4178 *Inorg. Chem.* **1995,** *34,* 4178−4181

A New Layered Mixed-Valent Potassium Vanadium Selenite, KV_2SeO_7

Kyu-Seok Lee and Young-Uk Kwon*

Department of Chemistry, Sung Kyun Kwan University, Suwon 440-746, Korea

Hae Namgung and Sei-Hwan Kim

Department of Chemistry, Kookmin University, Seoul 136-702, Korea

Received December 29, 1994[⊗]

A new layered mixed-valent compound, KV_2SeO_7, has been hydrothermally synthesized from V_2O_5, V_2O_3, SeO_2, and KOH with mole ratios of 2:2:15:15 or 3:1:15:15 (in millimoles) in 12 mL of H_2O at 230 °C. Slight changes of the reaction conditions yielded different phases as impurities. The crystal structure has been determined from single-crystal X-ray diffraction. KV_2SeO_7 crystallizes in the orthorhombic space group *Pnma* (No. 62) with $a = 17.954(8)$, $b = 5.360(3)$, and $c = 6.971(3)$ Å, $V = 670.8(6)$ Å^3, $Z = 4$, $R = 0.0459$. The structure is composed of alternating K^+ and $[V_2SeO_7]^-$ layers. The mixed-valent nature of this compound can be explained with two crystallographically distinct octahedral and tetrahedral sites for V^{4+} and V^{5+}, respectively. The magnetic susceptibility curve shows an antiferromagnetic coupling which can be explained with a 1-D Heisenberg model for $S = {}^1/_2$ with $g = 1.86$ and $J/k = 22.5$ K.

Introduction

There is a large volume of literature on vanadium phosphate compounds.[1−3] The diversity of the crystal chemistry of this class of materials is still attracting interest to their syntheses and characterizations. Recently, the hydrothermal technique has been applied to this system extensively. The crystal structures of these materials synthesized in this manner range from molecular[1] to two- or three-dimensional network types[2,3] and purely inorganic compounds and organic−inorganic composites.[2a−c,3b,c] Mixed-valence vanadium phosphates including V(III) and V(IV) species show varied magnetic behavior.[2d,3a]

In contrast, the known chemistry of metal selenites is very limited, even though many authors have pointed out that the lone pair on the selenium of selenite can behave similarly to the organic groups of organophosphates (RPO_3^{2-}) and phosphonates ($ROPO_3^{2-}$).[4,5] The diagonal relationship between P and Se also suggests that there is rich structural chemistry in metal selenites. Many metal selenite systems, notably those with manganese,[6] iron,[7] copper,[8] and rare earths,[9] have been studied. There are also reports on aluminum[10] and gallium selenites.[11] These are all synthesized under hydrothermal conditions. Jacobson and his group have reported the hydrothermal syntheses and the crystal structures of $VOSeO_3{\cdot}H_2O$[4] and $(NH_4)(VO_2)_3(SeO_3)_2$.[5] The former shows an antiferromagnetic coupling below ~50 K which is originated from $V^{4+}-V^{4+}$ dimers of edge-sharing vanadium octahedra.

In this paper, we report the synthesis, crystal structure, and magnetic properties of the layered compound KV_2SeO_7. Unlike previously reported vanadium selenites, this compound has mixed-valent vanadium atoms, IV and V, in distinct crystallographic sites.

Experimental Section

Synthesis. Crystalline single-phase KV_2SeO_7 was obtained from hydrothermal reactions. Teflon-lined stainless steel autoclaves with inside volumes of 20 mL were utilized. A mixture of V_2O_5, V_2O_3, SeO_2, and KOH in the mole ratio of 3:1:15:10 or 2:2:15:10 (in millimoles) was placed in an autoclave, and 12 mL of distilled water was added. The reactions were carried out at 230 °C for 3 days under autogenous pressure. The reactions were slowly cooled to room temperature, and the solid products were isolated by filtration. Pure dark-red crystalline products were obtained. The yields were 69% and 87%, based on vanadium metal for the V_2O_5/V_2O_3 = 3/1 and 2/2 reactions, respectively. The product was single phase according to

---

[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1995.

