The Chemistry of the Trivalent Actinoids.
Part 7 [1]. Crystal Structure Analysis of $[NH_4]U[SO_4]_2 \cdot 4H_2O$ and Comments on the Structure of $U_2[SO_4]_3 \cdot 9H_2O$

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The crystal structure of an hydrated uranium-(III) compound has been determined for the first time. Crystals of $[NH_4]U[SO_4]_2 \cdot 4H_2O$ are monoclinic with a = 6.7065(2), b = 19.0328(6), c = 8.8305(3) Å, β = 97.337(1)°, z = 4 and space group $P2_1/c$. The structure was solved by the heavy-atom method from Cu-K_α diffractometer data, and refined by full-matrix least squares to R = 0.096 for 1647 observed reflections. The compound is isostructural with $[NH_4]M[SO_4]_2 \cdot 4H_2O$ (M = La–Tb, except Pm). Each uranium atom is coordinated to nine oxygen atoms; six of them are contributed by four sulphate groups and the remaining three are from water molecules. The uranium–oxygen bond lengths were 2.37–2.60 Å (to sulphate ion) and 2.47–2.56 Å (to water). Each asymmetric unit contains a non-coordinated water molecule. The X-ray powder diffraction photograph of a substance previously reported as $U_2[SO_4]_3 \cdot 8H_2O$ and that of $La_2[SO_4]_3 \cdot 9H_2O$ showed that these compounds are isomorphous, with space group $P6_3/m$. Thus, the stoichiometry $U_2[SO_4]_3 \cdot 9H_2O$ is more likely with nine/twelve-coordination to the metal ions than is the eight-coordination found for the lanthanoid(III) sulphate octahydrates and $Am_2[SO_4]_3 \cdot 8H_2O$. By comparing the diffuse reflectance electronic spectra of the title compounds with those of various uranium(III) solutions, it is confirmed that both water and sulphate ion have similar nephelauxetic factors.

Introduction

Few structural data are available for uranium(III) compounds and are limited to simple, anhydrous compounds: UH_3 (a metallic- rather than salt-like substance with coordination number (C.N.) of 12) [2], UF_3 (C.N. = 11) [3], UCl_3 [4] and UBr_3 [5]

(both C.N. = 9), UOCl (no bond lengths quoted but isomorphous with PbClF) [6], and UI_3 (C.N. = 8) [7].

Most uranium(III) compounds are readily oxidised [8], but a few of the hydrated sulphates [8] are stable in air for a short period. By selecting $[NH_4]$-$U[SO_4]_2 \cdot 4H_2O$, previously reported [8] as $[NH_4]$-$U([SO_4]_2 \cdot 4.5H_2O$, we were able to manipulate the compound in air and, for the first time, to determine uranium(III)–oxygen bond lengths in an hydrated compound by crystallographic methods.

Previously [8] we had concluded that both title compounds contained the fully hydrated uranium-(III) ion (from a comparison of electronic spectra) and that the sulphate ions were non-coordinated (IR spectroscopy). These findings are shown to be in error by the present study, and the spectra are re-examined.

Experimental

Crystals of $[NH_4]U[SO_4]_2 \cdot 4H_2O$ were prepared as previously described [8], and were well-formed square prisms with approximate dimensions 0.2, 0.1, 0.1 mm measured along crystal edges parallel to *a* and at *ca.* 45° to *b* and *c* respectively.

Unit cell and space-group data were obtained from Weissenberg photographs and accurate unit-cell dimensions were obtained by a least-squares fit to the θ-values of 29 high-order reflections measured on a Siemens single-crystal diffractometer (A.E.D.), using nickel-filtered, Cu-K_α radiation ($\bar{\lambda} = 1.5418$ Å). Crystal data for $[NH_4]U[SO_4]_2 \cdot 4H_2O$ and the isomorphous La [9] and Sm [9] compounds are listed in Table I; the ammonium double sulphates $[NH_4]M[SO_4]_2 \cdot 4H_2O$ (M = La–Tb, except Pm) are isomorphous. The unit-cell dimensions for U fall between those of the La and Ce salts, and not between those of Ce and Pr as might have been expected from the published ionic radii [10]. The

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TABLE I. Crystal Data for $[NH_4]M[SO_4]_2 \cdot 4H_2O$.

