crystals that are strictly isomorphous with those of the same isomer of the tantalum analogue.[9] In both cases, the two chelate rings have the same (λ) conformation and the molecule is chiral. The two molecular structures have principal dimensions that do not differ significantly at the 3σ level. Thus, there are the following differences (esd's in parentheses): M–M, 0.004 (3) Å; M–P, 0.018 (8) Å; M–Cl$_b$, 0.009 (9) Å; M–Cl$_t$, 0.000 (10) Å. While corresponding Nb and Ta molecules of this class have previously been found to have similar dimensions, as in the comparison of **1** and **2** above, this is apparently the first case in which they have been so similar as to be identical within the 3σ criterion.

Comparison of 1 and 3. These two structures are surprisingly similar in view of the difference between dene and depe as ligands. The two Nb–Nb distances are different in a statistically significant sense, viz., 2.741 (3) Å in the depe compound (**3**) and 2.764 (1) Å in the dene compound (**1**), but in a chemical sense the difference is almost insignificant. The Nb–Cl distances do not differ from one compound to the other at the 3σ level. It must be concluded that the nature of the molecule, particularly its Nb–Nb bonding, is not sensitive to the change from depe to dene. Whether this would be true for comparable molecules with other metals, such as Mo or Re, remains to be seen, since there are no other dene/depe analogues available for comparison.

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Registry No. **1**, 111112-77-7; **2**, 111112-79-9; **3**, 111139-83-4; $Nb_2Cl_6(SMe_2)_3$, 61069-51-0; $Ta_2Cl_6(SMe_2)_3$, 77827-59-9; Nb, 7440-03-1; Ta, 7440-25-7.

Supplementary Material Available: For the crystal structures of $Nb_2Cl_6(dene)_2$, $Ta_2Cl_6(dene)_2$, and $Nb_2Cl_6(depe)_2$, full lists of bond distances, bond angles, and anisotropic displacement parameters (8 pages); tables of observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

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Crystal Structure of a Complex Basic Zirconium Sulfate

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A new complex basic zirconium sulfate, $Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6}\cdot 33H_2O$, has been characterized by single-crystal X-ray techniques. The crystals are hexagonal, C_{6h}^2-$P6_3/m$, with $a = 33.779$ (4) Å, $c = 17.522$ (3) Å, $V = 17322$ (3) Å^3, and $R(F) = 0.083$ for 7218 observations [$I > 2\sigma(I)$] and 775 variables. The unit cell contains six complex molecules each consisting of a folded sheet of 18 zirconium atoms linked via oxygen bridges. Large channels between the complexes contain water molecules involved in linking the complexes via hydrogen bonding. The Zr atoms are found in both 7- and 8-fold coordination. This compound is much more basic than the previously characterized basic sulfates, and the structure is distinguished by the presence of triply bridging hydroxyl groups and quadruply bridging oxide ions and by the diminished importance of the sulfate groups in the Zr framework. Systematic rules for the formation of basic zirconium sulfates are discussed in light of these results.

Introduction

The complexity of systems containing zirconium and sulfate ions is well-known.[1-4] An astonishing array of compounds has been obtained from both neutral and acidic zirconium sulfate solutions.[3-5] Structural characterization of a number of neutral[6-11] (Zr:SO$_4$ ratio = 1:2) and basic[12,13] (Zr:SO$_4$ ratio greater than 1:2) zirconium sulfates has revealed a diversity of interesting bonding features. However, the number of known structures is small compared to the large number of possible known compounds. Therefore in 1964, Clearfield attempted to explain how such a diversity of compounds could form from sulfate solutions and to predict their structure and formation.[14] Determination of additional crystal structures would help to establish or modify the proposed theory. In particular, little is known about the more basic compounds, i.e., those in which the Zr:SO$_4$ ratio is large. As part of our interest in this aspect of zirconium chemistry, we have characterized a new basic zirconium sulfate whose composition and structure represent a significant departure from those previously reported. We present here the synthesis and crystal structure of the compound $Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6}\cdot 33H_2O$ and discuss its relationship to the known zirconium sulfates.

Experimental Section

Synthesis. Single crystals of $Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6}\cdot 33H_2O$ were supplied by Magnesium Elektron, Ltd. Their preparative procedure was as follows. To an aqueous solution of zirconyl chloride (0.64 M, 250 mL, 0.16 mol) were added 4.4 mL of 12 M HCl (0.053 mol) and 5 mL of 18.8 M H_2SO_4 (0.094 mol). The solution was allowed to stand in a stoppered flask at ambient temperature for about 10 days during which time clear, colorless crystals formed. The product was then collected and allowed to air dry.