(1) (a) Mokry, L. M.; Thompson, J.; Bond, M. R.; Otieno, T.; Mohan, M.; Carrano, C. J. *Inorg. Chem.* **1994,** *33,* 2705. (b) Salta, J.; Chen, Q.; Chang, Y.-D.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1994,** *33,* 757 and references therein.

(2) (a) Khan, M. I.; Lee, Y.-S.; O'Conner, C. J.; Haushalter, R. C.; Zubieta, J. *J. Am. Chem. Soc.* **1994,** *116,* 4525. (b) Soghomonian, V.; Haushalter, R. C.; Chen, Q.; Zubieta, J. *Inorg. Chem.* **1994,** *33,* 1700. (c) Khan, M. I.; Lee, Y.-S.; O'Conner, C. J.; Haushalter, R. C.; Zubieta, J. *Inorg. Chem.* **1994,** *33,* 3855. (d) Haushalter, R. C.; Wang, Z.; Thomson, M. E.; Zubieta, J.; O'Conner, C. J. *Inorg. Chem.* **1993,** *32,* 3966. (e) Johnson, J. W.; Jacobson, A. J.; Brody, J. F.; Rich, S. M. *Inorg. Chem.* **1982,** *21,* 3820.

(3) (a) Haushalter, R. C.; Wang, Z.; Thomson, M. E.; Zubieta, J. *Inorg. Chem.* **1993,** *32,* 3700. (b) Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J.; O'Conner, C. J.; Lee, Y.-S. *Chem. Mater.* **1993,** *5,* 1690. (c) Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J. *Chem. Mater.* **1993,** *5,* 1595. (d) Lii, K. H.; Chueh, B. R.; Kang, H. Y.; Wang, S. L. *J. Solid State Chem.* **1992,** *99,* 72. (e) Kang, H. Y.; Lee, W. C.; Wang, S. L.; Lii, K. H. *Inorg. Chem.* **1992,** *31,* 4743. (f) Lii, K. H.; Mao, L. F. *J. Solid State Chem.* **1992,** *96,* 436.

(4) Huan, G.; Johnson, J. W.; Jacobson, A. J.; Goshorn, D. P. *Chem. Mater.* **1991,** *3,* 539.

(5) Vaughey, J. T.; Harrison, W. T.; Dussack, L. L.; Jacobson, A. J. *Inorg. Chem.* **1994,** *33,* 4370.

(6) (a) Wildner, M. *J. Solid State Chem.* **1993,** *103,* 341. (b) Giester, G.; Wildner, M. *J. Solid State Chem.* **1991,** *91,* 370. (c) Wildner, M. *J. Solid State Chem.* **1994,** *113,* 252.

(7) Giester, G. *J. Solid State Chem.* **1993,** *103,* 451.

(8) Effenberger, H. *J. Solid State Chem.* **1987,** *70,* 303 and references therein.

(9) (a) Castro, A.; Enjalbert, R.; de Pedro, M.; Trombe, J. C. *J. Solid State Chem.* **1994,** *112,* 418 and references therein. (b) Morris, R. E.; Wilkinson, A. P.; Cheetham, A. K. *Inorg. Chem.* **1992,** *31,* 4774 and references therein.

(10) (a) Harrison, W. T. A.; Stucky, G. D.; Morris, R. E.; Cheetham, A. K. *Acta Crystallogr.* **1992,** *C48,* 1365. (b) Morris, R. E.; Harrison, W. T. A.; Stucky, G. D.; Cheetham, A. K. *J. Solid State Chem.* **1991,** *94,* 227.

(11) Meunier, P. G.; Bertaud, M.; Galy, J. *Acta Crystallogr.* **1974,** *B30,* 2834.

