Discussion. The molecule is extended with a *trans* junction between the rings [average torsion angle across the ring junction is 177·5 (1·6)°]. The six-membered rings are both in a flattened chair conformation as shown by the average value for ring torsion angles, 44·0 (2·3)°, and the larger than normal ring angles [average internal ring angle is 114·7 (1·0)°]. The average C–N bond length is 1·44 (1) Å and the C–N–C angle is 117·8 (1·0)°. The average C–C bond length is 1·48 (1) Å and the average C–C–C angle is 115·6 (1·1)°.

The structure of the naturally occurring pumiliotoxin C (2-n-propyl-5-methyl-*cis*-decahydroquinoline hydrochloride) was reported earlier (Daly, Tokuyama, Habermehl, Karle & Witkop, 1969). The present molecule differs from pumiliotoxin C in the position of the methyl group [on C(5) in pumiliotoxin and on C(7) in the present molecule] and in the configuration of the junction of the fused rings (there is a *cis* junction in pumiliotoxin). The stereo configuration and molecular packing of (I) are illustrated in Fig. 1. The packing is very similar in both crystals and the hydrogen-bonding system is the same for both molecules, linking them into zigzag columns along the **b** direction. The N···Cl distances are 3·13 and 3·18 Å in pumiliotoxin C and 3·11 (1) and 3·27 (1) Å for (I) (see Fig. 1). In both cases these are the only intermolecular approaches less than van der Waals separations.

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Cobalt Vanadate, Co2V2O7, and Nickel Vanadate, Ni2V2O7

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Abstract. Cobalt divanadate: monoclinic, space group $P2_1/c$, $a=6\cdot594$ (2), $b=8\cdot380$ (1), $c=9\cdot470$ (9) Å, $\beta=100\cdot17$ (3)°, $Z=4$, $D_m=4\cdot29$, $D_x=4\cdot33$ g cm^{-3}. Nickel divanadate: monoclinic, space group $P2_1/c$, $a=6\cdot515$ (8), $b=8\cdot303$ (7), $c=9\cdot350$ (6) Å and $\beta=99\cdot86$ (8)°, $Z=4$, $D_m=4\cdot44$, $D_x=4\cdot41$ g cm^{-3}. The crystals were grown from the melt. The structures were refined by full-matrix least-squares methods from a model obtained from the Patterson function of Co2V2O7. The divalent cations are octahedrally coordinated to oxygen atoms and the anion consists of corner-sharing VO4 tetrahedra. The V–O–V angle is 117·5° in the cobalt salt and 117·6° in the nickel salt. The average V–O(–V) and terminal V–O bond lengths are 1·848 and 1·694 Å in Co2V2O7 and 1·853 and 1·683 Å in Ni2V2O7.

Introduction. A survey of the structures of stoichiometry M2X2O7, with the anion based upon corner sharing XO4 tetrahedra, by Brown & Calvo (1970), suggested that these compounds can be related to one of the known alkali metal dichromate series provided that the cation's radius exceeds a value near 1 Å and related to thortveitite below this boundary. Recent structural studies of the rare-earth disilicates, reviewed by Flesche (1973), shows that the boundary region between these two areas is rich in new structural types. At the lower end of the ionic radii scale the divanadates also show a variety of new structures as indicated by that of Mg2V2O7 (Gopal & Calvo, 1974), Cu2V2O7 (Calvo & Faggiani, 1974) and the present structures.

A crystal of Co2V2O7 with dimensions $0\cdot21 \times 0\cdot145 \times 0\cdot19$ mm and a ground sphere of Ni2V2O7 with radius 0·12 mm were used to collect 1162 and 1787 unique reflections of positive measure respectively using a Syntex $P\bar{1}$ automatic diffractometer (scintillation counter; graphite monochromatized Mo $K\alpha$, $\lambda=0\cdot71069$ Å).

For Co2V2O7, 990 reflexions had intensities greater than 3σ and 272 with $0<I\leq3\sigma$ were considered unobserved. For Ni2V2O7 the analogous values are 1487 and 300 respectively. Reflexions $h0l$ with l odd and $0k0$ with k odd were systematically absent. The intensities were corrected for absorption, Lorentz and polarization effects. $\mu_{Co_2V_2O_7}=90\cdot7$ cm^{-1} and $\mu_{Ni_2V_2O_7}=102\cdot3$ cm^{-1}. The structure of Co2V2O7 was determined from the Patterson function and both structures were refined by full-matrix least-squares methods. Atomic form factors for Ni^{2+}, Co^{2+}, V^{3+} and O$^-$ were taken from Cromer & Waber (1965) and corrected for anomalous dispersion. Weights were chosen as $w=[3\cdot26-0\cdot15F_o+0\cdot0027F_o^2]^{-1}$ for Co2V2O7 and $w=$

