All reagents were purchased commercially and used without further purification. The elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. The elemental analyses (V and Fe) were performed on a Perkin-Elmer Optima 3300DV spectrophotometer. The infrared spectra were recorded with a Perkin-Elmer SPECTRUM ONE FTIR spectrometer with KBr pellets in the 4000-200cm^{-1} region. XPS measurements were performed on single crystals with ESCALAB MARK II apparatus, using the Mg Kα (1253.6eV) achromatic X-ray radiation source. The powder XRD patterns were obtained with a Scintag X1 powder diffractometer system using Cu Kα radiation with a variable divergent slit and a solid-state detector. The UV-Vis spectra were recorded on a Shimadzu UV3100 spectrophotometer. The magnetic measurements were performed in the temperature range 1.9-300 K by using a Quantum Design MPMS XL-7 SQUID magnetometer. The TG curve was performed on a Perkin-Elmer TGA-7000 thermogravimetric analyzer in the flowing N_2 with a temperature ramp rate of 10°C min^{-1}.

Table S1. The bond valence sum results of the vanadium atoms in compound **1**.

V1	V2	V3	V4	V5	V6	V7	V8	V9	V10	V11	V12	V13	V14	V15	V16
4.10	4.87	4.33	4.33	4.87	4.53	4.70	4.45	4.52	4.13	4.04	4.89	4.34	4.94	4.97	5.03

The formulas applied for the bond valence summation are s =si, where s = valence of the vanadium ion, and si = $(R/R1)^{-N}$, where N and R1 are empirical values equal to 5.1 and 1.791 for V^{V} ions and 5.2 and 1.770 for V^{IV} ions, respectively, and R = cation-oxygen bond length; see: Brown, I. D.; Wu, K. K. Acta Crystallogr. 1976, B32, 1957. The average value of the BVS is 4.56, which is corresponding to the expected value 4.56 for the $V^{IV}{}_7V^{V}{}_9$.

Table S2. The O-H⋯O hydrogen bonds and the C-H⋯O hydrogen bonds in compound 1.

O-H⋯O hydrogen bonds	O⋯O distance (Å)
Ow(8)-H⋯O(26)	2.9317(6)
Ow(8)-H⋯Ow(7a, a: 1-x, -0.5+y, 0.5-z)	2.8222(6)
Ow(7)-H⋯O(2)	2.9076(6)
Ow(5)-H⋯O(2)	2.7576(4)
Ow(2)-H⋯Ow(4b, b: 1-x, 0.5+y, 0.5-z)	2.5622(6)
Ow(5)-H⋯Ow(4b, b: 1-x, 0.5+y, 0.5-z)	2.7200(5)
Ow(3)-H⋯O(39)	2.8278(5)
Ow(3)-H⋯Ow(3c, c: -x, -y, -z)	2.8341(5)
Ow(1)-H⋯O(15)	2.8960(60
C-H⋯O hydrogen bonds	C⋯O distance (Å)
C(3)-H⋯O(23d, d: 1-x, 1-y, -z)	2.9460(5)
C(15)-H⋯O(8e, e: 1+x, 0.5-y, -0.5+z)	3.0961(7)
C(17)-H⋯O(1e)	3.0727(6)
C(22)-H⋯O(5f, f: 1-x, -y, -z)	3.0272(5)
C(25)-H⋯O(5f)	3.1016(5)
C(33)-H⋯O(21g, g : 1-x, 1-y, -z)	3.0480(5)
C(34)-H⋯O(21g)	2.9209(5)
C(45)-H⋯O(12)	3.1084(5)
C(74)-H⋯O(8h, h : 1+x, y, z)	3.0031(6)
C(78)-H⋯O(21i, i : 1-x, -0.5+y, 0.5-z)	3.0645(6)

