further synthetic transformations, which are currently being investigated in our laboratory.

Experimental Section

Typical procedure for the α-alkylation: The enantiopure sulfonate **1** (1 mmol) was dissolved in dry THF (20 mL) and the solution cooled to $-(90-95)\,^{\circ}\mathrm{C}$. After 30 min *n*BuLi (1.0 equiv) was added dropwise. The solution was stirred for an additional hour after which the electrophile (1.5 equiv in 5 mL THF) was added dropwise. The mixture was stirred for 1 h at $-(90-95)\,^{\circ}\mathrm{C}$, then at $-78\,^{\circ}\mathrm{C}$. After 24 h the reaction was quenched by adding pH 7 buffer (2 mL). The mixture was partitioned between H_2O and CH_2Cl_2 and washed with brine. The aqueous layer was then extracted three times with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (SiO_2, pentane/diethyl ether).

Typical procedure for the removal of the chiral auxiliary: The sulfonate **2** (0.6 mmol) was dissolved in an $EtOH/H_2O$ solution (19 mL/1 mL). $Pd(OAc)_2$ (15 mol%) was added to the solution and the mixture was refluxed for four days (TLC control). The palladium residues were removed by filtration and washed twice with EtOH. The filtrate was treated with an ethereal solution of diazomethane until the yellow color persisted. The solvent was evaporated under reduced pressure and the crude product purified by flash column chromatography (SiO_2, pentane/diethyl ether).

Received: August 10, 2001 [Z17705]

---

[1] M. Yoshikawa, S. Yamaguchi, K. Kunimi, H. Matsuda, Y. Kuno, J. Yamahara, N. Murakami, *Chem. Pharm. Bull.* **1994**, *42*, 1226 – 1230.

[2] a) S. Morimoto, H. Nomura, T. Ishiguro, T. Fugono, K. Maeda, *J. Med. Chem.* **1972**, *15*, 1105 – 1108; b) S. Morimoto, H. Nomura, T. Fugono, T. Azuma, I. Minami, M. Hori, T. Masuda, *J. Med. Chem.* **1972**, *15*, 1108 – 1111.

[3] I. Minami, H. Akimoto, M. Kondo, H. Nomura, *Chem. Pharm. Bull.* **1983**, *42*, 482 – 489.

[4] a) D. R. Magnin, S. A. Biller, Y. Chen, J. K. Dickson, Jr., O. M. Fryszman, R. M. Lawrence, J. V. H. Logan, E. S. Sieber-McMaster, R. B. Sulsky, S. C. Traeger, D. C. Hsieh, S. Lan, J. K. Rinehart, T. W. Harrity, K. G. Jolibois, L. K. Kunselmann, L. C. Rich, D. A. Slusarchyk, C. P. Ciosek, Jr., *J. Med. Chem.* **1996**, *39*, 657 – 660; b) J. K. Dickson, Jr., S. A. Biller, D. R. Magnin, E. W. Petrillo, Jr., J. W. Hillyer, D. C. Hsieh, S. Lan, K. Rinehart, R. E. Gregg, T. W. Harrity, K. G. Jolibois, S. S. Kalinowski, L. K. Kunselman, K. A. Mookhtiar, C. P. Ciosek, Jr., *J. Med. Chem.* **1996**, *39*, 661 – 664.

[5] R. Yoshioka, K. Okamura, S. Yamada, K. Aoe, T. Da-te, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1109 – 1116.

[6] H. Kawanishi, H. Morimoto, T. Nakano, T. Watanabe, K. Oda, K. Tsujihara, *Heterocycles* **1998**, *49*, 181 – 189.

[7] E. B. Evans, E. E. Mabbott, E. E. Turner, *J. Chem. Soc.* **1927**, 1159 – 1168.

[8] E. J. Corey, K. A. Cimprich, *Tetrahedron Lett.* **1992**, *33*, 4099 – 4102.

[9] R. M. Lawrence, S. A. Biller, J. K. Dickson, J. V. H. Logan, D. R. Mignin, R. B. Sulsky, J. D. DiMarco, J. Z. Gougoutas, B. D. Beyer, S. C. Taylor, S. Lan, C. P. Ciosek, Jr., T. W. Harrity, K. G. Jolibois, L. K. Kunselman, D. A. Slusarchyk, *J. Am. Chem. Soc.* **1996**, *118*, 11668 – 11669. For the asymmetric synthesis of sulfonic acid derivatives see: a) M. H. H. Nkunya, B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 253 – 259; b) F. A. Davis, P. Zhou, *J. Org. Chem.* **1993**, *58*, 4890 – 4896; c) D. Enders, C. R. Thomas, G. Raabe, J. Runsink, *Helv. Chim. Acta* **1998**, *81*, 1329 – 1336; d) C. Huart, L. Ghosez, *Angew. Chem.* **1997**, *109*, 627 – 629; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 634 – 636.

