739(115)					
Cl13	0.5024(40)	0.3875(30)	0.0596(12)	0.0502(85)					
Cl14	0.2629(40)	0.3980(30)	0.0950(12)	0.0517(87)					
Cl15	0.3398(39)	0.3497(28)	0.1493(12)	0.0458(81)					
Cl16	0.4620(48)	0.4059(37)	0.1832(16)	0.0742(116)					
Cl17	0.5348(43)	0.3603(34)	0.2327(13)	0.0587(93)					
Cl18	0.4768(46)	0.2574(34)	0.2510(15)	0.0614(98)					
Cl19	0.3465(42)	0.2054(30)	0.2219(13)	0.0513(86)					
C20	0.2777(47)	0.2499(35)	0.1716(15)	0.0664(106)					

Note:

The error in the last digit is given in parentheses.
 The temperature parameter U is given either as isotropic U_{iso}
 or as anisotropic U_{ij} , referring to the expression
 $\exp[-2\pi^2(U_{11}h^2a^2 + \dots + 2U_{12}h_1h_2a^2b^2 + \dots)]$, i.e., in terms of
 mean-square amplitudes of vibration in Å^2 .

TABLE 2

Some distances and angles in the structure of (BTMA)_n[UO₂Cl₅O₇Cl₃UO₂]

The error in the last digit is given in parentheses.

	Distance, Å		Angle, °
U-U'	4,346 (38)	U'-U-01	88,8 (7)
U-01	1,784 (27)	U'-U-02	91,8 (8)
U-02	1,772 (28)	01-U-02	179,3 (1,0)
U-03	2,287 (30)	03-U-C13	76,8 (6)
U-03'	2,308 (28)	C13-U-C12	84,4 (4)
U-C11	2,687 (8)	C12-U-C11	82,8 (4)
U-C12	2,731 (28)	C11-U-03	78,6 (6)
U-C13	2,772 (10)	03'-U-03	37,9 (8)
03'-03	1,493 (29)	C11-03'-03	128,0 (1,5)
03-C11	3,166 (28)	03'-03-C13	127,8 (1,5)
C11-C12	3,583 (31)	03-C13-C12	93,4 (5)
C12-C13	3,664 (25)	C13-C12-C11	95,6 (4)
C13-03	3,140 (33)	C12-C11-03'	94,0 (5)
N1-C1	1,454 (53)	C1-N1-C2	110,8 (3,0)
N1-C2	1,516 (51)	C1-N1-C3	107,6 (3,0)
N1-C3	1,495 (51)	C1-N1-C4	109,0 (2,7)
N1-C4	1,508 (45)	C2-N1-C3	109,1 (2,9)
C4-C5	1,507 (44)	C2-N1-C4	110,7 (2,7)
C5-C6	1,394 (49)	C3-N1-C4	109,6 (2,7)
C6-C7	1,401 (66)	N1-C4-C5	115,0 (2,7)
C7-C8	1,306 (70)	C4-C5-C6	120,7 (2,9)
C8-C9	1,405 (64)	C4-C5-C10	121,9 (2,9)
C9-C10	1,342 (56)	C6-C5-C10	117,4 (3,0)
C10-C5	1,355 (47)	C5-C6-C7	118,1 (3,7)
		C6-C7-C8	124,1 (4,7)
		C7-C8-C9	116,1 (4,4)
		C8-C9-C10	121,3 (4,0)
		C9-C10-C5	122,5 (3,5)
N2-C11	1,499 (44)	C11-N2-C12	104,2 (2,6)
N2-C12	1,499 (47)	C11-N2-C13	108,5 (2,5)
N2-C13	1,509 (44)	C11-N2-C14	109,3 (2,5)
N2-C14	1,484 (42)	C12-N2-C13	106,7 (2,5)
C14-C15	1,494 (43)	C12-N2-C14	114,3 (2,7)
C15-C16	1,366 (49)	C13-N2-C14	113,4 (2,5)
C16-C17	1,374 (52)	N2-C14-C15	115,1 (2,6)
C17-C18	1,372 (52)	C14-C15-C16	123,3 (3,0)
C18-C19	1,346 (47)	C14-C15-C20	121,2 (2,9)
C19-C20	1,378 (50)	C16-C15-C20	115,0 (3,0)
C20-C15	1,409 (49)	C15-C16-C17	123,3 (3,5)
		C16-C17-C18	119,0 (3,3)
		C17-C18-C19	120,3 (3,4)
		C18-C19-C20	119,9 (3,3)
		C19-C20-C15	121,8 (3,2)

