determined by a study of some reflections in the ω–θ plane. Scanning speed adjusted to obtain $\sigma(I)/I <$ 0·018 or to approach it in a time limited to 60 s. Three standards (13,0,0, 0,16,0 and 0,0,17) for count every 7000 s and orientation every 1200 reflections: no decay. 4295 reflections measured, 1306 reflections ($h \pm 13$, k 16, l 17, $\theta \le 45°$) with $I \ge 3\sigma(I)$ used to solve and refine the structure. No correction made for extinction or absorption. All subsequent calculation on a MicroVAX II with the SDP (B. A. Frenz & Associates, Inc., 1985) system. Composition determined by refinement of the multiplicities of Co(1) and Co(2) and by microprobe analysis. All atoms refined anisotropically. Atomic scattering factors from International Tables for X-ray Crystallography (1974, Vol. IV). $(\Delta/\sigma)_{max} = 0·00$, $\Delta\rho < 0·675$ e Å^{-3}, $R = 0·029$, $wR = 0·034$, $w = 1$, $S = 1·335$. Atomic parameters are given in Table 1.*

Discussion. These results confirm the ability of $Mg_2P_2O_7$ and $Co_2P_2O_7$ to form a solid solution. The Mg and Co atoms are distributed at random over two sorts of sites. One can notice the large distortion of the $[MO_6]$ octahedra and $[MO_5]$ pyramids (Table 2) which can be considered as a $3 + 3$ and $4 + 1$ coordination for the metallic atoms respectively. The diphosphate groups have a staggered configuration, with usual P—O bonds, i.e. involving three short P—O distances with the terminal O atoms and a longer one with the bridging oxygen (Table 2).

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53929 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

This structure (Fig. 1) can be described as the stacking along [101] of two sorts of layers, mixed layers $[(Mg_{1-x}Co_x)_2O_3]_\infty$ built up from edge-sharing $[MO_6]$ octahedra and $[MO_5]$ pyramids and tetrahedral $[P_2O_4]_\infty$ formed of isolated diphosphate groups. In fact, this oxide exhibits a great similarity with the structure of β-$V_2P_2O_9$ (Gorbunova & Linde, 1978). The $[MO_5]$ pyramids form, with the oxygen O(6), a very distorted octahedron so that the atom M can also be described as being strongly off-centre in this octahedron with an $M(2)$—O(6) distance of 3·375 (3) Å (against 2·272 Å in β-$V_2P_2O_9$). A comparison of Figs. 1 and 2 shows the marked similarity of the two structures. β-$V_2P_2O_9$ can be described as units of two edge-sharing octahedra linked through $[P_2O_7]$ groups. Such an arrangement is also observed in $(Mg_xCo_{1-x})_2P_2O_7$, in the (014) plane, but in addition, these bi-octahedra share their edges in the orthogonal direction forming the $[(Mg_{1-x}Co_x)_2O_3]_\infty$ layers. (See Fig. 1.)

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Structure of Ho4Mo4O11

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Abstract. $Ho_4Mo_4O_{11}$, $M_r = 1219·47$, orthorhombic, *Pbam*, $a = 10·683$ (3), $b = 15·848$ (4), $c = 5·6592$ (1) Å, $V = 958·1$ (3) Å^3, $Z = 4$, $D_x = 8·453$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0·71073$ Å, $\mu = 380·3$ cm^{-1}, $F(000) = 2096$, $T = 295$ K, $R = 0·018$ for 1534 observed reflections. The title compound constitutes a new structure type containing infinite chains of *trans*-edge-shared Mo_6 octahedra clusters. The

latter show a pairwise distortion and are well separated from each other by the Ho^{3+} cations which are coordinated by seven O atoms forming a monocapped trigonal prism.

Introduction. The discovery of NaMo$_4$O$_6$ (Torardi & McCarley, 1979) comprising infinite chains of *trans*-edge-shared Mo$_6$ octahedra sparked a vigorous interest in the study of new reduced molybdenum oxides. Thus, over the last decade, various new compounds have been synthesized, containing as dominant structural features quasi-discrete clusters such as Mo$_4$ rhomboids (Torardi & McCarley, 1981), Mo$_6$ octahedra (Lindblom & Strandberg, 1989), bicapped octahedra Mo$_8$ (Leligny, Ledesert, Labbe, Raveau & McCarroll, 1990; Gougeon & McCarley, 1991), chain fragments of two, three, four and five *trans*-edge-shared Mo$_6$ octahedra (Hibble, Cheetham, Bogle, Wakerley & Cox, 1988; Dronskowski & Simon, 1989; Mattausch, Simon & Peters, 1986; Simon, Mertin, Mattausch & Gruehn, 1986) as well as infinite chains of *trans*-edge-shared Mo$_4$ (McCarley, Lii, Edwards & Brough, 1985) or Mo$_6$ clusters. Up to the present, four different structure types only containing infinite chains of condensed Mo$_6$ octahedral clusters have been identified: NaMo$_4$O$_6$ (Torardi & McCarley, 1979), Sc$_{0.75}$Zn$_{1.25}$Mo$_4$O$_7$ (McCarley, 1982), ZnMo$_8$O$_{10}$ (Lii, McCarley, Kim & Jacobson, 1986) and Mn$_{1.5}$Mo$_8$O$_{11}$ (Carlson, Brough, Edwards & McCarley, 1989). All of these compounds differ from each other in the way that the infinite cluster chains are coupled together through the O atoms to form the lattice. During our investigation of the rare-earth–Mo–O ternary system, a new structural type containing infinite chains of fused Mo$_6$ clusters was synthesized. Structure work on a single crystal of the Ho compound showed that the new compound was Ho$_4$Mo$_4$O$_{11}$.

