get their four nitrogen atoms from the macrocycle octaethylporphyrinate.

For comparative purposes the M–L bond distances of some hexacoordinated vanadium(II) compounds with bonds to oxygen- and/or nitrogen-containing ligands are provided in Table VIII. In general, the mean V–O distance is fairly constant, but significant deviations of the individual bond lengths appear in **2** and in $[V(THF)_4][V(CO)_6]_2$. In the latter case the vanadium-to-oxygen distance of the bridging carbonyl group is very short. This is also the case in **3**, where the corresponding bond distance is 2.071 (4) Å. However, the shortening of the bond is accompanied by a lengthening of the V–N bonds (2.184 [21] Å) as compared to the case where the nitrogen atoms are provided by a porphyrin ring as in $[V(oep)(THF)_2]$ and $[V(oep)(PPhMe_2)_2]$, in which the mean V–N bond distances are only 2.046 [1] and 2.050 [4] Å, respectively. In the case of the porphyrin ligand, it is possible that electrons in the plane formed by the VN_4 species can be delocalized, allowing π interaction between the electrons from the metal and those of the ring, thus making the V–N bonds shorter and the other V–L bonds longer, as is the case in $[V(oep)(THF)_2]$.

When the ligand is pyridine, the same extended delocalization is not possible. Perhaps this allows a clear contact with the axial ligands as in the case of the carbonyl oxygen atom of the saccharinate ligand. In this case, it is tempting to use the same argument and assume some electron delocalization over the saccharinate ring, which is planar, or π bonding to the chlorine atom in the case of $VCl_2(py)_4$. However, if that is the case, it does not manifest itself in a lengthening of the C–O bond.

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Registry No. **1** (CC entry), 22364-10-9; **1** (salt entry), 22257-76-7; **2**, 103563-29-7; **3**, 103563-31-1; **4**, 103563-32-2; $VOSO_4$, 27774-13-6.

Supplementary Material Available: Tables of anisotropic thermal parameters and all bond distances and angles for **1–4** and crystal data and positional parameters for **4** (17 pages); tables of observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

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$In_{11}Mo_{40}O_{62}$: A Molybdate with Units of Four and Five Condensed Mo_6 Octahedra and Linear In_5^{7+} and In_6^{8+} Ions

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$In_{11}Mo_{40}O_{62}$ is prepared from a stoichiometric mixture of In, Mo, and MoO_2 at 1100 °C. The crystal structure ($Pmc2_1$, a = 2887.8 (5) pm, b = 951.3 (1) pm, c = 988.3 (1) pm, Z = 2, R = 0.038 for 3017 reflections with $F > 2\sigma(F)$) of the metallic looking compound exhibits several novel features. Chains of four and five Mo_6 octahedra condensed via opposite edges occur that are surrounded by O atoms above all free octahedra edges (Mo–Mo distances between 264 and 312 pm). The channels between these cluster units are filled with chains of five and six In atoms with metal–metal-bonded In_5^{7+} and In_6^{8+} ions (In–In distances between 262 and 268 pm). The structure is discussed in terms of bond length–bond strength calculations.

Introduction

A large number of metal-rich compounds of d metals and p elements, e.g. halogens, chalcogens, etc., have structures that contain isolated or condensed clusters.[1] Oxides that exhibit these structural features are rather scarce. Triangular clusters of molybdenum atoms occur in the compounds $A_2Mo_3O_8$ (A = divalent elements like Mg, Mn, Zn, etc.)[2–4] and $LiZn_2Mo_3O_8$ or $ScZnMo_3O_8$.[5] Tetranuclear clusters were found in $Ba_{1.14}Mo_8O_{16}$[6] and $K_2Mo_8O_{16}$.[7] These tetranuclear clusters are condensed to form ribbons in $Na_{0.9}Mo_2O_4$.[8,9] The only oxides containing isolated octahedral M_6 units are $Mg_3Nb_6O_{11}$[10] and $Mn_3Nb_6O_{11}$.[11] The extreme of a 3-dimensional framework of condensed M_6 units was found in NbO[12,13] and TiO.[1,14] A fascinating group of structures was worked out by McCarley et al.[8] Compounds with the composition AMo_4O_6 (A = Na,[15] K,[16] Rb,[9] Sr,[9] Ba[6,9] Eu,[9] Pb,[6,9] In, Sn[8,9] as well as $Sc_{0.75}Zn_{1.25}Mo_4O_7$ and $Ti_{0.5}Zn_{1.5}Mo_4O_7$[17] contain infinite chains of trans-edge-sharing Mo_6 octahedra, the oxygen environment corresponding to the M_6X_{12} type cluster. The variation of the Mo/O ratio is due to different ways of interconnection of such chains via oxygen bridges. Combinations of different structural elements were found in $Ca_{5.45}Mo_{18}O_{32}$.[8] This compound contains chains of condensed M_6 and M_4 units together with chains of single atoms. By means of Extended Hückel calculations the chemical bonding in reduced molybdates containing such chains of octahedra has been discussed in detail.[18]