Analysis. Zirconium was determined by EDTA titration using Xylenol orange as indicator. A 0.1-g sample was dissolved in 10 mL of 5 M sulfuric acid and diluted to 20 mL. The solution was then brought to a boil while being stirred magnetically, and after 15 min of boiling, the solution was diluted to 60 mL. A few drops of indicator were then added, and the solution was kept at 90 °C while being titrated to an orange color with 0.1 M EDTA. The mixture was then cooled and 10 mL of 7 M NH_4OH added so that it returned to its original mauve color. The flask was then returned to the hot plate and the titration completed. The color went from mauve to orange to yellow. Sulfate was determined gravimetrically as $BaSO_4$. A 0.2-g sample of the basic sulfate was boiled with 20 mL of 1 M NaOH. The slurry was then diluted by addition of 30 mL of water and filtered to remove hydrous zirconium dioxide, and sulfate was determined in the filtrate. A TGA weight loss curve was obtained

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Table I. Crystallographic Data for $Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6}\cdot 33H_2O$

empirical formula (asymmetric unit)	$Zr_9S_{6.3}O_{63.1}H_{52.4}$
empirical fw	2085.4
a, Å	33.779 (4)
c, Å	17.522 (3)
V, Å^3	17322 (2)
Z	12
d_{calcd}, g/cm^3	2.40
d_{obsd}, g/cm^3	2.38 ($CHBr_3$–CCl_4)
space group	C_{6h}^2-$P6_3/m$
temp of data collcn, K	298
radiation	graphite-monochromated Mo Kα [$\lambda(K\alpha_1)$ = 0.709 30 Å]
crystal color, form	colorless, irregular needle
linear abs coeff μ, cm^{-1}	19
transmission factors	0.829–1.0 (ψ-scans)
data limits, deg	$0° \leq 2\theta$ (Mo Kα_1) $\leq 52°$
scan type	ω–2θ
scan range, deg in ω	0.3 below Kα_1 to 0.3 above Kα_2
scan speed, deg in ω min^{-1}	from 20.0 for strongest to 8.0 for weakest data
bkgd counts	$^1/_4$ of scan range on each side of reflcn
p factor	0.05
tot. no. of measd data	12 229
R(av)	0.011
no. of unique data (including $I < 0$)	11 712
no. of unique data [with $I > 2\sigma(I)$]	7218
no. of variables	775
R^a	0.083
R_w	0.107
error in observn of unit wt, S	2.38

[a] The function minimized was $\sum_i w_i(|F_{o_i}| - |F_{c_i}|)^2$ where $w = 1/\sigma^2(F_{o_i})$ and $\sigma(F_o) = [^1/_2(C + {}^1/_4(t_c/t_b)^2B + (PI)^2]^{1/2}$ (C = total counts; t_c = time spent counting peak intensity; t_b = time counting one side of background, B = background counts; P = p factor; I = net intensity).

on a Cahn R.H. electrobalance. The results of the analysis indicated an empirical formula of $ZrO_2\cdot 0.7SO_3\cdot 3.1H_2O$.

Crystallographic Study. Preliminary precession photographs (Cu Kα) established the hexagonal symmetry and approximate cell parameters. Accurate cell parameters were determined at 298 K from the setting angles of 23 reflections in the range $24° < 2\theta$ (Mo Kα_1) $< 43°$ accurately centered on an Enraf-Nonius CAD4 diffractometer. Intensity data were collected at room temperature with the ω–2θ scan technique. The intensities and orientation of three standard reflections, measured every hour throughout data collection, were stable. An empirical absorption correction employing the ψ-scan method (TEXSAN series of programs[15]) was applied. Cell data and other relevant crystallographic details are given in Table I.

Initial calculations were performed with the use of the SDP[16] crystallographic computing package while the final refinement was carried out with TEXSAN. The systematic absence ($00l$, $l = 2n + 1$) is consistent with the space groups C_6^6-$P6_3$, C_{6h}^2-$P6_3/m$, and D_6^6-$P6_322$. We selected the centrosymmetric group C_{6h}^2-$P6_3/m$ on the basis of intensity statistics ($N(Z)$ test) and the satisfactory residual of 0.011 that resulted from merging 1034 equivalent data in this space group. The structure was solved by a combination of direct methods and trial and error. In this way, the positions of the zirconium atoms were located. Successive difference Fourier syntheses were then used to locate the S and O atoms.

Once all of the O atoms had been located, it was apparent that the S and terminal O atoms on three of the doubly bridging sulfate groups had anomalously high isotropic thermal parameters ($B > 5$Å^2) while those for the two bridging O atoms on each sulfate were much smaller ($B \simeq$ 1–2 Å^2). Refinement of the occupancy factors for the S and terminal O atoms suggested disorder between SO_4^{2-} and OH^- groups, with two hydroxyl groups statistically replacing the bridging O atoms for each sulfate group to maintain full occupancy of the O sites. The net occupancy of the sulfate group was reflected in the occupancy factors of the S and terminal O atoms. Consequently, in the final stages of refinement the occupancy factors for the terminal O atoms on each of these sulfate groups were constrained to be equal to the variable occupancy factor of the S atom. The final cycle of refinement of the 7218 unique F_o values for which $I > 2\sigma(I)$ included variable occupancy factors for atoms S4, S6, and S9 and anisotropic thermal parameters for the 96 independent non-hydrogen atoms. No attempt was made to locate the H atoms. From the final refined occupancies, the composition of the crystal used in the X-ray experiment was $Zr_{18}O_4(OH)_{38.92(3)}(SO_4)_{12.55(3)}\cdot 33H_2O$. This composition yields an empirical formula, $ZrO_2\cdot 0.7SO_3\cdot 2.9H_2O$, which is deficient in water relative to that obtained by chemical and thermogravimetric analyses. We believe the additional water, amounting to 3.4 molecules per Zr_{18} formula unit, is present in the channels but is not detectable in the X-ray structure due to disorder or large thermal motion.