[10] W. Sowa, G. H. S. Thomas, *Can. J. Chem.* **1966**, *44*, 836 – 837.

[11] H. Kunz, J. Mohr, *J. Chem. Soc. Chem. Commun.* **1988**, *19*, 1315 – 1317.

[12] D. Brundish, A. Bull, V. Donovan, J. D. Fullerton, S. M. Garman, J. F. Hayler, D. Janus, P. D. Kane, M. McDonell, G. P. Smith, R. Wakeford, C. V. Walker, G. Howarth, W. Hoyle, M. C. Allen, J. Ambler, K. Butler, M. D. Talbot, *J. Med. Chem.* **1999**, *42*, 4584 – 4603.

[13] a) S. Otto, J. B. F. N. Engberts, J. C. T. Kwak, *J. Am. Chem. Soc.* **1998**, *120*, 9517 – 9525; b) H. Abdellaoui, P. Depreux, D. Lesieur, B. Pfeiffer, P. Bontempelli, *Synth. Commun.* **1995**, *25*, 1303 – 1311.

[14] Crystal data for **2d**: single crystals were obtained by recrystallization from ethyl acetate. The substance ($C_{30}H_{40}O_8S$, $M_r = 560.68$) crystallized in the monoclinic space group $P2_1$, $a = 17.624(2)$, $b = 18.704(2)$, $c = 26.905(5)$ Å, $\beta = 92.436(14)^{\circ}$, $V = 8861(2)$ Å^3, $Z = 12$, $\rho_{calcd} = 1.216\ \mathrm{g\,cm^{-3}}$, $F(000) = 3600$, $T = 173(2)$ K. Data collection: A single crystal (colorless transparent block with dimensions $0.12 \times 0.2 \times 1.3$ mm) was measured on a SIEMENS SMART diffractometer at a temperature of about $-100\,^{\circ}\mathrm{C}$. Repeatedly measured reflections remained stable. An empirical absorption correction was made by using the program SADABS. The correction factor ranged from 0.950 to 1.000. Equivalent reflections were averaged. Friedel opposites were not averaged. $R(I)_{int} = 0.092$. The structure was solved by direct methods using the program SHELXS. The H atoms were placed at calculated positions and were treated as riding atoms. The structure was refined on F^2 values using the program SHELXL-97. Max./min. resiual electron denisty $-0.25/+0.25$ e Å^{-3}. The absolute configuration of the structure was confirmed by the value of the Flack x parameter ($x = -0.04(3)$). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-168530. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[15] As the sugar auxiliary is rather cheap, it is acceptable at the present stage that the auxiliary cannot be recycled under these conditions.

[16] a) A. Windaus, E. Kuhr, *Liebigs Ann. Chem.* **1937**, *532*, 52 – 68; b) W. Treibs, I. Lorenz, *Chem. Ber.* **1949**, *82*, 400 – 405; c) G. Geiseler, R. Kuschmiers, *Chem. Ber.* **1958**, *91*, 1881 – 1891; d) H. C. Hansen, J. L. Kice, *J. Org. Chem.* **1983**, *48*, 2943 – 2949; e) H. Ishiyama, M. Ishibashi, A. Ogawa, S. Yoshida, J. Kobayashi, *J. Org. Chem.* **1997**, *62*, 3831 – 3836.

Protonated Sulfuric Acid: Preparation of Trihydroxyoxosulfonium Hexafluoroantimonate $H_3SO_4^+SbF_6^-$[**]

Rolf Minkwitz,[*] Raphael Seelbinder, and René Schöbel

Dedicated to Professor Karl Otto Christe on the occasion of his 65th birthday

One of the strongest acids is 100% sulfuric acid and this marks per definition the border to the superacids. Among the ions that are formed by the autoprotolysis of sulfuric acid according to Equation (1), only the structure of the hydrogensulfate ion in solid salts and that of sulfuric acid itself is known.[1, 2]

$$2\,H_2SO_4 \longrightarrow H_3SO_4^+ + HSO_4^- \qquad (1)$$

---

[*] Prof. Dr. R. Minkwitz, Dipl.-Chem. R. Seelbinder, R. Schöbel
Fachbereich Chemie, Anorganische Chemie
Universität Dortmund
Otto-Hahn-Strasse 6, 44227 Dortmund (Germany)
Fax: (+49) 231-755-5048
E-mail: minkwitz@citrin.chemie.uni-dortmund.de

[**] This work was supported by the Deutsche Forschungsgemeinschaft.

