Table 2. *Selected geometric parameters* (Å, °)

Si1—O1	1.626 (3)	C23—C22	1.357 (6)
Si1—C18	1.843 (5)	C12—C13	1.362 (6)
Si1—C30	1.882 (4)	C12—C11	1.498 (4)
Si1—C24	1.873 (5)	C9—C8	1.464 (6)
C3—C2	1.515 (4)	C9—C91	1.490 (6)
C3—C4	1.392 (5)	O5—C51	1.413 (5)
C3—C8	1.389 (5)	C8—C7	1.403 (6)
O1—C2	1.408 (4)	C6—C7	1.349 (6)
O6—C6	1.366 (4)	C30—C31	1.536 (8)
O6—C61	1.409 (6)	C30—C32	1.516 (8)
N10—C9	1.436 (5)	C30—C33	1.512 (8)
N10—C11	1.427 (4)	C13—C14	1.379 (6)
C5—C4	1.367 (5)	C22—C21	1.364 (6)
C5—O5	1.355 (5)	C24—C25	1.382 (6)
C5—C6	1.387 (5)	C24—C29	1.374 (6)
C18—C23	1.396 (6)	C14—C15	1.383 (6)
C18—C19	1.401 (6)	C15—C16	1.344 (7)
C20—C19	1.364 (6)	C25—C26	1.402 (6)
C20—C21	1.377 (6)	C26—C27	1.342 (8)
C17—C12	1.387 (6)	C27—C28	1.370 (7)
C17—C16	1.378 (6)	C28—C29	1.366 (6)
C2—C11	1.523 (6)		
C30—Si1—C24	111.6 (3)	C5—O5—C51	116.4 (4)
C18—Si1—C24	110.8 (3)	C3—C8—C9	122.4 (4)
C18—Si1—C30	109.7 (3)	C9—C8—C7	120.4 (4)
O1—Si1—C24	110.7 (2)	C3—C8—C7	117.1 (4)
O1—Si1—C30	108.6 (3)	O6—C6—C5	115.5 (4)
O1—Si1—C18	105.1 (3)	C5—C6—C7	119.3 (4)
C4—C3—C8	120.0 (4)	O6—C6—C7	125.2 (4)
C2—C3—C8	120.5 (4)	Si1—C30—C33	109.2 (4)
C2—C3—C4	119.5 (4)	Si1—C30—C32	110.8 (4)
Si1—O1—C2	134.9 (4)	Si1—C30—C31	111.4 (4)
C6—O6—C61	117.0 (4)	C32—C30—C33	111.0 (5)
C9—N10—C11	113.9 (4)	C31—C30—C33	108.1 (5)
O5—C5—C6	115.8 (4)	C31—C30—C32	106.3 (5)
C4—C5—C6	119.7 (4)	C12—C13—C14	120.8 (5)
C4—C5—O5	124.5 (4)	C18—C19—C20	121.9 (5)
Si1—C18—C19	123.1 (4)	C8—C7—C6	122.8 (4)
Si1—C18—C23	121.1 (4)	C2—C11—C12	114.1 (4)
C23—C18—C19	115.8 (4)	N10—C11—C12	110.2 (3)
C19—C20—C21	119.4 (5)	N10—C11—C2	105.9 (4)
C12—C17—C16	120.4 (5)	C23—C22—C21	119.3 (5)
C3—C2—O1	112.3 (3)	C20—C21—C22	120.7 (5)
O1—C2—C11	107.5 (3)	Si1—C24—C29	120.5 (4)
C3—C2—C11	108.6 (4)	Si1—C24—C25	122.7 (3)
C18—C23—C22	122.8 (5)	C25—C24—C29	116.8 (5)
C17—C12—C11	120.2 (4)	C24—C25—C26	120.4 (4)
C17—C12—C13	118.5 (4)	C25—C26—C27	121.4 (5)
C13—C12—C11	121.1 (4)	C26—C27—C28	118.3 (5)
C3—C4—C5	120.9 (4)	C27—C28—C29	121.0 (5)
N10—C9—C91	109.6 (4)	C17—C16—C15	120.9 (5)
N10—C9—C8	109.8 (4)	C24—C29—C28	122.1 (5)
C8—C9—C91	113.2 (4)	C13—C14—C15	120.0 (5)
C14—C15—C16	119.4 (5)		

Due to the poor quality of the crystal the data could be measured up to an angle $\theta = 25°$. This explains the poor relative number of parameters, number of reflections, the resulting high R value, and the large standard deviations.

Structure solution: *MULTAN*87 (Debaerdemaeker, Germain, Main, Tate & Woolfson, 1987). Structure refinement: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *SCHAKAL*88 (Keller, 1988). Preparation of material for publication: *PARST* (Nardelli, 1983).

The authors gratefully acknowledge Petronor, SA (Muskiz, Bizkaia), for the generous gift of hexane during the last years. Financial support of the University of the Basque Country (Project UPV 170.310-E076/90) and of the MEC (HA93-013) are gratefully acknowledged. One of us (IT) thanks the Basque Government for a fellowship.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving H atoms have been deposited with the IUCr (Reference: NA1106). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Arrieta, J. M., Badía, D., Domínguez, E., Lete, E., Igartua, A., Germain, G., Vlassi, M. & Debaerdemaeker, T. (1988). *Acta Cryst.* C**44**, 1931–1933.

Arrieta, J. M., Badía, D., Domínguez, E., Lete, E., Martínez de Marigorta, E., Germain, G., Vlassi, M. & Debaerdemaeker, T. (1988). *J. Chem. Res.* (*M*), pp. 591–597.

Badía, D., Domínguez, E. & Tellitu, I. (1992). *Tetrahedron*, **48**(21), 4419–4430.

Debaerdemaeker, T., Germain, G., Main, P., Tate, C. & Woolfson, M. M. (1987). *MULTAN*87. *A Computer Program for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, Louvain, Belgium, and Ulm, Germany.

