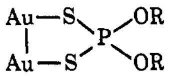
these it is helpful to view the dimers as consisting of two fused



five-membered rings sharing their Au–Au bonds. Both the five-ring configurations and the P–OR conformations are worthy of comment. First, it appears that the five-membered rings are all decidedly puckered. Whether this puckering is intrinsically associated with electron-pair avoidance in the five-ring itself (as it commonly is in the case of small rings which pucker spontaneously in the absence of external forces) or whether it is induced by the packing forces is not known. In either event, two puckering coordinates are possible which can be designated as A_2 (leading to C_2 symmetry) and B_1 (leading to C_s symmetry) relative to a planar C_{2v} reference structure.[33] It is evident that the interdimeric repulsion between isopropoxy groups leads to A_2 twisting deformations of the five-membered rings in dimer 2, and that the intrinsic linearity of S–Au–S bonds in the joined rings of the dimer makes the individual A_2 deformations cooperative, leading to a local C_2 symmetry of the dimer skeleton.[34] The two rings in dimer 1 pucker cooperatively, also, but the twist of dimer 2 provides holes in the cell for the isopropoxy groups of dimer 1 to enter *via* a B_1 bend (envelope flap) preserving local C_s symmetry of the dimer skeleton.[35]

A consequence of the above ring puckerings is that two of the isopropoxy groups in dimer 1 [namely, $C_3H_7(2)$ and $C_3H_7(3)$] but none of them in dimer 2 are compressed toward the –Au–Au– chain. The isopropoxy groups suffering this compression undergo hindered rotation about their P–O bonds to relieve their steric problem. They adopt what we may refer to as gauche locations when compared with the $(CH_3)_2$-C–O–P–O reference conformations. All other isopropoxy groups are found in trans locations.

In conclusion, we find that the material $\{[Au(dtp)]_2\}_n$ is strikingly different in structure from its copper analog,[5] $Cu_4(dtp)_4$, which exists as a discrete tetramer. On the other hand, both the gold and the copper derivatives display striking similarities in structure with the respective gold(I)[23] and copper (I)[36] *N,N*-dialkyldithiocarbamate complexes. A characteristic feature of each of these compounds is the presence of metal–metal bonding, albeit weak, which forms the nuclei or backbones of the molecular clusters or chains. A logical extension of this series of structural investigations to silver(I) *O,O'*-dialkylphosphorodithioates would now be of worthwhile interest in order to examine their polymerization tendencies and, specifically, to determine if hexamers form as in the case of silver(I) *N,N*-diethyldithiocarbamate, $[Ag(C_2H_5)_2NCS_2]_6$.[37]

Acknowledgments.—We are indebted to J. J. Dickert for supplying the purified crystals of this compound. Helpful discussions with J. J. Dickert, C. N. Rowe, Professor L. S. Bartell, and Professor J. C. Bailar, Jr., are gratefully acknowledged. We also extend our appreciation to Professor W. C. Fernelius for making available to us the revised (1971) IUPAC Rules for Nomenclature of Inorganic Chemistry prior to their publication. We also thank Mobil Research and Development Corporation for an undergraduate cooperative assistantship during 1970 for one of us (W. J. R.) in partial fulfillment of the requirements for the B.S. degree in chemistry from Drexel University. Finally, we thank Mrs. J. C. Mahley for her assistance with the data collection.

(33) Notation corresponding to conventional group theoretical tables with the out-of-plane axis taken in the *x* direction.

(34) The S(6)–Au(4)–S(8) twist about the –Au–Au– axis relative to S(5)–Au(3)–S(7) corresponds to 38°.

(35) The dihedral angles in dimer 1 formed by the flaps average 123.7°, compared with 180° if the dimer skeleton were strictly planar.

(36) R. Hesse, *Ark. Kemi*, **20**, 481 (1963).

(37) R. Hesse and L. Nilson, *Acta Chem. Scand.*, **23**, 825 (1969).