M	U^a	La^b	Sm^b
M_r	520.19	421.07	432.56
Crystal system	monoclinic	monoclinic	monoclinic
$a/Å$	6.7065(2)	6.719(1)	6.582(2)
$b/Å$	19.0328(6)	19.073(4)	18.886(7)
$c/Å$	8.8305(3)	8.843(2)	8.736(4)
β/deg	97.337(1)	97.45(2)	96.88(4)
$V_c/Å^3$	1117.9(5)	1123.7(6)	1078.1(11)
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
Z	4	4	4
$D_x/g\ cm^{-3}$	3.07	–	2.67
$\mu(CuK_\alpha)/cm^{-1}$	481	–	414
$F(000)$	956	–	–

[a]Present work.   [b]Ref. [9].

TABLE II(a). Final Positional Parameters.[a]

Atom	x	y	z
U(1)	3532(2)	1212(1)	2161(1)
S(1)	8198(13)	760(5)	2379(12)
S(2)	3801(17)	2771(5)	895(11)
O(1)	8743(52)	44(20)	2637(49)
O(2)	6590(41)	820(21)	992(45)
O(3)	7141(45)	1104(17)	3598(35)
O(4)	9982(45)	1192(11)	2097(38)
O(5)	1982(48)	2385(13)	1178(30)
O(6)	3751(55)	2952(14)	9270(29)
O(7)	5520(41)	2274(14)	1266(25)
O(8)	4051(52)	3403(14)	1850(31)
O(9)	2552(69)	1069(17)	−713(31)
O(10)	3181(48)	−66(18)	1704(37)
O(11)	3255(48)	542(15)	4650(26)
O(12)	8591(64)	3884(18)	1658(40)
N(1)	8461(54)	2771(20)	3903(49)

TABLE II(b). Final Thermal Parameters.[a,b]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U(1)	561(9)	277(7)	219(7)	−9(4)	25(5)	−15(3)
S(1)	461(45)	369(45)	575(54)	−30(34)	87(41)	6(38)
S(2)	754(64)	312(41)	290(48)	34(41)	−23(44)	−13(34)
O(1)	729(205)	605(217)	1500(286)	20(171)	89(189)	231(205)
O(2)	350(146)	866(257)	801(270)	−33(151)	−148(156)	−312(212)
O(3)	650(156)	900(197)	388(157)	160(135)	170(130)	234(140)
O(4)	805(171)	174(122)	658(207)	−118(104)	68(146)	−32(106)
O(5)	713(194)	322(118)	506(133)	102(124)	77(129)	17(98)
O(6)	1518(259)	381(135)	113(123)	217(153)	49(140)	−100(101)
O(7)	548(174)	642(155)	498(117)	54(133)	89(113)	26(106)
O(8)	1104(210)	430(136)	377(138)	54(144)	−23(140)	−73(115)

TABLE II(b). *(continued)*

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(9)	1699(348)	534(157)	109(131)	−45(200)	184(171)	7(120)
O(10)	816(184)	597(199)	543(178)	−85(154)	271(148)	−283(157)
O(11)	679(201)	457(158)	402(117)	−99(143)	153(123)	71(108)
O(12)	1134(290)	720(203)	500(177)	−88(183)	−84(170)	−108(147)
N(1)	553(201)	629(215)	321(272)	57(166)	−48(186)	−46(191)

[a]All values are multiplied by 10^4 and include estimated standard deviations in parentheses.   [b]Anisotropic temperature factors were of the form:

$$\exp\{-2\pi^2[h^2a^{*2}U_{11} + \cdots\cdots + 2hka^*b^*U_{12} + \cdots\cdots]\}.$$

TABLE III. Bond Lengths/Å and Angles/deg involving U(1).[a,b]