Keller, E. (1988). *SCHAKAL*88. *Fortran Program for the Graphic Representation of Molecular and Crystallographic Models*. Univ. of Freiburg, Germany.

Kinns, M. & Sanders, J. K. M. (1984). *J. Magn. Reson.* **56**, 518–520.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Ohta, S., Tachikawa, O., Makino, Y., Tasaki, Y. & Hirobe, M. (1990). *Life Sci.* **46**, 599–605.

Plywaczyk, M., Tykarsa, E., Jaskólski, M. & Kosturkiewicz, Z. (1984). *Acta Cryst.* C**40**, 1107–1109.

Sheldrick, G. M. (1976). *SHELX*76. *Program for Crystal Structure Determination*. Univ. of Cambridge, England.

Acta Cryst. (1995). C**51**, 1234–1240

Five Salts of Berberine

BENSON M. KARIUKI

Department of Chemistry, University of Liverpool, PO Box 147, Liverpool L69 3BX, England

WILLIAM JONES

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, England

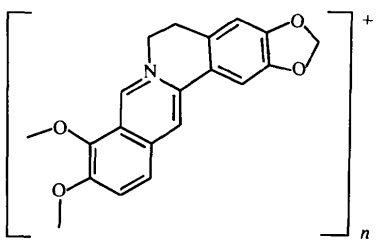
(*Received* 5 *July* 1994; *accepted* 2 *November* 1994)

Abstract

Structures of berberine chloride tetrahydrate, $C_{20}H_{18}NO_4^+.Cl^-.4H_2O$ (I), berberine chloride ethanol solvate hemihydrate, $C_{20}H_{18}NO_4^+.Cl^-.C_2H_5OH.0.5H_2O$ (II), berberine bromide dihydrate, $C_{20}H_{18}NO_4^+.Br^-.2H_2O$ (III), berberine iodide, $C_{20}H_{18}NO_4^+.I^-$ (IV) and bis(berberine) sulfate heptahydrate, $2C_{20}H_{18}NO_4^+.SO_4^{2-}.7H_2O$ (V) are reported. In all the salts, the cations pack in antiparallel pairs.

Comment

Berberine, 5,6-dihydro-9,10-dimethoxybenzo[*g*]-1,3-benzodioxolo[5,6-*a*]quinolizinium, which is an alkaloid of pharmacological interest, occurs in many plants (Abadi, Moss & Palmer, 1984). The crystal structures were obtained to determine the influence



$Cl^-.4H_2O$, $n = 1$ (I)

$Cl^-.C_2H_5OH.0.5H_2O$, $n = 1$ (II)

$Br^-.2H_2O$, $n = 1$ (III)

I^-, $n = 1$ (IV)

$SO_4^{2-}.7H_2O$, $n = 2$ (V)

of the counter-ion on the packing of the berberine cations. The effect of the mode of packing on the reactivity of crystalline materials has been extensively studied (Schmidt, 1971; Theocharis & Jones, 1987). The structure of berberine hydrogen sulfate has been reported and the molecular structure of the cation discussed (Abadi, Moss & Palmer, 1984). The atom identification scheme for (V) is shown in Fig. 1 [atom numbering for the other compounds is identical to molecule 1]. The asymmetric unit of each structure includes a cation and an anion [two for (V)]. In crystals of (II), ethanol molecules are incorporated in addition to those of water (which are disordered). (I), (III) and (V) contain water of hydration (four, two and seven molecules, respectively), although they were recrystallized from methanol. This is consistent with elemental analysis results. Cation bond distances and angles for (III) as well as selected contacts for (I), (II) and (V) are tabulated. The conformations assumed by the cations are very similar in all the structures. The interplanar angles between rings *A* and *CD* range from 10.31 (9)° (I) to 16.35 (13)° [(V), cation 2]. The maximum deviation of C19 from the plane of rings *CD* is 0.310 (6) Å (III). For C20, the deviation from the same plane falls between 1.106 (15) (IV) and 1.272 (6) Å (I). In all the structures, the cations pack in centrosymmetric pairs which in turn form columns parallel to one axis (Figs. 2–6). Similar pairing has been observed for other planar ions (Wang-Nang & Jones, 1987). The spaces between the columns are occupied by anions and solvent molecules. In addition to electrostatic forces, hydrogen-bonding contacts occur [except in (IV) which is not solvated].

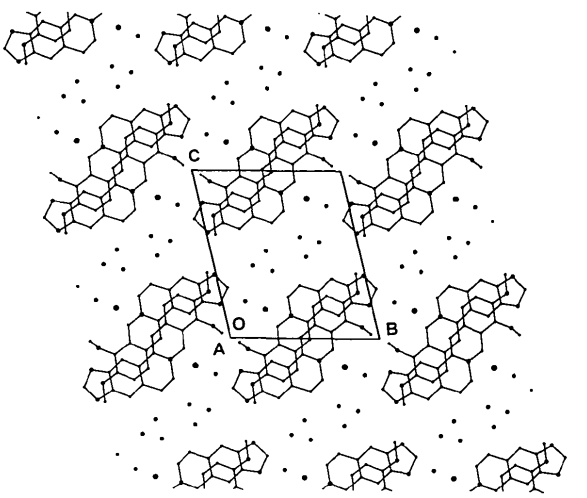


Fig. 2. The structure of (I) viewed down the *a* axis. H atoms have been omitted for clarity.

