Supporting Information

SU-79: A Novel Germanate with 2D 10-Ring Channels Templated by a Square-Planar Nickel Complex

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Contents

1. Chemical formula determination of SU-79

From the structure refinement result, we can deduce that the chemical formula of the SU-79 framework is $[Ge_{12.5}O_{26}(OH)_2]^{4-}$, and one 1,2-$H_2pda^{2+}$ ion at special positions and one $[Ni(C_3N_2H_{10})_2]^{2+}$ at general position also can be observed. The ICP result revealed that the Ge/Ni ratio (11.0) is much lower than the expected value (12.5), which means more Ni complexes may exist in channels. From the CHN analysis, the molar ratio of C/N=1.33 is lower than the ratio for 1,2-pda (C/N=1.5), indicating the decomposition of 1,2-pda. Based on the results of ICP and CHN analysis, as well as the residual peaks in the structure refinement, we deduced that Ni(1,2-pda)$^{2+}$ complexes and NH_4^+ ions can be occupied in channels with the occupancies of 0.1 and 0.8, which can also balance the chance from the framework, and additional 1.5 1,2-pda molecules also reside in channels. The water content was deduced from the ratio of H/N = 5.37, suggesting two water molecules per asymmetric unit. Finally, the chemical composition of SU-79 was determined $[Ge_{12.5}O_{26}(OH)_2][Ni(C_3N_2H_{10})_2]_{1.1}(NH_4)_{0.8}(C_3N_2H_{12})_{0.5}(C_3N_2H_{10})_{1.5}(H_2O)_2$. Anal. Calcd for SU-79: N 7.22%, C 8.47%, H 2.84%. Found: N 7.33%, C 8.38%, H 2.83%. Thermogravimetric analysis for SU-79 shows a weight loss of 22.08% between 40 and 900°C, as shown in Figure S5, which agrees well with the expected value (22.62%) of the removal of all guest molecules from the structure.

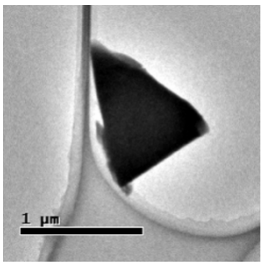

Fig. S1 TEM image of the selected micro-domain of the SU-79 crystal from which the RED data was collected.

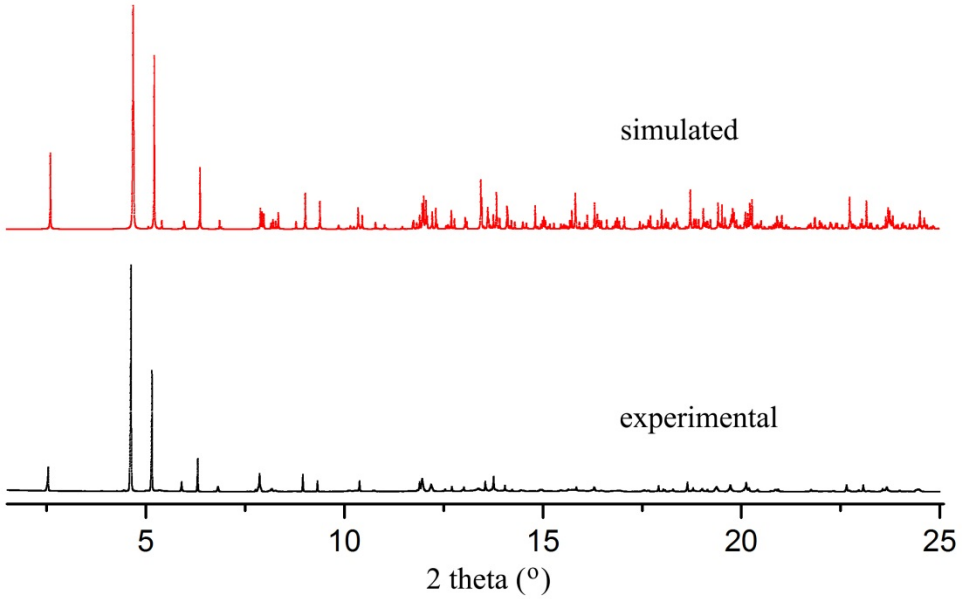

Fig. S2 Experimental and simulated powder X-ray diffraction patterns of SU-79 (λ=0.82695 Å). The difference of the intensity in experimental and simulated pattern is due to the preferred orientation of the as-synthesized SU-79 crystals.