U–O(2)	2.52(3)	U–O(7)	2.60(3)
U–O(3)	2.59(3)	U–O(9)	2.54(3)
U–O(4)[(i)]	2.37(3)	U–O(10)	2.47(3)
U–O(5)	2.57(3)	U–O(11)	2.56(3)
U–O(6)[(ii)]	2.44(3)		
O(2)–U–O(3)	54.4(1.0)	O(4)[(i)]–U–O(9)	81.0(1.3)
O(2)–U–O(4)[(i)]	148.3(1.1)	O(4)[(i)]–U–O(10)	84.6(0.9)
O(2)–U–O(5)	115.8(1.1)	O(4)[(i)]–U–O(11)	80.3(1.0)
O(2)–U–O(6)[(ii)]	122.1(1.2)	O(5)–U–O(6)[(ii)]	70.8(0.8)
O(2)–U–O(7)	68.3(1.1)	O(5)–U–O(7)	54.7(0.9)
O(2)–U–O(9)	71.5(1.3)	O(5)–U–O(9)	73.5(0.9)
O(2)–U–O(10)	73.0(1.2)	O(5)–U–O(10)	140.8(0.9)
O(2)–U–O(11)	110.7(1.1)	O(5)–U–O(11)	130.6(0.9)
O(3)–U–O(4)[(i)]	151.8(1.1)	O(6)[(ii)]–U–O(7)	74.9(0.9)
O(3)–U–O(5)	123.1(1.0)	O(6)[(ii)]–U–O(9)	144.1(1.0)
O(3)–U–O(6)[(ii)]	73.6(1.1)	O(6)[(ii)]–U–O(10)	139.7(1.0)
O(3)–U–O(7)	74.1(0.9)	O(6)[(ii)]–U–O(11)	71.2(0.9)
O(3)–U–O(9)	125.7(1.2)	O(7)–U–O(9)	81.9(1.0)
O(3)–U–O(10)	93.7(1.0)	O(7)–U–O(10)	139.3(1.0)
O(3)–U–O(11)	73.1(1.0)	O(7)–U–O(11)	138.0(0.8)
O(4)[(i)]–U–O(5)	69.1(0.9)	O(9)–U–O(10)	74.1(1.0)
O(4)[(i)]–U–O(6)	89.5(1.1)	O(9)–U–O(11)	139.4(1.0)
O(4)[(i)]–U–O(7)	123.8(0.8)	O(10)–U–O(11)	68.5(1.0)
O(1)–S(1)–O(2)	110.0(2.2)	O(5)–S(2)–O(6)	111.4(1.8)
O(1)–S(1)–O(3)	115.9(2.2)	O(5)–S(2)–O(7)	106.2(1.6)
O(1)–S(1)–O(4)	111.0(1.8)	O(5)–S(2)–O(8)	110.4(1.8)
O(2)–S(1)–O(3)	100.9(1.8)	O(6)–S(2)–O(7)	106.4(1.7)
O(2)–S(1)–O(4)	108.9(1.9)	O(6)–S(2)–O(8)	110.7(1.6)
O(3)–S(1)–O(4)	109.7(1.7)	O(7)–S(2)–O(8)	111.4(1.7)

[a]Atoms marked with a superscript are generated from the corresponding atom in Table II by the symmetry operations:

(i) *x*, −1, *y*, *z*

(ii) *x*, ½ − *y*, ½ + *z*.

[b]Standard deviations in parentheses.

calculated density for the uranium compound provides good evidence for $Z = 4$ when compared with the density of the samarium salt.

A crystal of dimensions 0.17, 0.08, 0.08 mm was selected for the intensity measurements. The intensities of 1893 symmetry-independent reflections were measured on the diffractometer using the five-value measurement technique [11] with $\lambda^{-1}\sin\theta < 0.56$. A reference reflection, monitored after every 20 reflections, decreased in intensity by about 10% in the

TABLE IV. Comparative Bond Lengths/Å to Oxygen.

(i) Internal sulphur to oxygen bonds.