CONTRIBUTION FROM THE TRANSURANIUM RESEARCH LABORATORY,
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Crystal Structure of Americium Sulfate Octahydrate[1]

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The structure of $Am_2(SO_4)_3 \cdot 8H_2O$ has been determined by single-crystal X-ray diffraction methods. All nonhydrogen atomic positions were deduced from 3035 diffractometer-measured intensities by means of Patterson and Fourier methods. Refinement by the method of least squares with anisotropic thermal motion for each atom resulted in an agreement index, R_F, of 0.035. The monoclinic unit cell has dimensions of a = 13.619 (7), b = 6.837 (2), c = 18.405 (4) Å, and β = 102° 40 (5)′; it contains four formula units. The space group is $C2/c$. Each americium atom is coordinated by four oxygen atoms belonging to sulfate ions at 2.382–2.509 Å and by four water molecules at 2.406–2.553 Å. These eight oxygen atoms form a polyhedron which is intermediate between an antiprism and a dodecahedron. Cross-linking of americium atoms occurs through sharing of sulfate ions, and extensive hydrogen bonding involving the water molecules is indicated.

Introduction

Important questions in the study of aqueous solutions of lanthanide and actinide ions are those of hydration number and of which anions form inner-sphere and which form outer-sphere complexes. Evidence for the hydration number in solution is provided by such methods as proton magnetic resonance[2] and absorption

(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

(2) A. Fratiello, V. Kubo, S. Peak, B. Sanchez, and R. E. Schuster, *Inorg. Chem.*, **10**, 2552 (1971).

spectroscopy,[3] among others. However, study of the structures of hydrated crystals obtained from aqueous solution provides indirect evidence for the type of complexes existing in solution, and often these data are needed as a reference point for comparison of the results found by the more direct methods.

Examples showing the variability with which water is included in the inner coordination sphere are given by $Nd(BrO_4)_3\cdot 9H_2O$,[4] in which the Nd^{3+} ion has nine H_2O neighbors to the exclusion of BrO_4^- ions, and by $La_2(SO_4)_3\cdot 9H_2O$,[5] in which one kind of La^{3+} ion is coordinated by 12 SO_4^{2-} oxygens and no H_2O. Other cases, in which both H_2O and anions are in the inner sphere, include $La_2(SO_4)_3\cdot 9H_2O$ in which one of the La^{3+} ions has six H_2O molecules and three SO_4^{2-} ions as neighbors and $AmCl_3\cdot 6H_2O$,[6] which has the Am^{3+} ion coordinated by two Cl^- ions and six H_2O molecules. The analysis to be described here was carried out to provide information of the type just discussed regarding the coordination of Am^{3+} in aqueous SO_4^{2-} solution and to add to the somewhat limited knowledge of americium stereochemistry. In the present case, indeed it was found that the Am^{3+} is coordinated by four SO_4^{2-} oxygens and four H_2O molecules.

Because our X-ray diffraction data showed $Am_2(SO_4)_3\cdot 8H_2O$ to be isostructural with $Nd_2(SO_4)_3\cdot 8H_2O$, the present work also served to clarify the details of this latter structure, for which a partial determination had been made[7] and subjected to question.[8] Unit-cell data on $Pr_2(SO_4)_3\cdot 8H_2O$[9] and $Sm_2(SO_4)_3\cdot 8H_2O$[10] had indicated these to also have the same structure.