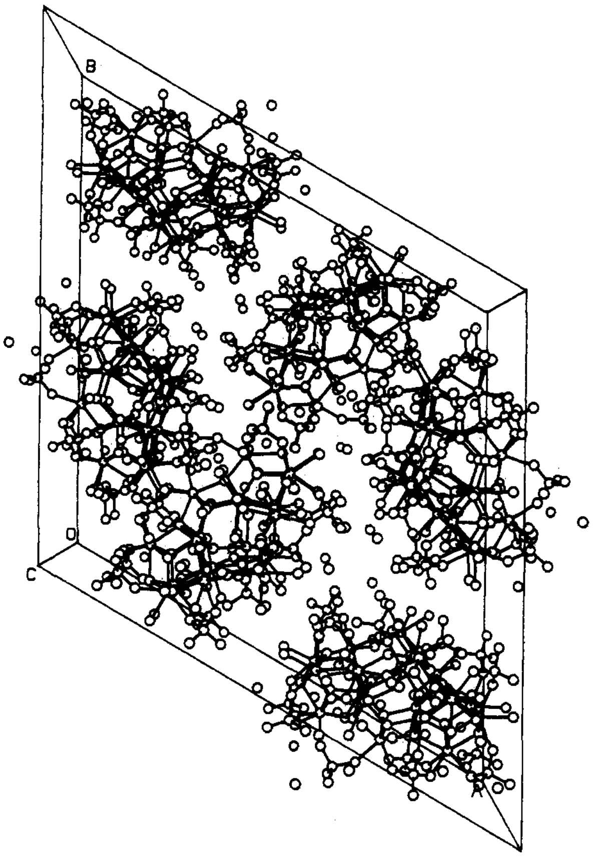

Figure 1. Perspective view of the $Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6}\cdot 33H_2O$ structure along [001], showing the outline of the unit cell.

The height of the largest peak in the final difference electron density map was <5% that of a Zr atom. No unusual trends were observed in an analysis of F_o vs F_c as a function of $(\sin \theta)/\lambda$ or Miller indices. Final agreement indices are given in Table I. Final positional parameters and equivalent isotropic thermal parameters are presented in Table II. Structure amplitudes (×10) and anisotropic thermal parameters are provided in Tables SI and SII,[17a] respectively.

Results

A packing diagram showing the contents of the unit cell is given in Figure 1, while the labeling scheme is shown for the asymmetric portion of a single molecule in Figure 2. Selected bond distances are presented in Table III. Each molecule consists of a folded, or wedge-shaped, sheet of 18 Zr atoms linked via oxygen bridges. The molecules are bisected by mirror planes at $z = {}^1/_4$ and $^3/_4$ with atoms Zr4, Zr7, Zr9, Zr6, O11, O26, O51, S3, O42, O72, O52, O24, O18, O33, O31, S4, O2S4,[17b] O1S4, S8, O1S8, O2S8, S7, O1S7, and O2S7 lying in the plane. Inspection of Figure 2 reveals, in addition, a pseudo-mirror symmetry between the left and right halves of the molecule as bisected by a line running through Zr atoms 6, 7, and 8. This pseudosymmetry is broken only by the different connectivities of the (ordered) sulfate groups containing atoms S2 and S3. The former is triply bridging while the latter bridges two Zr atoms.

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(15) "TEXSAN, Texray Structural Analysis Package"; Molecular Structure Corporation: College Station, Texas, 1987 (revised).

(16) "Structure Determination Package"; Enraf-Nonius: Delft, Holland, 1981 (revised).

(17) (a) Supplementary material. (b) This designation means oxygen number 2 bonded to sulfur number 4, etc.

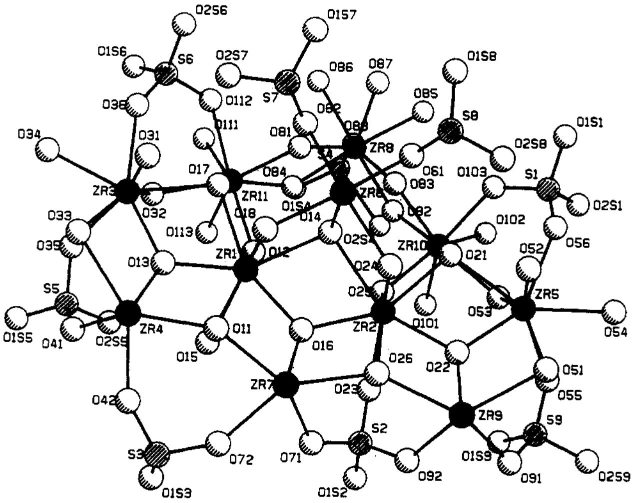

Figure 2. Asymmetric portion of a single molecule with the numbering scheme. Zirconium and sulfur atoms are shown as black and shaded circles, respectively. For clarity, symmetry-equivalent atoms generated by the mirror bisecting the molecule have been omitted from this view, which is along [001] perpendicular to the mirror plane.