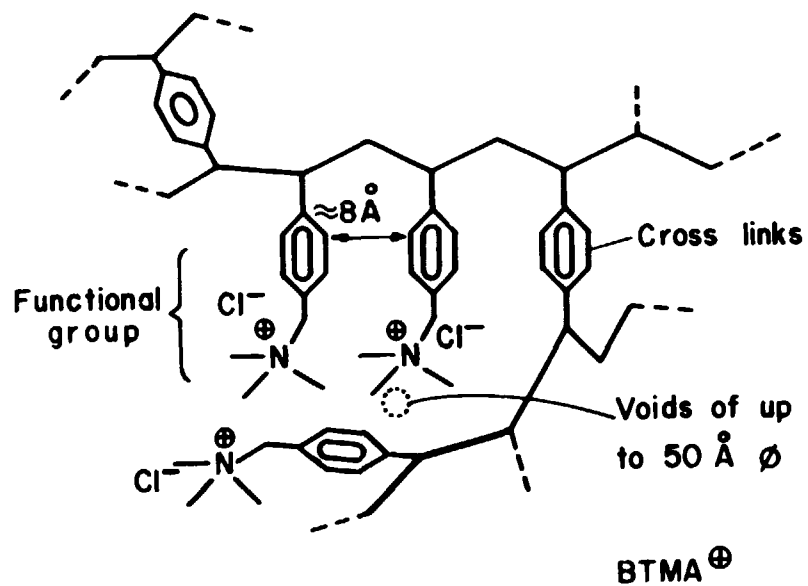


FIGURE 1 A typical strong-base anionic-exchange resin

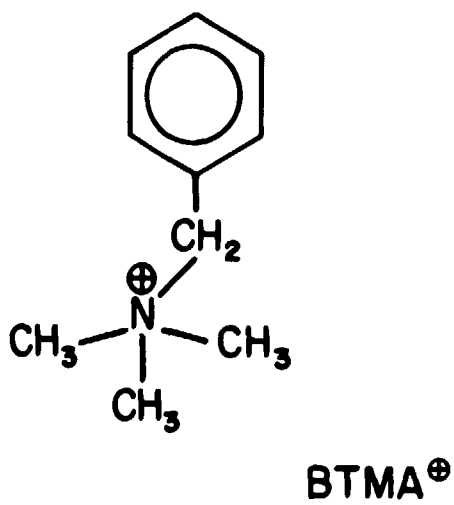


FIGURE 2 The benzyl-trimethylammonium (BTMA) cation

MODEL SYSTEMS IN ANIONIC EXCHANGE