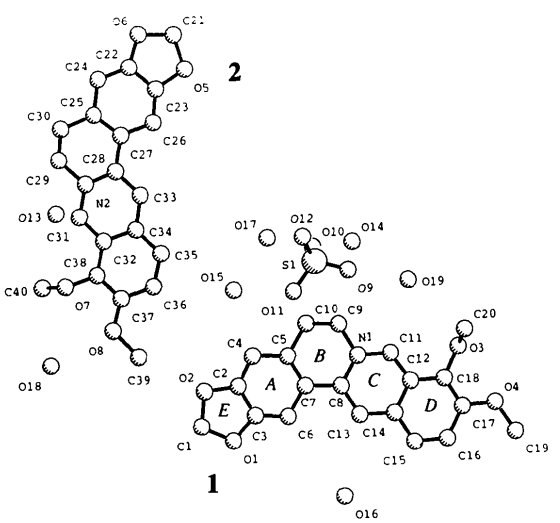


Fig. 1. The asymmetric unit of (V) showing the numbering scheme. H atoms have been omitted for clarity

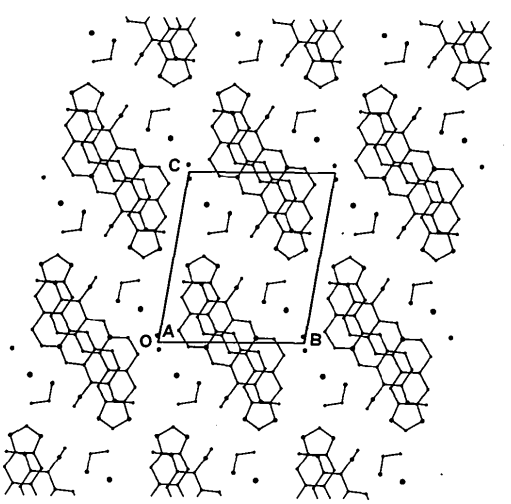


Fig. 3. The structure of (II) viewed along the *a* axis.

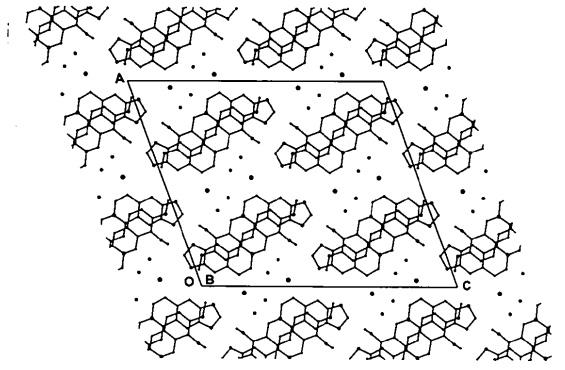


Fig. 4. The structure of (III) viewed down the *b* axis.

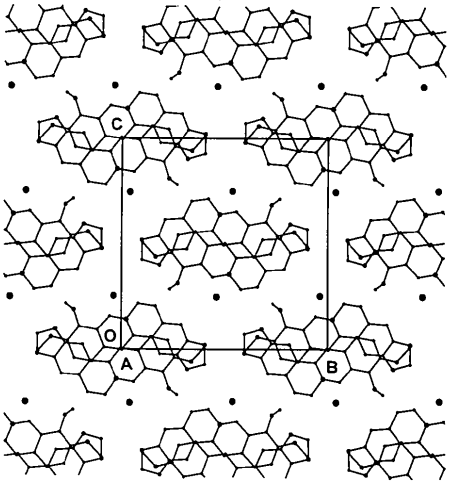


Fig. 5. The structure of (IV) viewed down the *a* axis.

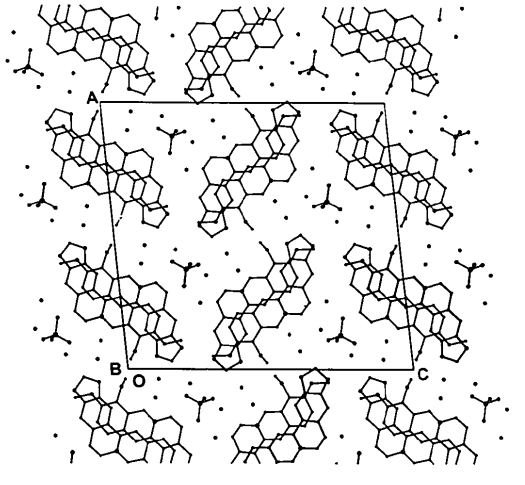


Fig. 6. The structure of (V) viewed down the *b* axis.

Experimental

Berberine chloride and sulfate were obtained from Aldrich Chemicals plc. Recrystallization of the chloride from methanol gave crystals of (I) and ethanol yielded (II). The bromide was prepared by precipitation from a warm aqueous solution of the chloride using potassium bromide. The solid was then washed and recrystallized from methanol to yield (III). The same procedure was repeated using potassium iodide instead of bromide to give (IV). Recrystallization of the sulfate from methanol resulted in two types of crystals. The first crop were those of the hydrogen sulfate whilst those obtained later were the sulfate (V). Recrystallization of all samples was carried out at 295 K.

Compound (I)

Crystal data

$C_{20}H_{18}NO_4^+.Cl^-.4H_2O$
$M_r = 443.87$
Triclinic
$P\bar{1}$
$a = 7.029\ (2)$ Å
$b = 11.598\ (3)$ Å
$c = 13.172\ (20)$ Å
$\alpha = 103.85\ (2)°$
$\beta = 89.14\ (2)°$
$\gamma = 95.87°$
$V = 1037.0\ (16)$ Å^3
$Z = 2$
$D_x = 1.422$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 7–15°$
$\mu = 0.232$ mm^{-1}
$T = 293\ (2)$ K
Plate
0.6 × 0.2 × 0.1 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$2\theta/\omega$ scans
Absorption correction: none
3834 measured reflections
3656 independent reflections
1970 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.0136$
$\theta_{max} = 24.97°$
$h = -8 \rightarrow 8$
$k = -13 \rightarrow 13$
$l = 0 \rightarrow 15$
3 standard reflections monitored every 100 reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0701$
$wR(F^2) = 0.1947$
$S = 1.238$
3654 reflections
264 parameters
$w = 1/[\sigma^2(F_o^2) + (0.1380P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.007$
$\Delta\rho_{max} = 0.443$ e Å^{-3}
$\Delta\rho_{min} = -0.466$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (I)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Cl1	0.1087 (2)	0.27592 (12)	1.16838 (11)	0.0800 (5)
N1	0.3137 (4)	0.5610 (3)	0.8669 (2)	0.0346 (7)
O1	0.1689 (5)	0.0199 (2)	0.8022 (2)	0.0595 (9)