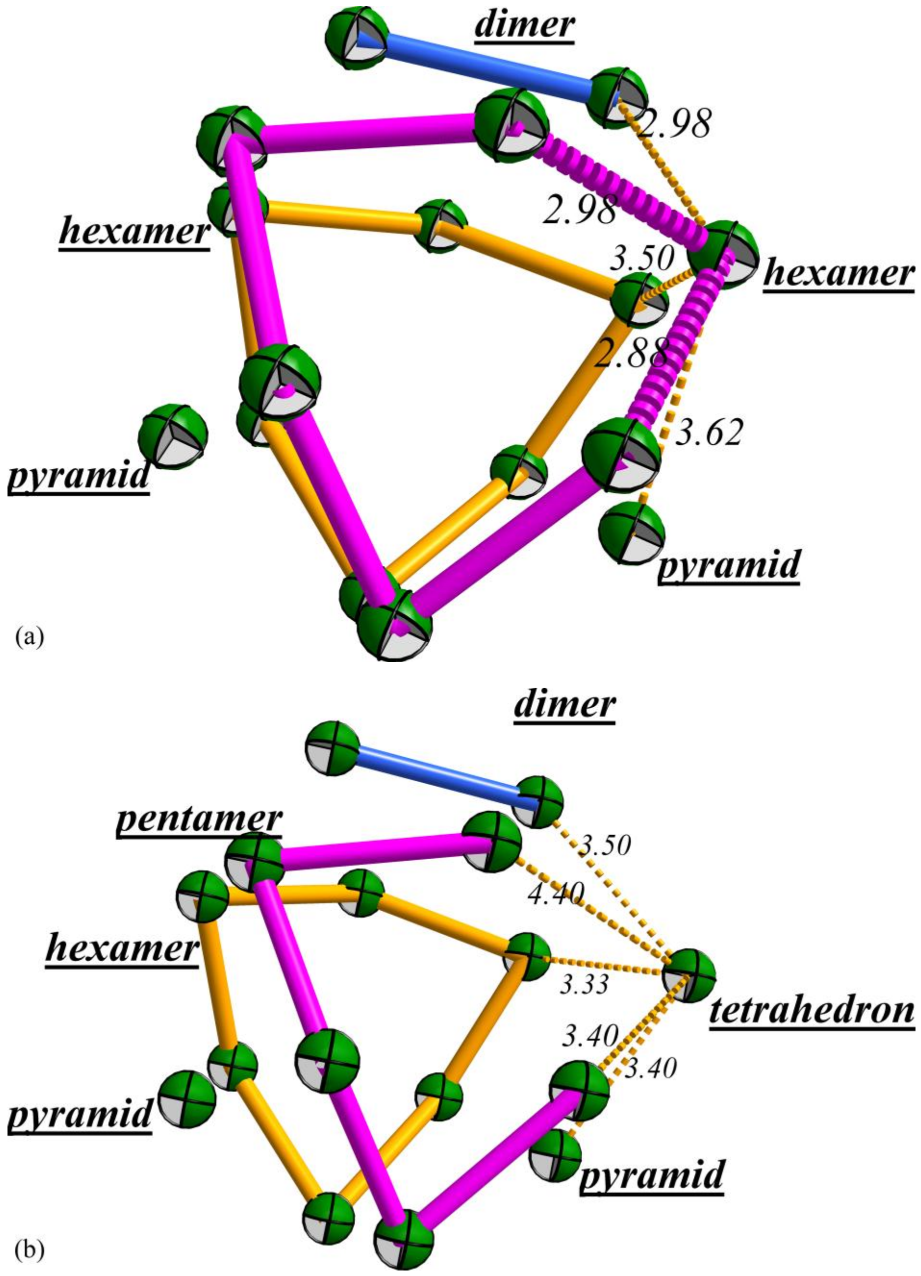


Fig. s1. (a) The skeleton of the $V_{16}O_{38}$; (b) the skeleton of the $V_{16}O_{39}$.

