Supporting Information

A New Salt-Inclusion Compound $CsCl\cdot(VOSe_2O_5)_4$ Showing Nearly Isolated Spin-1/2 Chain Structure with a Typical Square Lattice

Wenya Xiang[a,b,c], Guozhao Wang[a,b,c], Meiyan Cui[a], Zhiying Zhao[a], Zhangzhen He[a,*]

[a]State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002, China

[b]College of Chemistry and Materials, Fujian Normal University, Fuzhou, 350117, China

[c]Fujian College, University of Chinese Academy of Sciences, Fuzhou 350002, China

[*]*Corresponding authors: hcz1988@hotmail.com; hezz@fjirsm.ac.cn.*

Experimental section

Synthesis: Single crystal $CsCl{\cdot}(VOSe_2O_5)_4$ was prepared by conventional hydrothermal method. A mixture of CsF (0.95 mmol, 0.1443g), V_2O_3 (0.4 mmol, 0.0599g), SeO_2 (2.2 mmol, 0.2441g), $SbCl_3$ (0.45 mmol, 0.1026g), HF (0.05 mmol, 0.1g) and 1 mL of deionized water was sealed in an autoclave equipped with a Teflon liner (28 mL). The reaction procedure is set to rapid heating at room temperature to 265 °C, holding for four days, and then dropping to room temperature for two days. The dark green rod-like crystal were obtained. The purity of powered samples was confirmed by powder X-ray diffraction analysis (Fig. S1). The Rietveld refinement for structural parameters was performed by GSAS-EXPGUI software [1]. EDS (Fig. S2) confirmed that the compound contains the element Cs, Cl, V, Se and O, which is in accordance with the stoichiometric ratio of $CsCl{\cdot}(VOSe_2O_5)_4$. The calculated bond valences of V, Se1, and Se2 atoms are 4.17, 3.91, and 3.95, respectively. The valence state of V, Se1, and Se2 atoms were all proved to be + 4, respectively.

X-Ray crystallography: The single-crystal X-ray diffraction data of $CsCl{\cdot}(VOSe_2O_5)_4$ was obtained on a XtaLAB Synergy R, HyPix diffractometer with Mo Kα radiation (λ = 0.71073 Å) at 100 K. Using Olex2-1.5 [2], the structure was solved with the SHELXT 2018/2 structure solution program [3] using Intrinsic Phasing and refined with the olex2.refine refinement package using Levenberg-Marquardt minimisation [4]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The final refined structural parameters were checked by the PLATON program.[5] Crystallographic data and structural refinements are summarized in Table S1. The final refined atomic positions and structural parameters are seen in the Supporting Information (Tables S2−S4).

Magnetic Measurements: Magnetic measurements were performed using a commercial Quantum Design Physical Properties Measurement System (PPMS). Powdered samples of $CsCl{\cdot}(VOSe_2O_5)_4$ (18 mg) in a magnetic sample tube. Magnetic susceptibility was measured at 0.1 T from 300 to 2 K (temperature scan of 5 K/min). Isothermal magnetization was measured at 2 K in applied field from 0 to 8 T (field scan of 0.1 T/step). The measurement of specific heat was under zero field.

Diamagnetic corrections were estimated by Pascal constant, and background correction was measured on the sample holder.

Thermal Analysis: Thermogravimetric analysis (TGA) of $CsCl{\cdot}(VOSe_2O_5)_4$ was performed in the NETZSCH STA 449C instruments in a nitrogen atmosphere at a heating rate of 10 °C/min. The samples were placed in Al_2O_3 crucibles and heated from room temperature to 1000 °C.

$CsCl{\cdot}(VOSe_2O_5)_4$ is stable below 300 °C with no changes of the curve in this temperature range, while the curve decreases rapidly in the temperature range from 300 °C to 425 °C, with a total loss of about 65% (Figure S7). The loss may correspond to a loss of eight SeO_2, showing the process of decomposition of the Se_2O_5 groups. There are no any steps can be observed with further increasing temperature. It is noted that the final residuals of thermal analysis were difficult to be characterized due to the fact that the residuals were melted with the TGA bucket made of Al_2O_3.