The existence of the trihydroxyoxosulfonium cation $H_3SO_4^+$ was confirmed by cryoscopy, conductivity measurements, and mass spectrometry, and structural parameters were calculated by theoretical methods.[3–5] A complete protonation of sulfuric acid to $H_3SO_4^+$ is only possible by acids with a proton activity H_0 about six orders of magnitude greater than that of H_2SO_4. Theoretically the superacid HF/SbF_5 with a H_0 value of up to -21 should be able to protonate sulfuric acid, which has a H_0 value of -12, to give the $H_3SO_4^+$ ion. But it was shown by Gillespie and Robinson that about 0.1 % of the sulfuric acid also undergoes an ionic self-dehydration [Eq. (2)] at the same time to give oxonium ions.[5]

$$2\,H_2SO_4 \longrightarrow H_3O^+ + HS_2O_7^- \qquad (2)$$

Oxonium ions have a levelling effect on the superacid strength, which prohibits a complete protonation, as we confirmed by our own investigations. The reaction of pure sulfuric acid with HF/SbF_5 does not yield a homogeneous solid but a highly viscous residue, from which $H_3O^+SbF_6^-$ can be isolated. To avoid the dehydration leading to formation of H_3O^+ ions, the bis(trimethylsilyl) ester of sulfuric acid (**1**) was used as starting material, which reacts according to Equation (3).

$$\underset{\mathbf{1}}{[(CH_3)_3SiO]_2SO_2} + XF/SbF_5 \longrightarrow 2\,(CH_3)_3SiF + \underset{\mathbf{2}}{X_3SO_4^+SbF_6^-} \qquad (3)$$
$$(X = H, D)$$

This kind of reaction was successfully applied to the preparation of salts of protonated hydrogen peroxide and protonated carbonic acid.[6, 7] The formation of **2** is thermodynamically favored because of the high formation enthalpy of the Si–F bond and its preparation has the advantage that trimethylfluorosilane and HF can be removed easily at −78 °C in vacuum. ^1H NMR spectroscopy gave no indication of the formation of H_3O^+ ions and thus for a reaction according to Equation (2); the spectrum shows only a singlet at $\delta = 12.1$ for $H_3SO_4^+SbF_6^-$. After removal of **2** and excess of HF/DF a crystalline, colorless solid of $H_3SO_4^+SbF_6^-$ or $D_3SO_4^+SbF_6^-$, respectively, precipitates, from which crystals suitable for an X-ray structure analysis were obtained.[8] In contrast to $D_3SO_4^+SbF_6^-$, the results of the X-ray structure analysis of $H_3SO_4^+SbF_6^-$ did not lead to a satisfactory determination of the structure because all measured crystals displayed a disorder that we were unable to explain.

Efforts to obtain the compounds as hexafluoroarsenate salts by the use of the superacid XF/AsF_5 ($X = H, D$) were not successful and always yielded a highly viscous fluid, in which no oxonium salts were found. Evidently, the acid strength of this system is not sufficient to protonate the sulfuric acid completely.

The single-crystal structure determination of $D_3SO_4^+SbF_6^-$ shows, within the precision of the measurement, that three of the four S–O bonds are almost the same length (149.9(6)–151.2(6) pm). They are shorter than the S–O single bonds in sulfuric acid (153.7(1) pm) and longer than its S–O double bond, which infers delocalization of the positive charge over the SO_3 unit (Figure 1, Table 1). The length of the S–O double bond in $D_3SO_4^+SbF_6^-$ (141.3(6) pm) is comparable to the bond length in solid sulfuric acid (142.6(1) pm).[2] All deuterium atoms were found by Fourier synthesis. The Sb–F distances (Sb(1)–F(1) 188.9(5), Sb(1)–F(2) 191.4(5), Sb(1)–F(3) 190.4(5) pm) of the fluorine atoms that participate in the hydrogen (deuterium) bonds are significantly longer than the other Sb–F bond lengths (185.8(5)–187.1(5) pm), thus the anion is a distorted octahedron. Anions and cations are linked by three hydrogen bonds in the crystal, leading to 4-rings comprising 16 atoms. These rings are condensed to wavy bands arranged parallel to the *bc* plane (Figure 2).