$[1\cdot8+0\cdot005F_o+0\cdot0022F_o^2]^{-1}$ for $Ni_2V_2O_7$. A parameter was varied to account for the effects of extinction as suggested by Larson (1967). The final R and $R_w(=\{\sum w|F_o-F_c|^2/\sum wF_o^2\}^{1/2})$ are 0·034 and 0·042 for $Co_2V_2O_7$ and 0·048 and 0·069 for $Ni_2V_2O_7$. The final positional and thermal parameters are in Tables 1 and 2.* Note that the thermal parameters of the atoms in $Co_2V_2O_7$ are larger than those in $Ni_2V_2O_7$ by a factor of 2 or 3. This may be as a result of inadequate absorption corrections for $Co_2V_2O_7$ due to the irregular shape of the crystal.

Discussion. The structure contains two types of octahedrally coordinated M^{2+} ions with mean $M(1)$–O and $M(2)$–O bond lengths of 2·074 and 2·088 Å for $M=Co^{2+}$ and 2·039 and 2·052 Å for $M=Ni^{2+}$. The V ions are tetrahedrally coordinated to oxygen atoms which share a bridging oxygen atom, $O(1)$. Five of the six terminal oxygen atoms are shared with two divalent cations while the sixth, bonded to only one M ion shows the shortest V–O bond length in both structures. The bond lengths and angles are presented in Table 3.

The MO_6 polyhedra, as a result of edge sharing,

form linked chains running parallel to the c axis as shown in Fig. 1. Adjacent chains are connected by edge sharing across centres of symmetry at $0\frac{1}{2}0$ and those translationally equivalent along the chain. These edges are shared between centrosymmetrically related $M(1)O_6$ groups. Since the $O(1)$–$O(5)$ edge at the centre of the cell is not shared the structure does not form sheets of edge-sharing MO_6 groups characteristic of the thortveitite (Cruickshank, Lynton & Barclay, 1962) and $Er_2Si_2O_7$ (Smolin & Shepelov, 1970) structures. In these structures the anions share only terminal oxygen atoms with the cations. In contrast with the present
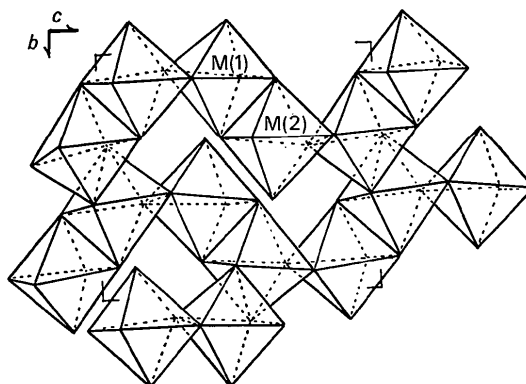
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* Tables of observed and calculated structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30638 (16 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Fig. 1. Projection of the cation octahedra in Ni and Co divanadate onto the bc plane.

Table 1. *Positional and thermal parameters* $(\mathring{A}^2 \times 10^4)$ *for* $Ni_2V_2O_7$ *with standard errors in parentheses*

The values of U_{ij} were obtained from $\beta_{ij}=2\pi^2b_ib_jU_{ij}$ where the β_{ij} appear in the structure factor expression as $\exp[-(\beta_{11}h^2+\ldots+2\beta_{12}hk+\ldots)]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni(1)	0·14645 (9)	0·12126 (8)	0·46331 (6)	26 (1)	22·2 (9)	19·8 (7)	−1·9 (6)	4·3 (7)	−0·3 (5)
Ni(2)	0·30510 (10)	0·38681 (7)	0·67944 (6)	25 (1)	22·4 (9)	19·8 (7)	0·0 (7)	4·1 (7)	0·4 (5)
V(1)	0·36206 (11)	0·76019 (10)	0·53125 (8)	23 (2)	20 (1)	20·4 (8)	0·9 (9)	3·5 (8)	−0·7 (6)
V(2)	0·19456 (12)	0·01854 (10)	0·81303 (8)	24 (2)	21 (1)	17·6 (8)	−1·0 (8)	2·8 (8)	−0·1 (6)
O(1)	0·6010 (5)	0·1313 (4)	0·1242 (4)	35 (6)	35 (4)	30 (3)	0 (4)	12 (4)	3 (3)
O(2)	0·4271 (5)	0·1249 (4)	0·3940 (4)	32 (6)	37 (4)	29 (3)	−7 (4)	5 (4)	0 (3)
O(3)	0·1689 (6)	0·3694 (4)	0·4608 (4)	57 (7)	27 (4)	28 (3)	−3 (4)	3 (4)	6 (3)
O(4)	0·2571 (5)	0·3600 (4)	0·1808 (4)	50 (7)	31 (4)	24 (3)	3 (4)	6 (4)	−2 (3)
O(5)	0·6820 (6)	0·3726 (4)	0·3486 (4)	69 (8)	31 (4)	33 (3)	−4 (4)	7 (4)	3 (3)
O(6)	0·0280 (5)	0·0849 (5)	0·2497 (4)	44 (7)	38 (4)	27 (3)	−12 (4)	6 (4)	−1 (3)
O(7)	0·8850 (5)	0·3793 (4)	0·0082 (4)	33 (7)	37 (4)	35 (3)	−3 (4)	7 (4)	−4 (3)

