Supporting Information

$Na_2Cu_7(SeO_3)_4O_2Cl_4$: A Selenite Chloride Compound With Cu_7 Units Showing Spin-frustration and Magnetization Plateau

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Experimental Section

Single crystals of $Na_2Cu_7(SeO_3)_4O_2Cl_4$ was synthesized by a conventional hydrothermal method. For $Na_2Cu_7(SeO_3)_4O_2Cl_4$, a mixture of 1.5 mmol $CuSO_4 \cdot 5H_2O$ (3N, 0.3745 g), 1 mmol $BaCl_2$ (3N, 0.2443 g), 0.3 mmol SeO_2 (3N, 0.0333 g), 0.7 mmol NaOH (3N, 0.028 g) and 1 mL deionized water was sealed in an autoclave equipped with a Teflon liner (28 mL). The autoclaves were put into a furnace which was heated at 210 °C for 5 days under autogenous pressure, and then cooled to room temperature at a rate of ~ 4 °C/h for 2 days. Some brown bulk crystals of $Na_2Cu_7(SeO_3)_4O_2Cl_4$ were obtained and further dried at 60 °C for 2 hours. With this procedure, the yield for $Na_2Cu_7(SeO_3)_4O_2Cl_4$ was estimated to be about 80%. (Note: during the synthetic procedure, barium sulfate was obtained as by-products in the form of white powder. $Na_2Cu_7(SeO_3)_4O_2Cl_4$ crystals were separated by the removal of the barium sulfate powder via ultrasonic cleaning in deionized water).

X-ray crystallographic studies.

A small crystal of $Na_2Cu_7(SeO_3)_4O_2Cl_4$ (~ 0.15 mm × 0.05 mm × 0.05 mm) was selected and mounted on glassy fibers for single crystal X-ray diffraction (XRD) measurements. Data collections were performed on Rigaku Mercury CCD diffractometer equipped with a graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 293 K. The data sets were corrected for Lorentz and polarization factors as well as for absorption by Multi-scan method.[1] The structure was solved by direct methods and refined by full-matrix least-squares fitting on F^2 by *SHELX*-97.[2] All non-hydrogen atoms were refined with anisotropic thermal parameters. The final refined structural parameters were checked by the *PLATON* program.[3] Crystallographic data and structural refinements are summarized in Table S1. The final refined atomic positions and structural parameters are seen in Tables S2-4.

Magnetic Measurements.

Magnetic measurements were performed using a commercial Quantum Design Physical Property Measurement System (PPMS). Powdered samples of $Na_2Cu_7(SeO_3)_4O_2Cl_4$ (52.45 mg) were placed in a gel capsule sample holder which was suspended in a plastic drinking straw. Magnetic susceptibility was measured at 0.1 T from 300 to 2 K (temperature scan of 5 K/min), and magnetization was measured at 2 K in applied field (0-8-0 T, field scan of 0.1 T/step). Low-temperature magnetic susceptibilities were also measured with field-cooling (FC) and zero-field-cooling (ZFC) regimes under 5000 Oe. Ac magnetic susceptibilities were measured at an amplitude of 3 Oe with frequencies from 1000 to 10000 Hz. Heat capacity was measured at zero field by a relaxation method using a pellet sample.

Thermal Analysis.

Thermogravimetric analysis (TGA) was performed in the NETZSCH STA 449C instruments in a nitrogen atmosphere at a heating rate of 10 °C/min. The sample was placed in Al_2O_3 crucible and heated from room temperature to 1000 °C.

Figure S1. View of the oxygen-coordination environments for (a) Cu1, (b) Cu2, (c) Cu3, (d) Cu4, (e) Se1, (f) Se2, and (g) Na atoms.

Figure S2. View of the connection of $[Cu_7O_{14}Cl_4]^{18-}$ cluster in $Na_2Cu_7(SeO_3)_4O_2Cl_4$. Color codes: Se1, cyan; Se2, blue.

Figure S3. Simulated (red line) and experimental (black line) powder X-ray (Cu Ka) diffraction patterns for $Na_2Cu_7(SeO_3)_4O_2Cl_4$.

Figure S4. Thermogravimetric curve for the decomposition of compound $Na_2Cu_7(SeO_3)_4O_2Cl_4$.

Figure S5. Heat capacity data of $Na_2Cu_7(SeO_3)_4O_2Cl_4$ obtained at zero field.

Figure S6. The field-cooling (FC) and zero-field-cooling (ZFC) regimes for $Na_2Cu_7(SeO_3)_4O_2Cl_4$.