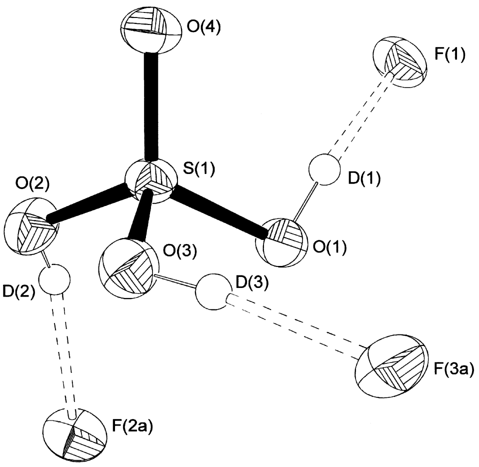

Figure 1. The $D_3SO_4^+$ ion with atom labels. Interionic contacts [pm]: O(1)-D(1)···F(1) 259.3(8), O(2)-D(2)···F(2a) 254.5(8), O(3)-D(3)···F(3a) 255.7(8). Symmetry operation: a: $-x, -y, -z$.

Table 1. Selected bond lengths and angles of $D_3SO_4^+SbF_6^-$. Only three F atoms are shown from the anion in Figure 1.[a]

Distances [pm]		Angles [°]	
S(1)-O(1)	151.1(5)	O(4)-S(1)-O(1)	115.6(3)
S(1)-O(2)	149.8(6)	O(4)-S(1)-O(2)	110.5(4)
S(1)-O(3)	150.6(6)	O(4)-S(1)-O(3)	115.7(3)
S(1)-O(4)	141.0(6)	O(1)-S(1)-O(2)	107.3(3)
		O(1)-S(1)-O(3)	103.6(3)
		O(2)-S(1)-O(3)	103.0(3)
Sb(1)-F(1)	188.9(5)	F(1)-Sb(1)-F(5)	177.3(2)
Sb(1)-F(2)	191.4(5)	F(2)-Sb(1)-F(6)	179.2(2)
Sb(1)-F(3)	190.4(5)	F(2)-Sb(1)-F(3)	88.0(2)
Sb(1)-F(4)	187.1(5)	F(3)-Sb(1)-F(4)	176.0(2)
Sb(1)-F(5)	185.8(5)		
Sb(1)-F(6)	186.9(5)		

[a] Standard deviations refer to the last digit of the number.

The vibrational spectroscopic characterization of $D_3SO_4^+SbF_6^-$ and $H_3SO_4^+SbF_6^-$ is given by their IR spectra, because during Raman investigations strong fluorescence occurred. The IR spectra (Figure 3, Table 2) of $X_3SO_4^+SbF_6^-$ ($X = H, D$) confirm the results of the X-ray structure analysis and are comparable to the spectra of the isoelectronic orthophosphoric acid. The position and contour of the bands, as well as their splitting is attributed to crystal effects. The broad band between 2173 and 2411 cm^{-1} is assigned to the O–D stretching modes (D_3PO_4: 2050–2350 cm^{-1}).[9] The

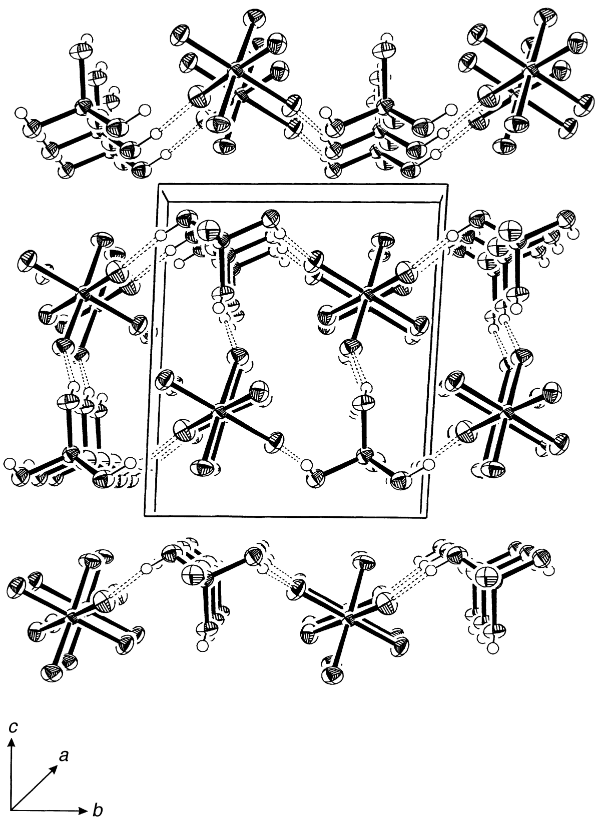

Figure 2. Section of the crystal packing of $D_3SO_4^+SbF_6^-$.