References:

1. B. H. Toby, *J. Appl. Cryst.*, 2001, **34**, 210-213.
2. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.* , 2009, 339-341.
3. Sheldrick and G. M., *Acta Cryst.*, 2015, **71**, 3-8.
4. L. J. Bourhis, O. V. Dolomanov, R. J. Gildea, J. A. K. Howard and H. Puschmann, *Acta Cryst.*, 2015, **71**, 59-75.
5. A. L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7-13.

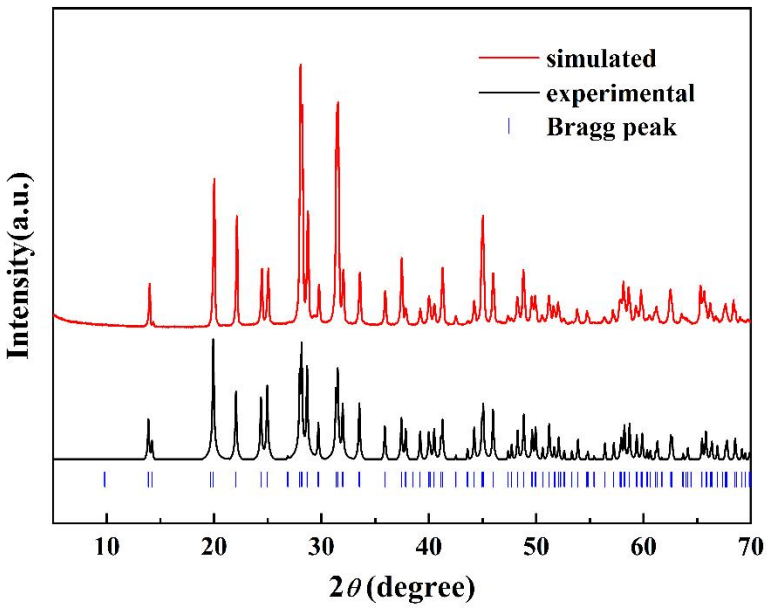

Fig.S1. Refinement of powder X-ray (Cu Kα) diffraction patterns for $CsCl{\cdot}(VOSe_2O_5)_4$.

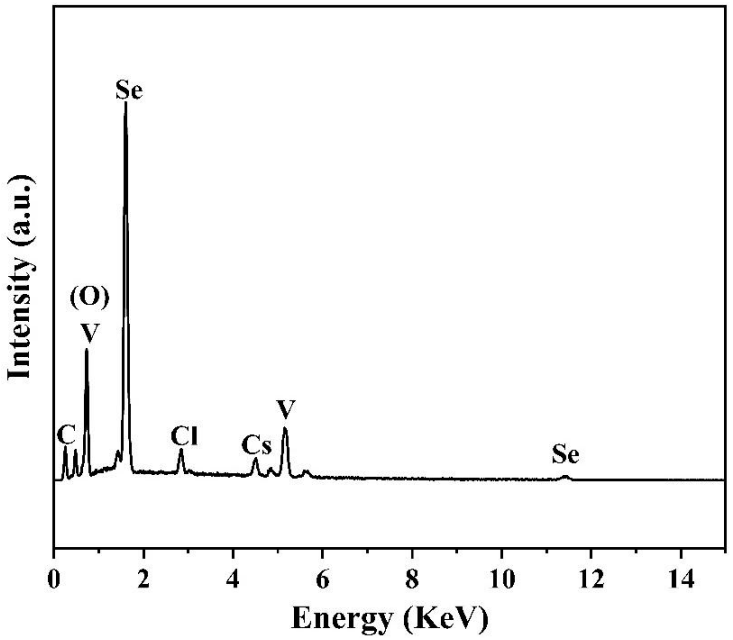

Fig.S2. The energy-dispersive spectrometry (EDS) elemental analyses of $CsCl{\cdot}(VOSe_2O_5)_4$.