Table 2. *Positional and thermal parameters* $(\mathring{A}^2 \times 10^4)$ *for* $Co_2V_2O_7$ *with standard errors in parentheses*

The values of U_{ij} were obtained from $\beta_{ij}=2\pi^2b_ib_jU_{ij}$ where the β_{ij} appear in the structure factor expression as $\exp[-(\beta_{11}h^2+\ldots+2\beta_{12}hk+\ldots)]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co(1)	0·1470 (1)	0·1215 (1)	0·46400 (6)	59 (3)	72 (3)	90 (4)	(3)	14 (3)	−11 (3)
Co(2)	0·3077 (1)	0·3784 (1)	0·68073 (6)	61 (3)	71 (3)	85 (4)	−2 (3)	15 (3)	−1 (2)
V(1)	0·3608 (1)	0·7588 (1)	0·53076 (8)	71 (3)	91 (3)	109 (3)	−7 (2)	23 (2)	1 (2)
V(2)	0·1941 (1)	0·0186 (1)	0·81435 (7)	75 (3)	96 (3)	106 (3)	−1 (2)	23 (2)	4 (2)
O(1)	0·6049 (5)	0·1308 (4)	0·1233 (3)	77 (14)	131 (14)	112 (14)	5 (12)	25 (11)	(12)
O(2)	0·4291 (5)	0·1277 (4)	0·3972 (3)	69 (13)	124 (14)	138 (14)	−7 (12)	30 (11)	6 (12)
O(3)	0·1709 (5)	0·3702 (4)	0·4602 (3)	124 (15)	124 (15)	110 (14)	139 (15)	21 (12)	−11 (11)
O(4)	0·2552 (5)	0·3603 (4)	0·1840 (3)	102 (14)	103 (14)	130 (15)	−7 (12)	89 (11)	8 (11)
O(5)	0·6794 (5)	0·3730 (4)	0·3489 (4)	158 (15)	119 (15)	144 (14)	−27 (13)	31 (12)	9 (12)
O(6)	0·0275 (5)	0·0820 (4)	0·2467 (3)	92 (14)	143 (14)	124 (14)	−16 (12)	42 (11)	−5 (12)
O(7)	0·8532 (5)	0·3781 (4)	0·0075 (4)	73 (14)	119 (14)	170 (15)	−5 (11)	31 (11)	2 (12)

structures, although the anions are accommodated between adjacent interconnected edge-sharing MO_6 groups in all these structures, the anions have a nearly eclipsed configuration whereas the centre of symmetry at the bridging oxygen atom confers the staggered configuration to these disilicates.

Although a number of the members of the $M_2V_2O_7$ family have the thortveitite (Cruickshank, Lynton &

Table 3. *Bond lengths and angles in* $Ni_2V_2O_7$ *and* $Co_2V_2O_7$ *with standard errors in parentheses*