The Zr atoms are found in both 7- and 8-fold oxygen coordination. The coordination geometries of the 11 crystallographically independent Zr atoms are shown in detail in Figure 3. Atoms Zr4 and Zr7 are 7-coordinate and set in a monocapped trigonal prism of O atoms. Among the 8-coordinate atoms, Zr9 is unique in that its coordination is best described as a bicapped trigonal prism. The remaining Zr atoms have somewhat irregular 8-fold geometries that are approximately square antiprismatic (atoms 6, 8, 10, and 11) or triangulated dodecahedral (atoms 1, 2, 3, and 5). The fragment consisting of Zr11, Zr8, and Zr10 resembles the structure present in the zirconyl halides[18] with one Zr atom missing.

There is a substantial variation in Zr–O distances, both in the structure as a whole (from 2.04 to 2.42 Å), and within the individual Zr coordination spheres. That there should be so many unusually long Zr–O interactions is not surprising given the disparate nature of the oxygen polyhedra that have joined to form the framework. Indeed, the uniqueness of this arrangement is underscored by the unusual polyhedral connectivities involving three types of oxygen bridges linking the Zr atoms. In addition to the doubly bridging hydroxyl groups that are typical of the basic sulfates,[12,13] as well as other basic salts,[12,18–20] there are also triply and quadruply bridging O atoms in the present structure. To our knowledge this is the first zirconium sulfate to exhibit such features. The 4-coordinate O atoms (O11 and O26), which sit in a distorted tetrahedron of Zr atoms, are clearly oxidic in nature, while the 10 3-coordinate O atoms, whose geometries are irregular, are assigned as hydroxyl groups on the basis of charge balance.

Of the nine independent sulfate groups, eight bridge two Zr atoms while the other bridges three. Unlike sulfate groups in the structurally characterized basic zirconium sulfates, the sulfate groups here are not an integral part of the zirconium atom network. Rather, they are located around the perimeter of the molecule and appear to serve mainly to cap loose ends at the edge of the sheet. No Zr atom is bound to more than two sulfate oxygen atoms, and each Zr atom is linked to at least two other zirconium atoms via non-sulfate oxygen bridges. The sulfates do play a critical role in propagating the structure by participation in hydrogen bonding. As shown in Figure 1, the unit cell contains six molecules, of composition $Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6}(H_2O)_{16}$, which pack so as to create sizable channels. The channels contain additional water molecules. Hydrogen bonds between terminal sulfate oxygen atoms and channel water molecules serve to link the Zr sheets together. Thus, a more descriptive formula for the compound would be $Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6}(H_2O)_{16}\cdot 17H_2O$. The large thermal parameters of the oxygen atoms of the channel water molecules (primed atoms in Tables II and SII[17a]) are not unreasonable considering that hydrogen bonds are weak and that the X-ray study was performed at room temperature.

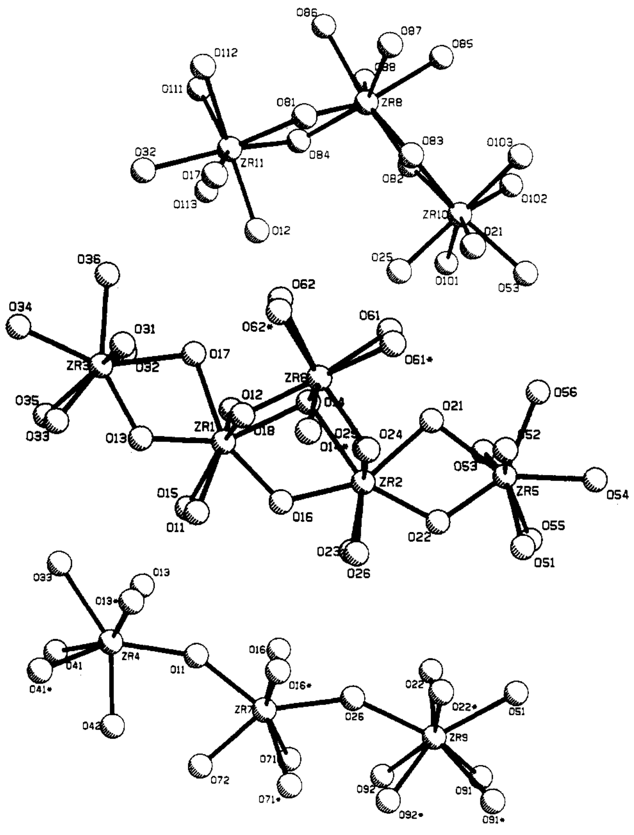

Figure 3. Coordination spheres of the zirconium atoms shown in detail, emphasizing the rows of metal atoms that comprise the framework. This "exploded" view is along the [001] direction.

The nonstoichiometry arises from disorder between sulfate and hydroxyl groups that can be viewed as a partial replacement of three of the SO_4^{2-} groups by OH^-, starting from an orginal ideal formula for each molecule of $Zr_{18}O_4(OH)_{36}(SO_4)_{14}(H_2O)_{16}$. This suggests that a dynamic replacement process involving the anions may have been taking place in solution and was frozen out at the time of crystallization.

Discussion

The sulfates of zirconium may be classified as anionic, neutral, or basic. The neutral compounds have a Zr:SO_4 ratio of exactly 1:2 while the basic salts are deficient in SO_4^{2-} with the balance made up by the presence of OH^- groups. Anionic complexes contain more than two sulfates per zirconium.