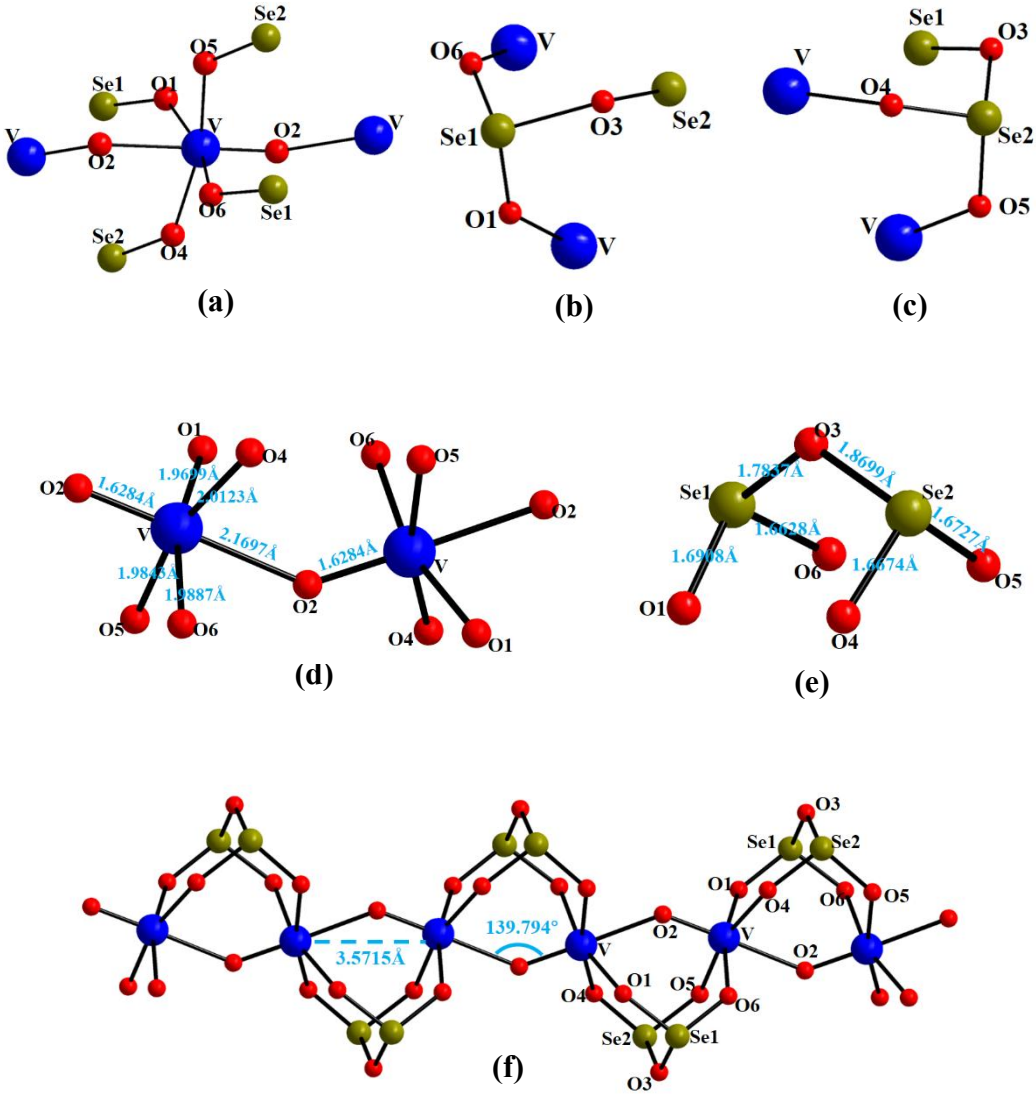

Fig.S3. Views of the coordination environments of (a) V, (b) Se1, and (c) Se2 atoms. The detailed linkages of (d) VO_6 octahedra, (e) $Se2O_5$ groups, and (f) one-dimensional chains of $CsCl{\cdot}(VOSe_2O_5)_4$.