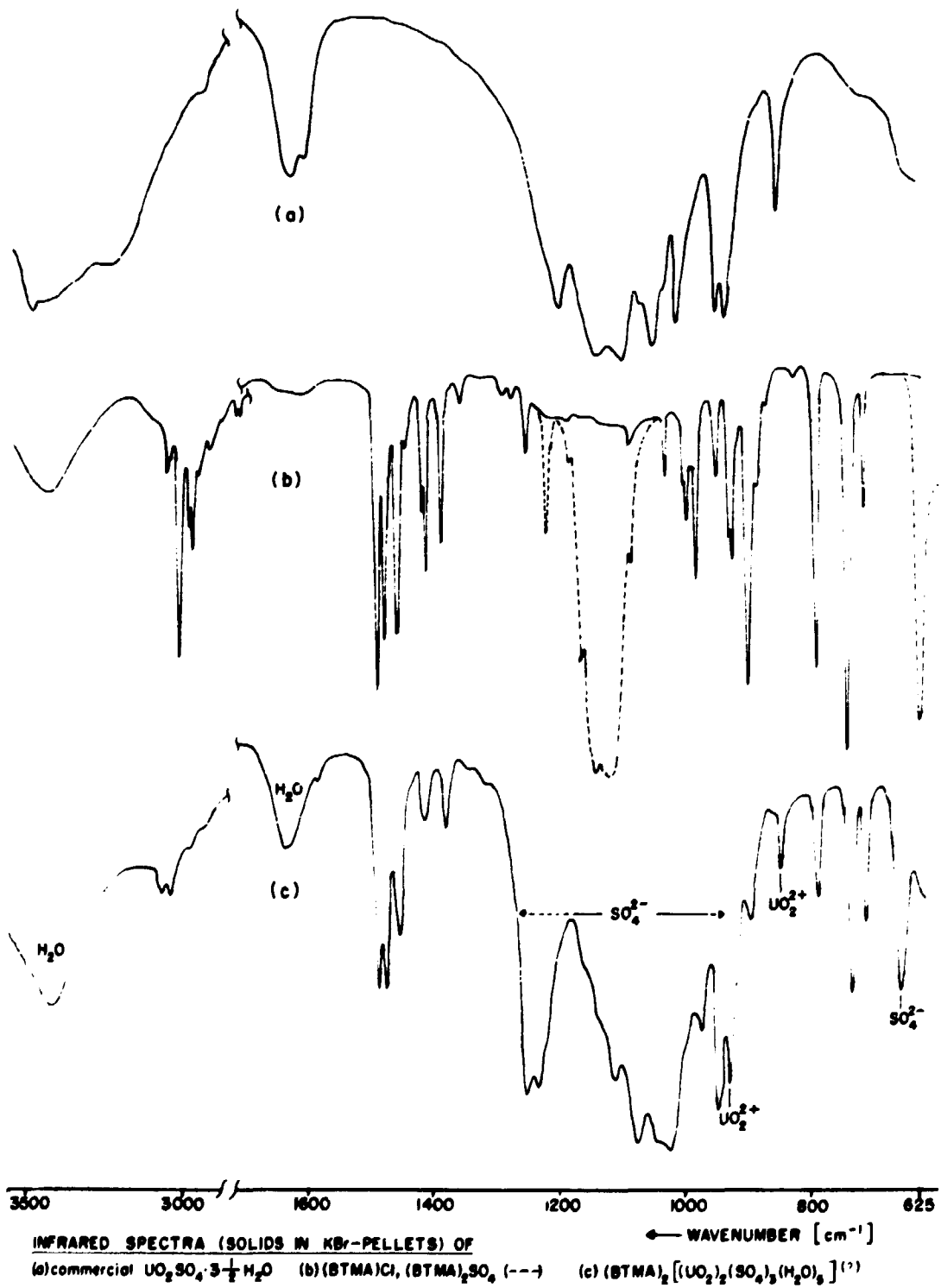


FIGURE 3 Comparison of the infrared spectra of some compounds containing UO_2^{2+} , (BTMA), SO_4^{2-} , and H_2O .

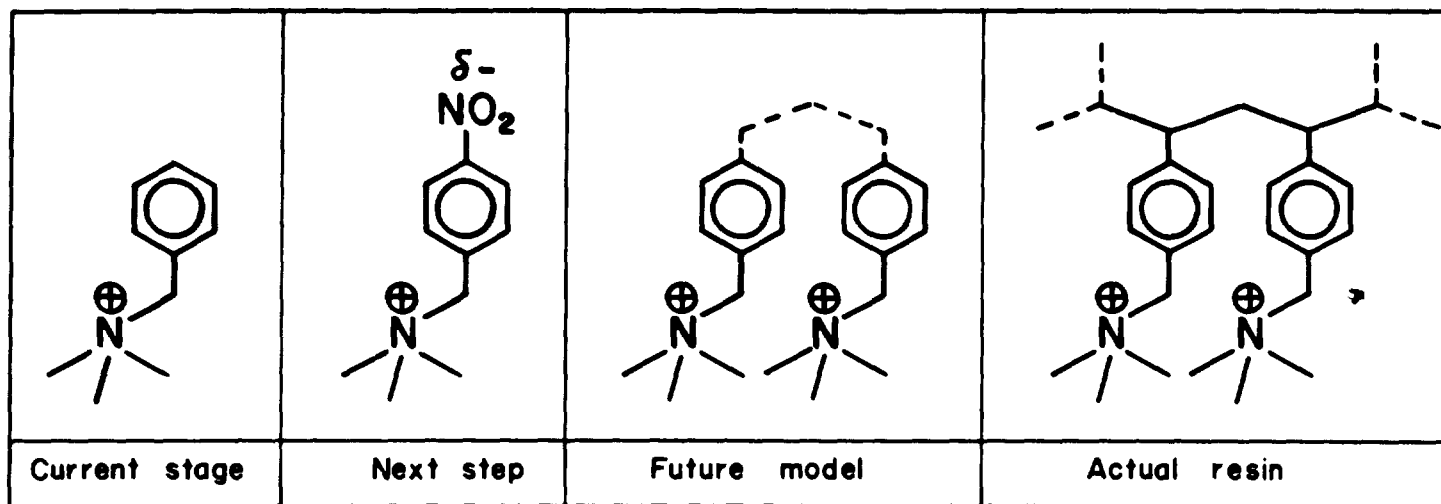
BTMA[⊕]