O2	0.1650 (5)	0.0135 (2)	0.6255 (2)	0.0538 (8)
O3	0.3798 (4)	0.8999 (2)	1.0691 (2)	0.0438 (7)
O4	0.3306 (4)	0.9259 (2)	1.2749 (2)	0.0485 (7)
O5	0.5300 (5)	0.8454 (3)	0.7854 (3)	0.0697 (9)
O6	0.5286 (6)	0.7410 (4)	0.5721 (3)	0.0883 (12)
O7	−0.1557 (6)	0.6194 (4)	0.6019 (3)	0.0876 (12)
O8	−0.1854 (6)	0.3687 (4)	0.5157 (3)	0.0943 (13)
C1	0.1277 (3)	−0.0571 (2)	0.7020 (2)	0.0621 (13)
C2	0.1893 (3)	0.1289 (2)	0.6828 (2)	0.0430 (10)
C3	0.1907 (3)	0.1321 (2)	0.7875 (2)	0.0401 (9)
C4	0.2116 (3)	0.2308 (2)	0.6460 (2)	0.0532 (11)
C5	0.2368 (6)	0.3390 (3)	0.7195 (3)	0.0439 (10)
C6	0.2185 (5)	0.2373 (3)	0.8611 (3)	0.0397 (9)
C7	0.2415 (5)	0.3433 (3)	0.8251 (3)	0.0348 (8)
C8	0.2621 (5)	0.4603 (3)	0.9031 (3)	0.0317 (8)
C9	0.3598 (8)	0.5512 (4)	0.7553 (3)	0.0594 (13)
C10	0.2454 (8)	0.4544 (4)	0.6852 (3)	0.0624 (13)
C11	0.3307 (5)	0.6700 (3)	0.9311 (3)	0.0384 (9)
C12	0.3019 (5)	0.6874 (3)	1.0391 (3)	0.0326 (8)
C13	0.2326 (5)	0.4726 (3)	1.0068 (3)	0.0340 (8)
C14	0.2530 (5)	0.5853 (3)	1.0796 (3)	0.0350 (9)
C15	0.2271 (5)	0.6009 (3)	1.1868 (3)	0.0375 (9)
C16	0.2551 (5)	0.7120 (3)	1.2516 (3)	0.0406 (9)
C17	0.3027 (5)	0.8136 (3)	1.2129 (3)	0.0370 (9)
C18	0.3249 (5)	0.8024 (3)	1.1076 (3)	0.0369 (9)
C19	0.3230 (7)	0.9416 (4)	1.3860 (3)	0.0578 (12)
C20	0.2259 (7)	0.9484 (4)	1.0283 (4)	0.0639 (13)

Table 2. *Selected geometric parameters* (Å, °) *for* (I)

Cl1···O7^{i}	2.987 (6)	O5···O6	2.780 (7)
Cl1···O5^{ii}	3.160 (4)	O6···O8^{iv}	2.743 (6)
O3···O5^{iii}	3.122 (4)	O6···O7^{v}	2.827 (6)
O4···O5^{iii}	3.013 (4)	O7···O8	2.845 (6)

Symmetry codes: (i) $-x, 1-y, 2-z$; (ii) $1-x, 1-y, 2-z$; (iii) $1-x, 2-y, 2-z$; (iv) $-x, 1-y, 1-z$; (v) $1+x, y, z$.

Compound (II)