Figure S7. In phase (χ') susceptibility measurements versus temperature at different frequencies for $Na_2Cu_7(SeO_3)_4O_2Cl_4$.

Figure S8. Magnetization curves measured at different temperatures for $Na_2Cu_7(SeO_3)_4O_2Cl_4$.

Table S1. Crystal data and structure refinements for $Na_2Cu_7(SeO_3)_4O_2Cl_4$.

Table S2. Atomic coordinates and equivalent isotropic displacement parameters for $Na_2Cu_7(SeO_3)_4O_2Cl_4$.

Table S3. Selected bond lengths and angles for $Na_2Cu_7(SeO_3)_4O_2Cl_4$.

Table S4. Anisotropic displacement parameters for $Na_2Cu_7(SeO_3)_4O_2Cl_4$.

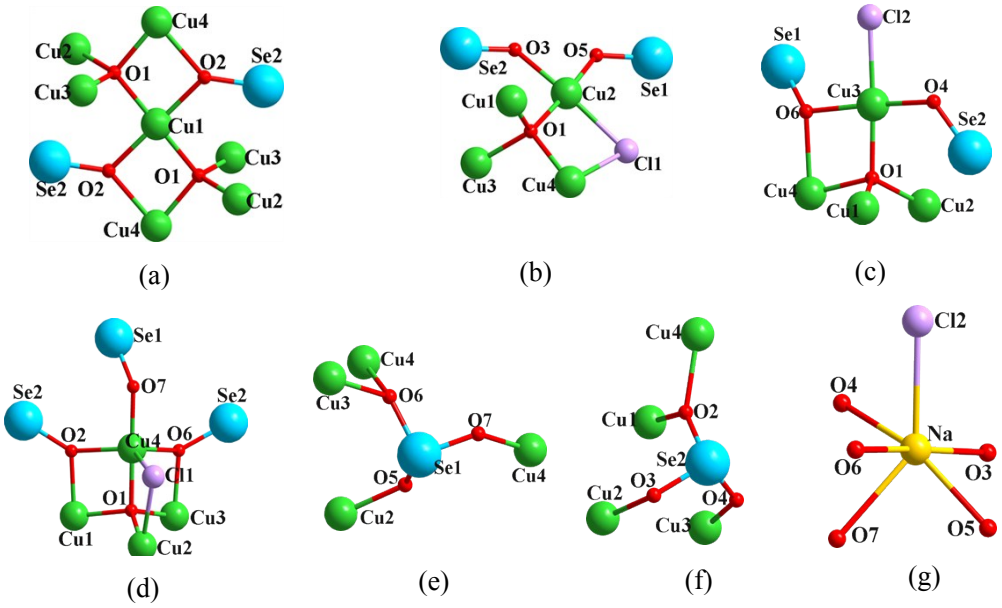

Figure S1. View of the oxygen-coordination environments for (a) Cu1, (b) Cu2, (c) Cu3, (d) Cu4, (e) Se1, (f) Se2, (g) Na atoms in $Na_2Cu_7(SeO_3)_4O_2Cl_4$.

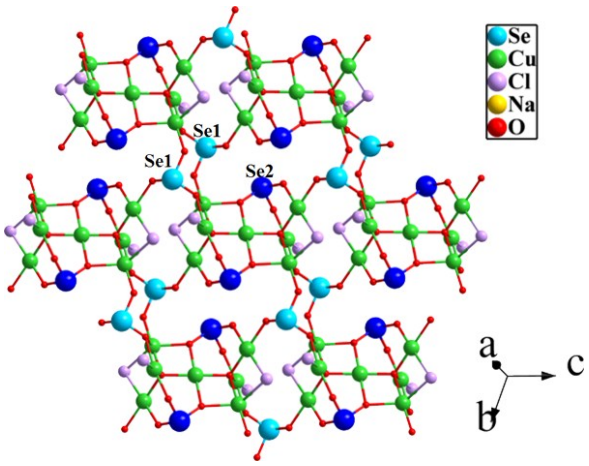

Figure S2. View of the connection of $[Cu_7O_{14}Cl_4]^{18-}$ cluster in $Na_2Cu_7(SeO_3)_4O_2Cl_4$. Color codes: Se1, cyan; Se2, blue.