Our interests in ternary molybdenum oxides were focused in two directions. On one side the close structural relationship of $NaMo_4O_6$ with metal-rich lanthanide halides[1,19] prompted the question as to whether the extent of condensation can be increased, leading to twin chains or ultimately layers of condensed octahedra.

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Figure 1. Crystals of $In_{11}Mo_{40}O_{62}$ exhibiting the twinning pattern that is characteristic for the compound. All crystals are threefold twinned.

On the other side we were interested in cutting the infinite Mo_4O_6 chain into finite pieces as is possible with the chain of trans-face-sharing Mo_6 units in ternary chalcogenides.[20,21] A number of different "oligomers" formed by condensing two, three, five, seven, and nine M_6X_8 clusters were found in the latter compounds as a kind of intermediate between the isolated cluster and the infinite cluster chain.[22] With the compound $In_{11}Mo_{40}O_{62}$ the last mentioned aim of cutting the Mo_4O_6 type chain could be reached. The compound contains "oligomeric" straight units of four and five trans-edge-sharing Mo_6 octahedra.

Experimental Section

Preparation. The compound $In_{11}Mo_{40}O_{62}$ is formed in quantitative yield by heating an intimate mixture of MoO_2, Mo powder, and In in the stoichiometric ratio at T = 1050–1100 °C.

Single crystals that were used for the X-ray structure analysis were taken from a sample of 6 mmol of In, 12 mmol of MoO_2, and 2 mmol of Mo enclosed in a quartz glass ampule (length 70 mm, diameter 10 mm) under vacuum and heated at 1100 °C for 8 days. An applied temperature gradient yielded crystals of approximately 2 mm in length at the colder end ($T \approx 1060$ °C) together with an excess of indium. An X-ray powder diagram shows MoO_2 to be present in the residue. As starting materials MoO_2 (Ventron, Karlsruhe, FRG) and Mo and In (Merck, Darmstadt, FRG, LAB quality) were used.

Characterization. $In_{11}Mo_{40}O_{62}$ forms brittle crystals with metallic reflectance, which are frequently twinned to form stars as shown in Figure 1. The compound is quite air stable and does not react in a visible extent with concentrated HCl or aqua regia, which only dissolves it upon heating. $In_{11}Mo_{40}O_{62}$ is a good conductor with a specific resistivity of $\rho = 6 \times 10^{-4}$ Ω cm at room temperature. The magnetic behavior is complicated. The effective moment increases with temperature and reaches a value $\mu_{eff} \approx 0.5\ \mu_B$ at room temperature. Further experiments are necessary to understand the strong field and temperature dependence of μ_{eff}. A Guinier diagram (Cu $K\alpha_1$, Si standard) has been used (12° $\leq 2\theta \leq$ 55°, 15 unique reflections; PARAM X-ray system, 1974) to determine the lattice constants a = 2887.8(5), b = 951.3 (1), and c = 988.3 (1) pm, which have been used for the calculation of distances. The compound diagram is characterized by the following d values (pm; estimated intensities checked vs. calculated values in parentheses): 686 (50), 668 (55), 488 (40), 476 (42), 340.7 (30), 311.6 (60), 309.9 (75), 302.3 (100), 300.7 (85), 271.2 (45), 249.4 (65), 241.3 (75), 239.6 (80), 238.2 (20), 223.9 (15), 219.5 (17), 197.7 (30), 196.1 (90), 195.2 (40), 187.1 (25), 186.7 (25), 182.6 (30), 179.3 (25), 171.6 (55), 160.9 (20), 151.4 (35), 150.9 (20), 144.4 (20), 143.2 (25).

