Introduction

The structure consists of a metal oxide/fluoride framework with highly disordered organic contents. The formula for the framework is $[Ge_2\ Zr\ O_6\ F_2]^{2-}$ and consists of *trans*-ZrF_2O_4 octahedra corner-sharing with GeO_4 tetrahedra. The tetrahedra form corner-sharing chains along the c-axis, joined together by the Zr atoms. Channels in the structure run along the a- and b- axes, but not in the c-direction, nor are the channels particularly "open".

The formula for the framework is based on the successful refinement of the fluorine atoms, combined with the Zr-X distances for the terminal atoms and the shared oxygen atoms. The fluorine atoms are disordered over two equally-occupied positions differing in the z coordinate and inspection of the anisotropic displacement parameters of the bridging atoms clearly shows that the rest of the octahedron shares the disorder, although the oxygen atoms do not move as much as the fluorines. However, the possibility exists that the atoms labeled as F are actually the O of hydroxyl groups. The only way to clarify this is via elemental analysis or some other non-crystallographic technique.

In addition to the disorder of the framework, the crystals were apparently twinned by mirror symmetry on the base diagonal. Inclusion of the twinning parameter dramatically improved the residuals and the refinement. The twinning fraction refined to 0.5 within 3σ.

The cavities contain electron density which was modeled as a nitrogen atom, a disordered carbon atom (C1A and C1B) and a group of carbon atoms with a common thermal parameter and variable occupancies. The metal-oxide framework has two negative charges per formula unit, so the contents of the voids needs to supply two positive charges. It could do this by protonating both ends of a diaminobutane or by protonating one end of two diaminobutanes. The disordered atoms fill the voids with electron density equivalent to 59 e^-, slightly more than the 52 e^- for one diprotonated diaminobutane but significantly less than the 102 e^- expected for a pair of mono-protonated amines. I expect that there is additional water, (either protonated or not) in the contents of the voids, but that the primary species is the diprotonated amine.

Experimental

Data Collection

A representative crystal of $C_{16}H_{32}F_4Ge_4N_4O_{12}Zr_2$ having approximate dimensions of 0.27 x 0.04 x 0.03 mm was mounted on a glass fiber using Paratone N hydrocarbon oil.

All measurements were made on a SMART[10] CCD area detector with graphite monochromated Mo-Kα radiation.

Cell constants and an orientation matrix , obtained from a least-squares refinement using the measured positions of 2027 reflections in the range of $3< 2\theta < 45°$.

a = 15.323(1) Å

c = 11.191(1) Å

V = 2627.73(12)Å^3

For Z = 4 and F.W. = 1021.26, the calculated density is 2.581 g/cm^3. The systematic absences of:

h0l: h+l $\neq$ 2n

0k0: k $\neq$ 2n

uniquely determine the space group to be:

$$I4_1/a$$

The data were collected at a temperature of 168(2)± 1°K. Frames corresponding to an arbitrary hemisphere of data were collected using ω scans of 0.3° counted for a total of 10 seconds per frame.

Data Reduction

Data were integrated by the program SAINT[11] to a maximum 2θ value of 49.4°. The data were corrected for Lorentz and polarization effects. Data were analyzed for agreement and possible absorption using XPREP[12]. An empirical absorption correction based on comparison of redundant and equivalent reflections as applied using SADABS[13] (Tmax = 0.85, Tmin = 0.59).

Structure Solution and Refinement

The structure was solved by direct methods[14] and expanded using Fourier techniques[15]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions but not refined. The final cycle of full-matrix least-squares refinement[3] was based on 912 reflections (all data) and 107 variable parameters and converged (largest parameter shift was 0.002 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma||Fo| - |Fc||/\Sigma|Fo| = 0.0225(\mathrm{F}^2 > 2\sigma(\mathrm{F}))$$

$$wR2 = \sqrt{(\Sigma w(|Fo|^2 - |Fc|^2)^2/\Sigma wFo^2)]} = 0.0432 \text{ (all data)}$$

The standard deviation of an observation of unit weight[4] was 0.891. The weighting scheme was based on counting statistics and included a factor (p = 0.02) to downweight the intense reflections. Plots of reflection order in data collection, $\sin\theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.569 and -0.349 $e^-/\mathring{A}^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[5] . Anomalous dispersion effects were included in Fcalc[6]; the values for Δf' and Δf" were those of Creagh and McAuley[7]. The values for the mass attenuation coefficients are those of Creagh and Hubbel[8]. All calculations were performed using the teXsan[9] crystallographic software package of Molecular Structure Corporation.