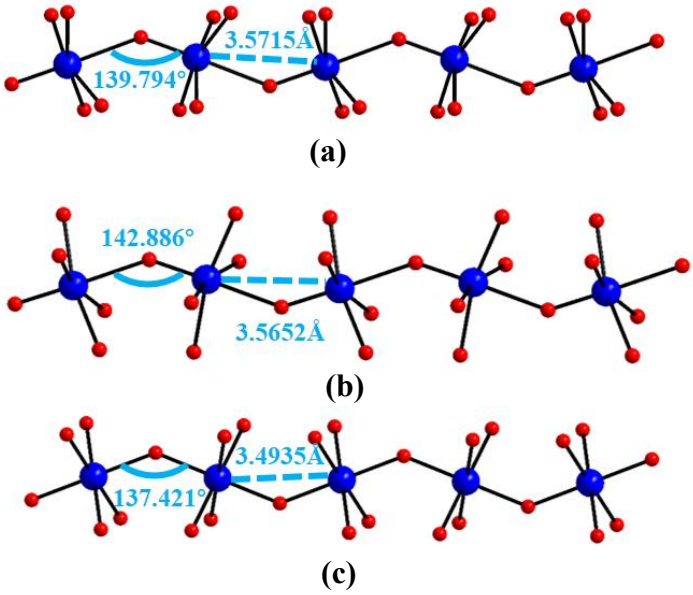

Fig.S4. Comparison of V-O-V bond angles and V-V distances of one-dimensional chains in (a) $CsCl{\cdot}(VOSe_2O_5)_4$, (b) $NaVO(PO_4)$, and (c) $Na_4VO(PO_4)_2$.

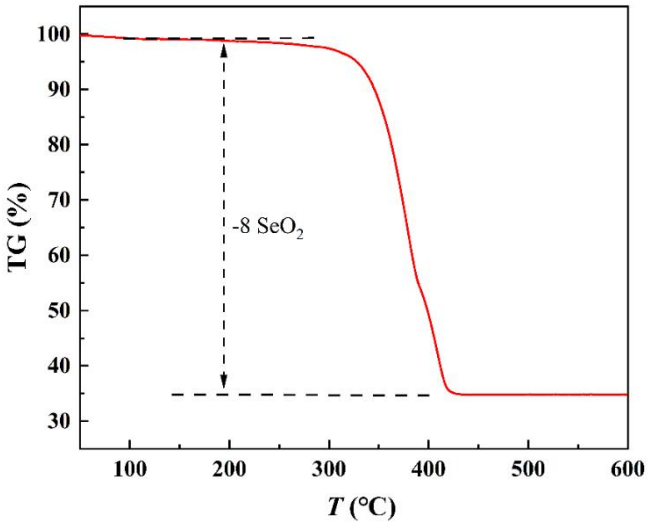

Fig.S5. Thermogravimetric analysis of $CsCl{\cdot}(VOSe_2O_5)_4$.

Table S1. Crystal data and structure refinements for $CsCl\cdot(VOSe_2O_5)_4$.

Compound	$CsCl\cdot(VOSe_2O_5)_4$
F_W	1387.785
T, K	100
λ, Å	0.71073
space group	$I\bar{4}$
a, Å	12.7443(4)
b, Å	12.7443(4)
c, Å	7.1295(4)
α, deg	90
β, deg	90
γ, deg	90
V, Å^3	1157.95(8)
Z	2
ρcalc, g cm^{-3}	3.980
μ, mm^{-1}	15.910
GOF on F^2	0.952
R_1, wR_2 $[I > 2\sigma(I)]^a$	0.0383, 0.0796
R_1, wR_2 (all data)	0.0481, 0.0832

$^aR_1 = \sum||F_o| - |F_c||/\sum|F_o|$, and $wR_2 = \{\sum w[(F_o)^2 - (F_c)^2]^2 / \sum w[(F_o)^2]^2\}^{1/2}$.