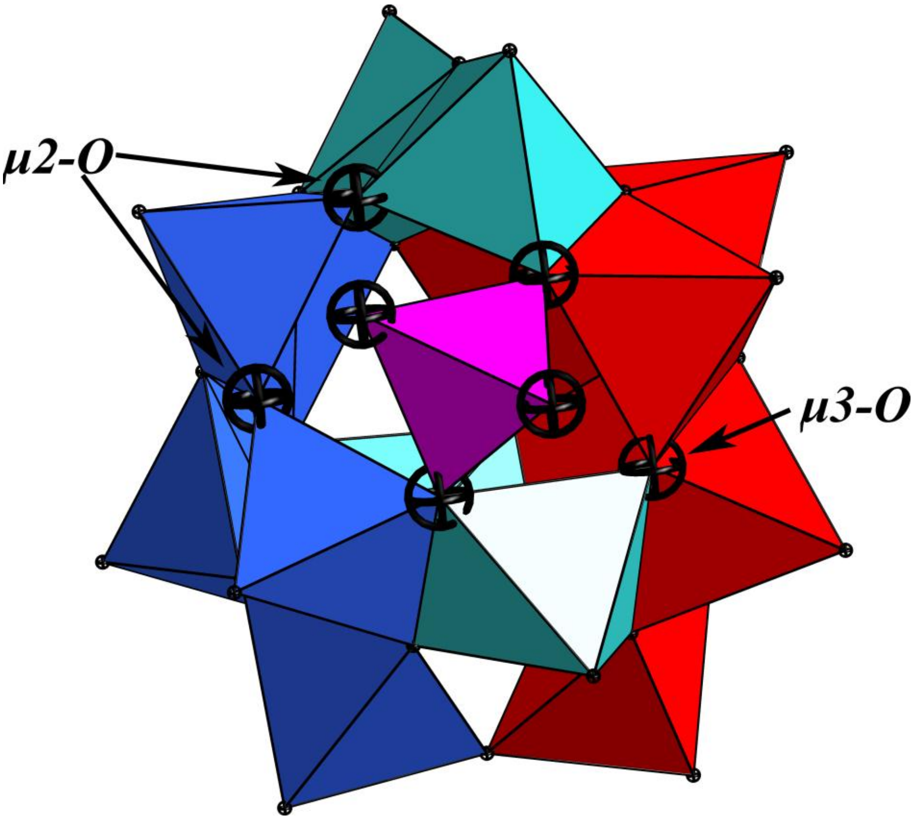


Fig. s2. The types of oxygen atoms around the VO_4 tetrahedron in our anion.

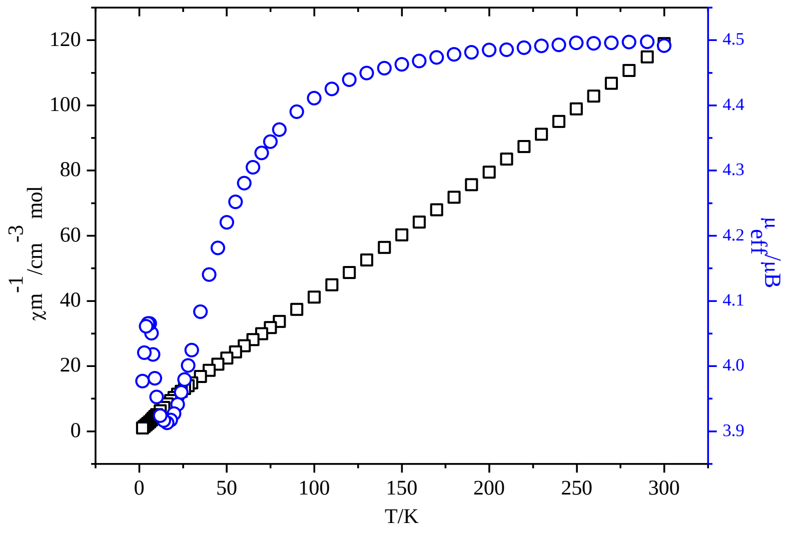


Fig. s3. Temperature dependences of the reciprocal magnetic susceptibility χ_m^{-1} (□) and the product μ_{eff} (○) for compound **1**. The average magnetic moment per V atom for the seven V(IV) from the value of the Curie constant is about 0.65μ_B.