FIGURE 4 Functional cationic groups

MODEL SYSTEMS IN ANIONIC EXCHANGE

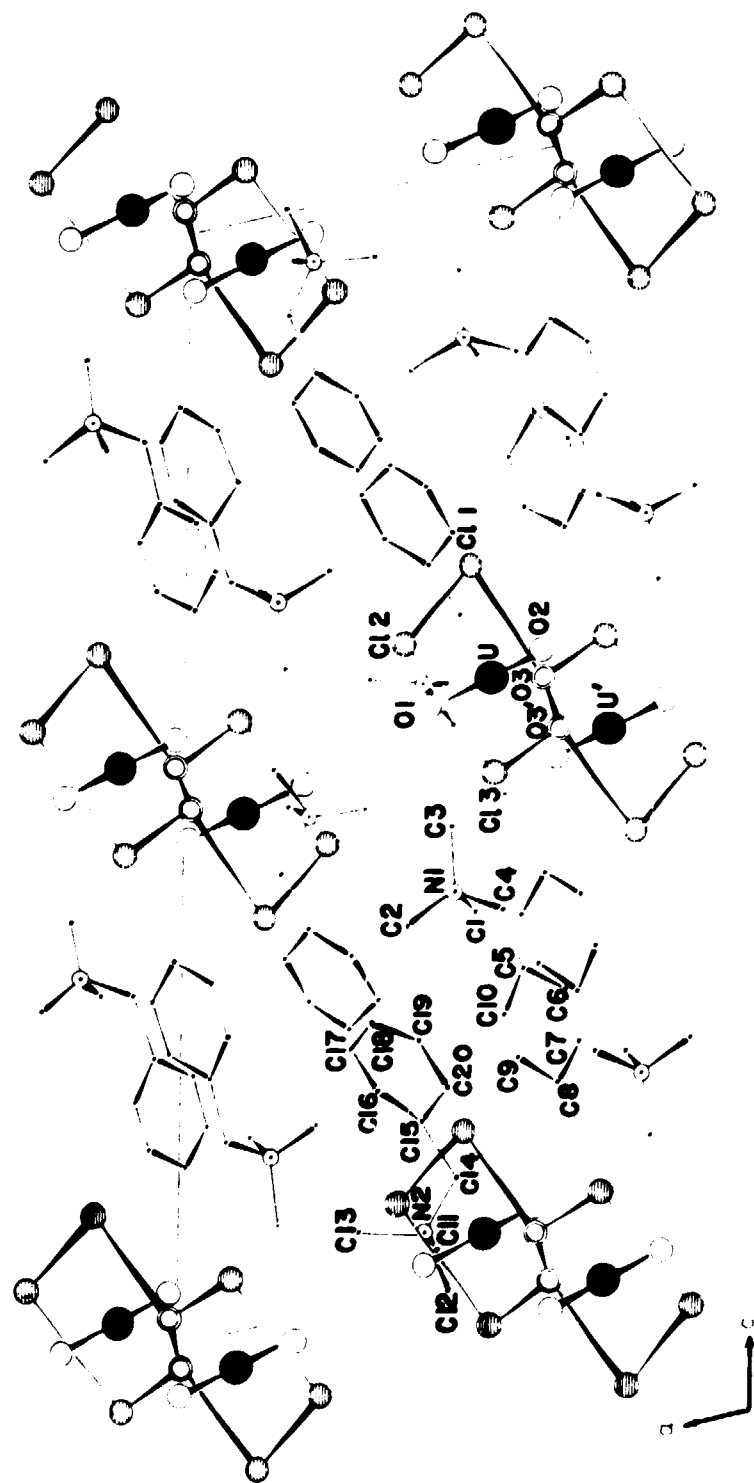


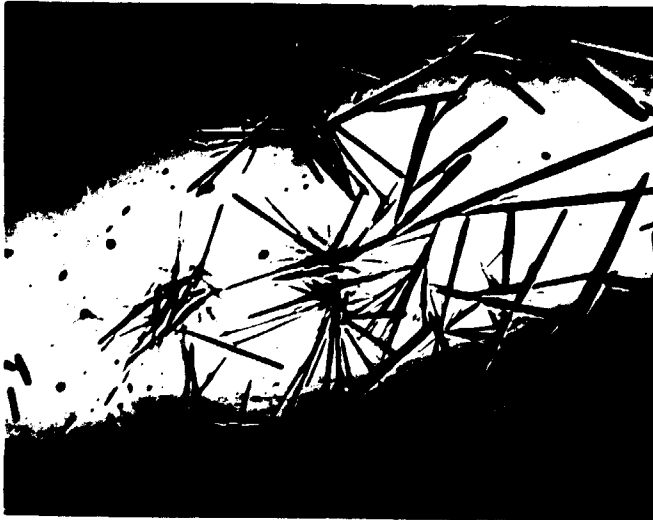
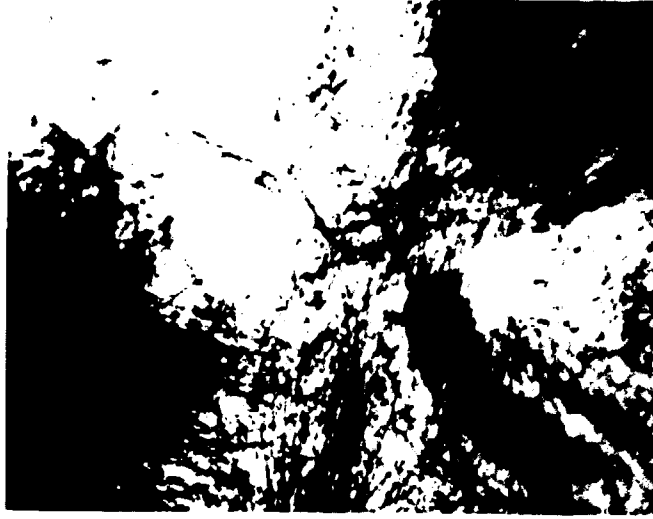
FIGURE 5 Projection of the unit cell along the monoclinic b -axis.

MODEL SYSTEMS IN ANIONIC EXCHANGE

PLATE I

Photomicrographs of $(\text{BTMA})_2[(\text{UO}_2)_2(\text{SO}_4)_3(\text{H}_2\text{O})_3]$

- Top: The original crystalline product.
Magnification 50 \times .
- Bottom: Crystals formed by slow diffusion into acetone of an aqueous solution of the original crystalline product.
Magnification 50 \times .



APPENDIX

THE DATA-REDUCTION ROUTINE, AND ATTEMPTS
TO SYNTHESIZE THE PEROXOCOMPOUND

The data reduction was done by use of a computer, which was programmed to allow for uneven background readings. Whenever the crystal is slightly disorientated during intensity measurements — by whatever effects, thermal or mechanical — it is useful to correct for misreadings caused by this disorientation. On the assumption that the peak profile is of Gaussian type and that the peak maximum lies inside the scanning range (see Figure 1-1.a), the following correction is applied:

$$P = P_u(1 + F^2), \text{ with } F = QU / \exp \{(QU-1)^2/QP^2\}$$

where P is the corrected intensity

P_u is the uncorrected intensity

$$QP = UNT/P_u$$

$$QU = |UDIF|UNT$$

UNT is the total background-reading

$UDIF$ is the difference between left and right background-readings.

The characteristic of the correction function $F_{QU, QP}$ is shown in Figure 1-1.b.

It is easily seen that, for the described correction to be applied, it is necessary for the peak maximum to remain inside the (linear) scanning range. However, if the disorientation is such that the maximum lies completely outside the range, i.e., if the crystal is misaligned in a more general, two-dimensional manner (see Figure 1-1.c.), the correction still improves the measurement, but will, of necessity, never come close to the true value.

A small FORTRAN programme has been written to apply a spherical absorption correction on measured intensity data. Tabulated factors for absorption correction are used. If the crystal under study contains heavy elements, it is always advisable to allow for absorption effects. It is simplest to assume that the crystal is a sphere, for which the correction is only θ -dependent. However, if the crystal is not a real sphere, an approximation can be made by conversion of the actual volume of the crystal to that of a sphere having equal volume, from which the radius of the latter is determined as

$$R = \sqrt[3]{\frac{3}{4\pi} \text{vol (crystal)}}.$$

Obviously, this simplification applies only to specimens having shapes that are not too extreme.

