

Supplementary Information

Efficient Capture of Sr²⁺ from Acidic Aqueous Solution by an 18-

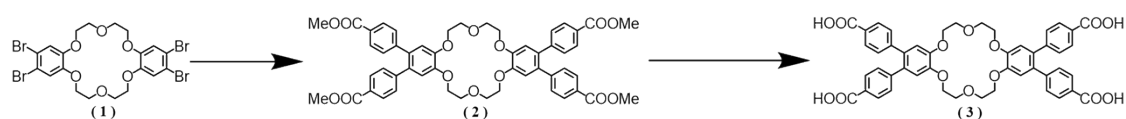
Crown-6-Ether based Metal Organic Framework

Chenglong Guo,^{ab} Mengjia Yuan,^b Linwei He,^b Liwei Chen,^b Xia Wang,^b Nannan Shen,^b Fuyin Ma,^{*b} Guolin Huang,^{*a} Shuao Wang^{*b}

a. *State Key Laboratory of Nuclear Resources and Environment, East China University of Technology, Nanchang 330013, China. E-mail: guolinhuang@sina.com.*

b. *State Key Laboratory of Radiation Medicine and Protection, School for Radiological and interdisciplinary Sciences (RAD-X) and Collaborative Innovation Center of Radiation Medicine of Jiangsu Higher Education Institutions, Soochow University, Suzhou 215123, China. E-mail: mafuyin@suda.edu.cn; shuaowang@suda.edu.cn*

Section 1. Synthesis



Scheme. 1 Synthetic routes to the ligand compound 3.

2.1.1 Synthesis of 4,4',5,5'-tetrabenzoate dibenzo-18-crown-6 (2)

4,4',5,5'-tetrabromodibenzo-18-crown-6 (1.0425 g, 1.54 mmol), methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (2.452 g, 9.35 mmol), K_2CO_3 (1.017 g, 7.36 mmol), and tetrakis(triphenylphosphine) palladium (0.202 g, 0.175 mmol) were added into a 100 mL Schleck flask. The flask was pumped under vacuum and refilled with N_2 three times, and then the degassed solvent of THF/ CH_3OH (30 mL/ 5 mL) were transferred into the Schleck flask. The mixture solution was heated at 90 °C for 48 h under a nitrogen atmosphere. After that the reaction mixture was cooled to room temperature, it was filtered and concentrated. The aqueous layer was extracted with chloroform (3×50 mL), and then the combined organic layer was dried over anhydrous $MgSO_4$. Hereafter, the solution was filtered and concentrated by a rotary evaporator. Finally, the crude product was recrystallized with ethyl acetate and chloroform to obtain a white solid. Yield: 0.8655 g (62.6%). 1H NMR (400 MHz, Chloroform- d) δ 7.86 (d, $J = 8.1$ Hz, 8H), 7.14 (d, $J = 8.1$ Hz, 8H), 6.93 (s, 4H), 4.27 (t, $J = 4.4$ Hz, 8H), 4.07 (t, $J = 4.5$ Hz, 8H), 3.89 (s, 12H).

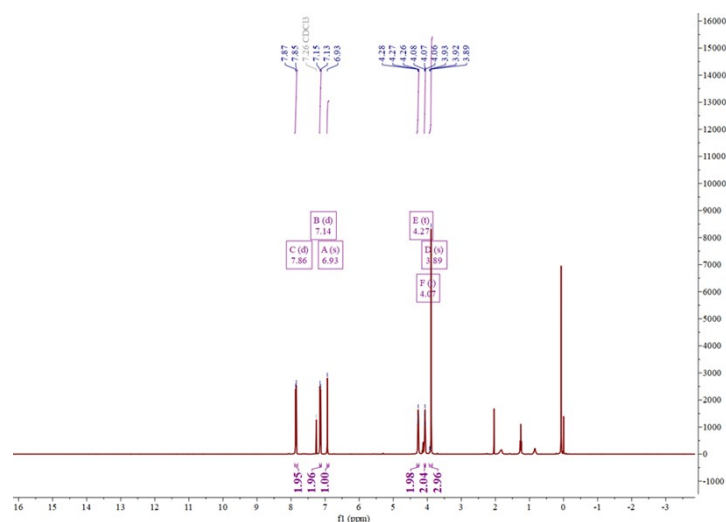


Fig. S1 1H NMR spectra of compound 2 in $CDCl_3$.