	[NH$_4$]Sm[SO$_4$]$_2$·4H$_2$O[a]	[NH$_4$]U[SO$_4$]$_2$·4H$_2$O[b]
S(1)–O(1)	1.42(1)	1.42(4)
S(1)–O(2)	1.50(1)	1.53(3)
S(1)–O(3)	1.49(1)	1.51(3)
S(1)–O(4)	1.50(1)	1.50(3)
S(2)–O(5)	1.49(1)	1.47(3)
S(2)–O(6)	1.47(1)	1.47(3)
S(2)–O(7)	1.49(1)	1.49(3)
S(2)–O(8)	1.46(1)	1.46(3)

(ii) Metal ion to oxygen distances

Compound	C.N.	Range of M–O	Ref.
[NH$_4$]Sm[SO$_4$]$_2$·4H$_2$O	9	2.38(1)–2.56(1)[c] 2.42(1)–2.51(1)[d]	[9]
Am$_2$[SO$_4$]$_3$·8H$_2$O	8	2.382(4)–2.509(4)[c] 2.406(5)–2.553(4)[d]	[14]
Pr$_2$[SO$_4$]$_3$·8H$_2$O	8	2.36(2)–2.52(2)[c] 2.37(1)–2.57(1)[d]	[15]
La$_2$[SO$_4$]$_3$·9H$_2$O	9, 12	2.51(1)[c,e] 2.59(1)[c,x] 2.55(1)[d,e] 2.80(1)[c,f]	[15]
AmCl$_3$·6H$_2$O	8	2.440(6)–2.471(5)	[16]
[NH$_4$]U[SO$_4$]$_2$·4H$_2$O	9	2.37(3)–2.60(3)[c] 2.47(3)–2.56(3)[d]	This work

[a]Ref. [9] numbering scheme changed to match ours.   [b]This work.   [c]To sulphate oxygen.   [d]To water oxygen.   [e]C.N. = 9.
[f]C.N. = 12.

course of data collection indicating slight crystal decomposition. The intensity data were scaled to a common value which allowed for the decomposition.

The intensity data were corrected for Lorentz and polarisation effects. The linear absorption coefficient, μ, was large and correction by the numerical integration method of Busing and Levy [12] was carried out, using a grid of 2400 points; transmission factors varied from 0.0374 to 0.1547.

Each measured intensity was assigned a variance based on counting statistics and 1647 reflections for which $I > 2.58\sigma(I)$ were used in the structure analysis.

Structure Determination and Refinement

The uranium atomic positions were deduced from a three-dimensional Patterson map. An electron density map phased on uranium then located the remaining non-hydrogen atoms. Weighted least-squares refinement, using anisotropic temperature factors, for all non-hydrogen atoms, with corrections for the anomalous dispersion of uranium and sulphur atoms, reduced R to 0.096. During the final cycle, the shifts in the parameters averaged to 0.005 Å. No attempt

was made to place hydrogen atoms. The final atomic and thermal parameters are listed in Table II. Bond lengths and angles are given in Tables III and IV, and the numbering scheme and environment about uranium are shown in Fig. 1. Figure 2 is a packing diagram of two unit cells projected on to the *ab* plane. In this structure, the electron density distribution around N(1) and O(12) was very similar, but there was no significant change in R on interchanging these atoms. The indicated positions are chemically the more probable, and are consistent with the isomorphous structure of ref. [9]. Observed and calculated structure factors can be obtained from the authors on request.