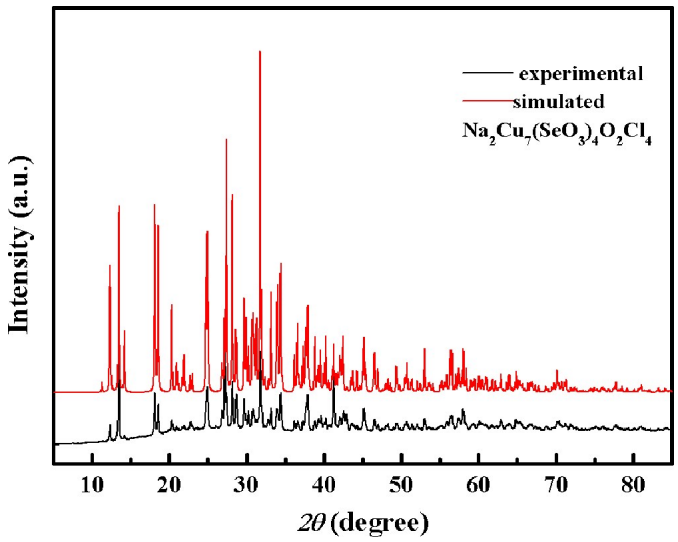

Figure S3. Simulated (red line) and experimental (black line) powder X-ray (Cu Ka) diffraction patterns for $Na_2Cu_7(SeO_3)_4O_2Cl_4$.

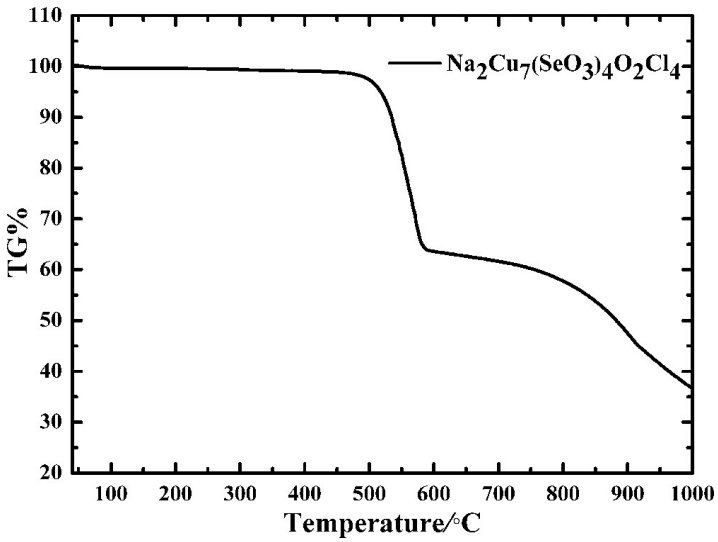

Figure S4. Thermogravimetric curve for the decomposition of compound $Na_2Cu_7(SeO_3)_4O_2Cl_4$.

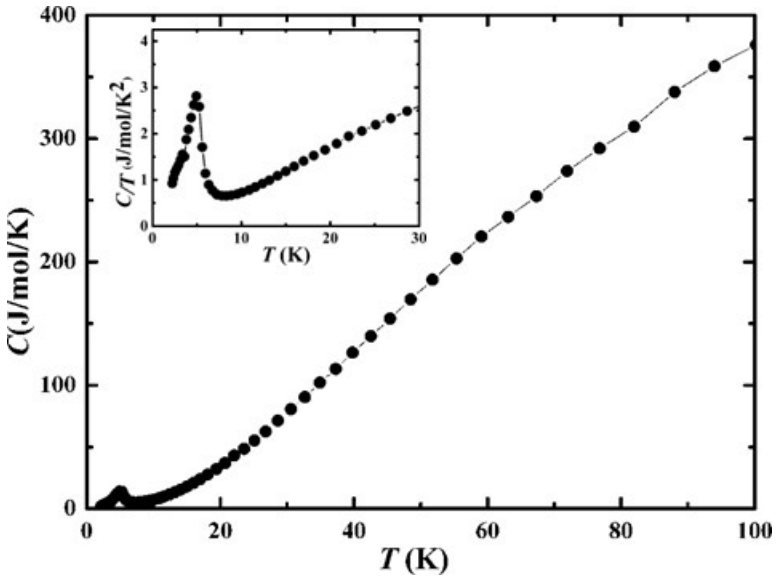

Figure S5. Heat capacity data of $Na_2Cu_7(SeO_3)_4O_2Cl_4$ obtained at zero field.