Neutral Zirconium Sulfates. Despite the apparent simplicity of the neutral sulfate composition, there actually exists a series of zirconium sulfate hydrates $Zr(SO_4)_2\cdot nH_2O$ (n = 0, 1, 4, 5, 7).[6–11] In addition, polymorphs exist for n = 0, 1, and 5. A comprehensive study of the structural chemistry of this series has been carried out by Bear and Mumme. The stable anhydrous polymorph α-$Zr(SO_4)_2$[11] and two of the monohydrates α-[10] and γ-$Zr(SO_4)_2\cdot H_2O$[9] have structures containing infinite sheets of 7-coordinate Zr atoms. In the monohydrates, the layers are held together by hydrogen bonds between the water molecules in the Zr coordination sphere and terminal sulfate oxygen atoms. The tetrahydrate $Zr(SO_4)_2\cdot 4H_2O$[8] also has an infinite sheet structure with interlayer hydrogen bonding, but the Zr coordination is 8-fold with four sulfate oxygen atoms and four water molecules forming a square antiprism about the metal. By contrast, the higher hydrates α- and β-$Zr(SO_4)_2\cdot 5H_2O$[7] and $Zr(SO_4)_2\cdot 7H_2O$[6] contain discrete dimers of composition $Zr_2(SO_4)_4(H_2O)_8$. The Zr atoms are in 8-fold dodecahedral coordination composed of four water

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Table II. Positional and Thermal Parameters for $Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6}\cdot 33H_2O$