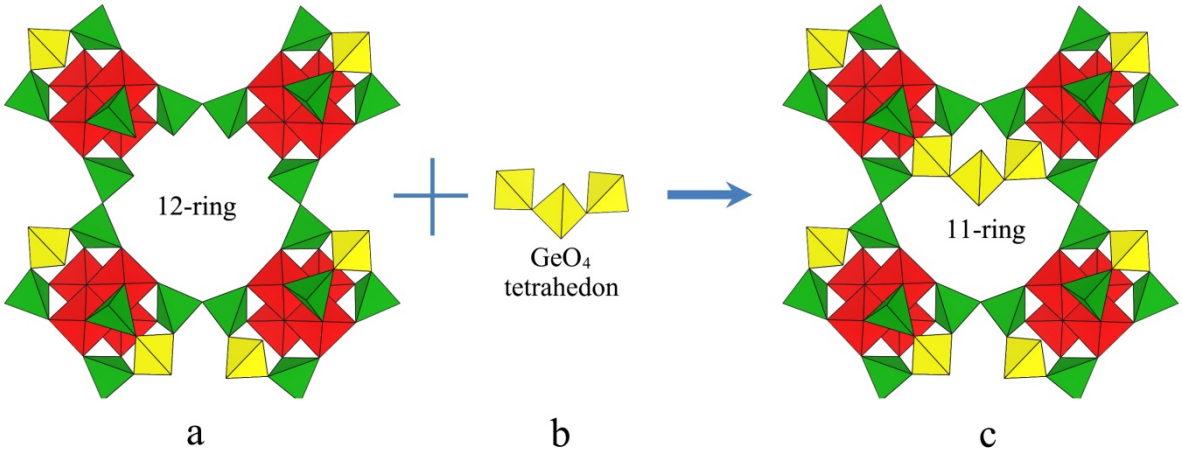

Fig. S3 Fan-shaped 11-ring in SU-79. Four Ge_{10} clusters link to each other by sharing corners to form a 12-ring (a), which is converted into a fan-shaped 11-ring (c) via connections of three additional tetrahedra (b).

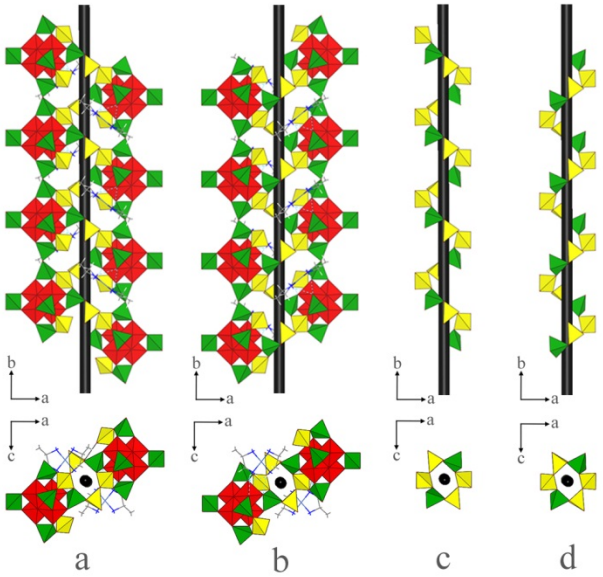

Fig. S4 Helical chains in SU-79.