Experimental Section

Compound Preparation.—A solution of americium-243 sulfate was prepared by titrating a solution of $AmCl_3$ with a hot solution of Ag_2SO_4 and filtering off the precipitate of AgCl. The americium sulfate solution was then evaporated to about 5 *M* and filtered again to remove traces of AgCl and Ag_2SO_4. Evaporation of the filtrate was continued using an infrared lamp and an argon jet sweeping the surface of the solution. Before evaporation was complete, it was possible to remove from the mother liquor thick, tabular, pale yellow-pink crystals of lengths up to 0.5 mm. After being dried in air these crystals of $Am_2(SO_4)_3\cdot 8H_2O$ showed no tendency to change their state of hydration over a period of several days. The remaining solution was evaporated to dryness yielding more crystals which were examined by thermogravimetric (tga) and differential thermal analyses (dta) to confirm the degree of hydration. The tga–dta data and an absorption spectroscopy study of the solid will be discussed elsewhere.[11] All chemistry and manipulation of crystals was carried out in glove boxes for containment of the α-active ^{243}Am.

Data Collection.—Several crystals of $Am_2(SO_4)_3\cdot 8H_2O$ were examined by X-ray diffraction photography from which the identity of the compound was established by its isomorphism with $Nd_2(SO_4)_3\cdot 8H_2O$.[7] From precession photographs preliminary values for the monoclinic unit-cell dimensions were obtained and the pattern of systematic absences was ascertained to be *hkl* for $h + k$ odd and *h*0*l* for *l* odd. These are characteristic of space groups *C*2/*c* and *Cc;* the former was assumed to be correct because it had been used in the previous work on $Nd_2(SO_4)_3\cdot 8H_2O$. While the earlier work was not definitive in itself, this was the proper choice, because its use led to a successful structure determination and refinement in the present case.

For measurement of intensity data a crystal in the shape of a rectangular parallelepiped with dimensions of 0.06 × 0.11 × 0.13 mm was sealed in a thin-walled glass tube to contain the α activity. This specimen was mounted with its *b* axis approximately 60° away from the φ axis of a Picker four-circle goniometer. This instrument and its diffractometer and scintillation-counter detector were all computer controlled for automatic operation. The PDP-8 computer programs were written by Busing, *et al.*[12] Niobium-filtered, Mo Kα X-rays were employed (λ 0.70926 Å).

Twelve reflections in the 2θ range of 55–65° were centered in the detector aperture and the angles were used to obtain the best values of the unit-cell dimensions by least-squares refinement.[12] Intensity measurements were made by θ–2θ scanning with steps of 0.03° and 2-sec counting times for each step. Scan ranges varied from 0.96 to 1.30°. Ten-second counting periods at each end of the scans were used in determining the background for each reflection. All independent reflections with $2\theta < 65°$ were measured and yielded some 3057 intensities. A reference reflection was measured hourly to follow changes in the X-ray source. Its intensity remained constant to ±1.7%, except for one period when a 25% increase occurred because of failure of the voltage regulation.

Calculations.—The diffraction intensities were corrected for absorption by use of the ORABS program.[13] A mass absorption coefficient of 60 cm^{-1} for Am was estimated by extrapolation of the values for actinide elements given by Roof.[14] Using this value a linear absorption coefficient for $Am_2(SO_4)_3\cdot 8H_2O$ of 119 cm^{-1} was derived, and the calculated transmission factors for the specimen used ranged from 0.26 to 0.53. Application of those factors plus Lorentz and polarization factors and normalization by interpolating between measurements of the reference reflections resulted in a set of squared structure factors.

A three-dimensional Patterson map was calculated and interpreted, with some aid from the reported structure of $Nd_2(SO_4)_3\cdot 8H_2O$,[7] to yield the positions of the Am and S(1) atoms in general positions 8(f) of space group *C*2/*c* and the S(2) atom in special positions 4(e). The coordinates of these atoms were refined by the method of least squares[15] (to $R = 0.17$), and the phases calculated from them were used in computing an electron density map using all observations. This map revealed the presence of ten oxygen atoms in general positions, thus completing the required stoichiometry.