Crystal data

$C_{20}H_{18}NO_4^+.Cl^-.C_2H_6O.0.5H_2O$
M_r = 426.88
Triclinic
$P\bar{1}$
a = 7.3712 (10) Å
b = 11.2724 (10) Å
c = 13.3998 (10) Å
α = 77.587 (7)°
β = 73.299 (7)°
γ = 78.228 (8)°
V = 1029.4 (2) Å^3
Z = 2
D_x = 1.377 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 7–15°
μ = 0.222 mm^{-1}
T = 293 (2) K
Needle
0.4 × 0.1 × 0.1 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$2\theta/\omega$ scans
Absorption correction: none
3788 measured reflections
3616 independent reflections
1916 observed reflections $[I > 2\sigma(I)]$
R_{int} = 0.0165
θ_{max} = 24.97°
$h = -8 \rightarrow 8$
$k = -13 \rightarrow 13$
$l = 0 \rightarrow 15$
3 standard reflections monitored every 100 reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0562
$wR(F^2)$ = 0.1534
S = 1.302
3615 reflections
277 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0941P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.071
$\Delta\rho_{max}$ = 0.590 e Å^{-3}
$\Delta\rho_{min}$ = −0.434 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (II)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Cl1	0.3006 (2)	−0.16466 (11)	1.19251 (9)	0.0843 (4)
N1	0.1119 (3)	0.6655 (2)	1.0291 (2)	0.0363 (6)
O1	0.2332 (4)	0.6883 (2)	0.5532 (2)	0.0600 (7)
O2	0.1256 (4)	0.8960 (2)	0.5482 (2)	0.0672 (8)
O3	0.1367 (3)	0.4666 (2)	1.3215 (2)	0.0491 (6)
O4	0.3028 (3)	0.2269 (2)	1.3416 (2)	0.0518 (6)
O5	0.3248 (4)	0.3295 (3)	0.7602 (2)	0.0680 (8)
O6	0.4026 (8)	0.0143 (5)	0.9589 (5)	0.084 (2)
C1	0.1514 (6)	0.7955 (4)	0.4937 (3)	0.0674 (12)
C2	0.1290 (5)	0.8411 (3)	0.6494 (3)	0.0468 (9)
C3	0.1927 (5)	0.7170 (3)	0.6528 (2)	0.0426 (8)
C4	0.0834 (5)	0.8957 (3)	0.7363 (3)	0.0555 (10)
C5	0.1019 (5)	0.8202 (3)	0.8309 (3)	0.0424 (8)
C6	0.2115 (5)	0.6418 (3)	0.7435 (2)	0.0403 (8)
C7	0.1650 (4)	0.6951 (3)	0.8357 (2)	0.0360 (7)
C8	0.1872 (4)	0.6165 (3)	0.9360 (2)	0.0333 (7)
C9	−0.0066 (6)	0.7898 (3)	1.0257 (3)	0.0544 (10)
C10	0.0648 (6)	0.8753 (3)	0.9288 (3)	0.0598 (10)
C11	0.1274 (4)	0.6025 (3)	1.1219 (2)	0.0381 (7)
C12	0.2191 (4)	0.4801 (3)	1.1340 (2)	0.0340 (7)
C13	0.2818 (4)	0.4984 (3)	0.9441 (2)	0.0343 (7)
C14	0.2996 (4)	0.4269 (3)	1.0414 (2)	0.0332 (7)
C15	0.3891 (4)	0.3039 (3)	1.0523 (3)	0.0380 (8)
C16	0.3919 (4)	0.2385 (3)	1.1503 (3)	0.0429 (8)
C17	0.3099 (4)	0.2902 (3)	1.2422 (2)	0.0393 (8)
C18	0.2267 (4)	0.4113 (3)	1.2344 (2)	0.0366 (7)
C19	0.3791 (6)	0.0991 (3)	1.3542 (3)	0.0614 (11)
C20	0.2591 (7)	0.4940 (4)	1.3760 (3)	0.0789 (13)
C21	0.2815 (9)	0.2146 (5)	0.6399 (5)	0.114 (2)
C22	0.3228 (6)	0.3304 (4)	0.6550 (3)	0.0690 (11)

Table 4. *Selected geometric parameters* (Å, °) *for* (II)

Cl1···O5^{i}	3.145 (4)	Cl1···O6^{i}	3.043 (4)
Cl1···O6	3.315 (4)	O6···O6^{i}	1.987 (4)

Symmetry code: (i) $1-x, -y, 2-z$.

Compound (III)

Crystal data

$C_{20}H_{18}NO_4^+.Br^-.2H_2O$
M_r = 452.30
Monoclinic
$I2/a$
a = 21.974 (3) Å
b = 7.200 (7) Å
c = 26.151 (3) Å
β = 110.180 (10)°
V = 3883.4 (38) Å^3
Z = 8
D_x = 1.547 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 7–15°
μ = 2.154 mm^{-1}
T = 293 (2) K
Plate
0.4 × 0.2 × 0.1 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$2\theta/\omega$ scans
Absorption correction: none
3485 measured reflections
3400 independent reflections
1454 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.0540$
$\theta_{max} = 24.97°$
$h = -26 \rightarrow 24$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 31$
3 standard reflections
monitored every 100 reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0471$
$wR(F^2) = 0.0839$
$S = 1.189$
3398 reflections
267 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0394P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.183$
$\Delta\rho_{max} = 0.340$ e Å^{-3}
$\Delta\rho_{min} = -0.310$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 5. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (III)

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Br1	0.46789 (3)	0.04315 (9)	0.15465 (2)	0.0550 (2)
N1	0.34419 (15)	0.0578 (6)	0.25951 (15)	0.0329 (9)
O1	0.2990 (2)	0.1342 (6)	0.47653 (15)	0.0673 (12)
O2	0.4105 (2)	0.1272 (6)	0.51686 (14)	0.0680 (12)
O3	0.27591 (14)	−0.0250 (5)	0.09475 (13)	0.0531 (10)
O4	0.1487 (2)	−0.1000 (5)	0.04144 (13)	0.0583 (11)
O5	0.5670 (2)	0.2033 (6)	0.2741 (2)	0.0682 (13)
O6	0.3699 (2)	0.4000 (7)	0.1663 (2)	0.0785 (15)
C1	0.3505 (3)	0.1613 (9)	0.5260 (2)	0.067 (2)
C2	0.3929 (2)	0.1064 (7)	0.4616 (2)	0.0406 (14)
C3	0.3273 (2)	0.1134 (7)	0.4375 (2)	0.0405 (14)
C4	0.4330 (2)	0.0865 (7)	0.4317 (2)	0.0423 (14)
C5	0.4036 (2)	0.0678 (7)	0.3754 (2)	0.0328 (11)
C6	0.2968 (2)	0.0953 (6)	0.3829 (2)	0.0406 (14)
C7	0.3365 (2)	0.0720 (7)	0.3510 (2)	0.0341 (12)
C8	0.3057 (2)	0.0432 (7)	0.2920 (2)	0.0311 (11)
C9	0.4121 (2)	0.1229 (7)	0.2853 (2)	0.0431 (14)
C10	0.4439 (2)	0.0347 (8)	0.3399 (2)	0.0394 (12)
C11	0.3225 (2)	0.0231 (7)	0.2067 (2)	0.0351 (12)
C12	0.2575 (2)	−0.0212 (6)	0.1793 (2)	0.0308 (11)
C13	0.2421 (2)	−0.0031 (6)	0.2662 (2)	0.0330 (13)
C14	0.2153 (2)	−0.0317 (7)	0.2100 (2)	0.0311 (11)
C15	0.1500 (2)	−0.0728 (7)	0.1818 (2)	0.0407 (13)
C16	0.1277 (2)	−0.0948 (6)	0.1269 (2)	0.0405 (13)
C17	0.1690 (2)	−0.0823 (7)	0.0961 (2)	0.0427 (14)
C18	0.2340 (2)	−0.0496 (7)	0.1221 (2)	0.0371 (11)
C19	0.0805 (2)	−0.1067 (8)	0.0108 (2)	0.064 (2)
C20	0.2958 (3)	−0.1895 (10)	0.0755 (3)	0.087 (2)