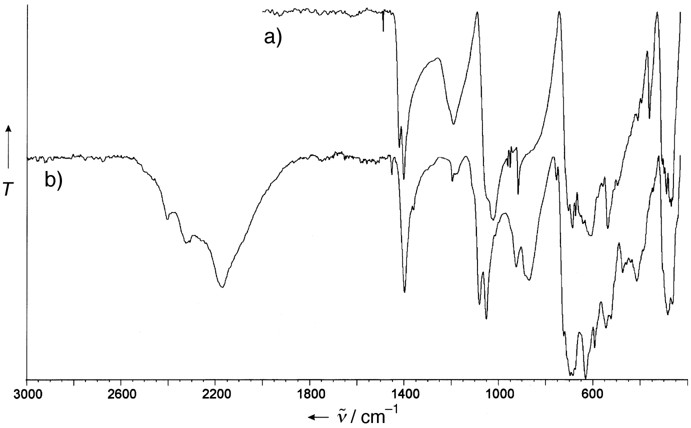

Figure 3. IR spectra of a) $H_3SO_4^+SbF_6^-$ and b) $D_3SO_4^+SbF_6^-$ as solids at −40 °C.

S=O stretching mode (1401 cm^{-1}) of the double bond occurs about 340 wavenumbers above the P–O valence mode of phosphoric acid (1165 cm^{-1}), but lower than in the isoelectronic triflourooxosulfonium cation in the hexaflouroantimonate salt (1540 cm^{-1}).[10] The asymmetric SO_3 valence stretches are detected at 1051 and 1085 cm^{-1} for $D_3SO_4^+$ and at 1123 cm^{-1} for the protonated sulfuric acid, whereas the symmetric valence modes are found at 930 and 922 cm^{-1}, respectively (D_3PO_4: $\nu_{as}(PO_3)$: 1012, $\nu_s(PO_3)$: 880 cm^{-1}; H_3PO_4: $\nu_{as}(PO_3)$: 1066–1074, 1007, $\nu_s(PO_3)$: 885 cm^{-1}). The SO_3 deformation modes for $D_3SO_4^+SbF_6^-$ are detected at 482 cm^{-1} for δ_{as} and at 417 cm^{-1} for δ_s. For $H_3SO_4^+SbF_6^-$ only one deformation mode at 410 cm^{-1} was observed.

Table 2. IR frequencies[a] [cm^{-1}] and assignment.

$H_3SO_4^+SbF_6^-$	$D_3SO_4^+$ SbF_6^-	Assignment
n.o.	2411 (w)	ν OH(D)
	2328 (m)	
	2173 (s)	
1401 (s)	1401 (s)	ν S=O
1195 (m)		δ_{as} SOH
1123 (vs)		ν_{as} SO_3
	1085 (s)	
	1051 (s)	
954 (s)		δ_s SOH
922 (s)	930 (m)	ν_s SO_3
	872 (s)	δ_{as} SOD
	546 (s)	δ O=SO
539 (vs)	521 (sh)	
	482 (m)	δ_{as} SO_3
410 (m)	417 (m)	δ_s SO_3
361 (m)		δ_{as} OSOH
	280 (s)	δ_{as} OSOD
688 (vs)	684 (vs)	ν SbF_6^-
610 (vs)	630 (vs)	
559 (sh)	588 (s)	
287 (s)	287 (s)	

[a] n.o. not observed; intensities (in parentheses): vs = very strong, s = strong, m = medium, w = weak, sh = shoulder.

One expects two vibrations for the SbF_6^- ion, but in both salts four vibrations are found. This is attributed to the decrease of the symmetry of the octahedron, which results from the different Sb–F bond lengths as established already in the crystal structure analysis.

Experimental Section

$(Me_3SiO)_2SO_2$ was prepared according to reference [11]. SbF_5 (Fluka) was triply distilled; DF was prepared from D_2SO_4 and CaF_2 and dried over F_2.