The positions and anisotropic thermal parameters of the 13 atoms of the asymmetric unit were then refined by full-matrix least squares,[15] along with a single scale factor and an isotropic extinction parameter. The function minimized was $\Sigma w(F^2 - F_o^2)^2$, where F_o is the observed structure factor and F is the calculated structure factor corrected for extinction using the Coppens and Hamilton formulation[16] of the Zachariasen approximation.[17] The weight, w, of an observation was taken as $1/\sigma^2(F_o^2)$, and the variance, $\sigma^2(F_o^2)$, was estimated from counting statistics plus a contribution of 3% of the intensity for possible systematic errors. Intensities measured to be less than background were set equal to zero. Twenty-two reflections having $2\theta \leq 12°$ were omitted from the refinement because they were judged to be inaccurate due to difficulty in measuring the background. Atomic scattering factors for neutral Am, S, and O were taken from Cromer and Waber[18] and anomalous dispersion corrections,[19] $\Delta f' = -7.42$ e and $\Delta f'' = 4.64$ e, were applied for Am.

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TABLE I

REFINED PARAMETERS[a] AND THEIR STANDARD ERRORS FOR $Am_2(SO_4)_3 \cdot 8H_2O$

Atom	x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Am	0.33150 (1)	0.02440 (2)	0.10730 (1)	15.1 (1)	48.5 (4)	8.5 (1)	−3.3 (1)	2.8 (1)	−1.6 (1)
S(1)	0.28476 (8)	0.03109 (15)	0.41113 (6)	16.2 (5)	49.1 (17)	8.2 (3)	1.6 (7)	3.0 (3)	−0.6 (5)
S(2)	0.5	0.32728 (22)	0.0	15.4 (7)	61.0 (27)	8.2 (4)	0.0	1.9 (4)	0.0
O(1)	0.4669 (3)	0.4497 (6)	0.3058 (3)	26 (2)	87 (8)	16 (1)	0 (3)	6 (1)	−13 (2)
O(2)	0.4156 (3)	0.2040 (7)	0.2138 (2)	30 (2)	152 (9)	10 (1)	−39 (3)	3 (1)	−14 (2)
O(3)	0.3568 (3)	0.0828 (6)	0.4823 (2)	25 (2)	99 (7)	8 (1)	2 (3)	1 (1)	2 (2)
O(4)	0.3381 (3)	0.0321 (7)	0.3510 (2)	23 (2)	175 (9)	8 (1)	6 (3)	5 (1)	0 (2)
O(5)	0.2026 (3)	0.1754 (5)	0.3967 (2)	20 (2)	69 (7)	15 (1)	12 (3)	2 (1)	0 (2)
O(6)	0.2556 (3)	0.3370 (6)	0.0780 (3)	30 (2)	55 (7)	24 (2)	10 (3)	7 (1)	0 (2)
W(1)[b]	0.0137 (3)	0.3350 (6)	0.3576 (3)	19 (2)	87 (8)	36 (2)	−1 (3)	1 (2)	−15 (3)
W(2)	0.4619 (3)	0.2375 (5)	0.0643 (2)	18 (2)	89 (7)	13 (1)	−4 (3)	3 (1)	0 (2)
W(3)	0.2395 (4)	−0.0056 (7)	0.2044 (3)	28 (2)	229 (12)	12 (1)	−32 (4)	7 (1)	−10 (3)
W(4)	0.3483 (3)	0.4849 (5)	0.4576 (2)	21 (2)	74 (7)	13 (1)	−2 (3)	0 (1)	−3 (2)

[a] Thermal parameters are for the expression $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}kl + 2\beta_{23}kl)]$. [b] The symbol W is used for an oxygen atom belonging to a water molecule.

Convergence of the refinement was rapid and in the final cycle all parameters varied less than 0.1 of their standard errors. The agreement index, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, was 0.035 for 3035 reflections and 0.031 for the 2831 reflections observed larger than one standard deviation. The standard deviation of an observation of unit weight was 1.41. The refined value of the extinction parameter g[16] was $(7.6 \pm 0.2) \times 10^{-4}$. The extinction correction that was applied to F^2_{obsd} amounted to less than 10% for 90.5% of the observations; its maximum value was a factor of 3.0. The final values of the structural parameters and their standard deviations are given in Table I, while the observed and calculated structure factor amplitudes are available elsewhere.[20]

After refinement was completed, a difference Fourier map was generated in an attempt to locate the hydrogen atoms. It was not possible, however, to distinguish them from background oscillations which ranged over approximately ±1 e/Å^3.