	$Ni_2V_2O_7$	$Co_2V_2O_7$
M(1)–O(2)*a*	2·041 (4) Å	2·068 (3) Å
–O(3)*a*	2·065 (4)	2·088 (3)
–O(4)*d*	2·041 (3)	2·085 (3)
–O(6)*a*	2·051 (3)	2·096 (3)
–O(7)*c*	2·026 (4)	2·055 (3)
–O(7)*d*	2·012 (4)	2·050 (3)
M(2)–O(1)*d*	2·083 (4)	2·130 (3)
–O(2)*d*	2·027 (4)	2·069 (4)
–O(3)*a*	2·087 (3)	2·129 (4)
–O(4)*d*	2·071 (4)	2·103 (3)
–O(5)*b*	2·017 (4)	2·029 (3)
–O(6)*d*	2·028 (4)	2·068 (3)
V(1) –O(1)*c*	1·853 (4)	1·855 (3)
–O(2)*b*	1·716 (3)	1·719 (4)
–O(5)*b*	1·634 (4)	1·640 (3)
–O(7)*c*	1·710 (4)	1·714 (3)
V(2) –O(1)*b*	1·840 (4)	1·842 (3)
–O(3)*d*	1·697 (4)	1·695 (3)
–O(4)*d*	1·699 (4)	1·700 (3)
–O(6)*b*	1·693 (3)	1·697 (3)
O(1)–V(1)–O(2)	115·9 (3)°	115·4 (3)°
–V(2)–O(4)	112·5 (3)	112·9 (3)
–V(1)–O(5)	102·3 (3)	102·4 (3)
–V(2)–O(3)	106·2 (3)	106·0 (3)
–V(1)–O(7)	112·3 (3)	112·4 (3)
–V(2)–O(6)	107·0 (3)	107·5 (3)
O(2)–V(1)–O(5)	108·5 (3)	108·3 (3)
O(4)–V(2)–O(3)	109·7 (4)	109·3 (3)
O(2)–V(1)–O(7)	109·8 (3)	109·7 (3)
O(4)–V(2)–O(6)	110·8 (4)	110·4 (3)
O(5)–V(1)–O(7)	107·5 (4)	108·1 (3)
O(3)–V(2)–O(6)	110·6 (3)	110·7 (3)
V(1)–O(1)–V(2)	117·1 (2)	117·6 (2)

Symmetry transformations:
$a = x, y, z$; $b = \bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$; $c = \bar{x}, \bar{y}, \bar{z}$; $d = x, \frac{1}{2} - y, \frac{1}{2} + z$.
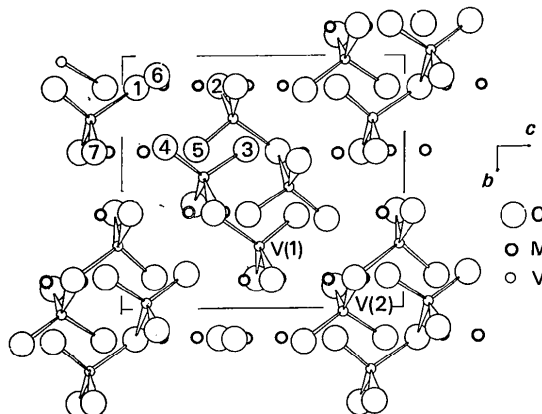

Fig. 2. Projection of the structure of Ni and Co divanadate onto the *bc* plane.

Barclay, 1962) or thortveitite-like structures, $Ni_2V_2O_7$ and $Co_2V_2O_7$ have more features related to the dichromate or large cation series (Brown & Calvo, 1970). In addition, to the nearly eclipsed anion configuration and the concomitant small V–O–V bond angle the anions are arranged in a manner similar to that in α-$Sr_2P_2O_7$ (Hagman, Jansson & Magnéli, 1968). That is, the anions pack in columns whose dimensions are defined by the repulsion between the backbone oxygen atoms. These atoms, consisting of the bridging oxygen atoms and one terminal oxygen atom at each end of the anion, define a plane which contains or nearly contains the pentavalent ions.

These columns of anions are arranged in the same centred pattern as in α-$Sr_2P_2O_7$ with the columns at the centre rotated by 90° from those at the corner (see Fig. 2). Further, one of the cations, M(2) bridges across the anion sharing terminal oxygen atoms, O(3) and O(5), with the anion. The Sr(2) site in α-$Sr_2P_2O_7$ is similarly bonded to P_2O_7. In this latter system Mn^{2+} preferentially substitutes into the Sr(1) site (Calvo, Leung & Stager, 1968). Similar differential substitution might be possible in these vanadates.

These studies indicate the limited usefulness of a plot of X^{5+} and M^{2+} radii in defining structural types since it does differentiate successfully among the $M_2V_2O_7$ series. There are indications that a number of these divanadates are polymorphs and that some of these might be thortveitite-like in character. Pedregosa, Baran & Aymonino (1973) have reported monoclinic phases for $Mg_2V_2O_7$ and $Cu_2V_2O_7$ prepared at temperatures lower than the melting points. The powder pattern of the former seems to be isotypic with that of thortveitite-like α-$Mg_2P_2O_7$ (Calvo, 1967), and that of $Cu_2V_2O_7$ seems to be isotypic with thortveitite.

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