Structure Investigation. A wedge-shaped crystal with maximum dimensions of 0.30 × 0.12 × 0.08 mm was investigated on a Model P$\bar{1}$ single-crystal diffractometer (Syntex). The lattice constants refined on the basis of 15 reflections are a = 2887.8 (9), b = 952.6 (3), and c = 989.5 (2) pm. The intensities of 3105 reflections hkl were measured in the ω-scan mode (Mo $K\alpha$, graphite monochromator, 3° $\leq 2\theta \leq$ 55°; h = 0–37, k = 0–12, l = 0–12; $\Delta\omega$ = 0.75°, scan speeds 0.75–29.3° min^{-1}) and corrected for absorption effects by applying ψ scans for 11 reflections. A total of 3017 reflections with $F > 2\sigma(F)$ were used for the refinements. The systematically absent reflections $hk0$ ($h00$) with $h = 2n + 1$ led to the possible space groups $Pmma$ (No. 51) and $P2_1ma$ (No. 26); the acentric space group was finally taken and transformed to the conventional setting $Pmc2_1$. The structure was solved with direct methods, yielding the positions of all metal atoms. In a following ΔF synthesis at the stage where R = 0.14, all oxygen atoms could be localized. The oxygen atom positions could only be refined isotropically, and in part they exhibited very small temperature coefficients. Inspection of the F_o/F_c list indicated extinction, which was accounted for in the final cycle. Least-squares refinements yielded final reliability factors R = 0.038[38a] and R_w = 0.037.[38b] With an extinction correction,[38c] all atoms could be refined anisotropically. Occupancy factors for all In atoms lead to values of unity within standard deviations. All calculations were performed on an Eclipse computer using the SHELXTL program system.[23] Table I summarizes the crystal data for $In_{11}Mo_{40}O_{62}$. The atomic parameters are listed in Table II, and Table III contains all interatomic distances up to 340 pm.

Table I. Summary of Single-Crystal Data and X-ray Intensity Collection for $In_{11}Mo_{40}O_{62}$

formula	$In_{11}Mo_{40}O_{62}$
molar wt, g	6092.58
space group	$Pmc2_1$
a,[a] pm	2887.8 (9)
b,[a] pm	952.6 (3)
c,[a] pm	989.5 (2)
V, pm^3	2722.03 × 10^6
temp, °C	24 ± 1
d_{calcd}, g cm^{-3}	7.43
Z	2
abs coeff, cm^{-1}	132.85
color	metallic luster
habit	wedgelike
dimens, mm	0.30 × 0.12 × 0.08 mm
λ(Mo $K\alpha$), Å	0.7107
method	ω-scan
scan speed, deg min^{-1}	0.75–29.3
monochromator	graphite
bkgd time/scan time	0.5
std reflcns	802 every 1.75 h
range of data, deg	$3 \leq 2\theta \leq 55$
no. of reflcns	3105
no. of reflcns with $F > 2\sigma(F)$	3017
$R = \sum\lvert F_o - \lvert F_c\rvert\rvert/\sum F_o$	
counter aperture width, mm	5
incident beam collimator diam, mm	0.5

[a] The lattice constants a = 2887.8 (5), b = 951.3 (1) and c = 988.3 (1) pm derived from Guinier patterns have been used for the calculation of interatomic distances.

Structure Description and Discussion

The crystal structure of $In_{11}Mo_{40}O_{62}$ is shown in Figure 2. It exhibits novel features in the bonding both of the transition metals and of the main-group metals. The occurrence of characteristic clusters consisting of four and five trans-edge-sharing Mo_6 octahedra is evident from Figure 2. These oligomeric clusters form parts of the infinite chains known from the compounds AMo_4O_6 and thus are interesting intermediate steps in cluster condensation.