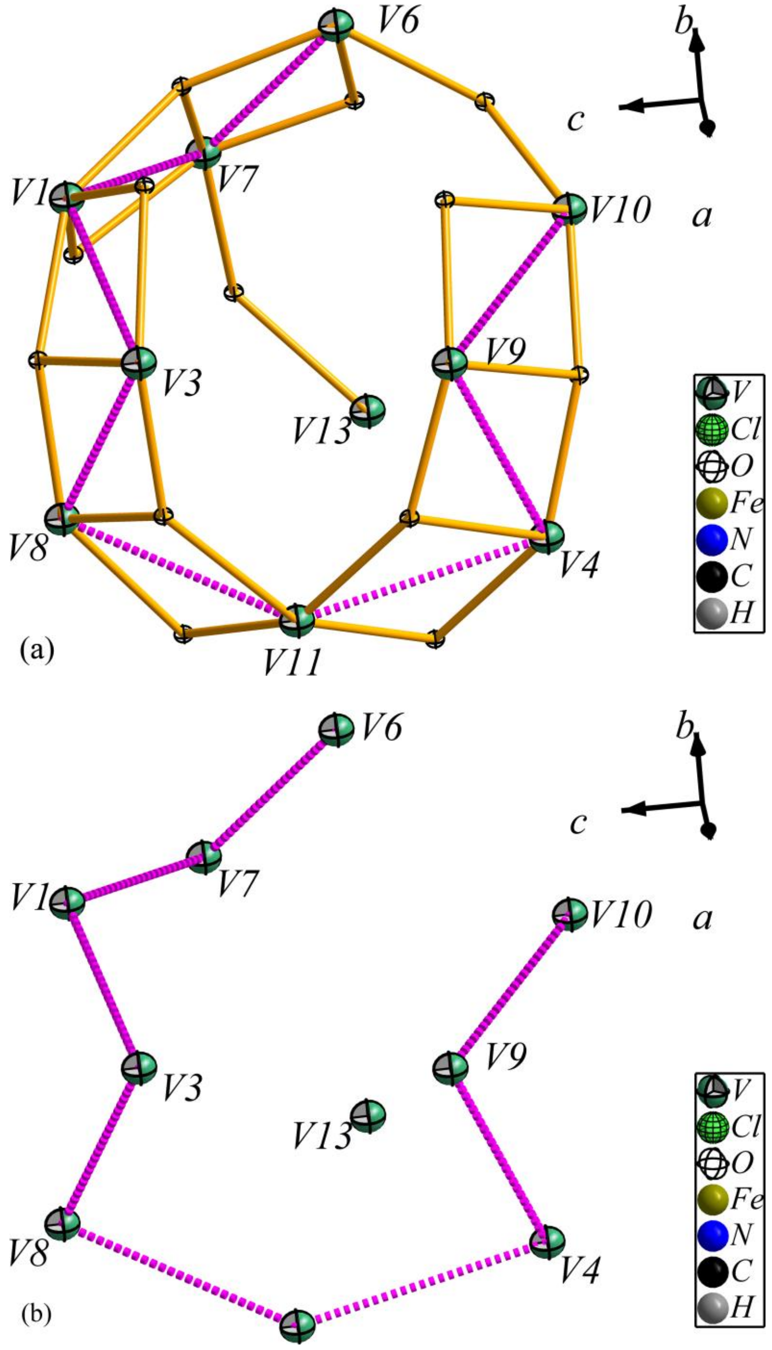


Fig. s4. The positions of different V^{4+} and V$^{4+/5+}$ atoms in compound **1** with oxygen atoms (a) and without oxygen atoms (b). the V(1) ion is bonded to V(7) and V(3) through two (μ_3-O)-V bonds, the V(11) ion is bonded to V(8) and V(4) via two (μ_3-O)-V bonds, while the V(10) ion is only bonded to V(9) via two (μ_3-O)-V bonds and the V(6) is only bonded to V(7) via two (μ_3-O)-V bonds. The V-V distances of V(6)-V(7), V(7)-V(1), V(1)-V(3), V(3)-V(8), V(8)-V(11), V(11)-V(4), V(4)-V(9) and V(9)-V(10) are 2.95Å, 3.05Å, 3.14Å, 2.88Å, 3.03Å, 2.97Å, 2.76Å and 2.89Å, respectively, and V-O-V angles are in the range of 92.0(3)-102.2(3)º, considered in the literature as acceptable for charge delocalization among the vanadium centers.

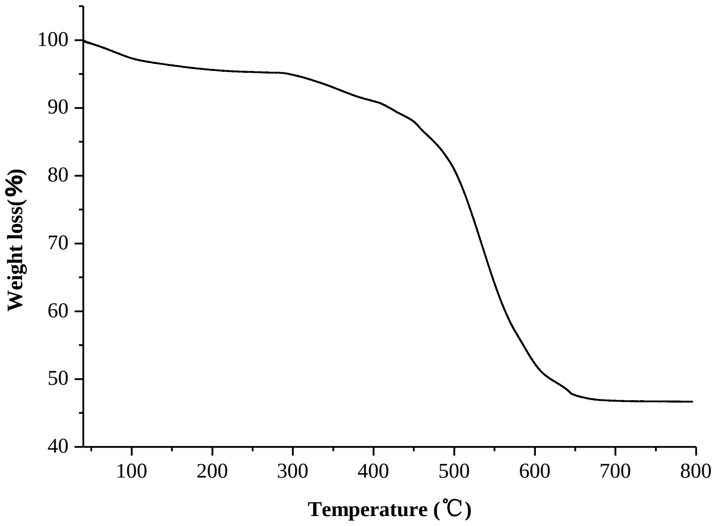


Fig. s5. The TG curve of compound **1**. We assumed that the residue should be the mixture of 7 VO_2, 4.5 V_2O_5 and 3FeO.