References

(1) SAPI91: Fan Hai-Fu (1991). Structure Analysis Programs with Intelligent Control, Rigaku Corporation, Tokyo, Japan.

(2) DIRDIF94: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M. (1994). The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(3) Least-Squares:

Function minimized: $\Sigma w(|Fo|^2 - |Fc|^2)^2$

(4) Standard deviation of an observation of unit weight:

$$\sqrt{\Sigma w(Fo^2 - Fc^2)^2/(No - Nv)}$$

where: No = number of observations

Nv = number of variables

(5) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(6) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(7) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(8) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(9) teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1992).

(10) SMART: Area-Detector Software Package, Bruker Analytical X-ray Systems, Inc.: Madison, WI, (1995-99)

(11) SAINT: SAX Area-Dectector Integration Program, V5.04; Siemens Industrial Automation, Inc.: Madison, WI, (1995)

(12) XPREP:(v 5.03) Part of the SHELXTL Crystal Structure Determination Siemens Industrial Automation, Inc.: Madison, WI, (1995)

(13) SADABS: Siemens Area Detector ABSorption correction program, George Sheldrick, (1996). Advance copy, private communication.

(14) XS: Program for the Solution of X-ray Crystal Structures, Part of the SHELXTL Crystal Structure Determination, Bruker Analytical X-ray Systems, Inc.: Madison, WI, (1995-99)

(15) XL: Program for the Refinement of X-ray Crystal Structures, Part of the SHELXTL Crystal Structure Determination, Bruker Analytical X-ray Systems, Inc.: Madison, WI, (1995-99)

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	C16 H32 F4 Ge4 N4 O12 Zr2
Formula Weight	1021.26
Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.27 X 0.04 X 0.03mm
Crystal System	tetragonal
Lattice Type	Body-centered
Lattice Parameters	a = 15.323(1) Å b = 15.323(1) Å c = 11.191(1) Å V = 2627.73(12) Å^3
Space Group	$I4_1/a$
Z value	4
D*calc*	2.581 g/cm^3
F000	1984
μ(MoKα)	5.38 cm^{-1}

B. Intensity Measurements

Diffractometer	SMART CCD
Radiation	MoKα (λ = 0.71069 Å) graphite monochromated
Detector Position	60.00 mm
Exposure Time	10 seconds per frame.
Scan Type	ω (0.3 degrees per frame)
θ max	24.71°

No. of Reflections Measured	Total: 5870 Unique: 1102 ($Rint$ = 0.0365)
Corrections	Lorentz-polarization Absorption (Tmax = 0.85, Tmin = 0.59)

C. Structure Solution and Refinement

Structure Solution	direct (SHELXS-97 (Sheldrick, 1990))
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w(\|Fo\| - \|Fc\|)^2$
Least Squares Weights	$w = \frac{1}{\sigma^2(Fo^2)+(p*P)^2+q*P}$ where P = $\frac{(Fo^2+2Fc^2)}{3}$
p-factors	p = 0.02, q = 0
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>2.00σ(I))	912
No. Variables	107
Reflection/Parameter Ratio	8.52
Residuals: R	0.0225
Goodness of Fit Indicator	0.891
Max Shift/Error in Final Cycle	0.002
Maximum peak in Final Difference Map	0.569 $e^-/\AA^3$
Minimum peak in Final Difference Map	-0.349 $e^-/\AA^3$