Table 6. *Selected geometric parameters* (Å, °) *for* (III)

N1—C11	1.320 (5)	C6—C7	1.409 (6)
N1—C8	1.393 (5)	C7—C8	1.470 (6)
N1—C9	1.485 (5)	C8—C13	1.368 (6)
O1—C3	1.376 (5)	C9—C10	1.499 (6)
O1—C1	1.409 (6)	C11—C12	1.395 (6)
O2—C2	1.370 (5)	C12—C18	1.417 (6)
O2—C1	1.439 (6)	C12—C14	1.424 (6)
O3—C18	1.358 (5)	C13—C14	1.398 (6)
O3—C20	1.414 (7)	C14—C15	1.400 (6)
O4—C17	1.349 (5)	C15—C16	1.358 (6)
O4—C19	1.435 (6)	C16—C17	1.408 (6)
C2—C3	1.359 (6)	C17—C18	1.375 (6)
C2—C4	1.373 (6)	Br1···O5^i	3.323 (5)
C3—C6	1.358 (6)	Br1···O5	3.337 (4)
C4—C5	1.397 (6)	Br1···O6	3.433 (5)
C5—C7	1.390 (6)	O5···O6^i	2.763 (6)
C5—C10	1.506 (5)		
C11—N1—C8	123.2 (4)	C13—C8—N1	116.8 (4)
C11—N1—C9	118.6 (3)	C13—C8—C7	124.9 (4)
C8—N1—C9	118.2 (4)	N1—C8—C7	118.2 (4)
C3—O1—C1	105.7 (4)	N1—C9—C10	111.4 (4)
C2—O2—C1	104.7 (4)	C9—C10—C5	109.9 (4)
C18—O3—C20	115.3 (4)	N1—C11—C12	121.2 (4)
C17—O4—C19	119.7 (4)	C11—C12—C18	120.8 (4)
O1—C1—O2	108.4 (4)	C11—C12—C14	118.1 (4)
C3—C2—O2	110.7 (4)	C18—C12—C14	121.1 (4)
C3—C2—C4	121.8 (5)	C8—C13—C14	122.8 (4)
O2—C2—C4	127.5 (5)	C13—C14—C15	124.6 (4)
C2—C3—C6	122.9 (5)	C13—C14—C12	117.8 (4)
C2—C3—O1	109.8 (4)	C15—C14—C12	117.6 (4)
C6—C3—O1	127.2 (5)	C16—C15—C14	120.8 (4)
C2—C4—C5	117.1 (4)	C15—C16—C17	121.9 (4)
C7—C5—C4	121.0 (4)	O4—C17—C18	116.6 (4)
C7—C5—C10	118.5 (4)	O4—C17—C16	123.9 (4)
C4—C5—C10	120.5 (4)	C18—C17—C16	119.5 (4)
C3—C6—C7	116.9 (4)	O3—C18—C17	122.6 (4)
C5—C7—C6	120.4 (4)	O3—C18—C12	118.0 (4)
C5—C7—C8	120.6 (4)	C17—C18—C12	119.0 (4)
C6—C7—C8	118.9 (4)		

Symmetry code: (i) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$.

Compound (IV)

Crystal data

$C_{20}H_{18}NO_4^+.I^-$
$M_r = 463.25$
Monoclinic
$P2_1/n$
$a = 7.0814$ (10) Å
$b = 15.917$ (2) Å
$c = 16.154$ (2) Å
$\beta = 99.126$ (10)°
$V = 1797.8$ (4) Å^3
$Z = 4$
$D_x = 1.712$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 7–15°$
$\mu = 1.807$ mm^{-1}
$T = 293$ (2) K
Needle
0.2 × 0.1 × 0.1 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$2\theta/\omega$ scans
Absorption correction: none
4009 measured reflections
3871 independent reflections
1055 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.0487$
$\theta_{max} = 27.47°$
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 20$
$l = 0 \rightarrow 19$
3 standard reflections
monitored every 100 reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0666$
$wR(F^2) = 0.1000$
$S = 1.277$
3870 reflections
147 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0342P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.510$ e Å^{-3}
$\Delta\rho_{min} = -0.598$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 7. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (IV)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
I1	0.16270 (11)	0.03786 (5)	0.74750 (4)	0.0535 (2)
O1	0.4215 (9)	0.8179 (4)	0.5959 (4)	0.050 (2)
O2	0.3304 (9)	0.9033 (4)	0.4803 (4)	0.049 (2)
O3	0.1178 (9)	0.2718 (4)	0.3119 (4)	0.041 (2)
O4	0.1357 (10)	0.1624 (4)	0.4417 (4)	0.055 (2)
C1	0.3917 (15)	0.9022 (6)	0.5718 (6)	0.058 (3)
C2	0.2947 (13)	0.8199 (6)	0.4607 (6)	0.036 (2)
C3	0.3526 (13)	0.7701 (6)	0.5274 (6)	0.038 (3)
N1	0.1990 (8)	0.5233 (4)	0.3577 (4)	0.025 (2)
C4	0.2229 (13)	0.7891 (6)	0.3830 (6)	0.043 (3)
C5	0.2031 (13)	0.7013 (6)	0.3761 (6)	0.035 (2)
C6	0.3334 (12)	0.6852 (5)	0.5221 (5)	0.034 (2)
C7	0.2601 (13)	0.6489 (5)	0.4446 (6)	0.029 (2)
C8	0.2395 (11)	0.5578 (5)	0.4370 (5)	0.022 (2)
C9	0.2011 (14)	0.5795 (5)	0.2832 (5)	0.044 (3)
C10	0.1079 (13)	0.6623 (5)	0.2952 (5)	0.035 (3)
C11	0.1707 (11)	0.4425 (5)	0.3435 (5)	0.030 (2)
C12	0.1781 (12)	0.3847 (5)	0.4087 (5)	0.023 (2)
C13	0.2499 (13)	0.5032 (5)	0.5030 (6)	0.033 (3)
C14	0.2257 (13)	0.4170 (6)	0.4917 (6)	0.028 (3)
C15	0.2374 (12)	0.3574 (6)	0.5582 (6)	0.037 (3)
C16	0.2077 (13)	0.2749 (6)	0.5430 (6)	0.039 (3)
C17	0.1611 (13)	0.2436 (6)	0.4609 (5)	0.035 (2)
C18	0.1510 (12)	0.2981 (5)	0.3929 (5)	0.029 (2)
C19	0.1661 (14)	0.1002 (6)	0.5081 (6)	0.062 (3)
C20	−0.0658 (16)	0.2331 (7)	0.2838 (6)	0.066 (3)