0020-1669/95/1334-4178$09.00/0

Table 1. Crystallographic Data of KV_2SeO_7

empirical formula	KO_7SeV_2	λ(Mo Kα), Å	0.710 73
fw	331.9	μ(Mo Kα), cm^{-1}	88.17
space group	*Pnma*	ϱ(calcd), g cm^{-3}	3.287
a, Å	17.954(8)	T, °C	20(2)
b, Å	5.360(3)	$R_1{}^a$	0.0459
c, Å	6.971(3)	w$R_2{}^b$	0.1258
V, Å^3	670.8(6)	S (goodness of fit)	1.147
Z	4		

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma|w(F_o{}^2 - F_c{}^2)^2|/\Sigma|w(F_o{}^2)^2|]^{1/2}$, $w = [\sigma^2(F)]^{-1}$.

Table 2. Atomic Positional and Isotropic Thermal Parameters for KV_2SeO_7

atom	x	y	z	$U_{eq}{}^a$
Se	0.1504(1)	0.2500	0.0263(2)	0.022(1)
V(1)	0.1864(1)	0.2500	0.5667(3)	0.023(1)
V(2)	0.3820(1)	0.2500	0.7788(3)	0.022(1)
K	0.4633(2)	0.2500	0.2611(4)	0.031(1)
O(1)	0.2746(5)	0.2500	0.6294(14)	0.041(2)
O(2)	0.1653(5)	0.0015(21)	0.4405(15)	0.089(4)
O(3)	0.1313(5)	0.2500	−0.2173(14)	0.062(4)
O(4)	0.0948(3)	0.0106(12)	0.0798(11)	0.044(2)
O(5)	0.4639(5)	0.2500	0.8707(14)	0.052(3)

[a] $U_{eq} = {}^1/_3(U_{11} + U_{22} + U_{33})$.

Table 3. Selected Bond Distances (Å) and Angles (deg) for KV_2SeO_7

Se(1)−O(4) × 2	1.669(6)	Se(1)−O(3)	1.732(10)
V(1)−O(2) × 2	1.640(9)	V(1)−O(1)	1.643(9)
V(1)−O(3)	1.802(9)		
V(2)−O(5)	1.603(9)	V(2)−O(2) × 2	1.952(8)
V(2)−O(4) × 2	2.012(8)	V(2)−O(1)	2.192(9)
K−O(5)	2.723(8)	K−O(4) × 2	2.823(8)
K−O(4)′ × 2	2.907(7)	K−O(5)′	3.120(5)
K−O(3) × 2	3.176(6)		
O(2)−V(1)−O(2)	108.6(8)	O(2)−V(1)−O(1)	111.4(3)
O(2)−V(1)−O(3)	108.8(4)	O(1)−V(1)−O(3)	107.9(5)
O(5)−V(2)−O(2)	99.7(4)	O(2)−V(2)−O(2)	87.3(7)
O(5)−V(2)−O(4)	94.9(3)	O(2)−V(2)−O(4)	90.5(4)
O(4)−V(2)−O(4)	87.9(4)	O(5)−V(2)−O(1)	175.2(5)
O(2)−V(2)−O(1)	83.8(3)	O(4)−V(2)−O(1)	81.6(3)
V(1)−O(1)−V(2)	167.0(6)	V(1)−O(2)−V(2)	166.1(6)
O(4)−Se−O(4)	100.5(5)	O(4)−Se−O(3)	95.7(3)
Se−O(3)−V(1)	135.3(6)	Se−O(4)−V(2)	124.3(3)

optical microscopic and powder X-ray diffraction investigations and was stable in air indefinitely.

Single-Crystal Structure Determination. The crystal structure of KV_2SeO_7 was determined from single-crystal X-ray diffraction data. A 0.4 × 0.2 × 0.15 mm size crystal was mounted on a glass fiber with epoxy, and intensity data were collected on a CAD4 automated four-circle diffractometer equipped with monochromated Mo Kα (λ = 0.710 73 Å) radiation. The 25 reflections found in the initial search in the range $2\theta = 3.7-20.1°$ could be indexed with an orthorhombic unit cell of a = 17.954(2), b = 5.360(2), and c = 6.971(1) Å. Data collection was performed with a $2\theta-\omega$ mode on an octant ($1° < 2\theta < 46°$). The systematic absence conditions ($0kl$, $k + l = 2n$; $hk0$, $h = 2n$; $0k0$, $k = 2n$; $00l$, $l = 2n$) suggested space groups $Pn2_1a$ (No. 33) and *Pnma* (No. 62). Both space groups were tried, and the refinement results proved that the latter was the correct one.