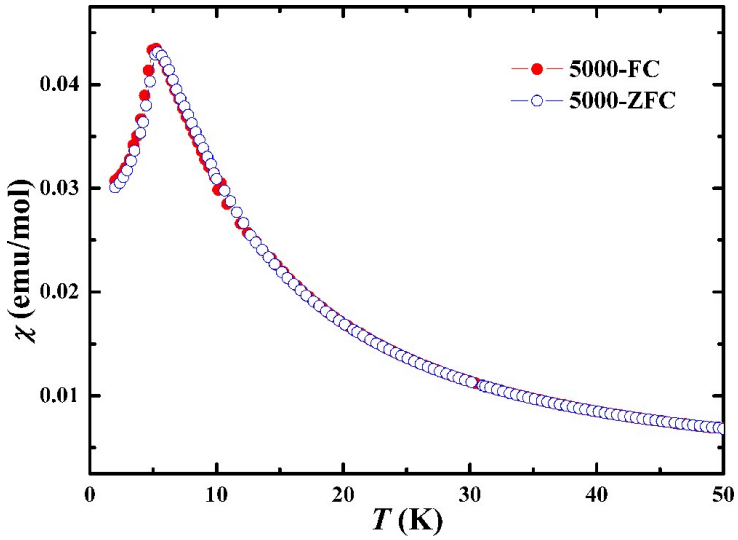

Figure S6. The field-cooling (FC) and zero-field-cooling (ZFC) regimes for $Na_2Cu_7(SeO_3)_4O_2Cl_4$.

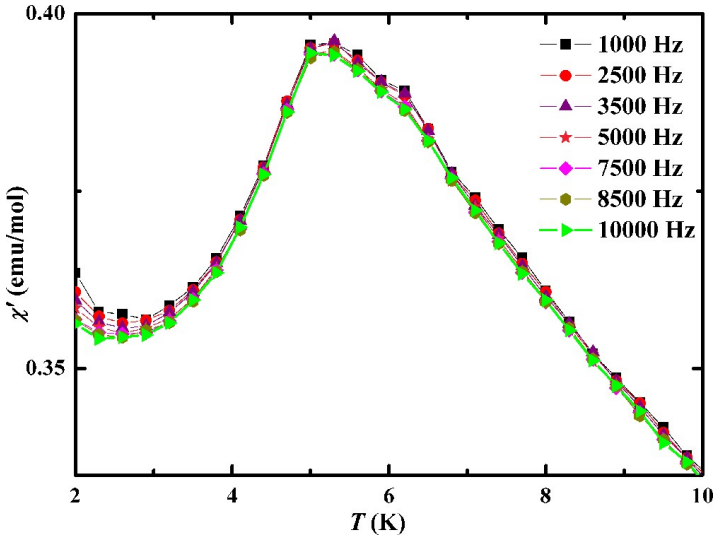

Figure S7. In phase (χ') susceptibility measurements versus temperature at different frequencies for $Na_2Cu_7(SeO_3)_4O_2Cl_4$.

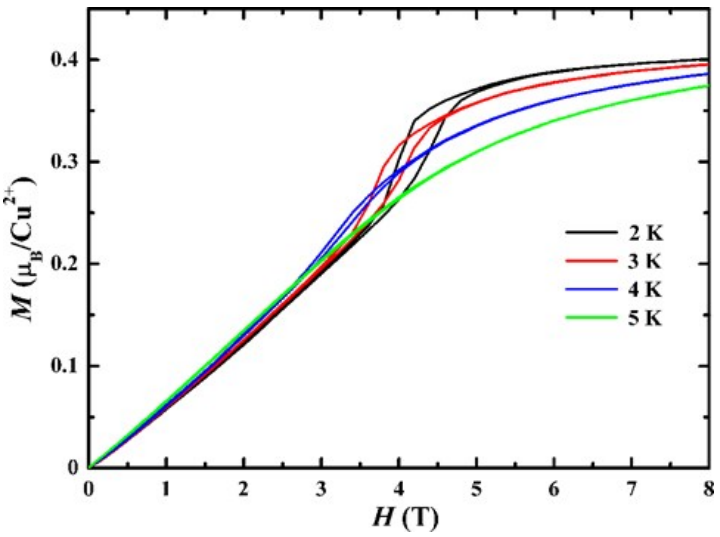

Figure S8. Magnetization curves measured at different temperatures for $Na_2Cu_7(SeO_3)_4O_2Cl_4$.