Results and Discussion

The Structure of [NH$_4$]U[SO$_4$]$_2$·4H$_2$O

This compound is isostructural with [NH$_4$]M-(SO$_4$)$_2$·4H$_2$O (M = La–Tb). A full structure analysis has been carried out for the samarium compound [9] and thus the geometry of this structure and ours differ in only minor details. The coordination sphere about uranium is made up by six oxygen atoms from
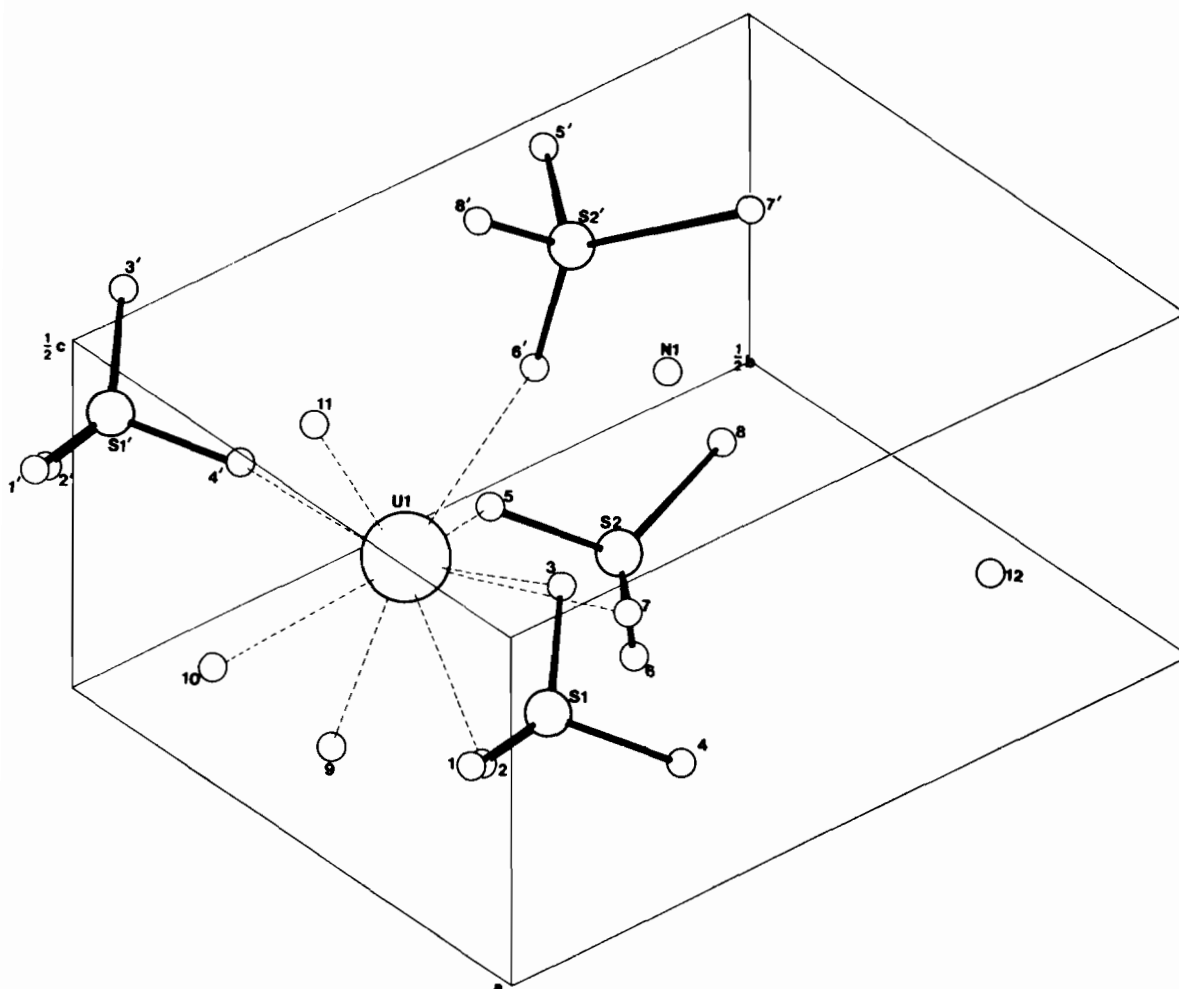
Fig. 1. Numbering scheme for $[NH_4]U[SO_4]_2 \cdot 4H_2O$ showing the environment around uranium.

four sulphate ions and three oxygen atoms from water molecules. The remaining water molecule, O(12), is not coordinated. There are two crystallographically-independent types of sulphate ion, $[S(1)O_4]^{2-}$ and $[S(2)O_4]^{2-}$. Both, however, coordinate in the same sense since O(2) and O(3), or O(5) and O(7), form a chelate ring to a single uranium atom and O(4), or O(6), makes a bridge to an adjacent uranium atom, with the remaining sulphate oxygen atom O(1), or O(8), non-coordinated. The stereochemistry about uranium is intermediate between two idealised polyhedra, namely, the tricapped trigonal prism and the monocapped square antiprism. Detailed calculations connecting these two geometries were presented [9] for the samarium compound. The short sulphate bite would impose restrictions on the lengths of the polyhedral edges involving bidentate sulphate groups formed by O(2), O(3) and O(5), O(7).