2.1.2 Synthesis of 4,4',5,5'-terabenzoic acid dibenzo-18-crown-6 ($H_4TBADB-18Cr6$) (3)

The compound 2 (0.8002, 0.966 mmol) was dissolved in 30 mL of CH_3OH , and 10 mL of 6 M NaOH aqueous solution was added. The mixture was stirred under reflux for 24 h. After cooling to room temperature, it was concentrated under vacuo to remove methanol, and then acidified by adding 3 M HCl solution dropwise to the above clear solution and adjusted to pH=1. Finally, a white precipitate was obtained, which was filtered, washed with water, and dried in an oven at 80 °C for 12 h. Yield: 0.6685 g (88.9%). 1H NMR (400 MHz, $DMSO-d_6$) δ 7.77 (d, $J = 8.1$ Hz, 8H), 7.21 (d, $J = 8.1$ Hz, 8H), 7.03 (s, 4H), 4.22 (d, $J = 5.6$ Hz, 8H), 3.87 (d, $J = 7.3$ Hz, 8H). ^{13}C NMR (101 MHz, $DMSO$) δ 167.17, 147.77, 145.23, 131.38, 129.95, 129.03, 128.81, 114.49, 68.82, 67.91.

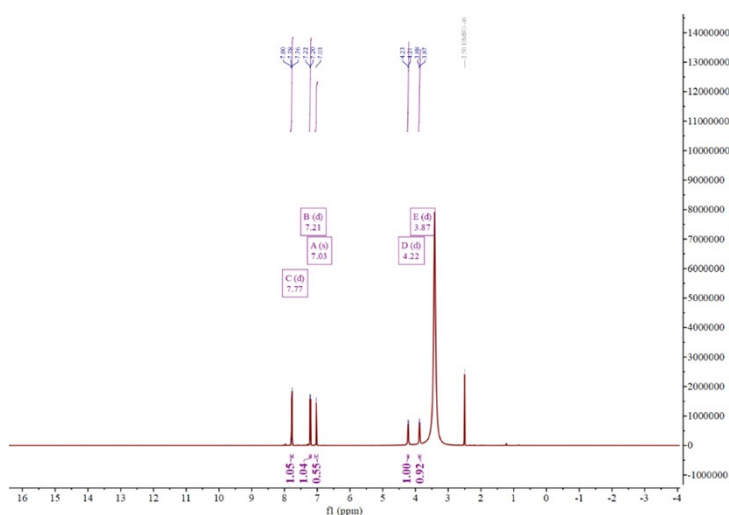


Fig. S2 1H NMR spectra of compound 3 in $[D_6]DMSO$

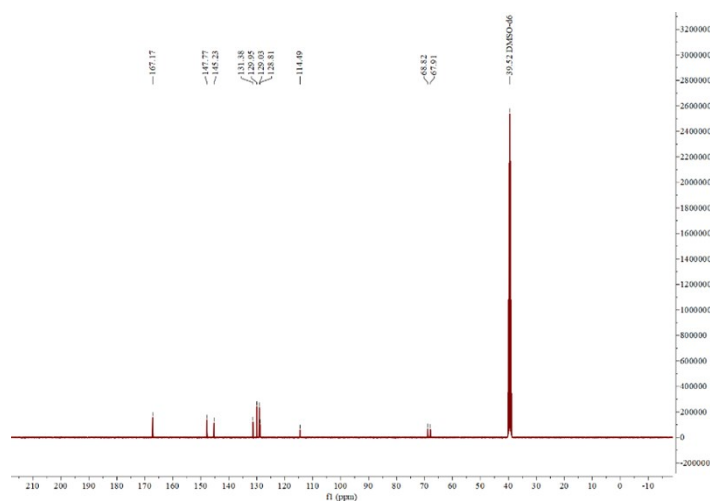


Fig. S3 ^{13}C NMR spectra of compound 3 in $[D_6]DMSO$.