Experimental. Single crystals were obtained by heating a stoichiometric mixture of Ho$_2$O$_3$, MoO$_3$ and Mo in a sealed molybdenum crucible at about 1980 K for 48 h, cooling it at 50 K h^{-1} to 1300 K and finally furnace cooling to room temperature.

A crystal with dimensions 0·04 × 0·07 × 0·26 mm was selected for data collection, carried out on an Enraf–Nonius CAD-4 diffractometer equipped with graphite-monochromatized Mo $K\alpha$ radiation. Accurate cell parameters were obtained by a least-squares refinement of the setting angles of 25 reflections with $13 \leq 2\theta \leq 60°$. The systematic absences ($h0l$, $h = 2n$ + 1 and $0kl$, $k = 2n + 1$) allow the space group to be *Pbam* or *Pba*2; the former was assumed and confirmed by the successful analysis. 3544 reflections were recorded in the range $2 \leq 2\theta \leq 64°$ with h: 0→15, k: 0→23, l: −8→8; ω–2θ mode was used with scan width $\Delta\omega = (0·95 + 0·35\tan\theta)°$ and counter

aperture $\Delta l = (2 + 0·5\tan\theta)$ mm. Three orientation and three intensity control reflections were checked every 250 reflections and every hour, respectively, and showed no significant variation. Data were corrected for Lorentz–polarization and an empirical absorption correction following the *DIFABS* procedure (Walker & Stuart, 1983) was applied to isotropically refined data. The min. and max. correction factors were 0·841 and 1·271. After averaging (R_{int} = 0·017) 1773 unique data were used to solve the structure with the aid of *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and a subsequent difference Fourier synthesis. The function minimized in the least-squares program was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 4F_o^2/[\sigma^2(F_o^2) + (0·03F_o^2)^2]$. The refinement of all atoms anisotropically and an extinction coefficient (103 variables) converged to $R = 0·018$, $wR = 0·025$, $S = 1·036$ for 1534 reflections with $F_o^2 > 2\sigma(F_o^2)$. The largest shift/e.s.d. was $< 0·01$. Max. and min. electron density in final difference Fourier map was $+1·56$ and $-1·96$ e Å^{-3}, respectively; final value of g was 1·66 × 10^{-7} (Stout & Jensen, 1968). A refinement of the occupancy factors for the Ho sites confirmed that they are fully occupied. Scattering factors for neutral atoms and f', f'' were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were performed with the *SDP* (B. A. Frenz & Associates, Inc., 1985) programs on a Digital MicroVAX 3100. Final atomic coordinates and B_{eq} are reported in Table 1 and selected interatomic distances in Table 2.*

Discussion. The structure of Ho$_4$Mo$_4$O$_{11}$ is dominated by Mo—Mo bonding manifested in infinite chains composed of edge-shared Mo$_6$ octahedal clusters with O atoms above all free edges and corners (Fig. 1). Thereby, the Mo atoms are coordinated to eleven atoms. The apical Mo(1) atom is bonded to six Mo and five O atoms, and the two waist Mo(2) and Mo(3) atoms to seven Mo and four O atoms. The uniqueness of the title compound with respect to the known infinite chain structures resides in the dilution of the chains with the Ho atoms (Fig. 2). Indeed, in the previous compounds, the infinite metal chains are always connected through bridging O atoms in at least one direction perpendicular to the chains. In this new compound, the cluster chains do not share O atoms since we always have the sequence Mo–O–Ho–O–Mo. Moreover, two crystallographically independent O atoms O(3) and O(8) are

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Table 1. *Positional parameters and equivalent iso-tropic thermal parameters*