Table S1. Crystal data and structure refinements for the $Na_2Cu_7(SeO_3)_4O_2Cl_4$.

formula	$Na_2Cu_7(SeO_3)_4O_2Cl_4$
fw	1172.47
T, K	room temp
λ, Å	0.71073
space group	*P*-1
a, Å	7.446(2)
b, Å	8.349(3)
c, Å	9.137(3)
α, deg	110.335(7)
β, deg	106.166(3)
γ, deg	105.161(7)
V, Å^3	469.3(2)
Z	1
D_{calcd}, g cm^{-3}	4.149
μ, cm^{-1}	162.15
F(000)	541
θ range(deg)	2.60 - 27.47°
Limiting indices	-8≤ h ≤9 -10≤ k ≤10 -11≤ l ≤11
Reflns collected/unique	5788 / 1887 [R(int) = 0.0354]
Completeness to θ (%)	98.9 %
Refinement method	Full-matrix least-squares on F^2
Data/restraints/params	2122/0/142
Max.and Min. transimissions	1.0000, 0.4580
GOF on F^2	1.032
R1,wR2 [I >2σ(I)]a	0.0221, 0.0486
R1,wR2 (all data)	0.0269, 0.0501
Largest diff. peak and hole	0.601 and -0.796 e.A^{-3}

[a]R1 = $\sum||F_o| - |F_c||/\sum|F_o|$, wR2 = $\{\sum w[(F_o)^2 - (F_c)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$

Table S2. Atomic coordinates (×10^4) and equivalent isotropicdisplacement parameters (Å^2 ×10^3) for $Na_2Cu_7(SeO_3)_4O_2Cl_4$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

atom	x	y	z	U(eq)
Se(1)	1962(1)	7953(1)	9608(1)	12(1)
Se(2)	-8020(1)	822(1)	3894(1)	12(1)
Cu(1)	-5000	5000	5000	12(1)
Cu(2)	-4449(1)	3356(1)	7777(1)	14(1)
Cu(3)	1713(1)	4438(1)	6473(1)	14(1)
Cu(4)	-6068(1)	2574(1)	1359(1)	14(1)
Cl(1)	-2384(2)	6121(1)	10352(1)	19(1)
Na	-2992(3)	909(2)	3170(2)	23(1)
O(1)	-4555(4)	510	3064(3)	10(1)

O(2)	-6499(4)	2332(3)	3428(3)	19(1)
O(3)	-6331(4)	1085(3)	5715(3)	17(1)
O(4)	-9407(4)	1976(3)	4591(3)	20(1)
O(5)	3797(4)	8411(3)	11441(3)	18(1)
O(6)	2947(4)	7100(3)	8154(3)	13(1)
O(7)	2419(4)	10060(3)	9642(3)	20(1)
Cl(2)	-1531(2)	4092(1)	6210(1)	20(1)

Table S3. Bond lengths [A] and angles [deg] for $Na_2Cu_7(SeO_3)_4O_2Cl_4$.