Calculations of interatomic distances and angles and their standard deviations were performed with the ORFFE program,[21] and the illustrations of the structure and thermal motions were prepared using ORTEP.[22]

Results and Discussion

The refined values for the monoclinic unit-cell dimensions at 23° are a = 13.619 (7) Å, b = 6.837 (2) Å, c = 18.405 (4) Å, and β = 102° 40 (5)′. Four formula units in the cell yield a calculated density of 3.65 g cm^{-3}.

The americium atoms, all of which are crystallographically equivalent, are coordinated by eight oxygen atoms at distances shown in Table II. Four of these belong to sulfate groups and four are in water molecules. The next nearest neighbor to americium is a sulfate oxygen, O(6), at 3.49 Å; thus the nine-coordination proposed (for Nd[23]) by Fitzwater and Rundle[7] was not correct. The symmetry of the polyhedron of eight oxygens (Figure 1a) was examined by applying the criteria devised by Lippard and Russ[24] for distinguishing between the antiprism and the dodecahedron when the symmetries are only approximate. Briefly, the result of this examination was that the angles between two possible sets of intersecting trapezoidal best planes are 84.0 and 84.8°, either of which is clearly an intermediate case between the antiprism (77.4°) and the dodecahedron (90°). Thus it is immaterial whether the coordination is called dodecahedral or antiprismatic as it must be considered distorted in either case.

TABLE II

BOND LENGTHS IN $Am_2(SO_4)_3 \cdot 8H_2O$

Bond	Length, Å	Bond	Length, Å
Am–O(2)	2.382 (4)	S(1)–O(4)	1.452 (5)
O(6)	2.384 (4)	O(6)	1.467 (4)
W(3)	2.406 (5)	O(5)	1.472 (4)
O(5)	2.429 (4)	O(3)	1.497 (4)
W(1)	2.438 (5)		
W(4)	2.493 (4)	S(2)–O(2)	1.463 (4)
O(3)	2.509 (4)	O(1)	1.470 (4)
W(2)	2.553 (4)		

TABLE III

BOND ANGLES IN THE SO_4 GROUPS

Angle	Value, deg	Angle	Value, deg
O(3)–S(1)–O(4)	108.9 (3)	O(2)–S(2)–O(1)	108.4 (3)
O(3)–S(1)–O(5)	109.1 (3)	O(2)–S(2)–O′(1)	109.9 (3)
O(3)–S(1)–O(6)	106.7 (3)	O(2)–S(2)–O′(2)	109.6 (4)
O(4)–S(1)–O(5)	110.3 (3)	O(1)–S(2)–O′(1)	110.6 (4)
O(4)–S(1)–O(6)	111.9 (3)	O(1)–S(2)–O′(2)	109.9 (3)
O(5)–S(1)–O(6)	109.8 (3)	O′(1)–S(2)–O′(2)	108.4 (3)

TABLE IV

POSSIBLE HYDROGEN BONDS IN $Am_2(SO_4)_3 \cdot 8H_2O$

Acceptor	d, Å	Water	d, Å	Acceptor	Angle, deg
O(4)	2.72	W(1)	2.83	O(1)	108.4
O(4)	2.75	W(3)	2.79	O(1)	110.1
O(1)	2.78	W(2)	2.92	W(4)	105.8
O(1)	2.78	W(2)	2.98	O(3)	106.1
O(3)	2.98	W(2)	2.92	W(4)	112.8
O(3)	2.78	W(4)	2.92	W(2)	122.4
O(3)	2.78	W(4)	3.04	O(6)	106.6
W(2)	2.92	W(4)	3.19	W(2)	96.1
O(5)	3.11	W(4)	3.19	W(2)	105.2