atom	*x*	*y*	*z*	B_{eq}, Å^2	occupancy	atom	*x*	*y*	*z*	B_{eq}, Å^2	occupancy
Zr1	0.67982 (6)	0.08834 (6)	0.6482 (1)	1.42 (6)		O33	0.5447 (6)	0.0456 (6)	3/4	1.8 (6)	
Zr2	0.79870 (6)	0.11814 (6)	0.65043 (9)	1.35 (6)		O34	0.5078 (5)	0.0879 (6)	0.658 (1)	4.8 (8)	
Zr3	0.57623 (6)	0.09283 (7)	0.6449 (1)	1.97 (7)		O35	0.5245 (4)	0.0254 (5)	0.5970 (7)	2.5 (5)	
Zr4	0.58731 (8)	0.01013 (9)	3/4	1.59 (9)		O36	0.5815 (5)	0.1610 (5)	0.624 (1)	3.5 (6)	
Zr5	0.91995 (6)	0.18294 (6)	0.6445 (1)	1.68 (6)		O41	0.5342 (4)	−0.0307 (5)	0.6691 (7)	2.4 (5)	
Zr6	0.76073 (8)	0.18510 (8)	3/4	1.43 (9)		O42	0.5885 (6)	−0.0513 (7)	3/4	3 (1)	
Zr7	0.71743 (8)	0.02635 (8)	3/4	1.34 (8)		O51	0.9307 (6)	0.1474 (6)	3/4	2.3 (7)	
Zr8	0.77472 (6)	0.23536 (6)	0.4446 (1)	1.83 (6)		O52	0.9145 (6)	0.2103 (7)	3/4	2.3 (7)	
Zr9	0.86188 (8)	0.07954 (9)	3/4	1.51 (9)		O53	0.9069 (4)	0.1829 (4)	0.5251 (7)	2.0 (5)	
Zr10	0.85322 (6)	0.19559 (6)	0.4902 (1)	1.58 (6)		O54	0.9963 (5)	0.2200 (5)	0.6591 (8)	3.3 (6)	
Zr11	0.66007 (6)	0.14785 (7)	0.4908 (1)	2.19 (7)		O55	0.9468 (5)	0.1413 (5)	0.5918 (8)	3.0 (6)	
S1	0.6594 (2)	−0.0530 (2)	0.4382 (3)	2.4 (2)		O56	0.6900 (5)	−0.0519 (5)	0.3767 (8)	2.8 (6)	
S2	0.7819 (2)	0.0098 (2)	0.6213 (2)	1.7 (2)		O61	0.8190 (5)	0.2434 (5)	0.6855 (7)	3.4 (6)	
S3	0.6134 (2)	−0.0769 (2)	3/4	2.3 (3)		O62	0.7283 (6)	0.2203 (5)	0.6856 (8)	3.4 (6)	
S4	0.7628 (6)	0.2182 (5)	1/4	11.5 (7)	0.95 (2)	O71	0.7393 (4)	−0.0090 (4)	0.6669 (6)	1.8 (5)	
S5	0.5212 (2)	−0.0203 (2)	0.5935 (3)	2.9 (2)		O72	0.6631 (6)	−0.0434 (6)	3/4	1.8 (7)	
S6	0.6031 (2)	0.1996 (2)	0.5698 (4)	2.8 (3)	0.76 (2)	O81	0.7232 (4)	0.2061 (5)	0.5295 (7)	2.6 (5)	
S7	0.7134 (2)	0.2388 (2)	3/4	2.2 (3)		O82	0.8131 (4)	0.2041 (4)	0.4057 (7)	2.0 (5)	
S8	0.8477 (2)	0.2735 (2)	3/4	2.2 (3)		O83	0.8104 (4)	0.2223 (4)	0.5332 (7)	2.2 (5)	
S9	0.9366 (4)	0.0945 (4)	0.5965 (6)	3.5 (5)	0.54 (2)	O84	0.7163 (5)	0.1743 (5)	0.4093 (7)	2.8 (5)	
O1′	0.7300 (5)	0.0691 (5)	0.4432 (8)	3.1 (6)		O85	0.8396 (5)	0.2996 (5)	0.4145 (8)	3.6 (6)	
O2′	0.8324 (6)	0.0623 (5)	0.4443 (9)	4.4 (7)		O86	0.7389 (5)	0.2732 (5)	0.4183 (8)	3.3 (6)	
O3′	0.6156 (8)	0.2528 (7)	3/4	4 (1)		O87	0.7925 (5)	0.2921 (6)	0.5389 (7)	3.5 (6)	
O4′	0.8942 (8)	0.1668 (9)	1/4	4 (1)		O88	0.7750 (5)	0.2433 (5)	0.3173 (7)	3.1 (6)	
O5′	0.4520 (8)	−0.011 (1)	3/4	5 (1)		O91	0.9081 (6)	0.0641 (8)	0.677 (1)	8 (1)	
O6′	0.5802 (7)	0.0028 (7)	0.392 (1)	5.9 (9)		O92	0.8210 (4)	0.0206 (4)	0.6741 (7)	2.0 (5)	
O7′	0.636 (1)	−0.013 (1)	1/4	7 (2)		O101	0.8467 (5)	0.1437 (4)	0.3988 (7)	2.5 (5)	
O8′	0.591 (1)	0.115 (1)	1/4	9 (2)		O102	0.6711 (5)	−0.0966 (4)	0.6075 (7)	2.5 (5)	
O9′	0.928 (1)	0.106 (1)	1/4	9 (2)		O103	0.6343 (4)	−0.0998 (4)	0.4699 (7)	2.0 (5)	
O10′	0.663 (2)	0.076 (1)	1/4	17 (4)		O111	0.6302 (7)	0.1700 (9)	0.397 (1)	8 (1)	
O11′	0.7044 (9)	0.3204 (8)	0.533 (2)	12 (2)		O112	0.6416 (5)	0.2008 (5)	0.532 (1)	4.3 (7)	
O12′	0.5324 (9)	−0.113 (1)	0.444 (3)	19 (3)		O113	0.6348 (6)	0.0942 (6)	0.3963 (8)	5.0 (7)	
O11	0.6594 (5)	0.0367 (6)	3/4	2.0 (7)		O1S1	0.6251 (5)	−0.0421 (5)	0.4061 (8)	3.3 (6)	
O12	0.6834 (4)	0.1034 (4)	0.5272 (6)	2.1 (5)		O2S1	0.6866 (5)	−0.0195 (5)	0.4972 (8)	3.0 (6)	
O13	0.6097 (4)	0.0571 (4)	0.6617 (6)	1.9 (5)		O1S2	0.7791 (4)	−0.0223 (4)	0.5661 (7)	2.1 (5)	
O14	0.7518 (4)	0.1532 (4)	0.6358 (6)	1.6 (4)		O1S3	0.6046 (7)	−0.1028 (7)	0.683 (1)	9 (1)	
O15	0.6460 (4)	0.0149 (4)	0.5902 (6)	2.0 (5)		O1S4	0.7180 (9)	0.177 (1)	1/4	5 (1)	0.95 (2)
O16	0.7287 (4)	0.0689 (4)	0.6586 (6)	1.7 (4)		O2S4	0.805 (1)	0.189 (2)	1/4	13 (2)	0.95 (2)
O17	0.6539 (4)	0.1385 (4)	0.6192 (6)	1.7 (4)		O1S5	0.4751 (5)	−0.0554 (6)	0.5756 (8)	4.5 (6)	
O18	0.6976 (6)	0.1264 (6)	3/4	1.7 (6)		O2S5	0.5545 (5)	−0.0184 (6)	0.5356 (8)	4.2 (7)	
O21	0.8570 (4)	0.1907 (4)	0.6207 (6)	1.5 (4)		O1S6	0.5696 (7)	0.1918 (7)	0.512 (1)	4 (1)	0.76 (2)
O22	0.8623 (4)	0.1213 (4)	0.6632 (6)	1.4 (4)		O2S6	0.6198 (8)	0.2435 (6)	0.611 (1)	4 (1)	0.76 (2)
O23	0.7894 (4)	0.0525 (4)	0.5854 (6)	2.0 (5)		O1S7	0.7351 (8)	0.2881 (8)	3/4	4 (1)	
O24	0.8006 (5)	0.1534 (5)	3/4	1.0 (6)		O2S7	0.6647 (7)	0.2187 (7)	3/4	6 (1)	
O25	0.8014 (4)	0.1327 (4)	0.5289 (6)	1.7 (4)		O1S8	0.8507 (7)	0.3178 (7)	3/4	3 (1)	
O26	0.7919 (5)	0.0730 (5)	3/4	1.2 (6)		O2S8	0.8910 (7)	0.2760 (8)	3/4	8 (2)	
O31	0.6002 (6)	0.1281 (6)	3/4	2.1 (7)		O1S9	0.911 (1)	0.070 (1)	0.510 (2)	6 (2)	0.54 (2)
O32	0.5904 (4)	0.1006 (5)	0.5255 (7)	2.8 (5)		O2S9	0.983 (2)	0.098 (1)	0.595 (2)	8 (2)	0.54 (2)

molecules and four sulfate oxygen atoms. These discrete dimers are linked by hydrogen bonds involving additional water molecules, which occupy spaces between the Zr units. Thus these compounds are more accurately described by the formula $Zr_2(SO_4)_4(H_2O)_8\cdot nH_2O$ where $n = 2$ (pentahydrate) or 6 (heptahydrate). Two general trends accompanying the increase in hydration are evident from these results: the Zr coordination number increases from 7 to 8 and the dimensionality of the Zr framework decreases dramatically from 2 (infinite sheet) to 0 (discrete dimers).