Table 1. Atomic coordinates and U_{iso}/U_{eq}

atom	x	y	z	U_{iso}	occ
Zr1	0.2500	0.2500	0.2500	0.017(1)	
Ge1	0.2070(1)	0.4499(1)	0.1101(1)	0.014(1)	
F1A	0.3822(3)	0.2526(7)	0.2358(6)	0.029(2)	
F1B	0.3724(4)	0.2576(5)	0.1735(6)	0.024(2)	
O1	0.2216(5)	0.3391(3)	0.1194(3)	0.053(2)	
O2	0.2646(3)	0.5026(2)	0.2246(2)	0.019(1)	
O3	0.0997(3)	0.4793(4)	0.1172(3)	0.041(2)	
N1	0.5023(7)	0.3808(5)	0.1885(8)	0.060(3)	
C1A	0.5367(7)	0.4430(9)	0.1088(8)	0.053(3)	0.77
C1B	0.480(2)	0.465(3)	0.055(3)	0.061(3)	0.23(2)
C2	0.5032(18)	0.3948(10)	-0.0292(15)	0.061(3)	0.45(1)
C3	0.4713(10)	0.5290(12)	0.1034(14)	0.061(3)	0.51(2)
C4	0.4036(16)	0.3631(17)	-0.0645(17)	0.061(3)	0.35(1)
C5	0.5520(19)	0.5736(19)	0.174(2)	0.061(3)	0.29(2)
C6	0.3897(13)	0.2988(13)	-0.0221(18)	0.061(3)	0.42(2)
C7	0.451(2)	0.384(2)	0.054(3)	0.061(3)	0.25(2)
C8	0.529(3)	0.357(3)	0.199(4)	0.061(3)	0.30(2)
C9	0.588(4)	0.465(4)	0.147(5)	0.061(3)	0.17(2)

U_{eq} is defined as one third of the orthoganalized U_{ij} tensor

Table 2. Anisotropic Displacement Parameters

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zr1	0.0188(4)	0.0100(3)	0.0223(4)	0.0025(4)	0.0005(3)	-0.0008(5)
Ge1	0.0189(4)	0.0133(3)	0.0110(2)	0.0021(2)	-0.0033(2)	-0.0018(2)
O1	0.122(6)	0.005(2)	0.033(3)	0.0026(18)	-0.037(3)	-0.004(3)
O2	0.028(3)	0.0155(18)	0.0140(16)	-0.0001(15)	-0.0024(16)	-0.0079(17)
O3	0.021(3)	0.084(5)	0.018(2)	0.017(2)	0.0038(17)	-0.002(3)
N1	0.039(5)	0.036(4)	0.104(6)	-0.021(4)	0.003(6)	0.011(5)
C1A	0.047(6)	0.083(9)	0.030(5)	0.001(6)	-0.009(5)	0.001(7)

The general temperature factor expression:

$$\exp(-2\pi^2(a^{*2}U11h^2 + b^{*2}U22k^2 + c^{*2}U33l^2 + 2a^*b^*U12hk + 2a^*c^*U13hl + 2b^*c^*U23kl))$$

Table 3. Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
Zr1	F1A#1	2.033(5)	Zr1	F1A	2.033(5)
Zr1	O3#2	2.038(4)	Zr1	O3#3	2.038(4)
Zr1	O1	2.046(4)	Zr1	O1#1	2.046(4)
Zr1	F1B	2.065(5)	Zr1	F1B#1	2.065(5)
Ge1	O3	1.708(5)	Ge1	O1	1.715(5)
Ge1	O2	1.753(3)	Ge1	O2#4	1.756(3)
F1A	F1B	0.717(7)	O2	Ge1#3	1.756(3)
O3	Zr1#4	2.038(4)	N1	C8	0.56(3)
N1	C1A	1.409(13)	N1	C7	1.70(3)
N1	C9	1.90(6)	C1A	C9	0.96(5)
C1A	C1B	1.11(4)	C1A	C3	1.66(2)
C1A	C8	1.66(5)	C1A	C7	1.70(4)
C1A	C2	1.79(2)	C1B	C3	1.13(4)
C1B	C7	1.31(5)	C1B	C2	1.47(4)
C1B	C1B#5	1.75(6)	C1B	C3#5	1.93(4)
C1B	C9	1.95(7)	C2	C7	1.23(4)
C2	C3#5	1.49(2)	C2	C4	1.65(4)
C2	C5#5	1.89(3)	C3	C2#5	1.49(2)
C3	C5	1.62(3)	C3	C1B#5	1.93(4)
C4	C6	1.11(2)	C4	C7	1.55(4)
C4	C5#5	1.70(3)	C5	C4#5	1.70(3)
C5	C9	1.78(6)	C5	C2#5	1.89(3)
C5	C6#3	1.94(3)	C6	C7	1.82(4)
C6	C5#4	1.94(3)	C8	C9	1.97(7)