In a KEL-F reactor SbF_5 (1.5 mmol) was dissolved in HF or DF (ca. 140 mmol) and cooled to −196 °C. Under a dry nitrogen atmosphere $(Me_3SiO)_2SO_2$ (1.5 mmol) was added. The mixture was allowed to warm to −78 °C and volatile products as well as the excess of HF/DF were removed in dynamic vacuum. $D_3SO_4^+SbF_6^-$ or $H_3SO_4^+SbF_6^-$, respectively, precipitated as colorless solids, which decomposed at −5 °C.

Apparatus employed: Raman: Jobin-Yvon T64000, Ar$^+$-Laser (λ = 514.5 nm) Spectra Physics; IR: Bruker-IFS 113v; NMR: Bruker DPX300; X-ray diffractometer: Nonius-Kappa-CCD (1152 × 1242 Pixel).

Received: July 5, 2001 [Z17431]

---

[1] F. A. Cotton, B. A. Frenz, D. L. Hunter, *Acta Crystallogr. Sect. B* **1975**, *31*, 302–304.

[2] E. Kemnitz, C. Werner, S. Trojanov, *Acta Crystallogr. Sect. C* **1996**, *52*, 2665–2668.

[3] C. A. Pommerening, S. M. Bachrach, *J. Phys. Chem.* **1999**, *103*, 1214–1220.

[4] K. Do, T. P. Klein, C. A. Pommerening, S. M. Bachrach, L. S. Sunderlin, *J. Am. Chem. Soc.* **1998**, *120*, 6093–6096.

[5] R. J. Gillespie, E. A. Robinson in *Advances in Inorganic Chemistry and Radiochemistry, Vol. 1* (Eds.: H. J. Emeleus, A. G. Sharpe), Academic Press, New York, **1959**, p. 385.

[6] R. Minkwitz, S. Schneider, *Angew. Chem.* **1999**, *111*, 749–751; *Angew. Chem. Int. Ed.* **1999**, *38*, 714–715.

[7] R. Minkwitz, C. Hirsch, *Angew. Chem.* **1998**, *110*, 1776–1779; *Angew. Chem. Int. Ed.* **1998**, *37*, 1681–1684.

[8] a) Single-crystal X-ray analysis of $H_3SO_4^+SbF_6^-$ at 173 K: monoclinic, a = 979,7(1), b = 1416,1(1), c = 521,3(1) pm, β = 99.67(1); b) single-

crystal X-ray analysis of $D_3SO_4^+SbF_6^-$ at 173 K: triclinic, space group $P\bar{1}$ (no. 2), $a = 505.9(1)$, $b = 790.7(1)$ $c = 963.9(1)$ pm, $\alpha = 86.88(1)$, $\beta = 74.98(1)$, $\gamma = 88.89(1)^\circ$, $Z = 2$, $V = 371.8(1) \times 10^6$ pm^3, $\rho_{calcd} = 2.991(1)$ g cm^{-3}, crystal dimensions: $0.15 \times 0.12 \times 0.12$ mm^3, $2\theta/\omega$ scans, $2\theta_{max} = 54.92^\circ$, $T = 173(2)$ K, reflections collected 2543, 1639 independent reflections, σ-limit 2.0, $\mu(Mo_{K\alpha}) = 5.433$ mm^{-1}, structure solution: Patterson method, difference Fourier synthesis; SHELXS-86, SHELXL-93, PARST, PLATON, MISSYM, DENZO, SCALEPACK; 112 free parameters, deuterium atoms from the difference Fourier map ΔF, $R = 0.0476$, $wR2 = 0.1601$, $R = \Sigma||F_o| - |F_c||/\Sigma|F_0|$, structure refinement: full-matrix least-squares on F^2, largest difference peak and hole $-2.61/1.36$ e Å^{-3} from difference Fourier synthesis. For technical reasons we are not able to perform an experimental absorption correction. Using the data reduction software SCALEPACK (Minor and Otwinowski), each measured frame is multiplied by a certain scale factor that is generated by comparing the intensity of symmetrically related reflections.[12] Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-412007.

[9] A. C. Chapman, L. E. Thirlwell, *Spectrochim. Acta* **1964**, *20*, 937–947.

[10] R. J. Gillespie, E. A. Robinson, *Can. J. Chem.* **1962**, *40*, 644–657.

[11] N. Duffeaut, R. Calas, J. Donoguès, *Bull. Soc. Chim. Fr.* **1963**, 512.

[12] Z. Otwinoski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307–326.