Basic Zirconium Sulfates. Though an exhaustive study of the basic sulfate salts has not been performed, our results, together with those reported previously, suggest that similar trends obtain upon increasing replacement of SO_4^{2-} by OH^- and increasing hydration of these materials as well. To date only three basic zirconium sulfate structures have been reported. $Zr_2(OH)_2(SO_4)_3(H_2O)_4$[12] contains an infinite two-dimensional network of Zr atoms bridged by sulfate groups. These layers are linked by hydroxyl bridges. The Zr coordination is a dodecahedron formed by four sulfate oxygen atoms, two hydroxyl groups, and two water molecules. Hydrogen bonding is not important in this structure. $Zr(OH)_2SO_4$[12] and $Zr(OH)_2SO_4\cdot H_2O$[13] have similar structures in which the Zr atoms are bridged by hydroxyl groups to form infinite chains that are joined by sulfate groups. In $Zr(OH)_2SO_4$ the Zr coordination is 8-fold antiprismatic while in $Zr(OH)_2SO_4\cdot H_2O$ it is 7-fold pentagonal bipyramidal. In the hydrate, the layers formed by the linked chains are held together by hydrogen bonding. These compounds are all lower basic sulfates in that half, or fewer, of the SO_4^{2-} groups have been replaced by OH^- and the Zr:SO_4 ratio is still ≤1. As such they (together with similar basic zirconium chromates and nitrates[12,19]) have as a common feature an infinite Zr framework in which the hydroxyl groups participate exclusively in double bridges.

The crystal structure of $Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6}\cdot 33H_2O$ makes it clear that the higher basic sulfates differ markedly in this regard. As we have shown, this compound, which has a much higher Zr:SO_4 ratio (1.43:1) than the others, contains discrete 18 zirconium atom units rather than an infinite network. Moreover, the oxygen bridges that build these Zr sheets comprise quadruply bridging oxides and triply bridging hydroxides in addition to the doubly bridging hydroxides that were the rule before. As in the higher neutral sulfate hydrates, the channels in between the discrete Zr units contain hydrogen-bonded water molecules that are critical to the stability of the structure.

General Observations. It is clear from this extraordinary structural variation with composition that a complex chemistry is associated with the formation of the basic zirconium sulfates. Although many gaps in the picture remain, our results provide new clues to the nature of this crystal chemistry.

We have previously shown[14] that the best known basic sulfates (Chauvenet's, Leuch's, and Hauser's salts) belong to a series of

Table III. Selected Bond Distances (Å) in $Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6}\cdot 33H_2O$

Zr1–O16	2.07 (1)	Zr6–O24	2.10 (2)
Zr1–O13	2.07 (1)	Zr6–2 O14	2.22 (1)
Zr1–O18	2.103 (9)	Zr6–2 O61	2.27 (1)
Zr1–O12	2.17 (1)	Zr6–2 O62	2.28 (1)
Zr1–O17	2.32 (1)	Zr7–2 O16	2.06 (1)
Zr1–O14	2.33 (1)	Zr7–O72	2.14 (2)
Zr1–O11	2.35 (1)	Zr7–O11	2.16 (2)
Zr1–O15	2.38 (1)	Zr7–O26	2.20 (2)
Zr2–O24	2.09 (1)	Zr7–2 O71	2.23 (1)
Zr2–O16	2.11 (1)	Zr8–O84	2.11 (1)
Zr2–O22	2.11 (1)	Zr8–O81	2.12 (1)
Zr2–O25	2.18 (1)	Zr8–O83	2.14 (1)
Zr2–O26	2.25 (1)	Zr8–O82	2.15 (1)
Zr2–O21	2.31 (1)	Zr8–O86	2.20 (1)
Zr2–O23	2.37 (1)	Zr8–O85	2.24 (1)
Zr2–O14	2.42 (1)	Zr8–O88	2.25 (1)
Zr3–O13	2.05 (1)	Zr8–O87	2.37 (1)
Zr3–O31	2.121 (9)	Zr9–2 O22	2.07 (1)
Zr3–O32	2.13 (1)	Zr9–2 O92	2.21 (1)
Zr3–O35	2.23 (1)	Zr9–O26	2.26 (2)
Zr3–O34	2.24 (1)	Zr9–2 O91	2.27 (2)
Zr3–O36	2.25 (1)	Zr9–O51	2.31 (2)
Zr3–O33	2.32 (1)	Zr10–O25	2.08 (1)
Zr3–O17	2.33 (1)	Zr10–O82	2.12 (1)
Zr4–2 O13[a]	2.07 (1)	Zr10–O53	2.15 (1)
Zr4–O42	2.10 (2)	Zr10–O83	2.18 (1)
Zr4–O11	2.13 (2)	Zr10–O103	2.21 (1)
Zr4–2 O41	2.16 (1)	Zr10–O102	2.29 (1)
Zr4–O33	2.29 (2)	Zr10–O101	2.30 (1)
Zr5–O22	2.04 (1)	Zr10–O21	2.30 (1)
Zr5–O52	2.11 (1)	Zr11–O12	2.11 (1)
Zr5–O53	2.14 (1)	Zr11–O81	2.16 (1)
Zr5–O55	2.22 (1)	Zr11–O32	2.17 (1)
Zr5–O54	2.25 (1)	Zr11–O84	2.18 (1)
Zr5–O56	2.25 (1)	Zr11–O111	2.25 (2)
Zr5–O21	2.31 (1)	Zr11–O17	2.27 (1)
Zr5–O51	2.33 (1)	Zr11–O112	2.28 (2)
Zr6–O18	2.06 (2)	Zr11–O113	2.28 (2)