Section 2. Experimental method and characterization

2.1 The effect of pH on Sr²⁺ adsorption

By studying the solid-to-liquid ratio $m:V=1 \text{ g L}^{-1}$, 5 mg of SNU-200 sample was added to 5 mL solution containing $50 \text{ mg L}^{-1} \text{ Sr}^{2+}$. When the contact time was 12 h, the adsorption capacity of Sr²⁺ in the solution with pH value of 2 to 10. Then, the solid-liquid was separated by the aqueous $0.22 \mu\text{m}$ nylon membrane, and the concentration in the remaining liquid after adsorption was measured by ICP-OES. Finally, the Sr²⁺ adsorption capacities and removal rates were calculated.

2.2 Adsorption kinetics

Added 5 mg of SNU-200 sample into a 5 mL aqueous solution of Sr²⁺ with pH = 3 and an initial concentration of 50 mg L^{-1} . The mixture was stirred for a series of contact times. The adsorption capacities and concentrations of Sr²⁺ with different time were obtained. Then, the pseudo first-order and pseudo-second-order kinetic models were used to determine the adsorption kinetic curve. The equations are as follows:

pseudo first-order model: $\ln(q_e - q_t) = \ln q_e - k_1 t$

pseudo-second-order model: $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$

In the formula, q_e (mg g^{-1}) is the adsorption capacity of the adsorbent at the completion of the reaction; q_t (mg g^{-1}) is the adsorption capacity of the adsorbent at any moment; k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$) are the rate constants of pseudo-first-order and pseudo-second-order kinetic adsorption, respectively.

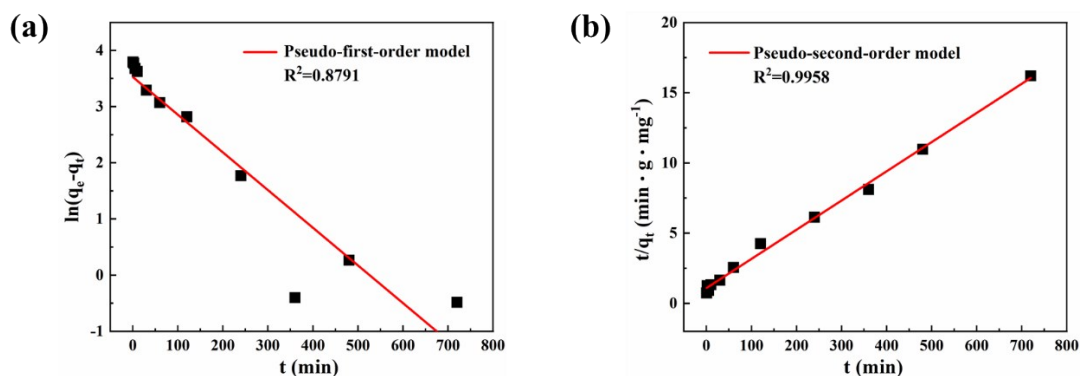


Fig. S4 (a) pseudo-first-order model. (b) pseudo-second-order model.

Table S1. pseudo-first-order and pseudo-second-order kinetic model fitting parameters.

pseudo-first-order			pseudo-second-order		
k_1 (min ⁻¹)	q_e (mg g ⁻¹)	R^2	k_2 (g mg ⁻¹ min ⁻¹)	q_e (mg g ⁻¹)	R^2
0.00671	34.01	0.8791	0.0004	48.08	0.9958

2.3 The effect of coexisting ions

The effect of coexisting metal ions represented by Na⁺, K⁺, Mg²⁺, Ca²⁺, and Cs⁺ were studied. By studying competing ions from low concentrations to high concentrations, the selective removal effect of SNU-200 for Sr²⁺ were obtained. Specifically, the influence of coexisting alkali metal ions represented by Na⁺, K⁺ and Cs⁺ was studied. 5 mg SNU-200 sample were stirred with 5 mL solution of Sr²⁺ at pH = 3 with that the molar ratio of Sr²⁺: Na⁺/K⁺ were 1:1, 1:10, 1:100, and 1:1000, respectively. After contacting for 6 h, the concentrations of Sr²⁺ in the remaining solutions were tested to obtain the removal rates. In the same way, the effect of adsorption and separation under the coexistence of alkaline-earth metal ions presented by Mg²⁺ and Ca²⁺ were also studied in the similar way.