For the sulphate ion centred on S(1), the S(1)–O(1) bond length is shorter than the other three S(1)–O bond lengths, but not significantly (3σ) so unlike the corresponding bonds in the samarium compound [9] which were significantly different. This may result from O(1) being non-coordinated. In contrast, for the sulphate ion centred on S(2), the S–O bond lengths show no significant (3σ) differences in either structure although it was claimed [9] that a slightly longer S(2)–O(8) bond as compared with S(1)–O(1) was attributable to interaction of O(8) *via* hydrogen bonds with water molecules (see Table IV(i)).

Average bond lengths in a number of relevant compounds are compared in Table IV(ii). There are few significant differences between these M–O bond lengths and those reported in the present work. This is attributable mainly to the high standard deviations found in our and other work so that changes caused by different coordination numbers are not marked. An exception is the twelve-coordinate lanthanum atom in $La_2[SO_4]_3 \cdot 9H_2O$ where the M–O bonds to sulphate oxygen atoms are significantly
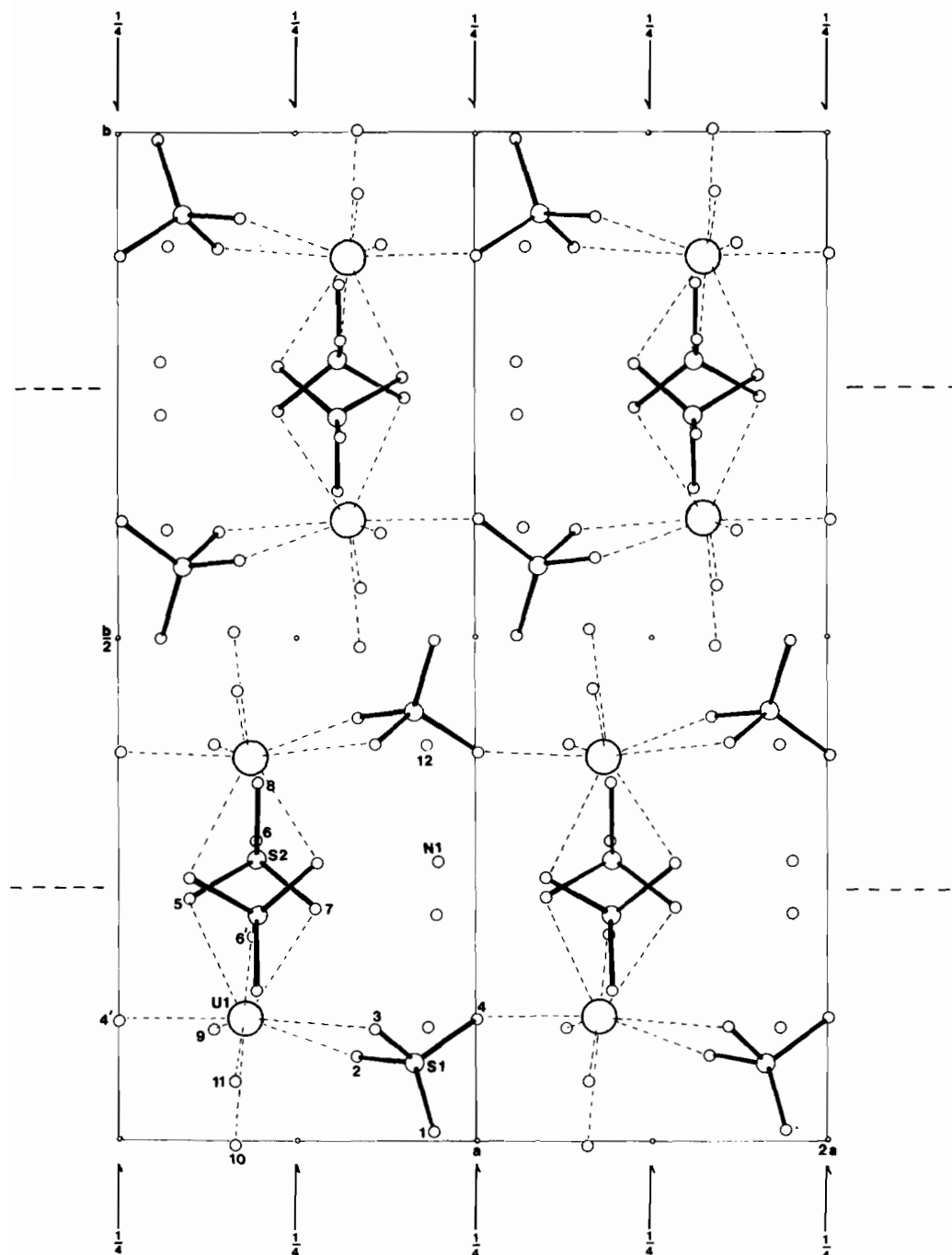
Fig. 2. Packing diagram of two unit cells projected on to the *ab* plane.