In $Am_2(SO_4)_3 \cdot 8H_2O$ the average Am–O(sulfate) distance is 2.43 Å, significantly shorter than the average Am–O(water) distance of 2.47 Å. This finding is in agreement with two other structures involving this kind of bonding, namely, in $AmCl_3 \cdot 6H_2O$[6] where the average Am–O(water) distance is 2.46 Å and in

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[20] A listing of structure factor amplitudes (×0.5) will appear immediately following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-2233. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

[21] W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, a Fortran Crystallographic Function and Error Program," Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

[22] C. K. Johnson, "ORTEP, a Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," Report ORNL-3794, Revised, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

[23] That $Nd_2(SO_4)_3 \cdot 8H_2O$ and $Am_2(SO_4)_3 \cdot 8H_2O$ are isostructural is indicated by their identical space groups, close unit-cell dimensions, and the fact that the original film data for the Nd compound gave an agreement index of 0.16 when compared to the final structure given here.

[24] S. J. Lippard and B. J. Russ, *Inorg. Chem.*, **7**, 1686 (1968).

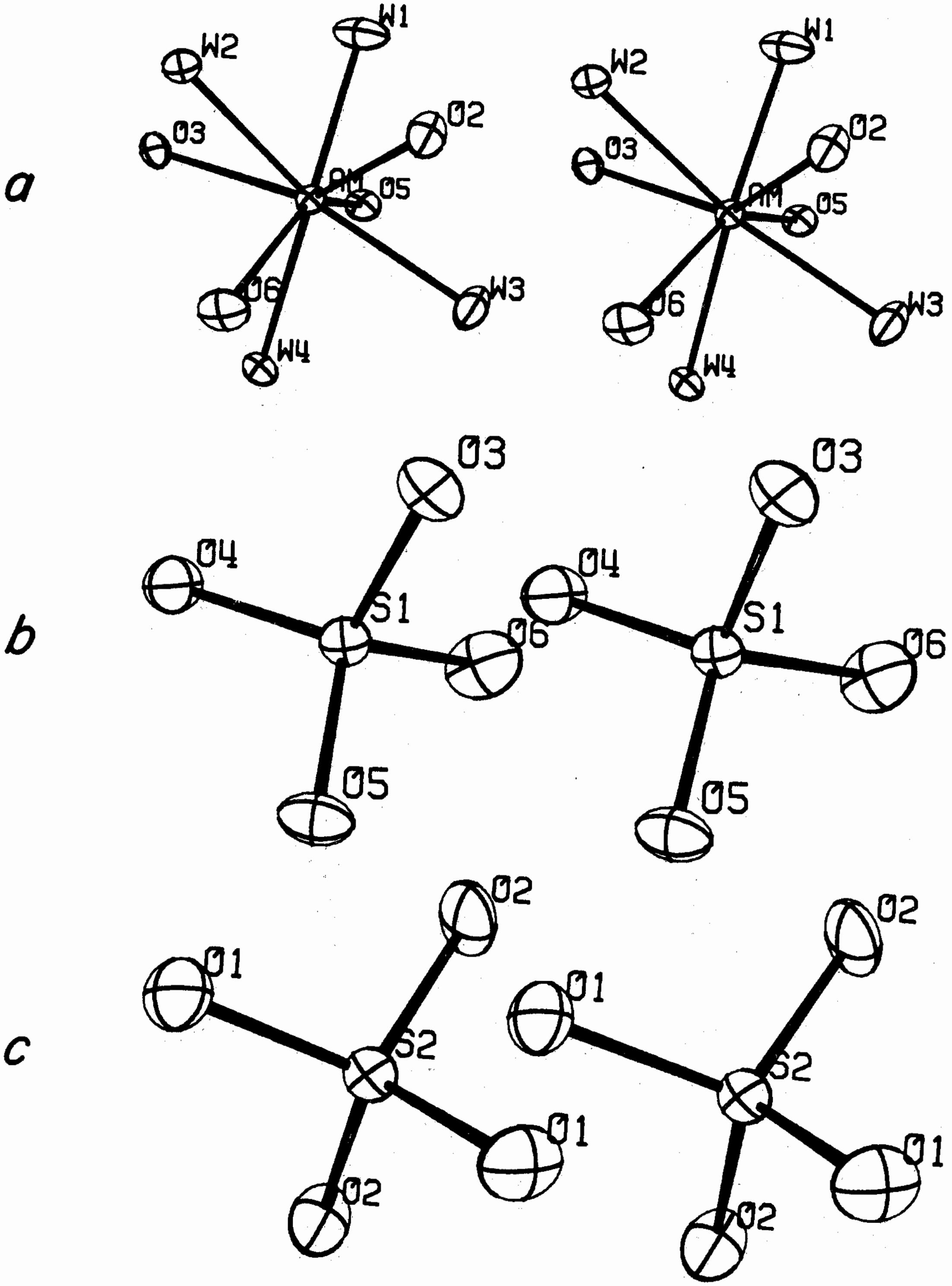