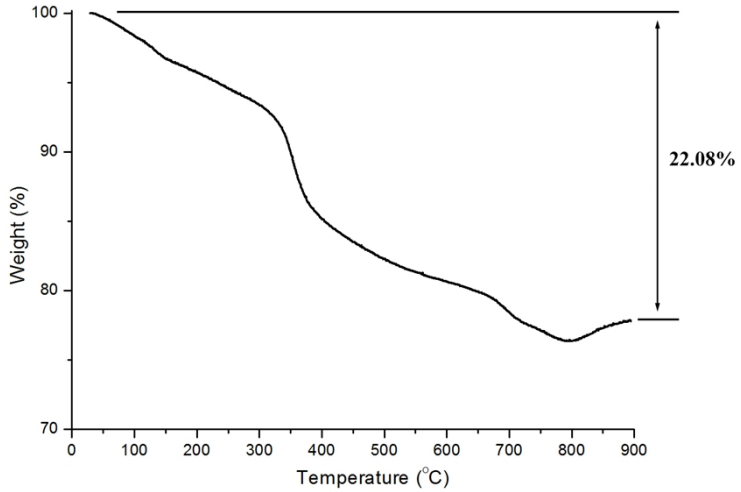

Fig. S5 Thermogravimetric analysis of SU-79. The weight loss of 22.08% between 40 and 900°C agrees well with the calculated value (22.62%) of the removal of all guest molecules from the structure. The weight lost and increase between 650 ºC and 900 ºC can be attributed to the reduction and reoxidization of germanium and nickel under the air condition. (J. Su, et al. *Inorg. Chem.*, 2010, **49**, 9765–9769.)

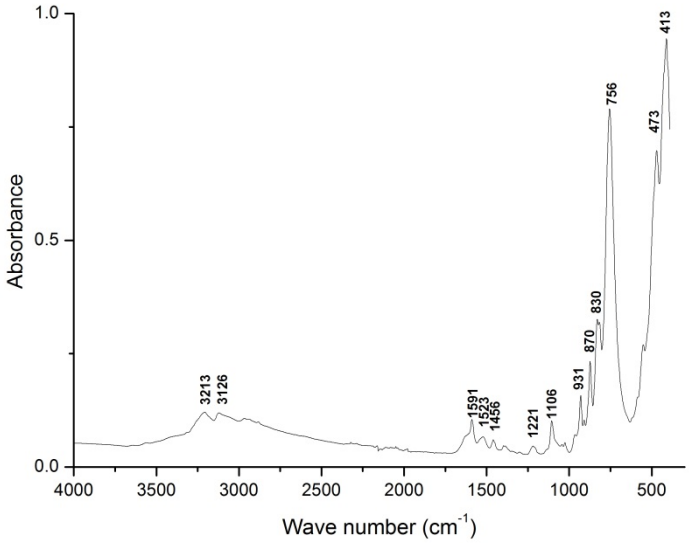

Fig. S6 FT-IR spectrum of SU-79. The peaks at 3213, 3126 and 2883-2984 cm^{-1} correspond to the stretching vibrations of OH, NH_2 and CH_2 groups. The bending bands of NH_2 and CH_2 are observed at around 1591 and 1456 cm^{-1}. The peaks at 931, 870 and 830 cm^{-1} can be assigned to Ge-O vibrations of the tetrahedral and octahedral germanium polyhedral. The symmetrical vibrations of Ge-O are observed at 756 cm^{-1}. The absorption bands at 473 and 413 cm^{-1} can be assigned to the asymmetric stretching vibrations of Ge-O bonds. (H. Zhang, et al. *Inorg. Chem.*, 2003, **42**, 6595; Z. Lin, et al. *Angew. Chem. Int. Ed.*, 2005, **44**,6881.)

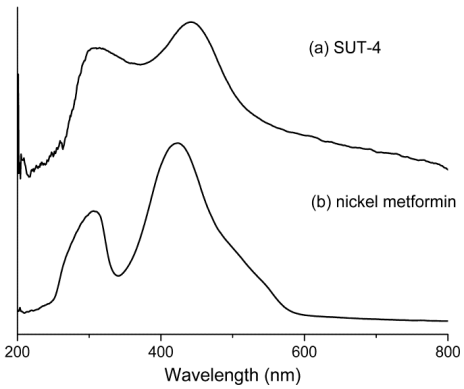

Fig. S7 UV-Vis diffuse-reflection spectrum of (a) SU-79 and (b) a standard nickel complex with the square-planar geometry. Peak positions: 331nm and 441nm in SU-79; 306 nm and 423 nm in nickel metfomin.