The SHELXS-86 program was utilized for the direct method.[12] The structure refinements were performed with the SHELXL-93 program on F^2 data.[13] The direct method yielded the atomic positions for K, V, and Se. Refinements with these atoms and subsequent difference Fourier synthesis produced the atomic positions for the oxygen atoms. These were included in the refinements. A numerical absorption correction was applied with the DIFABS program (corrections, min 0.847, max 1.349, av 1.007).[14] Anisotropic thermal parameters for all the atoms were included in the refinements. The site occupation factor for K was refined to get 1.005(12), implying that the K site was fully occupied. Therefore, the site occupation factors for all atoms were fixed at full occupations in the following refinements. The secondary extinction coefficient was not refined. The full-matrix least-squares refinement finally converged with R_1 = 0.0459, wR_2 = 0.1258 (on F^2).

The crystallographic parameters are given in Table 1. The atomic positional and isotropic thermal parameters and important bond distances are given in Tables 2 and 3, respectively.

Magnetic Properties and Thermogravimetric Measurements. Magnetization data of a powdered sample enclosed in a diamagnetic plastic capsule were obtained on a SQUID (Quantum Design) in the temperature range 10−300 K with a magnetic field of 5000 G. Magnetic susceptibility (χ_m) data were calculated from these and diamagnetic correction values.

Thermogravimetric analysis (TG) was made in a N_2 atmosphere with a Perkin-Elmer TGA-7. Weight losses of 1.4% and 30.9% are observed at 360 and 520 °C, respectively. The total weight loss of 32.3% was close to the theoretical value of 33.4%, corresponding to SeO_2 loss per formula unit.

Results and Discussion

The title compound was first encountered during our investigation of the hydrothermal reactions of the V_2O_3, SeO_2, KOH system. Deep-red block crystals were obtained in very low yields, along with other unidentified phases. Single-crystal structure refinement of this crystal revealed the present structure and the composition KV_2SeO_7. The formal oxidation state of vanadium was 4.5+, indicating a mixed valency of 4+ and 5+. Since this compound was obtained repeatedly, we concluded that the V^{3+} in the starting V_2O_3 had been oxidized by SeO_2 (in fact, H_2SeO_3) under the reaction conditions.

We have subsequently performed hydrothermal reactions including the V_2O_3 and V_2O_5 mixture in the starting materials. A good yield of the crystalline single-phase product could be obtained when the $V_2O_3/V_2O_5/SeO_2$/KOH ratio was 1/3/15/15 or 2/2/15/15 at 230 °C. In each case, there was excess SeO_2 and KOH in the reaction mixture compared to the target KV_2SeO_7 composition. This probably is related to the lower solubilities of V_2O_3 and V_2O_5 than those of SeO_2 or KOH. The V_2O_3/V_2O_5 = 2/2 combination has given a higher yield (87% based on total vanadium metal) than the "right on" composition of V_2O_3/V_2O_5 = 1/3 (69%). We interpret this observation in terms of the redox reactions between V_2O_3 and SeO_2 as well as between V_2O_3 and V_2O_5 to produce V^{4+} during the reaction.