Figure 1.—Stereoscopic views of portions of the $Am_2(SO_4)_3 \cdot 8H_2O$ crystal structure with atoms represented by 50% probability thermal ellipsoids.[22] Part a shows the eight-coordination of oxygen atoms around Am. The group is oriented identically to the one in the lower left of Figure 2. Parts b and c show the sulfate groups.

$CsAm(HFA)_4$ (HFA = hexafluoroacetylacetone)[25] where the average Am–O(diketone) distance is 2.41 Å. (In each case the Am is eight-coordinated, although in $AmCl_3 \cdot 6H_2O$ two of the eight are Cl atoms.) Thus the ionic bonds to the charged oxygen atoms are seen to be shorter and presumably stronger than those between the Am and the dipolar water molecules.

The Am atoms are cross-linked in the structure by sharing of their sulfate ions with other Am atoms as can be seen in Figure 2. Layers approximately parallel to $(10\bar{1})$ are connected internally by linkages of the type Am–O(2)–S(2)–O(2)–Am, Am–O(3)–S(1)–O(5)–Am, Am–O(3)–S(1)–O(6)–Am, and Am–O(5)–S(1)–O(6)–Am. Atoms O(1) and O(4) are not shared with Am atoms. Successive layers are held together by hydrogen bonds to be described later. The geometries of the sulfate groups are described by the bond lengths (Table II) and angles (Table III) and are depicted by

(25) J. H. Burns and M. D. Danford, *Inorg. Chem.*, **8**, 1780 (1969).

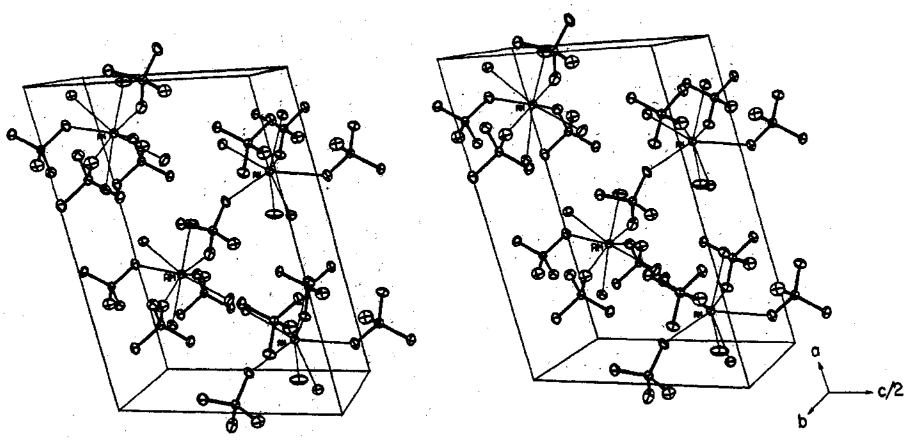

Figure 2.—A stereoscopic view of one-half of a unit cell content showing part of the cross-linking within layers. Atoms are identified by reference to Figure 1.