Figure 3 represents the clusters and their interconnection along [100] in more detail. The clusters are derived from M_6X_{12} type units, which typically occur in a wealth of reduced Nb and Ta halides. Such clusters carry X atoms above all 12 edges of the octahedron (X^i) and can have six additional X atoms above all corners of the octahedron (X^a).[13] Examples where all these positions are occupied are, e.g., $K_4Nb_6Cl_{18}$[24] or $K_4Nb_6Br_{18}$,[25] containing the clusters $Nb_6X^i_{12}X^a_6$. In a number of cases X atoms have a bridging function between adjacent clusters as, e.g., in

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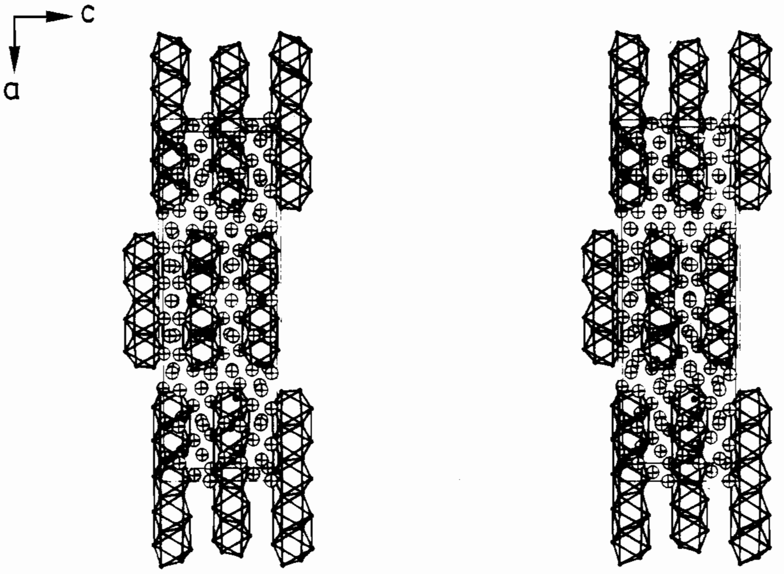

Figure 2. Stereoview of unit cell of $In_{11}Mo_{40}O_{62}$ along [010]. Mo atoms are interconnected, In atoms are represented by filled small circles, and O atoms are represented by open large circles.

Nb_6Cl_{14},[26] where according to $Nb_6Cl^i_{10}Cl^{i-a}_2Cl^{a-a}_{4/2}$ the Cl atoms of type X^a link clusters via corners (Cl^{a-a}) but some of the Cl atoms of type X^i coordinate to free corners of a neighboring octahedron (Cl^{i-a}). The two kinds of molybdenum clusters in $In_{11}Mo_{40}O_{62}$ will be referred to as $(M_6)_4$ and $(M_6)_5$.

In particular, the top and bottom of the oligomeric clusters in $In_{11}Mo_{40}O_{62}$ (Figure 3) indicate the almost identical X atom environment of the M_6 unit as in isolated $M_6X^i_{12}X^a_6$ clusters except for that part of the unit which is involved in cluster condensation. In the central parts of the oligomeric clusters all free corners and edges of the M_6 units are also surrounded by X atoms in the same manner.

With the symbolism explained before, the oligomeric clusters in $In_{11}Mo_{40}O_{62}$ can be described as $Mo_{18}O^i_{14}O^{i-i}_{4/2}O^{i-a}_{24/2}$ for the $(M_6)_4$ unit and $Mo_{22}O^i_{18}O^{i-i}_{4/2}O^{i-a}_{28/2}$ for the $(M_6)_5$ unit. The formulation means that the majority of oxygen atoms lie above octahedra edges but coordinate neighboring clusters in corner positions (X^{i-a}). Four oxygen atoms per cluster are shared (O(24), O(25), O(28), O(29)) in positions above edges of adjacent clusters (X^{i-i}). Chains of edge-sharing octahedra of different length that are only surrounded by X^i atoms have a general composition $M_{2(2n+1)}X_{6(n+1)}$, where n represents the number of condensed octahedra $(M_6)_n$. Out of this series the trivial case $n = 1$ has been known for a long time and $n = 2$ has been realized in the structure of $Gd_{10}Cl_{18}(C_2)_2$,[27] containing isolated clusters with C_2 unis in the centers of the M_6 octahedra, and also $Gd_{10}Cl_{17}(C_2)_2$,[28] where two Cl atoms have the X^{i-i} function, or $Gd_{10}I_{16}(C_2)_2$,[19] where four I atoms have the X_{i-i} function. The limiting case $n \rightarrow \infty$ is realized in the structures of compounds AMo_4O_6.[15]