Se(1)-O(5)	1.681(3)	Se(1)-O(7)	1.690(2)
Se(1)-O(6)	1.724(3)	Se(2)-O(4)	1.692(3)
Se(2)-O(3)	1.684(3)	Se(2)-O(2)	1.717(3)
Cu(1)-O(1)#3	1.915(2)	Cu(1)-O(1)	1.915(2)
Cu(1)-O(2)	1.963(2)	Cu(1)-O(2)#3	1.963(2)
Cu(2)-O(1)#3	1.912(2)	Cu(2)-O(3)	1.941(3)
Cu(2)-O(5)#4	1.959(3)	Cu(2)-Cl(1)	2.3625(12)
Cu(3)-O(4)#5	1.930(3)	Cu(3)-O(1)#1	1.942(3)
Cu(3)-O(6)	1.979(2)	Cu(3)-Cl(2)	2.2890(13)
Cu(4)-O(7)#6	1.904(2)	Cu(4)-O(1)	1.911(2)
Cu(4)-O(2)	2.071(3)	Cu(4)-O(6)#1	2.163(3)
Cu(4)-Cl(1)#3	2.4075(11)	Na-O(3)#2	2.256(3)
Na-O(6)#1	2.370(3)	Na-O(4)#5	2.372(3)
Na-O(5)#6	2.357(3)	Na-O(7)#1	2.604(3)
Na-Cl(2)	2.764(2)	O(5)-Se(1)-O(7)	103.66(12)
O(5)-Se(1)-O(6)	101.13(13)	O(7)-Se(1)-O(6)	97.45(13)
O(4)-Se(2)-O(3)	102.87(13)	O(4)-Se(2)-O(2)	102.56(13)
O(3)-Se(2)-O(2)	101.14(13)	O(1)#3-Cu(1)-O(1)	180.000(1)
O(1)#3-Cu(1)-O(2)	96.88(10)	O(1)-Cu(1)-O(2)	83.12(10)
O(1)#3-Cu(2)-O(3)	93.08(11)	O(1)#3-Cu(2)-O(5)#4	172.60(11)
O(3)-Cu(2)-O(5)#4	82.30(11)	O(1)#3-Cu(2)-Cl(1)	85.83(8)
O(3)-Cu(2)-Cl(1)	175.32(9)	O(5)#4-Cu(2)-Cl(1)	98.31(8)
O(4)#5-Cu(3)-O(1)#1	96.34(11)	O(4)#5-Cu(3)-O(6)	171.20(11)
O(1)#1-Cu(3)-O(6)	81.37(10)	O(4)#5-Cu(3)-Cl(2)	88.66(9)
O(1)#1-Cu(3)-Cl(2)	174.30(8)	O(6)-Cu(3)-Cl(2)	94.09(8)
O(7)#6-Cu(4)-O(1)	179.41(10)	O(7)#6-Cu(4)-O(2)	100.13(11)
O(1)-Cu(4)-O(2)	80.38(10)	O(7)#6-Cu(4)-O(6)#1	102.68(11)
O(1)-Cu(4)-O(6)#1	77.44(10)	O(2)-Cu(4)-O(6)#1	104.77(11)
O(7)#6-Cu(4)-Cl(1)#3	94.86(8)	O(1)-Cu(4)-Cl(1)#3	84.58(8)
O(2)-Cu(4)-Cl(1)#3	128.94(9)	O(6)#1-Cu(4)-Cl(1)#3	119.01(7)
O(3)#2-Na-O(6)#1	169.08(12)	O(3)#2-Na-O(4)#5	93.91(11)
O(6)#1-Na-O(4)#5	96.71(11)	O(3)#2-Na-O(5)#6	67.56(10)
O(6)#1-Na-O(5)#6	103.79(11)	O(4)#5-Na-O(5)#6	149.32(12)
O(3)#2-Na-O(7)#1	121.72(11)	O(6)#1-Na-O(7)#1	61.87(9)

O(4)#5-Na-O(7)#1	85.71(11)	O(5)#6-Na-O(7)#1	84.16(10)
O(3)#2-Na-Cl(2)	95.26(9)	O(6)#1-Na-Cl(2)	86.03(8)
O(4)#5-Na-Cl(2)	69.89(8)	O(5)#6-Na-Cl(2)	133.40(11)
O(7)#1-Na-Cl(2)	137.26(9)		

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z+1; #2 -x-1,-y,-z+1; #3 -x-1,-y+1,-z+1; #4 -x,-y+1,-z+2; #5 x+1,y,z; #6 x-1,y-1,z-1.

Table S4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $Na_2Cu_7(SeO_3)_4O_2Cl_4$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^*b^*U12]$

atom	U11	U22	U33	U23	U13	U12
Se(1)	13(1)	10(1)	11(1)	4(1)	4(1)	5(1)
Se(2)	16(1)	8(1)	10(1)	3(1)	4(1)	3(1)
Cu(1)	18(1)	9(1)	9(1)	4(1)	6(1)	4(1)
Cu(2)	18(1)	10(1)	12(1)	6(1)	3(1)	6(1)
Cu(3)	12(1)	10(1)	14(1)	2(1)	3(1)	4(1)
Cu(4)	19(1)	9(1)	10(1)	3(1)	2(1)	5(1)
Cl(1)	23(1)	16(1)	14(1)	8(1)	1(1)	5(1)
Na	23(1)	18(1)	20(1)	13(1)	0(1)	0(1)
O(1)	13(1)	9(1)	9(1)	4(1)	5(1)	6(1)
O(2)	31(2)	11(1)	11(1)	5(1)	12(1)	1(1)
O(3)	23(2)	10(1)	15(1)	8(1)	3(1)	5(1)
O(4)	15(2)	15(1)	21(2)	2(1)	3(1)	5(1)
O(5)	25(2)	14(1)	13(1)	8(1)	3(1)	9(1)
O(6)	16(1)	11(1)	11(1)	3(1)	8(1)	7(1)
O(7)	33(2)	9(1)	10(1)	3(1)	3(1)	8(1)
Cl(2)	13(1)	22(1)	21(1)	6(1)	4(1)	7(1)

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2 G. M. Sheldrick, *Crystallographic Software Package*, SHELXTL, version 5.1; Bruker-AXS: Madison, WI, 1998.

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