Besides the initial oxidation state of vanadium, the mole ratio of other reagents appears to be critical for the synthesis of pure KV_2SeO_7. Reactions with smaller amounts of KOH, while keeping the concentrations of the others the same as above, produced green crystals and a yellow microcrystalline powder as impurities. The amount of impurity phase increased with decreasing KOH/SeO_2 ratio down to KOH/SeO_2 = 1/3. This green crystal is different from the reported green $VOSeO_3{\cdot}H_2O$.[4] In fact, its crystal structure is partly solved, and the composition appears to be $KHVSe_2O_7$. The yellow powder has the color and crystal habit similar to those of $KV_3Se_2O_{12}$, a K analogue of $(NH_4)(VO_2)_3(SeO_3)_2$ reported by Jacobson and his group.[5] The synthesis and crystal chemistry of these and other related compounds will be reported later. A synthetic temperature lower than 230 °C increased the amounts of impurity phases. Even though undetectable with X-ray diffraction, the two-step weight loss in the TG implies that there may be a small amount of impurity in the final product. Incidentally, the green compound mentioned above decomposes at 360 °C, the same

---

(12) Sheldrick, G. M. *SHELXS-86 User Guides*; Crystallographic Department, University of Gottingen: Gottingen, Germany, 1985.

(13) Sheldrick, G. M. *SHELXS-93 User Guides*; Crystallographic Department, University of Gottingen: Gottingen, Germany, 1993.

(14) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

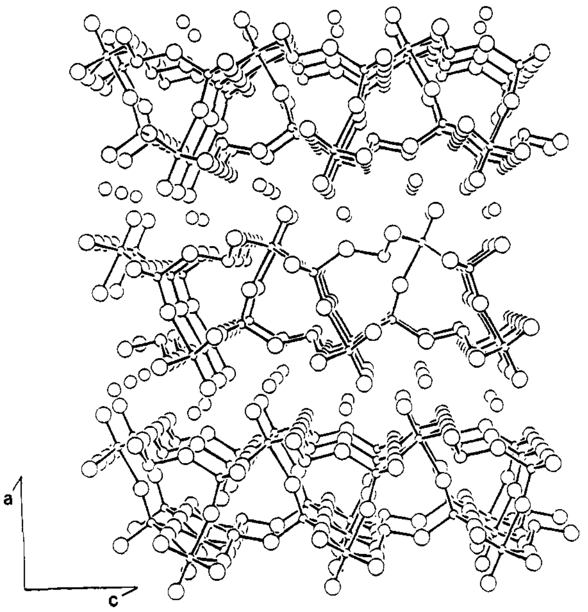

Figure 1. Structure of KV_2SeO_7 viewed in the [010] direction. Small, medium, and large circles in the bonded networks are vanadium, selenium, and oxygen atoms, respectively, and isolated atoms are potassium atoms.

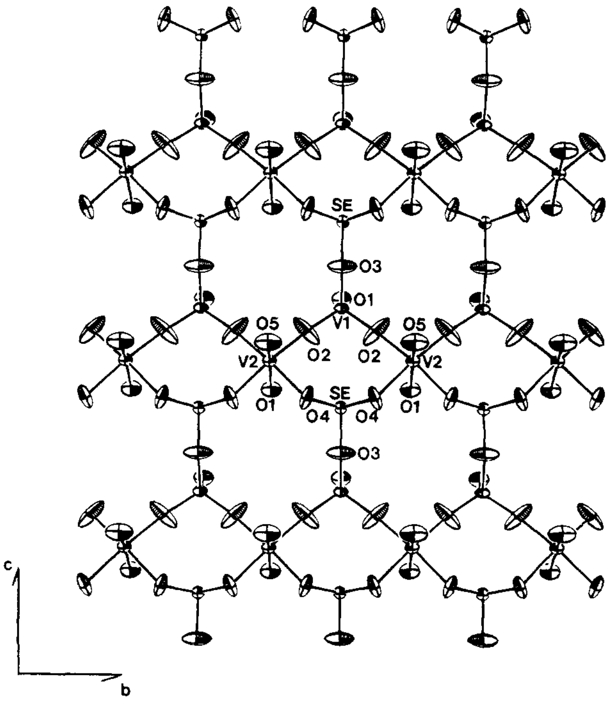

Figure 2. Sublayer of $[V_2SeO_7]^-$ viewed in the [100] direction.

temperature as the first weight-loss step. Assuming this phase as the only impurity, our sample purity is 98 wt %.