longer than any of the other M–O bonds reported in Table IV.

Stoichiometry of $[NH_4] U[SO_4]_2 \cdot 4H_2O$

Conventional chemical analysis gave [8] the composition $[NH_4] U[SO_4]_2 \cdot 4.5H_2O$ which is now amended by means of the crystallographic work.

Comments on the Structure of $U_2[SO_4]_3 \cdot nH_2O$

The trivalent lanthanides (except La and Pm) form octahydrates, $M_2[SO_4]_3 \cdot 8H_2O$. The cerium salt [17] is orthorhombic (*Cmca*) and the rest [15] are monoclinic and isomorphous. The structure of $Pr_2[SO_4]_3 \cdot 8H_2O$ has been successfully refined [15] in the non-centrosymmetric space group *Cc* (see

Table IV). Each praseodymium is eight coordinated to four oxygen atoms from four sulphate ions and to four oxygen atoms from water molecules. However, some authors [14, 18] have shown that the structures of the monoclinic compounds refine equally well in the centrosymmetric space group $C2/c$ and this was found for $Am_2[SO_4]_3 \cdot 8H_2O$ [18] using the same type of unit cell (except space group) as found [15] earlier. In either Cc [15] or $C2/c$ [14, 18] the coordination about the metal atoms was the same, and the earlier report [18] that the neodymium atom in $Nd_2[SO_4]_3 \cdot 8H_2O$ is nine-coordinate is incorrect.

In contrast, La(III) and Ce(III) form nonahydrates $M_2[SO_4]_3 \cdot 9H_2O$ which are hexagonal and isomorphous in space group $P6_3/m$. For the La salt [15], one type of metal ion is co-ordinated to twelve oxygen atoms from six sulphate ions with six short (2.59(7) Å) and six long (2.800(5) Å) bonds. The other type of metal ion is nine-coordinate, with three bonds to oxygen from three separate sulphate ions and six bonds to water oxygen atoms. The remaining three water molecules occupy holes in the structure (see Table IV).
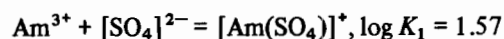
Analyses of our original preparation [8] of $U_2[SO_4]_3 \cdot nH_2O$ gave a uranium to sulphate ratio of 1:1.50 and, typically, over a number of preparations, 8.4 water molecules determined by difference; we reported the compound as $U_2[SO_4]_3 \cdot 8H_2O$. The preparation and analyses were repeated during the course of the present work with similar results. Because the unit-cell dimensions of $[NH_4]U[SO_4]_2 \cdot 4H_2O$ fell between those of the isomorphous La and Ce compounds, it occurred to us that the simple uranium(III) sulphate, $U_2[SO_4]_3 \cdot nH_2O$ (n = 8–9) might be structurally related to the La and Ce non-anhydrates rather than to the more numerous lanthanoid(III) sulphate octahydrates and to $Am_2[SO_4]_3 \cdot 8H_2O$. This was confirmed by X-ray powder diffraction studies. The photograph of $U_2[SO_4]_3 \cdot nH_2O$ was quite different from that of $Nd_2[SO_4]_3 \cdot 8H_2O$ but the same, even at high angles, as that obtained for $La_2[SO_4]_3 \cdot 9H_2O$ which had been prepared by repeated crystallisation from a solution of La_2O_3 in dilute sulphuric acid. We make the reasonable conclusions, therefore, that the uranium and lanthanum compounds are isomorphous ($P6_3/m$), and that the stoichiometry $U_2[SO_4]_3 \cdot 9H_2O$ is to be preferred. The latter compound is the first example of a uranium(III) salt containing a twelve-coordinate metal ion. Because of the general complexity of the powder patterns, no calculations were made on them.