Table 4. Bond Angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
F1A#1	Zr1	F1A	180.0	F1A#1	Zr1	O3#2	83.1(3)
F1A	Zr1	O3#2	96.9(3)	F1A#1	Zr1	O3#3	96.9(3)
F1A	Zr1	O3#3	83.1(3)	O3#2	Zr1	O3#3	179.999(1)
F1A#1	Zr1	O1	81.8(3)	F1A	Zr1	O1	98.2(3)
O3#2	Zr1	O1	90.41(14)	O3#3	Zr1	O1	89.59(14)
F1A#1	Zr1	O1#1	98.2(3)	F1A	Zr1	O1#1	81.8(3)
O3#2	Zr1	O1#1	89.59(14)	O3#3	Zr1	O1#1	90.41(14)
O1	Zr1	O1#1	180.0	F1A#1	Zr1	F1B	159.86(19)
F1A	Zr1	F1B	20.14(19)	O3#2	Zr1	F1B	85.2(3)
O3#3	Zr1	F1B	94.8(3)	O1	Zr1	F1B	81.9(3)
O1#1	Zr1	F1B	98.1(3)	F1A#1	Zr1	F1B#1	20.14(19)
F1A	Zr1	F1B#1	159.86(19)	O3#2	Zr1	F1B#1	94.8(3)
O3#3	Zr1	F1B#1	85.2(3)	O1	Zr1	F1B#1	98.1(3)
O1#1	Zr1	F1B#1	81.9(3)	F1B	Zr1	F1B#1	180.00(12)
O3	Ge1	O1	112.6(2)	O3	Ge1	O2	109.2(2)
O1	Ge1	O2	110.3(2)	O3	Ge1	O2#4	109.96(17)
O1	Ge1	O2#4	107.9(2)	O2	Ge1	O2#4	106.75(12)
F1B	F1A	Zr1	82.5(7)	F1A	F1B	Zr1	77.4(7)
Ge1	O1	Zr1	137.0(2)	Ge1	O2	Ge1#3	127.14(18)
Ge1	O3	Zr1#4	137.1(2)	C8	N1	C1A	107(6)

Table 5. Torsion Angles(°)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
F1A#1	Zr1	F1A	F1B	-49(9)	O3#2	Zr1	F1A	F1B	55.2(12)
O3#3	Zr1	F1A	F1B	-124.8(12)	O1	Zr1	F1A	F1B	-36.3(12)
O1#1	Zr1	F1A	F1B	143.7(12)	F1B#1	Zr1	F1A	F1B	180.0
F1A#1	Zr1	F1B	F1A	179.998(1)	O3#2	Zr1	F1B	F1A	-125.1(12)
O3#3	Zr1	F1B	F1A	54.9(12)	O1	Zr1	F1B	F1A	143.8(12)
O1#1	Zr1	F1B	F1A	-36.2(12)	F1B#1	Zr1	F1B	F1A	94.2(16)
O3	Ge1	O1	Zr1	-96.1(6)	O2	Ge1	O1	Zr1	26.1(7)
O2#4	Ge1	O1	Zr1	142.4(5)	F1A#1	Zr1	O1	Ge1	89.9(7)
F1A	Zr1	O1	Ge1	-90.1(7)	O3#2	Zr1	O1	Ge1	172.9(7)
O3#3	Zr1	O1	Ge1	-7.1(7)	O1#1	Zr1	O1	Ge1	133(4)
F1B	Zr1	O1	Ge1	-101.9(6)	F1B#1	Zr1	O1	Ge1	78.1(6)
O3	Ge1	O2	Ge1#3	102.6(3)	O1	Ge1	O2	Ge1#3	-21.6(4)
O2#4	Ge1	O2	Ge1#3	-138.53(17)	O1	Ge1	O3	Zr1#4	-90.8(5)
O2	Ge1	O3	Zr1#4	146.4(4)	O2#4	Ge1	O3	Zr1#4	29.6(6)

The ADC (atom designator code) specifies the position of an atom in a crystal. The 5-digit number shown in the table is a composite of three one-digit numbers and one two-digit number: TA (first digit) + TB (second digit) + TC (third digit) + SN (last two digits). TA, TB and TC are the crystal lattice translation digits along cell edges a, b and c. A translation digit of 5 indicates the origin unit cell. If TA = 4, this indicates a translation of one unit cell length along the a-axis in the negative direction. Each translation digit can range in value from 1 to 9 and thus ± 4 lattice translations from the origin (TA=5, TB=5, TC=5) can be represented.