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
Ho(1)	0·31426 (3)	0·27642 (2)	0·500	0·291 (5)
Ho(2)	0·07854 (3)	0·09893 (2)	0·500	0·297 (5)
Ho(3)	0·09729 (3)	0·23767 (2)	0·000	0·286 (5)
Ho(4)	0·88182 (3)	0·07728 (2)	0·000	0·327 (5)
Mo(1)	0·36636 (4)	0·08458 (2)	0·27217 (8)	0·208 (6)
Mo(2)	0·59167 (6)	0·06799 (4)	0·500	0·225 (9)
Mo(3)	0·58308 (6)	0·06009 (4)	0·000	0·228 (9)
O(1)	0·2257 (3)	0·1747 (2)	0·2626 (7)	0·46 (6)
O(2)	0·1851 (3)	0·3640 (2)	0·2411 (7)	0·47 (6)
O(3)	0·4597 (3)	0·3265 (2)	0·2470 (7)	0·52 (6)
O(4)	0·4596 (5)	0·1641 (3)	0·500	0·58 (9)
O(5)	0·2570 (5)	0·0143 (3)	0·500	0·36 (8)
O(6)	0·4516 (5)	0·1519 (3)	0·000	0·33 (8)
O(7)	0·2711 (5)	0·0237 (3)	0·000	0·32 (8)
O(8)	0·500	0·500	0·2454 (9)	0·44 (8)

Table 2. *Selected bond distances* (Å)

Mo(1)—Mo(1)	2·5786 (9)	Mo(1)—Mo(1)	3·0806 (9)
Mo(1)—Mo(2)	2·7432 (9)	Mo(2)—Mo(2)	2·912 (1)
Mo(1)—Mo(2)	2·7767 (7)	Mo(2)—Mo(3)	2·8339 (1)
Mo(1)—Mo(3)	2·8078 (7)	Mo(3)—Mo(3)	2·604 (1)
Mo(1)—Mo(3)	2·8144 (6)		
Mo(1)—O(4)	2·060 (4)	Mo(2)—O(2)	2 × 2·075 (4)
Mo(1)—O(5)	2·066 (4)	Mo(2)—O(4)	2·077 (5)
Mo(1)—O(1)	2·073 (3)	Mo(2)—O(5)	2·077 (5)
Mo(1)—O(6)	2·083 (3)	Mo(3)—O(6)	2·022 (5)
Mo(1)—O(7)	2·083 (3)	Mo(3)—O(7)	2·047 (5)
		Mo(3)—O(2)	2 × 2·121 (4)
Ho(1)—O(3)	2 × 2·257 (4)	Ho(3)—O(1)	2 × 2·256 (4)
Ho(1)—O(1)	2 × 2·302 (4)	Ho(3)—O(3)	2 × 2·269 (4)
Ho(1)—O(4)	2·362 (5)	Ho(3)—O(6)	2·343 (5)
Ho(1)—O(2)	2 × 2·445 (4)	Ho(3)—O(2)	2 × 2·598 (4)
Ho(2)—O(3)	2 × 2·249 (4)	Ho(4)—O(3)	2 × 2·230 (3)
Ho(2)—O(8)	2 × 2·289 (3)	Ho(4)—O(8)	2 × 2·241 (3)
Ho(2)—O(5)	2·332 (5)	Ho(4)—O(7)	2·287 (5)
Ho(2)—O(1)	2 × 2·391 (4)	Ho(4)—O(2)	2 × 2·673 (4)

only bonded to Ho^{3+} cations. As already observed in ZnMo$_8$O$_{10}$ (Lii *et al.*, 1986) and Gd$_4$Mo$_{18}$O$_{32}$ (Gall & Gougeon, 1990), the infinite chains are markedly distorted with a repeat unit of 2/*m* symmetry comprising two Mo$_6$ octahedra. Indeed, distortions are expected when the number of electrons per |Mo$_2$Mo$_{4/2}$| fragment is greater than 13 e$^-$ (14 e$^-$ in Ho$_4$Mo$_4$O$_{11}$) and it has been shown that the excess electrons occupy antibonding states involving $d_{x^2-y^2}$ orbitals of the apex Mo atoms (Hughbanks & Hoffmann, 1983). Consequently, we observe a pairing of the apical Mo(1) atoms which leads to alternate short and long distances between the Mo(1) atoms [2·5786 (9) and 3·0806 (9) Å, respectively] as well as between Mo atoms in the shared edges of the octahedra [Mo(2)—Mo(2) 2·912 (1) Å and Mo(3)—Mo(3) 2·604 (1) Å]. The other Mo—Mo distances are between 2·7432 (9) and 2·8339 (1) Å. The average of the Mo—Mo distances within the Mo$_8$O$_{16}$ repeat unit is 2·798 Å which differs little from that observed in the previous infinite chain compounds (*e.g.* 2·803 in NaMo$_4$O$_6$, 2·790 in Mn$_{1.5}$Mo$_8$O$_{11}$, 2·799 in Sc$_{0.5}$Zn$_{1.5}$Mo$_4$O$_7$ and 2·809 Å in ZnMo$_8$O$_{10}$). The