Table S2. Atomic coordinates ($\times10^4$) and equivalent isotropic displacement parameters (Å$^2\times10^3$) for $CsCl\cdot(VOSe_2O_5)_4$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cs1	5000	5000	-69.5(19)	45.3(3)
Se2	6573.3(4)	9490.7(4)	5010.0(17)	6.07(13)
Se1	5307.8(4)	7305.4(4)	4991.5(18)	5.62(14)
V1	7422.7(12)	7538.1(14)	7836(2)	7.2(2)
Cl1	5000	5000	4912(9)	9.6(6)
O1	6069(5)	7040(5)	6843(9)	7.3(13)
O4	7218(5)	9001(5)	6939(9)	7.1(13)
O2	7059(3)	7764(3)	9988(11)	7.2(8)
O3	5373(3)	8771(3)	5032(10)	9.1(8)
O5	7213(5)	8965(5)	3157(0)	7.2(13)
O6	6075(5)	7076(5)	3142(10)	8.4(13)

Table S3. Anisotropic displacement parameters ($Å^2×10^3$) for $CsCl·(VOSe_2O_5)_4$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cs1	60.3(5)	60.3(5)	15.1(5)	-0	-0	-0
Se2	6.7(2)	5.3(2)	6.2(2)	0.70(17)	-0.2(3)	0.1(3)
Se1	4.6(2)	6.9(2)	5.3(3)	-0.04(18)	0.5(4)	-0.7(5)
V1	7.8(6)	6.5(5)	7.2(6)	-1.2(4)	-3.4(6)	1.4(7)
Cl1	9.2(7)	9.2(7)	10.4(15)	-0	-0	0
O1	7.3(15)	7.5(15)	6.9(16)	0.1(5)	-0.2(5)	0.0(5)
O4	7.9(15)	6.9(15)	6.3(15)	-0.1(5)	-0.1(5)	0.1(5)
O2	6.0(17)	7.4(17)	8.2(19)	0.5(14)	0(3)	1(4)
O3	6.4(17)	5.1(17)	16(2)	-1.7(14)	-2(4)	2(3)
O5	9.5(18)	6.2(18)	5.8(19)	0.8(9)	1.2(9)	0.8(9)
O6	8(3)	11(2)	7(3)	-0.9(18)	1(2)	2(2)

Table S4. Bond lengths [Å] and angles [deg] for $CsCl·(VOSe_2O_5)_4$.

Atom-Atom	Length/Å	Atom-Atom	Length/Å
Cs1-Cl1	3.552(8)	Se2-O3	1.783(4)
Cs1-Cl1[1]	3.578(8)	Se2-O5	1.691(7)
Cs1-O1[2]	3.669(7)	Se1-O1	1.673(7)
Cs1-O1[3]	3.669(7)	Se1-O3	1.870(4)
Cs1-O1[1]	3.669(7)	Se1-O6	1.667(7)
Cs1-O1[4]	3.669(7)	V1-O1	1.970(7)
Cs1-O6	3.757(7)	V1-O4	2.012(7)
Cs1-O6[5]	3.757(7)	V1-O2[8]	2.170(8)
Cs1-O6[6]	3.757(7)	V1-O2	1.628(8)

Cs1-O6^{7}	3.757(7)	V1-O5^{9}	1.984(7)
Se2-O4	1.663(6	V1-O6^{9}	1.989(7)