Figures 1b and 1c. There is very little distortion from regular tetrahedra, and the S–O bond lengths are in good agreement with other determinations, such as $Cu(NH_4)_2(SO_4)_2\cdot 6H_2O$.[26]

With four water molecules per americium to act as donors and these plus numerous sulfate oxygens present to act as acceptors there may be extensive hydrogen bonding in this structure. Since attempts to interpret difference Fourier maps to obtain hydrogen positions were unsuccessful, even when plausible sites were deduced geometrically, the possibilities for hydrogen bonds were analyzed by surveying the close O···O distances (less than 3.25 Å) and the reasonable O···O···O angles (105 ± 10°). The results are summarized in Table IV. In each of two cases, W(1) and W(3), a single, highly probable orientation for the water molecule emerged. In the other two cases, W(2) and W(4), a decision could not be made among three and four possibilities, respectively; but the existence of these short distances and suitable angles suggests that these water molecules are also involved in hydrogen bonding, possibly in a disordered arrangement including several of the directions.

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[26] G. M. Brown and R. Chidambaram, *Acta Crystallogr., Sect. B*, **25**, 676 (1969), and references therein.

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The Crystal and Molecular Structure of Carbonylchlorobis(trimethylphosphine)-(1,2,3-triphenylpropenylium-1,3-diyl)iridium(1+) Tetrafluoroborate(1 −)-Dichloromethane, $[Ir(C_3(C_6H_5)_3)Cl(CO)(P(CH_3)_3)_2][BF_4]\cdot CH_2Cl_2$, an Oxidative Addition Derivative Formed by Carbon–Carbon Bond Cleavage

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The crystal and molecular structure of $[Ir(C_3(C_6H_5)_3)Cl(CO)(P(CH_3)_3)_2][BF_4]\cdot CH_2Cl_2$ has been determined from three-dimensional single-crystal X-ray data collected by counter methods. This compound crystallizes as discrete molecular units in the orthorhombic space group $P2_12_12_1$ with four formula units in a unit cell of dimensions a = 9.808 (1), b = 17.758 (2), and c = 19.971 (3) Å. The structure has been refined by full-matrix least-squares methods to a conventional R factor of 0.060 for the 3248 intensities above background. In reacting with $IrCl(CO)(P(CH_3)_3)_2$ the cyclopropenium ring is cleaved to give the monopositive bidentate propenylium-1,3-diyl group. This group, the trans phosphines, the chlorine, and the carbonyl are disposed about the six-coordinate iridium(III) ion in a distorted octahedral fashion. Iridium–phosphorus distances are 2.360 and 2.369 (5) Å; iridium–chlorine, 2.472 (5) Å; iridium–carbon (carbonyl), 1.94 (2) Å; and iridium–carbon (propenylium), 2.099 and 1.990 (15) Å. Carbon–carbon distances in the propenylium group are 1.36 and 1.41 (2) Å. A 1,3 $p\pi$–$p\pi$ interaction is suspected to occur in the propenylium group.

Investigations of transition metal triphenylcyclopropenyl derivatives[2,3] have shown some striking similarities between cyclopropenyl and nitrosyl metal complexes. This is perhaps not surprising when the electronic structures of $C_3(C_6H_5)_3^+$ and NO^+ are compared. Both cations are thought to have a highest occupied orbital of π symmetry and a lowest unoccupied π^* orbital which is energetically accessible. Although NO^+ is considered to be a good π-acceptor ligand,[4] further

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[4] See, for example, P. T. Manoharan and H. B. Gray, *ibid.*, **5**, 823 (1966).