2.4 Adsorption isotherm experiment

The initial Sr²⁺ concentrations were set from 1 to 300 mg L⁻¹, and the adsorption isotherm experiment of SNU-200 for Sr²⁺ was carried out. In a typical experiment, 5 mg of the adsorbent SNU-200 was added into 5 mL of an aqueous solution containing a certain concentration of Sr²⁺ with pH = 3. The above mixture was shaken for 6 h to ensure balance, and then a 0.22 μm water-based nylon membrane was used to filter to separate solid and liquid. The concentrations of Sr²⁺ in the filtrate solution were measured by ICP-OES, and the adsorption capacity and distribution coefficient also be calculated. In order to further understand the absorption model of Sr²⁺ on SNU-200, the Langmuir and Freundlich isotherm models were calculated, which were expressed as follows:

$$\text{Langmuir model: } \frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_l}$$

$$\text{Freundlich model: } \ln q_e = \ln k_F + \frac{1}{n} \ln C_e$$

Where q_m (mg g⁻¹) is the theoretical maximum adsorption capacity of a single layer, C_e

(mg L^{-1}) is the ion concentration at equilibrium, q_e (mg g^{-1}) is the equilibrium adsorption capacity obtained from the experiment, and K_L (mL mg^{-1}) is the Langmuir constant. K_F (mg g^{-1}) and n are Freundlich constants describing adsorption capacity and adsorption strength, respectively.

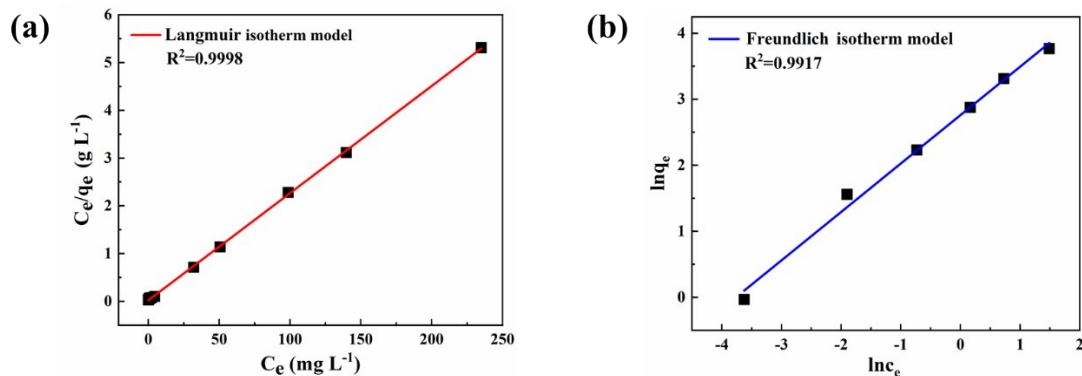


Fig. S5 (a) Langmuir isotherm model. (b) Freundlich isotherm model.

Table. S2 Langmuire and Freundlich isotherm model fitting parameters.

Langmuir			Freundlich		
q_m (mg g^{-1})	K_d (L mg^{-1})	R^2	K_F ($\text{L}^n/\text{mol}^{n-1} \text{ g}$)	n	R^2
44.8	1.007	0.9998	15.8	1.36	0.9917

2.5 Characterizations

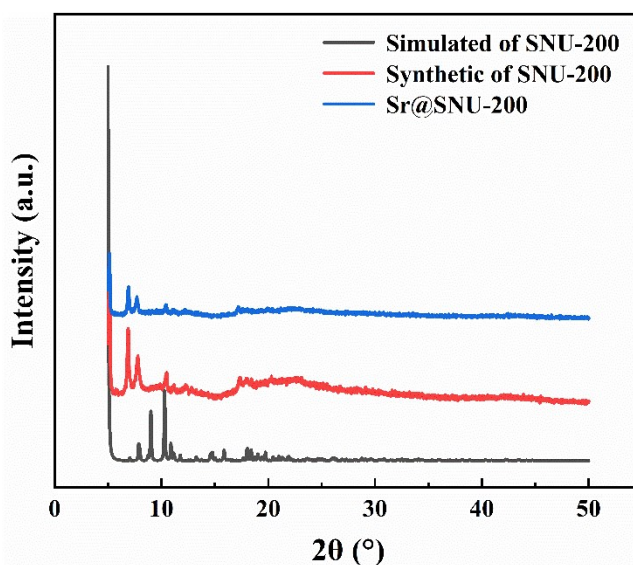


Fig. S6 PXRD patterns of SNU-200 before and after adsorption of Sr^{2+} .