The crystal structure of KV_2SeO_7 can be described as a double layer of $[V_2SeO_7]^-$ composed of corner-sharing VO_4 tetrahedral, VO_6 octahedral, and SeO_3 pyramidal units. Each double layer has two glide-mirror related sublayers (Figure 1). Within a sublayer, a sequence of VO_4, VO_6, and SeO_3 units is repeated along the *c*-axis and each individual unit is repeated along the *b*-axis (Figure 2). Two of the sublayers are fused into a double layer via oxygen bridges (O1) that are shared by VO_4 and VO_6 units of different sublayers. A potassium layer is located between the double layers to give a two-dimensional structure. There are nine oxygen atoms around a potassium ion in the distance range 2.72–3.18 Å.

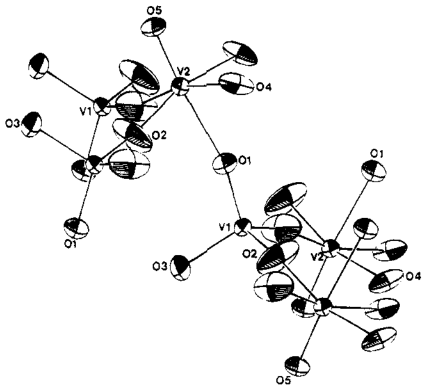

Figure 3. Local environments for V1 and V2. Additional vanadium and oxygen atoms are included for clarity. Upper and lower three vanadium atoms belong to different sublayers.

The coordination environments for vanadium atoms are shown in Figure 3. Each vanadium polyhedron is heavily distorted from the respective ideal geometry. It is easier to describe the local structure in terms of (noncrystallographic) point symmetries. The tetrahedral VO_4 unit for V1 has approximate C_{3v} point symmetry with three short and one long V–O bond distances. Two of the three short bonds are crystallographically identical, and these oxygens (O2) are corner bridges to the next octahedra of V2 in the same sublayer. The remaining oxygen (O1) of the three is also connected to octahedral V2 but in the other sublayer. The unique polar O3 of the long V–O distance is bonded to Se in the same sublayer.

The point symmetry for the octahedral VO_6 unit of V2 is C_s, with the mirror plane bisecting the O2–V–O2 and O4–V–O4 bond angles. Each O2 is a bridge to the V1 of a neighboring tetrahedron, and each O4 is bonded to a Se atom. On the mirror plane of C_s point symmetry are O1 and O5. The role of O1 is described above as a bridge between two sublayers. The V2–O5 bond has a very short bond distance of 1.603(9) Å, and the O5 atoms form the surfaces of the double layers. The waist oxygen atoms are shifted toward O1 of the long V–O bond as a result of the stronger electron cloud repulsion of the short V2–O5 bond.

The oxidation states of the two vanadium atoms were deduced from bond valence sum calculations.[15] The power of bond valence calculations in assigning oxidation states for mixed-valence compounds has been demonstrated in some examples.[16] Although the calculations resulted in positive deviations by as large as 10% for both vanadiums, we could assign oxidation states of 5+ for tetrahedral V1 and 4+ for the octahedral V2. A few sample calculations for known V^{4+} and V^{5+} compounds also showed positive deviations by 2.5–7%, partly justifying our calculation results. Our oxidation state assignments also agree with the generally accepted idea that the higher the charge on the metal atom, the stronger the covalent contribution to the bond and the stronger the tendency to adopt lower coordination numbers of the metal. On the basis of the crystal structure and oxidation states, KV_2SeO_7 belongs to the class I type of mixed-valence compounds in the Day and Robin classification; that is, different oxidation states are associated with different environments, and there are no interactions between different oxidation states.[17]

Magnetic susceptibility data in the temperature range 10–300 K are plotted in Figure 4. The χ_m vs T (Figure 4a) clearly

---

(15) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244.

(16) Warner, J. K.; Cheetham, A. K.; Cox, D. E.; Von Dreele, R. B. *J. Am. Chem. Soc.* **1992**, *114*, 6074.