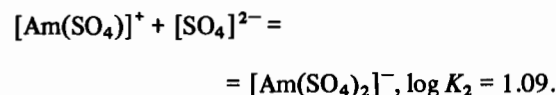*Electronic Spectra of the Uranium(III) Ion*

The solid-state diffuse reflectance electronic spectra of $[NH_4]U[SO_4] \cdot 4H_2O$ and $U_2[SO_4]_3 \cdot 9H_2O$ and of aqueous solutions of the uranium(III) ion in dilute sulphuric (1 M) or hydrochloric (0.3 M) acids

are very similar to each other with no relative nephelauxetic shifts greater than the experimental errors [8, 19]. Moreover, the IR spectra of $[NH_4]U$-$[SO_4]_2 \cdot 4H_2O$ and $U_2[SO_4]_3 \cdot 9H_2O$ showed no evidence of splitting in the antisymmetric stretching vibration, $\nu_3(F_2)$, of the sulphate ion near 1100 cm^{-1}, and the symmetric stretching vibration, $\nu_1(A_1)$, was weak, which indicated $T_d(\overline{4}3m)$ symmetry and non-coordination of the sulphate ions.

Interestingly, there is evidence for splitting of ν_3 in the samarium double sulphate [9]. These observations led us to conclude [8] that the sulphates contained the fully-hydrated uranium(III) ion. There is speculative evidence [20] for assuming this is $[U(H_2O)_9]^{3+}$. Clearly, our conclusions were incorrect. A more likely explanation is that the nephelauxetic factors of sulphate ion and water are nearly equal. Support for this view is obtained on examining the stability constants [21] for the reactions ($I = 1.0$ M, water molecules omitted):

$$Am^{3+} + [SO_4]^{2-} = [Am(SO_4)]^+, \log K_1 = 1.57$$

and

$$[Am(SO_4)]^+ + [SO_4]^{2-} =$$
$$= [Am(SO_4)_2]^-, \log K_2 = 1.09.$$

If we make the assumption that the uranium(III) constants are approximately the same, then the sulphuric acid solution (U = 0.15 M, H_2SO_4 = 1 M) used [8] to record the spectrum mentioned earlier contained *ca.* 90% $[U(SO_4)_2]^-$ and *ca.* 10% $[U(SO_4)]^+$, with little or no free uranium ions; thus the observed spectrum is clearly not that of the fully hydrated ion. On the other hand, the hydrochloric acid solution (U = 0.08 M, HCl = 0.3 M) contained *ca.* 80% of the fully hydrated ion and *ca.* 20% of $[UCl]^{2+}$ if the stability constant for

$$U^{3+} + Cl^- = [UCl]^{2+}$$
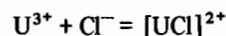
is the same [21] as for americium(III), $\log K_1 = 0.05$.

For trivalent lanthanoids, it is reasonably well-established [22] that changes in coordination number lead to modifications of the electronic spectra, and nephelauxetic effects are greater [19] for the uranium(III) and neptunium(III) ions than for the corresponding lanthanoids. Because of the striking similarity of the uranium(III) spectra mentioned above, it is tempting to conclude that they are derived from predominantly nine-coordinate species and that the hydrated ion is thus $[U(H_2O)_9]^{3+}$. This is tempered by the fact that half of the uranium ions in $U_2[SO_4]_3 \cdot 9H_2O$ are likely to be twelve-coordinate although the bond lengths to uranium are

noticeably longer than those usually found (Table IV) in related systems.

References

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