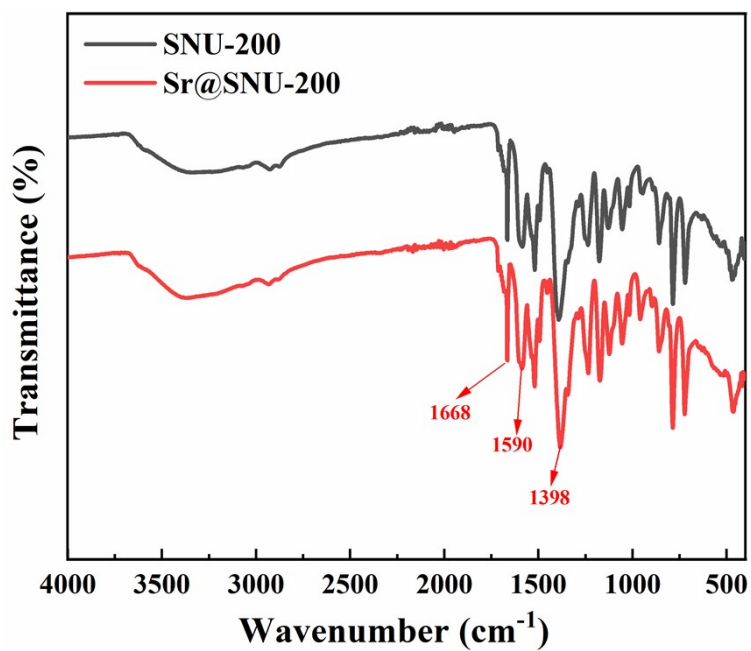


Fig. S7 FT-IR spectra of SNU-200 before and after adsorption of Sr²⁺.

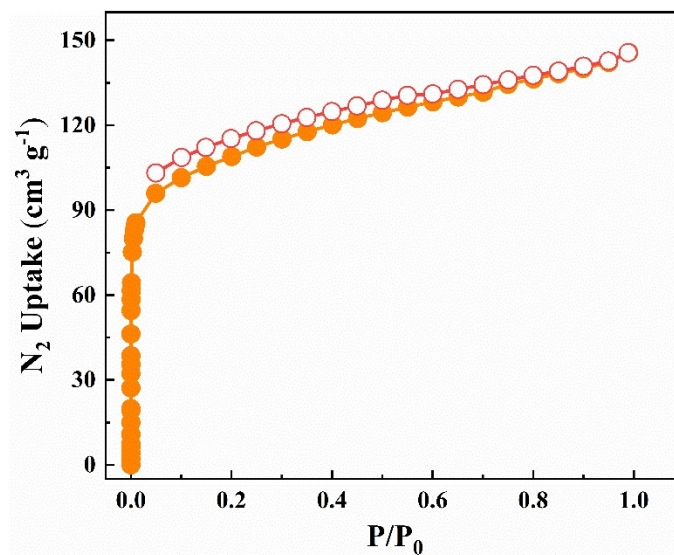


Fig. S8 N₂ sorption isotherms at 77 K of the SNU-200 activated with supercritical CO₂. Filled shape: adsorption; open shape: desorption.