It is interesting to note that the kind of interconnection of clusters as found in $In_{11}Mo_{40}O_{62}$ according to $In_{11}(Mo_{18}O_{26}O_{4/2})(Mo_{22}O_{32}O_{4/2})$ is identical with the interconnection principle in $Gd_{10}I_{16}(C_2)_2$ ($=Gd_{10}I_{14}I_{4/2}(C_2)_2$).

The channels between the clusters in $In_{11}Mo_{40}O_{62}$ are occupied by In atoms in a peculiar way. These are arranged in short chains of five and six In atoms associated to the $(M_6)_4$ and $(M_6)_5$ clusters, respectively, as shown in Figure 4. The coordination figure is exactly planar with cn = 4 for In(6) and becomes pyramidal with a progressive decrease of the pyramidal angle as a function of distance from the mirror plane. The coordination of the central In atoms in the chains is very similar to that in the structure of $InMo_4O_6$,[8,9] although a detailed knowledge of the cationic distribution in the latter compound is still obscured due to disorder problems. $In_{11}Mo_{40}O_{62}$ according to its structure obviously contains two kinds of metal–metal bonds, namely Mo–Mo and In–In bonds. Both the molybdenum clusters and the short chains

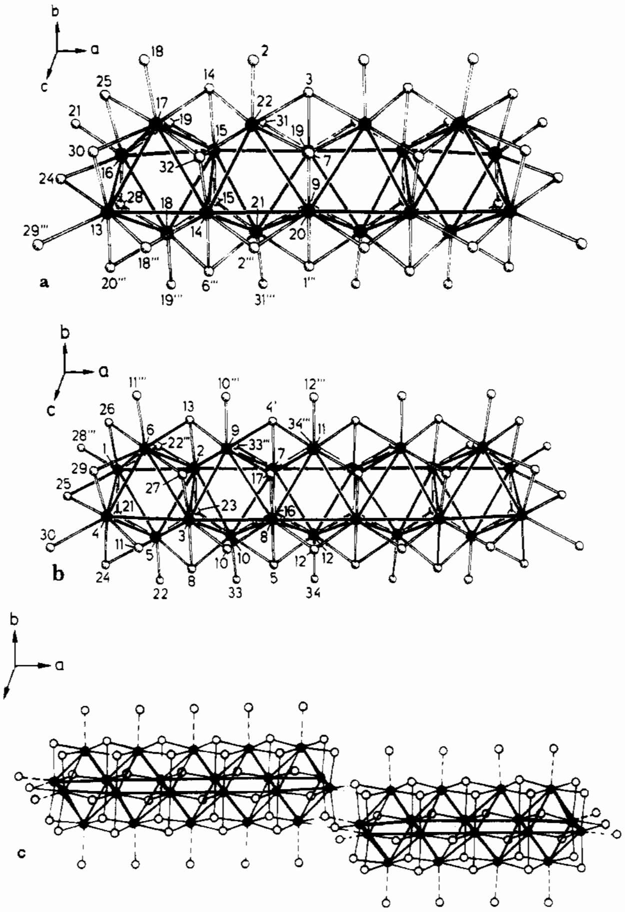

Figure 3. Structures of (a) the $(M_6)_4$ unit and (b) the $(M_6)_5$ unit in $In_{11}Mo_{40}O_{62}$. Filled circles symbolize Mo atoms, open circles O atoms. The numbering of the atoms is identical with that in Table III. (c) Interconnection between the $(M_6)_4$ and the $(M_6)_5$ units. Broken lines indicate the coordination of O atoms belonging to neighboring clusters (X^{i-a}).