eight independent O atoms can be divided into five distinct types according to their coordination geometries. Oxygen O(1) is coordinated by one Mo atom and three Ho cations forming a distorted tetrahedron. Oxygen O(2) is surrounded by two Mo atoms and three cations. O(3) and O(8) are only surrounded by four Ho cations in approximately tetrahedral symmetry. O(4) and O(5) are coordinated by three Mo and one Ho atoms in a sawhorse geometry. Finally, O(6) and O(7) are also bound to one Ho and three Mo atoms but in a very distorted tetrahedral geometry. The Mo—O range between 2·022 (5) and 2·121 (4) Å with an average value of 2·075 Å.

The environments of the four crystallographically inequivalent Ho cations are similar and consist of seven O atoms placed at the vertices of a distorted monocapped trigonal prism. The average Ho—O distances are 2·339, 2·313, 2·370, and 2·368 Å for Ho(1)—O, Ho(2)—O, Ho(3)—O and Ho(4)—O respectively. The shortest distance between Ho atoms is 3·4291 (5) Å and occurs between Ho(3) and Ho(4).

The estimation of the number of electrons per Mo$_4$ unit using separately the bond-length bond-strength formula (Brown & Wu, 1976) for the Mo—O bonds

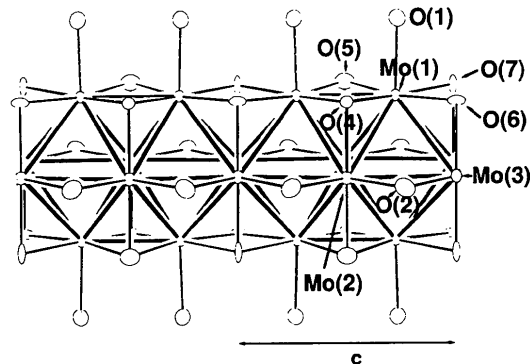Fig. 1. A section of one molybdenum oxide cluster chain. The repeat unit comprises two Mo$_6$ octahedra and has 2/*m* symmetry.
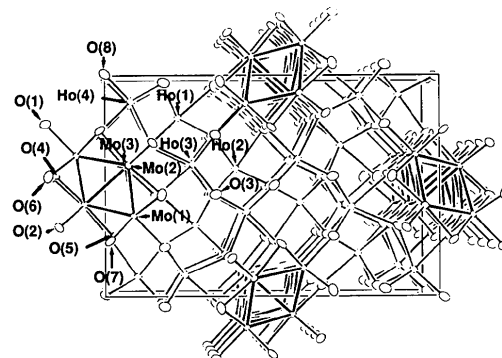

Fig. 2. The structure of Ho$_4$Mo$_4$O$_{11}$ as viewed down the *c* axis parallel to the direction of chain growth. Mo—Mo bonds in the octahedral cluster unit are shown by thick lines, Mo—O and Ho—O bonds by thin lines.

$[s = (d_{\text{Mo}-\text{O}}/1\cdot882)^{-6\cdot0}]$ and the Pauling bond order (PBO) equation $d_n = d_1 - 0\cdot6 \log n$ (Pauling, 1960) for the Mo—Mo bonds, yields 14·0 (1) and 14·05 (5) e^- per Mo₄, respectively, which are in excellent agreement with the value of 14 e^- based on the stoichiometry. Moreover, the number of antibonding electrons being one-half of the difference between the number of electrons per Mo₄ derived from PBO sums and that derived from the stoichiometry (McCarley, 1986), Ho₄Mo₄O₁₁ has no electrons in antibonding states. Thus this compound is perfectly bonded with all valence electrons of the Mo atoms involved in Mo—Mo or Mo—O bonding states.

Isostructural compounds are also formed with Nd, Sm, Gd, Tb, Dy, Er, Tm, Yb, Lu and Y as ternary element (Gall, Gougeon, Nagaki, Schimek & McCarley, 1990).

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Modulated Structure of Zirconium Titanate

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Abstract. $Zr_{0\cdot992}Hf_{0\cdot008}TiO_4$, $M_r = 203\cdot81$, orthorhombic, $P^{Pbc2_1}_{\bar{1}1\bar{1}}$, $a = 4\cdot821$ (2), $b = 5\cdot341$ (7), $c = 5\cdot022$ (3) Å, $\mathbf{k} = 0\cdot43\mathbf{a}^*$, $V = 129\cdot31$ (1) Å³, $Z = 2$, $D_x = 5\cdot2346$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71073$ Å, $\mu = 72\cdot4$ cm^{-1}, $F(000) = 188\cdot51$, $T = 298$ K, $R = 0\cdot093$ for all, 0·067 for 565 main and 0·113 for 1082 first order satellite reflections. The structure can be