Compound (V)

Crystal data

$2C_{20}H_{18}NO_4^+.SO_4^-.7H_2O$	Mo $K\alpha$ radiation
M_r = 894.88	λ = 0.71069 Å
Monoclinic	Cell parameters from 25 reflections
$P2_1/a$	θ = 7–15°
a = 23.198 (30) Å	μ = 0.169 mm^{-1}
b = 6.918 (10) Å	T = 293 (2) K
c = 24.963 (30) Å	Needle
β = 96.65 (9)°	0.4 × 0.1 × 0.1 mm
V = 3979.0 (91) Å^3	Orange
Z = 4	
D_x = 1.494 Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4 diffractometer	θ_{max} = 22.51°
$2\theta/\omega$ scans	$h = 0 \rightarrow 24$
Absorption correction: none	$k = 0 \rightarrow 7$
5360 measured reflections	$l = -26 \rightarrow 26$
5193 independent reflections	3 standard reflections monitored every 100 reflections
1319 observed reflections [$I > 2\sigma(I)$]	frequency: 180 min
R_{int} = 0.1112	intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max}$ = 0.003
$R[F^2 > 2\sigma(F^2)]$ = 0.0764	$\Delta\rho_{max}$ = 0.342 e Å^{-3}
$wR(F^2)$ = 0.1649	$\Delta\rho_{min}$ = −0.308 e Å^{-3}
S = 1.321	Extinction correction: none
5193 reflections	Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
380 parameters	
$w = 1/[\sigma^2(F_o^2) + (0.0844P)^2 + 3.7773P]$ where $P = (F_o^2 + 2F_c^2)/3$	

Table 8. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (V)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
S1	0.87341 (13)	0.4785 (5)	0.23974 (11)	0.0371 (8)
N1	0.3051 (3)	0.3843 (13)	0.0715 (3)	0.029 (2)
N2	0.2078 (3)	0.6378 (13)	0.5709 (3)	0.030 (2)
O1	0.0483 (3)	0.3566 (12)	0.1055 (3)	0.042 (2)
O2	0.0792 (3)	0.4295 (12)	0.1949 (3)	0.050 (2)
O3	0.4349 (3)	0.4082 (12)	−0.0296 (3)	0.046 (2)
O4	0.4065 (3)	0.3962 (11)	−0.1370 (2)	0.042 (2)
O5	0.4721 (3)	0.6220 (12)	0.6034 (3)	0.047 (2)
O6	0.4630 (3)	0.6712 (12)	0.6950 (3)	0.051 (2)
O7	0.0514 (2)	0.6003 (12)	0.4685 (2)	0.036 (2)
O8	0.0513 (3)	0.6313 (11)	0.3626 (2)	0.037 (2)
O9	0.9012 (4)	0.5459 (16)	0.1942 (3)	0.097 (4)
O10	0.8919 (3)	0.2842 (13)	0.2556 (3)	0.070 (3)
O11	0.8099 (3)	0.4814 (13)	0.2263 (3)	0.059 (3)
O12	0.8905 (3)	0.6161 (12)	0.2854 (3)	0.058 (3)
O13	0.1303 (3)	0.1173 (15)	0.5779 (3)	0.077 (3)
O14	0.0526 (3)	0.0554 (13)	0.7891 (3)	0.063 (3)
O15	0.7533 (3)	0.2426 (13)	0.7220 (3)	0.059 (3)
O16	0.1060 (3)	0.3965 (17)	−0.0838 (3)	0.092 (4)
O17	0.8519 (3)	0.9743 (13)	0.3092 (3)	0.058 (3)
O18	0.5672 (3)	1.0621 (13)	−0.3898 (3)	0.052 (2)
O19	0.0363 (3)	0.0530 (14)	−0.1028 (3)	0.065 (3)
C1	0.0297 (5)	0.404 (2)	0.1563 (4)	0.060 (4)
C2	0.1255 (4)	0.4232 (16)	0.1641 (4)	0.032 (3)
C3	0.1073 (4)	0.3841 (16)	0.1110 (4)	0.030 (3)
C4	0.1815 (4)	0.4493 (17)	0.1841 (4)	0.040 (3)
C5	0.2229 (4)	0.4395 (16)	0.1459 (4)	0.028 (3)
C6	0.1449 (4)	0.3694 (16)	0.0745 (4)	0.030 (3)
C7	0.2047 (4)	0.3948 (16)	0.0915 (4)	0.027 (3)
C8	0.2465 (4)	0.3958 (16)	0.0525 (4)	0.028 (3)
C9	0.3225 (4)	0.3566 (17)	0.1298 (3)	0.034 (3)
C10	0.2862 (3)	0.4748 (16)	0.1635 (4)	0.030 (3)
C11	0.3465 (4)	0.3902 (15)	0.0378 (3)	0.026 (3)
C12	0.3346 (4)	0.3973 (15)	−0.0178 (3)	0.024 (3)
C13	0.2311 (4)	0.4026 (16)	−0.0022 (4)	0.033 (3)
C14	0.2743 (4)	0.4001 (15)	−0.0389 (4)	0.024 (3)
C15	0.2604 (4)	0.4080 (17)	−0.0954 (4)	0.040 (3)
C16	0.3034 (4)	0.4082 (16)	−0.1280 (4)	0.036 (3)
C17	0.3624 (4)	0.3970 (18)	−0.1056 (4)	0.039 (3)
C18	0.3777 (4)	0.3931 (16)	−0.0522 (4)	0.028 (3)
C19	0.3925 (4)	0.4228 (16)	−0.1952 (4)	0.042 (3)
C20	0.4632 (4)	0.2323 (19)	−0.0129 (5)	0.055 (4)
C21	0.5035 (5)	0.636 (2)	0.6567 (4)	0.057 (4)
C22	0.4092 (4)	0.6735 (17)	0.6649 (4)	0.032 (3)
C23	0.4135 (4)	0.6463 (16)	0.6098 (4)	0.032 (3)
C24	0.3578 (4)	0.7044 (17)	0.6830 (4)	0.039 (3)
C25	0.3066 (4)	0.6965 (15)	0.6443 (3)	0.023 (3)
C26	0.3668 (4)	0.6434 (16)	0.5719 (4)	0.039 (3)
C27	0.3119 (4)	0.6662 (15)	0.5906 (3)	0.023 (3)
C28	0.2601 (4)	0.6612 (16)	0.5525 (4)	0.034 (3)
C29	0.2064 (4)	0.6105 (18)	0.6290 (4)	0.042 (3)
C30	0.2492 (4)	0.7325 (16)	0.6621 (4)	0.029 (3)
C31	0.1585 (4)	0.6267 (16)	0.5379 (4)	0.033 (3)
C32	0.1563 (4)	0.6433 (15)	0.4814 (3)	0.024 (3)
C33	0.2588 (4)	0.6696 (16)	0.4974 (4)	0.031 (3)
C34	0.2090 (4)	0.6691 (16)	0.4597 (4)	0.030 (3)
C35	0.2082 (4)	0.6810 (16)	0.4034 (4)	0.034 (3)
C36	0.1565 (4)	0.6712 (15)	0.3716 (4)	0.024 (3)
C37	0.1029 (4)	0.6486 (17)	0.3921 (4)	0.034 (3)
C38	0.1040 (4)	0.6295 (16)	0.4475 (4)	0.027 (3)
C39	0.0482 (4)	0.6567 (16)	0.3033 (3)	0.039 (3)
C40	0.0244 (4)	0.7713 (18)	0.4887 (4)	0.052 (4)