Attempts have been made to synthesize directly the described peroxocompound. After nearly stoichiometric amounts of $\text{UO}_2\text{Cl}_2 \cdot x \text{H}_2\text{O} + 4(\text{BTMA})\text{Cl} + \text{UO}_4 \cdot x \text{H}_2\text{O}$ (these substances having been prepared especially for this purpose) were mixed in water, or diluted H_2O_2 was added to an aqueous solution of $\text{UO}_2\text{Cl}_2 + 2(\text{BTMA})\text{Cl}$ (whereupon pale-yellow uranium peroxide, $\text{UO}_4 \cdot x \text{H}_2\text{O}$, is precipitated instantaneously), and slight heating of the mixtures, which were then allowed to stand open to the air, a microcrystalline orange solid formed after several days. However, for KCl instead of $(\text{BTMA})\text{Cl}$, neither a change of colour nor crystallization took place. Attempts to recrystallize the orange solid from water or methanol, or a mixture of both, failed, and large green crystals formed instead. If it is assumed that a peroxide-containing complex is formed initially, it seems that this complex decomposes in favour of a simple chloride complex. Any physical experiments with the microcrystalline solid appeared senseless: no uniform product could be expected since the water content of the starting material, and thus the exact stoichiometry of the mixture, were unknown.

The orange colour of the obtained solid seems to indicate the formation of the required compound, but its subsequent slow decomposition during recrystallization does not support this view. As mentioned earlier, the original crystals on which the determination of the structure was carried out were obtained by recrystallization from methanol. However, in the open air, these crystals also formed a green product after a time. Therefore, it is possible that a certain partial pressure of oxygen is necessary to prevent decomposition of the peroxide. Further investigations in this direction were abandoned when the project was terminated.

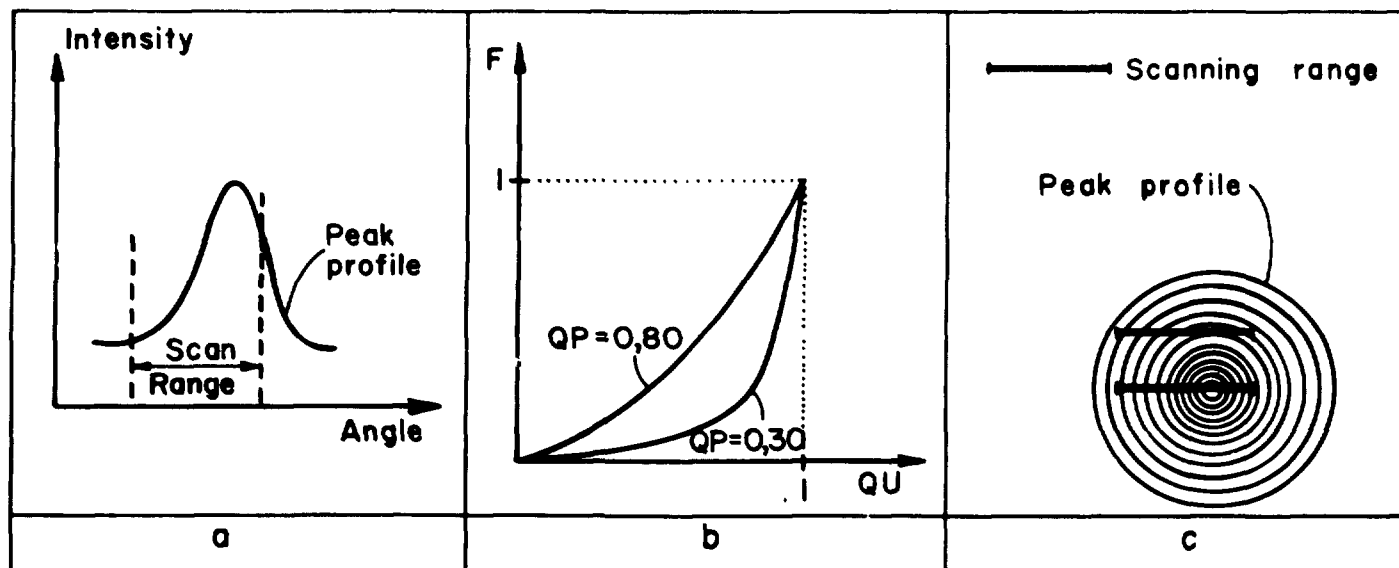


FIGURE I-1 Correction of misreadings during intensity measurements