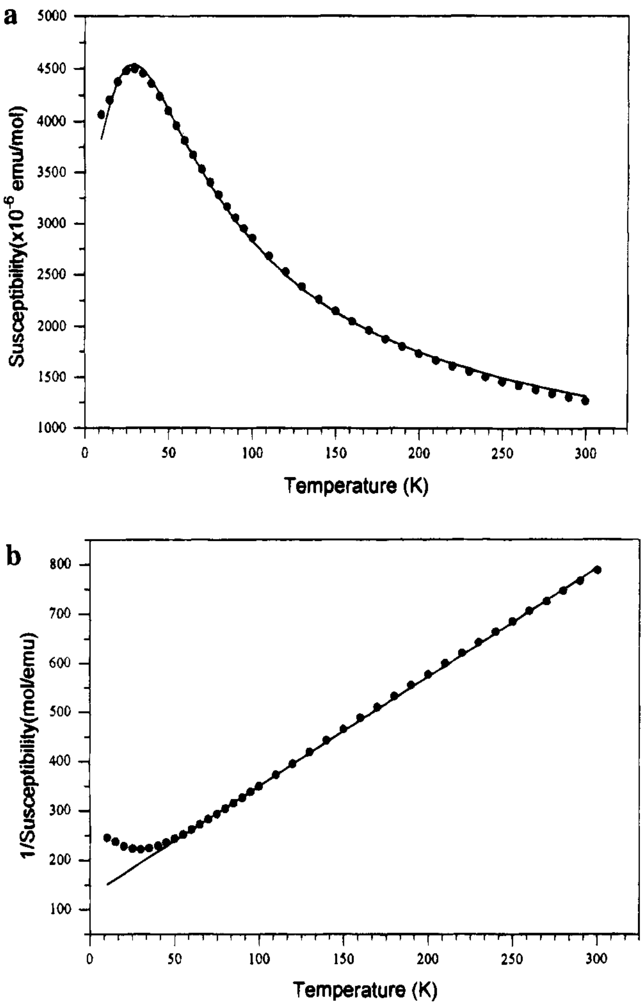

Figure 4. (a) Magnetic susceptibility vs temperature plot for KV_2SeO_7: (●) experimental data; (—) best fit using 1-D Heisenberg model for $S = {}^1/_2$ (see text). (b) Inverse magnetic susceptibility vs temperature plot for KV_2SeO_7: (●) experimental data; (—) fit to the Curie–Weiss law for data of 50–300 K.

shows an antiferromagnetic coupling below ~27 K. The origin of the magnetic coupling mechanism can be found from the crystal structure. The sublayer structure in Figure 2 shows that the magnetic V2 ions in VO_6 octahedra are arranged linearly along the *b*-axis, with a V2–V2 distance of 5.360(2) Å. This is a rather long distance to have an effective magnetic coupling directly between metal atoms. The structure does not have oxygen bridges of V2–O–V2 type for a superexchange mechanism. However, the oxygen atoms O2 and O4, of the VO_6 and SeO_3 bridges between V2 atoms, are arranged in such a way that a super-superexchange mechanism is in operation.[18,19] The magnetic V2 atoms are located slightly above (0.251(6) Å) the least-squares plane defined by the O2 and O4 atoms, and the bond angle O2–V2–O4 is 90.5°, close to the ideal value of 90° for this type of magnetic interaction. In this arrangement, d-electrons of V2 can interact with one another through the p-orbitals of O2 and O4. In view of this structural analysis, there must be a one-dimensional magnetic coupling between the V2 ions through super-superexchange and, maybe, direct metal–metal interaction mechanisms. The magnetic susceptibility data could be successfully fitted to a 1-D Heisenberg model with $S = {}^1/_2$,

$$\chi_m = \frac{N\bar{g}^2{\mu_B}^2}{kT}\,\frac{A + BX^{-1} + CX^{-2}}{1 + DX^{-1} + EX^{-2} + FX^{-3}} + \chi_{TIP}$$