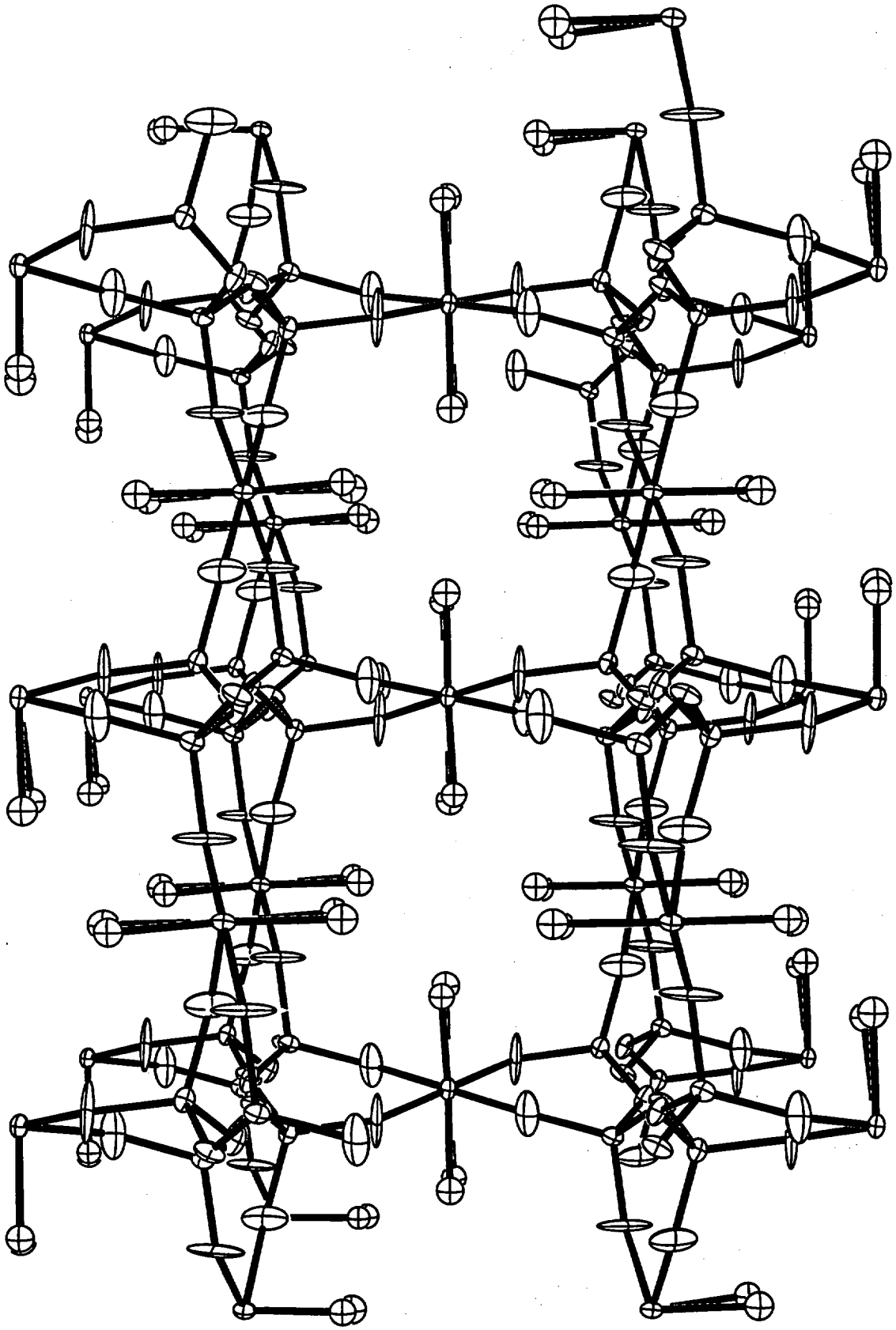
The SN, or symmetry operator number, refers to the number of the symmetry operator used to generate the coordinates of the target atom. A list of symmetry operators relevant to this structure are given below.