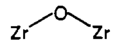
[a] Denotes two identical bonds to symmetry-related oxygen atoms.

general formula $Zr_n(OH)_{2n+2}(SO_4)_{n-1}$ ($n > 1$). Other series are also possible, for example, $Zr_n(OH)_{2n}(SO_4)_n$, of which examples have been given, and $Zr_n(OH)_{2n-2}(SO_4)_{n+1}$, to represent such compositions as $2ZrO_2\cdot 3SO_3\cdot 5H_2O$[5] or $Zr_2(OH)_2(SO_4)_3\cdot 4H_2O$. Still other series would contain correspondingly less sulfate such as $Zr_n(OH)_{2n+4}(SO_4)_{n-2}$ ($n > 2$). The present compound would nominally belong to the series $Zr_n(OH)_{2n+8}(SO_4)_{n-4}$, assuming ideal composition $Zr_{18}(OH)_{44}(SO_4)_{14}\cdot xH_2O$. This composition is further modified by oxolation and partial hydrolysis of sulfate groups. Thus, formation of four oxo groups results in loss of eight hydroxyls, yielding $Zr_{18}O_4(OH)_{36}(SO_4)_{14}$, while the partial displacement of 1.4 sulfates by OH^- yields the formula found in the present study.

We believe that almost all of the known basic zirconium sulfates can be fitted into one of these series and that certain rules apply to dictate how the different series arise. These rules are imperfectly formulated at present but arise from the following considerations. Sulfate ion strongly complexes zirconium[20,21] and can displace -ol groups when sulfate is present in high concentrations. Solutions containing Zr(IV) and SO_4^{2-} contain a multiplicity of species rather than a single preferred one. This is indicated by the fact that the sulfate solutions almost never reach equilibrium. Small changes in conductivity and precipitation of solids have been observed to occur over long periods of time.[5,22] Thus the larger polymers, such as the one described in this study, arise from the hydrolytic polymerization of the smaller soluble species. Evidence for the existence and mode of polymerization of small soluble fragments that arise from the dissolution of neutral (1:2) sulfates has been presented earlier.[14] The following rules arise from these considerations and the known sulfate structures:

1. Sulfate ion prefers to bridge across zirconium atoms under conditions where neutral and basic sulfate structures form. The bridging may be bidentate, tridentate, or quadridentate.
2. At high acidity and high sulfate ion concentrations, the sulfate ion may participate in bidentate chelation.[21,24]
3. The preferred coordination numbers in the solid phase are seven and eight.
4. Monodentate or nonbridged sulfate ions represent unstable situations and lead to further polymerization by bridging or displacement by a hydroxyl group.
5. Unbridged hydroxyl groups also represent an unstable condition. The hydroxyl group may be displaced by water or sulfate or may participate in further olation with another hydroxyl containing fragment.
6. Two hydroxyl groups displace one sulfate group followed by olation.
7. Oxolation takes place between olated chains or sheets by splitting out of water to produce an oxygen coordinated by four Zr atoms.

Rule 2 allows for the fact that solids with $Zr:SO_4$ ratios of 1:3 are known.[3,4] $Zr(SO_4)_2\cdot 4H_2O$ consists of infinite sheets of zirconium atoms linked together by sulfate bridging. In order for this sulfate to dissolve, the infinite sheets must break down into simpler units by scission of the bonds between Zr and sulfate oxygens. Since the solutions are highly acidic, the hydrolysis must occur by displacement of sulfate by OH^-.[14] The present structure confirms this. Because of the different types of subsequent displacement reactions that may occur, a polydisperse solution is to be expected. Several types of equilibria that may occur in such solutions have been given by Clearfield[14] and by Baglin and Breger.[25] Some ideas on how these species might polymerize to yield basic sulfates have also been presented.[14] It should be noted that the formation of oxo-groups results in a 4-coordinate oxygen rather than a 2-coordinate or



type. This was also found to be the case in the formation of cubic ZrO_2 by hydrolytic polymerization of the tetrameric zirconyl ion.[14,26-28]

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Note Added in Proof. We have recently become aware of the existence of a basic Hf sulfate that is essentially isomorphous with the Zr compound. The structure was determined by film techniques[29] and differs from the present structure only in the occupancies of some of the sulfate groups and water molecules of hydration.

Supplementary Material Available: Table SII, listing anisotropic thermal parameters (3 pages); Table SI, listing calculated and observed structure amplitudes (49 pages). Ordering information is given on any current masthead page.

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