where $X = kt/|J|$, $\bar{g}$ is the powder-averaged g factor, and J is the exchange constant.[20] The first term is from Hatfield, and it evaluates the susceptibility for a 1-D $S = {}^1/_2$ Heisenberg system. The last term is a correction for temperature-independent paramagnetism. The constants $A = 0.25$, $B = 0.149\,95$, $C = 0.300\,94$, $D = 1.9862$, $E = 0.688\,54$, and $F = 6.0626$ calculated theoretically for the 1-D $S = {}^1/_2$ Heisenberg system were used for the fit. The best fit to the observed data was obtained with $\bar{g} = 1.855$, $J/k = -22.5$ K, and $\chi_{TIP} = 339 \times 10^{-6}$ cm/mol. The g value is comparable to that obtained from an EPR study, 1.90. However, the EPR spectrum shows many complicated features such as an asymmetric peak shape and shoulder. Further study of this compound with angle-resolved EPR and solid state vanadium NMR is currently in progress. The high-temperature paramagnetic data of $50 < T < 300$ K could be fitted to the Curie–Weiss law $\chi = C/(T - \theta)$, with $C = 0.451$ K cm^3/mol and $\theta = -58$ K (Figure 4b). The corresponding magnetic moment for the paramagnetic region is $\mu_{eff} = 1.90$ μ_B, slightly larger than the spin-only value 1.73. Spin–orbit coupling does not seem to be responsible for this discrepancy because it usually lowers the magnetic moment for V^{4+}.[21] There are some examples of V^{4+} compounds that show similarly large magnetic moments. Their origins are attributed to the presence of V^{3+} impurities in the samples.[22] Contamination by V^{3+} and/or V^{4+} impurities in our sample also seems likely because V_2O_3 has been utilized as the starting material and the TG curve implies a V^{4+} impurity of 2%.

We have tried ion-exchange reactions to replace K^+ by Na^+ by refluxing KV_2SeO_7 powder in NaOH or NaCl solutions. The results are inconclusive. However, attempts to synthesize the Rb analogue with the hydrothermal method gave positive results ($a = 18.444(8)$, $b = 5.415(3)$, and $c = 7.070(4)$ Å, $V = 707.1(6)$ Å^3). However, the crystallinity and yield of this compound were so poor that we cannot make any definitive comment on it. We are currently studying the reaction conditions to synthesize this analogue compound in a pure phase.

In conclusion, we have synthesized a new layered mixed-valent KV_2SeO_7 compound as a single phase by the hydrothermal method. The right choice of reaction condition parameters such as temperature, concentration, and mole ratio are critical for successful synthesis. The structure of this compound can be characterized as a double layer of $[V_2SeO_7]^-$ composed of VO_4 tetrahedra of V^{5+} and VO_6 octahedra of V^{4+}. The magnetic properties of KV_2SeO_7 are well described by antiferromagnetic coupling of V(IV) ions arranged in one dimension.

Acknowledgment. This research is supported by the Korean Science and Engineering Foundation (KOSEF 931-0200-008-2).

Supporting Information Available: Table of crystal data for KV_2SeO_7 (Table S1); table of thermal parameters for KV_2SeO_7 (Table S2); table of bond distances and angles for KV_2SeO_7 (Table S3) (7 pages). Ordering information is given on any current masthead page.

IC941495U

---

(17) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.

(18) Buffat, B.; Demazeau, G.; Pouchard, M.; Dance, J. M.; Hagenmuller, P. *J. Solid State Chem.* **1983**, *50*, 33.

(19) Demazeau, G.; Pouchard, M.; Chevreau, N.; Thomas, M.; Menil, F.; Hagenmuller, P. *Mater. Res. Bull.* **1981**, *16*, 689.

(20) Hatfield, W. E. *J. Appl. Phys.* **1981**, *52*, 1985.

(21) Banerjea, D. *Coordination Chemistry*; McGraw-Hill: Delhi, 1993; pp 211–214.

(22) Liu, G.; Greedan, J. E. *J. Solid State Chem.* **1993**, *103*, 139.