Atom-Atom-Atom	Angle/°	Atom-Atom-Atom	Angle/°
O11-Cs1-Cl^{1}	126.87(11)	O6^{6}-Cs1-O1^{1}	111.26(17)
O1^{2}-Cs1-Cl1	126.87(11)	O6^{5}-Cs1-O1^{3}	179.3(2)
O13-Cs1-Cl1^{1}	53.13(11)	O6^{6}-Cs1-O1^{4}	179.3(2)
O1^{3}-Cs1-Cl1	126.87(11)	O6^{7}-Cs1-O1^{2}	74.42(8)
O1^{4}-Cs1-Cl1	126.87(11)	O6^{5}-Cs1-O1^{2}	111.26(17)
O1^{2}-Cs1-Cl1^{1}	53.13(11)	O6^{6}-Cs1-O1^{3}	74.42(8)
O1^{1}-Cs1-Cl1^{1}	53.13(11)	O6^{7}-Cs1-O6^{6}	68.20(11)
O1^{4}-Cs1-Cl1^{1}	53.13(11)	O6^{6}-Cs1-O6	68.20(11)
O1^{3}-Cs1-O1^{4}	106.3(2)	O6^{7}-Cs1-O6	104.9(2)
O1^{2}-Cs1-O1^{3}	68.90(11)	O6^{5}-Cs1-O6	68.20(11)
O1^{2}-Cs1-O1^{4}	68.90(11)	O6^{7}-Cs1-O6^{5}	68.20(11)
O1^{3}-Cs1-O1^{1}	68.90(11)	O6^{6}-Cs1-O6^{5}	104.9(2)
O1^{4}-Cs1-O1^{1}	68.90(11)	O3-Se2-O4	102.9(3)
O1^{2}-Cs1-O1^{1}	106.3(2)	O5-Se2-O4	103.07(18)
O6-Cs1-Cl1	52.45(11)	O5-Se2-O3	102.5(3)
O6^{5}-Cs1-Cl1	52.45(11)	O3-Se1-O1	99.4(3)
O6^{6}-Cs1-Cl1^{1}	127.55(11)	O6-Se1-O1	104.39(19)
O6^{6}-Cs1-Cl1	52.45(11)	O6-Se1-O3	99.3(3)
O6^{5}-Cs1-Cl1^{1}	127.55(11)	O4-V1-O1	93.3(3)

O6^{7}-Cs1-Cl1^{1}	127.55(11)	O2^{8}-V1-O1	82.7(2)
O6-Cs1-Cl1^{1}	127.55(11)	O2-V1-O1	98.4(3)
O6^{7}-Cs1-Cl1	52.45(11)	O2-V1-O4	97.6(2)
O6^{5}-Cs1-O1^{1}	111.63(17)	O2^{8}-V1-O4	82.7(2)
O6-Cs1-O1^{2}	179.3(2)	O5^{9}-V1-O1	86.3(3)
O67-Cs1-O1^{3}	111.26(17)	O5^{9}-V1-O4	164.9(3)
O6-Cs1-O1^{4}	111.26(17)	O5^{9}-V1-O2^{8}	82.3(2)
O6^{7}-Cs1-O1^{1}	179.3(2)	O5^{9}-V1-O2	97.4(3)
O6^{7}-Cs1-O1^{4}	111.63(17)	O6^{9}-V1-O1	164.2(4)
O6^{6}-Cs1-O1^{2}	111.63(17)	O6^{9}-V1-O4	86.2(2)
O6^{5}-Cs1-O1^{4}	74.42(8)	O6^{9}-V1-O2^{8}	81.6(2)
O6-Cs1-O1^{3}	111.63(17)	O6^{9}-V1-O2	97.3(3)
O6-Cs1-O1^{1}	74.42(8)	O6^{9}-V1-O5^{9}	90.0(3)

Symmetry transformations used to generate equivalent atoms:
^{1}+X,+Y,-1+Z;^{2}1-X,1-Y,-1+Z;^{3}+Y,1-X,-1+Z;^{4}1-Y,+X,-1+Z;^{5}1-Y,+X,+Z;^{6}+Y,1-X,+Z;^{7}1-X,1-Y,+Z;^{8}3/2-X,3/2-Y,-1/2+Z;^{9}3/2-X,3/2-Y,1/2+Z;^{10}+X,+Y,1+Z