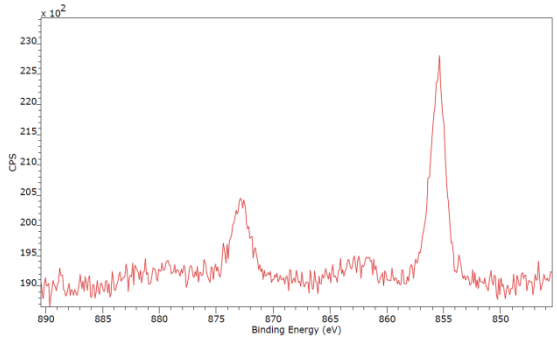

Fig. S8 Ni 2p XPS spectrum of SU-79. The two peaks around the banding energy 873eV and 856eV confirm the presence of Ni2+ in the SU-79.

Table S1. Crystallographic Data for SU-79

Sample Name	SU-79
Chemical Formula	$[Ge_{12.5}O_{26}(OH)_2][Ni(C_3N_2H_{10})_2]_{1.1}(NH_4)_{0.8}(C_3N_2H_{12})_{0.5}(C_3N_2H_{10})_{1.5}(H_2O)_2$[a]
Formula weight[a]	1075.26
Temperature (K)	150(2)
Wavelength (Å)	0.6889
Crystal system	Monoclinic
Space group	*C*2/*c*
Unit cell	a = 37.7974(11) Å, b = 10.4874(2) Å, c = 20.9666(4) Å, β = 106.765(3) °
Volume (Å^3)	7957.8(3)
Z	4
Density (calculated)	2.743
Absorption coefficient	9.853
F(000)	6239
Crystal size (mm^3)	0.50×0.50×0.10
Crystal color	Yellow
Theta range	2.19-26.41
Index ranges	-47 ≤ h ≤ 46, -13 ≤ k ≤ 13, -26 ≤ l ≤ 26
Completeness	0.977
Reflections collected	35737
Unique reflections	7998
R_{int}	0.0449
Observed reflections	7414
GOF	1.033
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0599, wR_2 = 0.1750
R indices (all data)	R_1 = 0.0633, wR_2 = 0.1784

[a] The formula here includes 1,2-pda and water, which could not be located in the structure refinement but were estimated from elemental analysis.

Table S2. Hydrogen bond lengths (Å) and angles (°) for SU-79

D-H…A	D(D-H)	D(H…A)	D(D…A)	∠(DHA)
O27-H27…O28	0.820	2.073	2.787	145.39
O28-H28…O16	0.820	2.445	3.219	157.66
O28-H28…O4	0.820	2.626	3.208	129.22
N1-H1B…O11	0.900	2.192	2.969	144.15
N1-H1B…O16	0.900	2.586	3.200	126.06
N2-H2A…O15	0.900	2.364	3.192	153.01
N2-H2A…O8	0.900	2.438	3.189	141.14
N2-H2B…O18	0.900	2.429	3.196	143.30
N2-H2B…Ow1	0.900	2.431	2.940	116.08
N3-H3A…O10	0.900	2.232	3.053	151.41
N3-H3A…O11	0.900	2.401	3.135	138.79
N3-H3B…O25	0.900	2.276	3.071	147.12
N4-H4A…Ow1	0.900	2.180	2.923	139.43
N4-H4B…O8	0.900	2.226	3.037	149.81
N4-H4B…O14	0.900	2.587	3.190	129.97
Ow1-Hw1A…O14	0.962	1.784	2.738	170.51
Ow1-Hw1B…O27	0.963	1.861	2.676	140.54
N5-H5A…O13	0.890	2.305	3.100	148.68
N5-H5B…O6	0.890	2.370	2.947	122.71
N6-H6D…O9	0.890	2.272	3.093	153.33
N6-H6D…O5	0.890	2.276	2.977	135.62
N6-H6E…O5	0.890	2.222	2.977	142.46
N6-H6E…O9	0.890	2.313	3.093	146.34