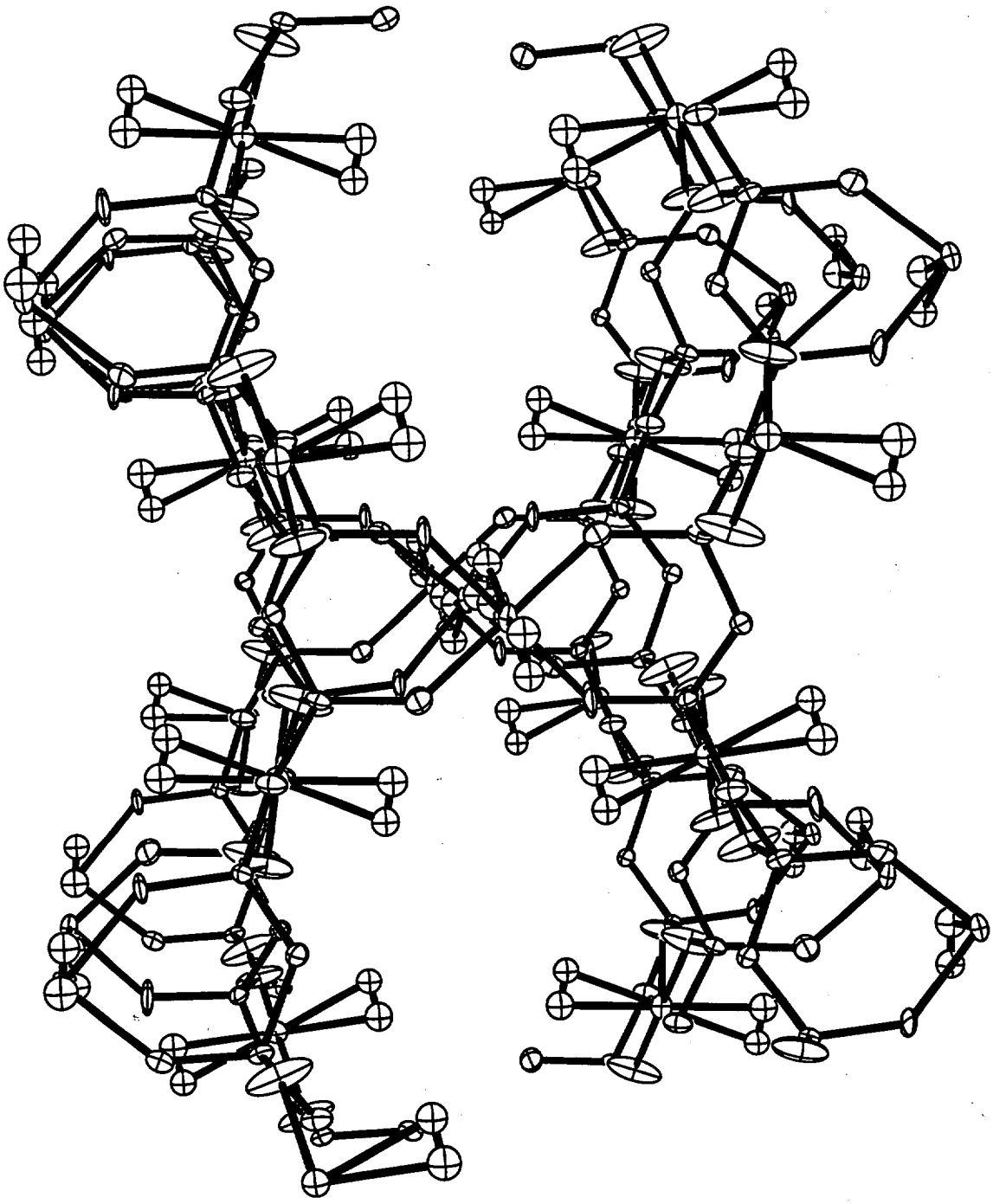
For a given intermolecular contact, the first atom (origin atom) is located in the origin unit cell and its position can be generated using the identity operator (SN=1). Thus, the ADC for an origin atom is always 55501. The position of the second atom (target atom) can be generated using the ADC and the coordinates of the atom in the parameter table. For example, an ADC of 47502 refers to the target atom moved through symmetry operator two, then translated -1 cell translations along the a axis, +2 cell translations along the b axis, and 0 cell translations along the c axis.