Table 9. *Selected geometric parameters* (Å, °) *for* (V)

S1—O9	1.448 (7)	O12···O18^{viii}	2.702 (10)
S1—O10	1.452 (9)	O12···O17	2.723 (12)
S1—O11	1.472 (7)	O12···O14^{iv}	3.307 (12)
S1—O12	1.502 (7)	O13···O18^{ix}	2.825 (12)
O4···O19^{i}	3.055 (10)	O13···O17^{iv}	2.871 (11)
O8···O18^{ii}	2.947 (9)	O14···O19^{x}	2.769 (10)
O9···O16^{iii}	2.769 (11)	O14···O12^{iv}	3.307 (12)
O9···O14^{iv}	2.972 (14)	O15···O11^{xi}	2.742 (11)
O10···O17^{v}	2.745 (12)	O15···O17^{xi}	2.948 (12)
O10···O14^{vi}	2.958 (13)	O16···O19	2.883 (14)
O11···O15^{vii}	2.742 (11)		

Symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}-y, z$; (ii) $\frac{1}{2}-x, y-\frac{1}{2}, -z$; (iii) $1-x, 1-y, -z$; (iv) $1-x, 1-y, 1-z$; (v) $x, y-1, z$; (vi) $1-x, -y, 1-z$; (vii) $\frac{3}{2}-x, \frac{1}{2}+y, 1-z$; (viii) $\frac{3}{2}-x, y-\frac{1}{2}, -z$; (ix) $x-\frac{1}{2}, \frac{3}{2}-y, 1+z$; (x) $x, y, 1+z$; (xi) $\frac{3}{2}-x, y-\frac{1}{2}, 1-z$.

All cation H atoms were placed in calculated positions. For (I), (II) and (III), all non-H atoms were assigned anisotropic displacement parameters. Hydroxyl and water [except the disordered one in (II)] H atoms were located in the difference Fourier synthesis map. For (IV) and (V) only the anions, water and cation O atoms, C1, C19 and C20 [and C21, C39, C40 for (V)] were refined anisotropically. Water H atoms were not located for (V).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*92 (Sheldrick, 1992). Molecular graphics: *DTMM* (Crabbe & Appleyard, 1991). Software used to prepare material for publication: *SHELXL*92.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1131). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Abadi, B. E. A., Moss, D. S. & Palmer, R. A. (1984). *J. Cryst. Spec. Res.* **14**, 269–281.

Crabbe, M. J. C. & Appleyard, J. R. (1991). *DTMM. Desktop Molecular Modeller* 2.0. Oxford Univ. Press.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Schmidt, G. M. J. (1971). *Pure Appl. Chem.* **27**, 647–678.

Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.

Sheldrick, G. M. (1992). *SHELXL*92. *Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.

Theocharis, C. R. & Jones, W. (1987). *Organic Solid State Chemistry*, edited by G. R. Desiraju, pp. 47–68. Amsterdam: Elsevier.

Wang-Nang, W. & Jones, W. (1987). *Tetrahedron*, **43**, 1273–1279.