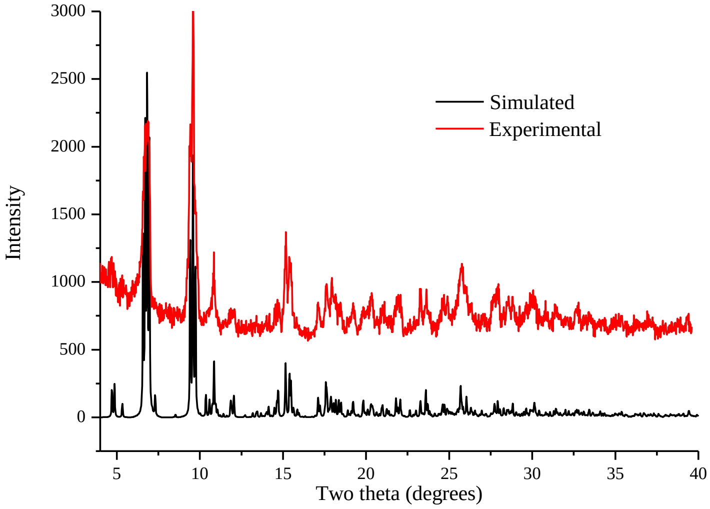
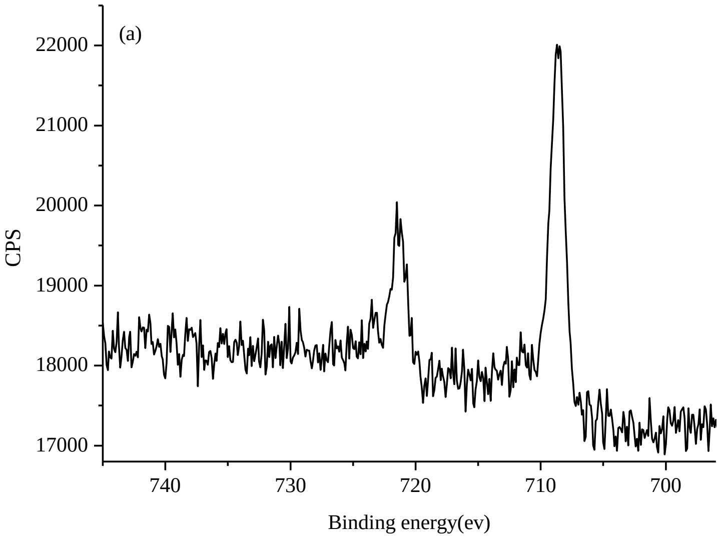


Fig. s6. The experimental and simulated XRD patterns for compound **1**.



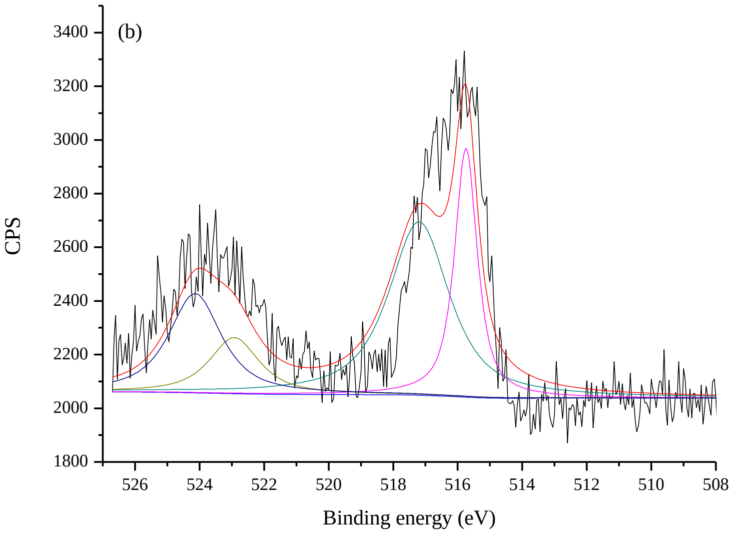


Fig. s7. The XPS spectra of compound **1** in the Fe 2p (a) region and V 2p (b) region.