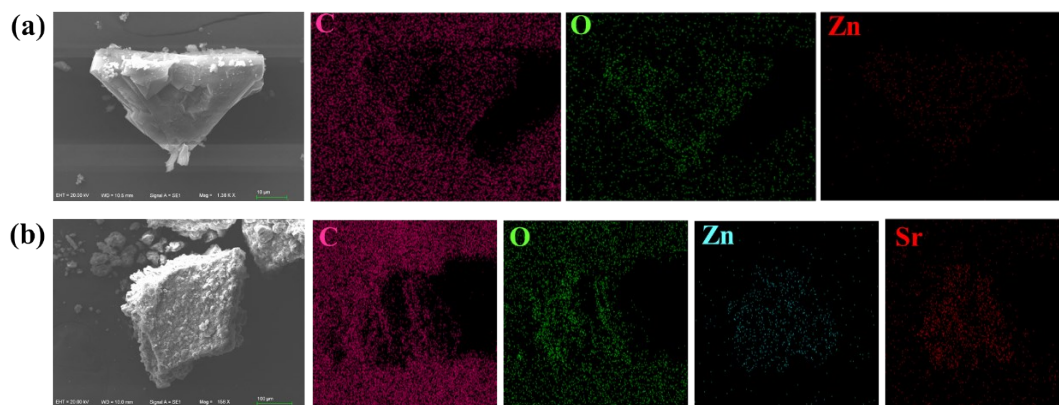


Fig. S9 SEM/EDS spectra of SNU-200 before and after adsorption of Sr²⁺.

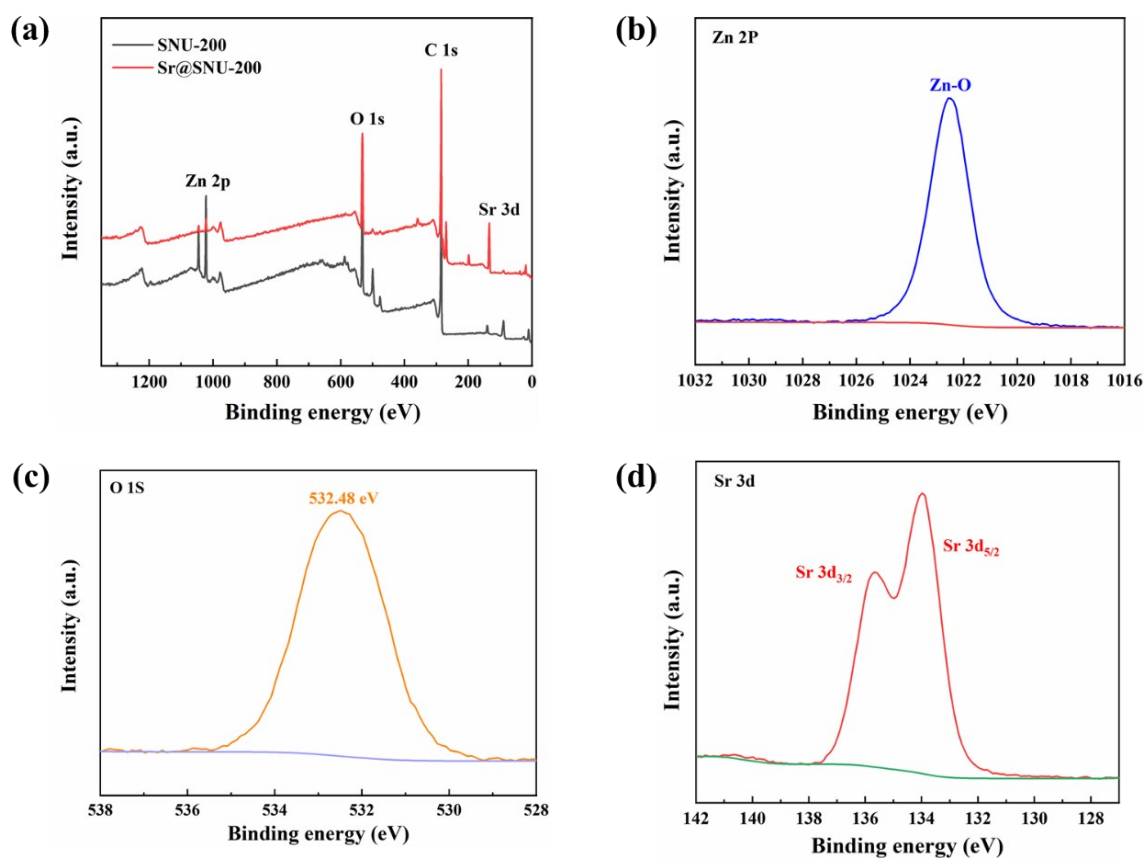


Fig. S10 (a) XPS spectrum of SNU-200 before and after adsorption of Sr²⁺. (b) Zn 2p XPS for SNU-200. (c) O 1s XPS for SNU-200. (d) Sr 3d XPS for Sr@SNU-200.