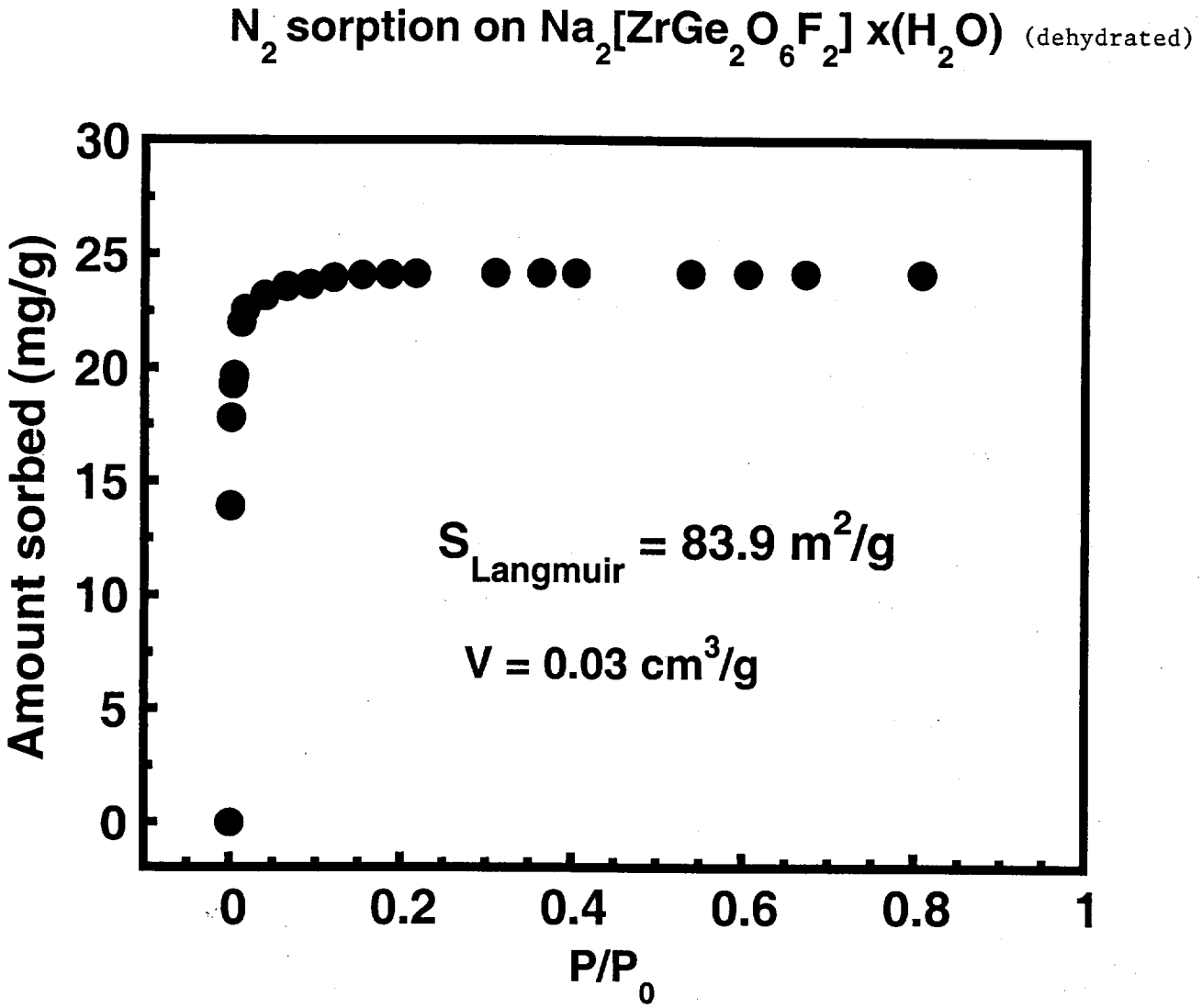
An ADC of 1 indicates an intermolecular contact between two fragments (eg. cation and anion) that reside in the same asymmetric unit.

Symmetry Operators:

x, y, z -x+1/2, -y, z+1/2 -y+3/4, x+1/4, z+1/4 y+3/4, -x+3/4, z+3/4 x+1/2, y+1/2, z+1/2 -x+1, -y+1/2, z+1 -y+5/4, x+3/4, z+3/4 y+5/4, -x+5/4, z+5/4 -x, -y, -z x-1/2, y, -z-1/2 y-3/4, -x-1/4, -z-1/4 -y-3/4, x-3/4, -z-3/4 -x+1/2, -y+1/2, -z+1/2 x, y+1/2, -z y-1/4, -x+1/4, -z+1/4 -y-1/4, x-1/4, -z-1/4






N2 sorption on Na2[ZrGe2O6F2] x(H2O) (dehydrated)
Amount sorbed (mg/g)
30
25
20
15
10
5
0
0
0.2
0.4
0.6
0.8
1
P/P0
SLangmuir = 83.9 m2/g
V = 0.03 cm3/g