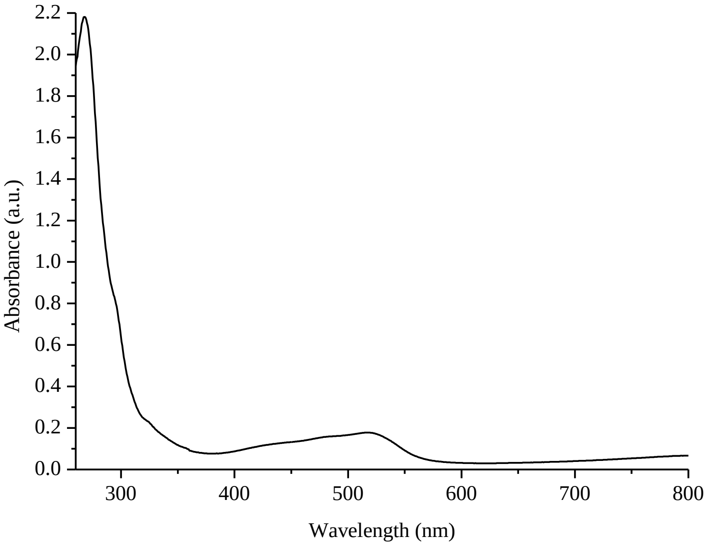
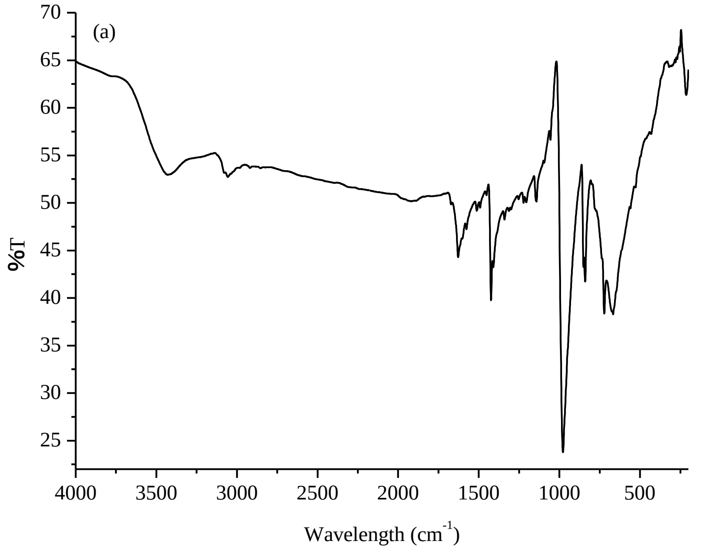


Fig. s8. The UV-Vis spectrum of compound **1**.



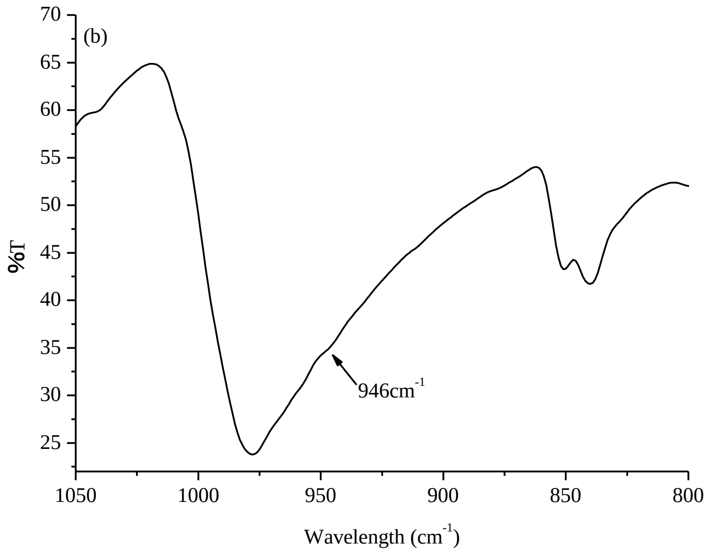


Fig. s9. The IR spectrum of compound **1** in the range of 200-4000cm^{-1} (a) and in the range of 800-1050cm^{-1} (b).