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Table IIa. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($pm^2 \times 10^{-1}$)

	x	y	z	U^a
In(1)	462 (1)	2481 (2)	−4056 (2)	34 (1)
In(2)	1381 (1)	2586 (1)	−4177 (2)	31 (1)
In(3)	2285 (1)	2059 (1)	−3764 (2)	30 (1)
In(4)	3206 (1)	2946 (1)	−1932 (2)	29 (1)
In(5)	4097 (1)	2401 (1)	−1474 (2)	29 (1)
In(6)	5000	2623 (2)	−1691 (2)	35 (1)
Mo(1)	2434 (1)	1378 (1)	36 (2)	25 (1)
Mo(2)	1474 (1)	1382 (1)	−17 (2)	24 (1)
Mo(3)	1467 (1)	3665 (1)	1787 (1)	24 (1)
Mo(4)	2424 (1)	3763 (1)	1664 (2)	26 (1)
Mo(5)	1964 (1)	1269 (1)	2466 (2)	25 (1)
Mo(6)	1969 (1)	3835 (1)	−649 (2)	27 (1)
Mo(7)	492 (1)	1406 (1)	11 (2)	24 (1)
Mo(8)	491 (1)	3597 (2)	1795 (2)	23 (1)
Mo(9)	1017 (1)	3821 (2)	−628 (2)	29 (1)
Mo(10)	1039 (1)	1199 (1)	2431 (2)	23 (1)
Mo(11)	0	3822 (2)	−603 (2)	27 (1)
Mo(12)	0	1185 (2)	2411	23 (1)
Mo(13)	3066 (1)	3625 (1)	−5702 (2)	25 (1)
Mo(14)	4022 (1)	3648 (1)	−5661 (2)	24 (1)
Mo(15)	4032 (1)	1345 (2)	−7468 (2)	25 (1)
Mo(16)	3079 (1)	1240 (1)	−7323 (2)	26 (1)
Mo(17)	3541 (1)	3730 (1)	−8133 (2)	25 (1)
Mo(18)	3537 (1)	1168 (1)	−5003 (2)	24 (1)
Mo(19)	5000	1421 (2)	−7431 (2)	26 (1)
Mo(20)	5000	3591 (2)	−5713 (2)	24 (1)
Mo(21)	4463 (1)	1195 (1)	−5034 (2)	23 (1)
Mo(22)	4459 (1)	3793 (1)	−8102 (2)	26 (1)
O(1)	5000	−2304 (17)	967 (22)	36 (6)
O(2)	4497 (6)	5166 (22)	215 (18)	65 (6)
O(3)	5000	2786 (14)	950 (15)	23 (4)
O(4)	−498 (4)	2749 (11)	−1587 (11)	23 (3)
O(5)	494 (3)	2244 (12)	3423 (15)	31 (4)
O(6)	4002 (4)	−2444 (11)	1084 (13)	27 (3)
O(7)	5000	−4996 (15)	2701 (14)	16 (3)
O(8)	1488 (4)	2448 (11)	3556 (14)	28 (3)
O(9)	5000	62 (22)	4159 (21)	46 (6)
O(10)	980 (5)	4790 (22)	2692 (19)	56 (6)
O(11)	1989 (6)	4878 (21)	2607 (18)	60 (6)
O(12)	0	4712 (22)	2730 (24)	48 (7)
O(13)	1500 (4)	2669 (11)	−1658 (11)	23 (3)
O(14)	4015 (4)	2585 (12)	825 (12)	26 (3)
O(15)	3987 (4)	−149 (15)	4036 (15)	36 (4)
O(16)	512 (4)	7 (17)	1568 (16)	41 (4)
O(17)	493 (3)	5060 (12)	247 (11)	17 (3)
O(18)	3495 (7)	5127 (21)	176 (18)	65 (6)
O(19)	3511 (3)	129 (10)	1628 (10)	11 (2)
O(20)	3014 (4)	−2402 (11)	960 (14)	31 (3)
O(21)	2520 (3)	137 (10)	1657 (10)	15 (2)
O(22)	1998 (3)	−129 (9)	4102 (9)	12 (2)
O(23)	1534 (3)	−52 (13)	1528 (12)	25 (3)
O(24)	2528 (4)	2465 (12)	3390 (14)	33 (4)
O(25)	2975 (4)	2575 (11)	995 (12)	25 (3)
O(26)	2475 (4)	2619 (11)	−1598 (12)	27 (3)
O(27)	1480 (4)	5147 (12)	246 (13)	27 (3)
O(28)	2983 (3)	−45 (12)	−5853 (11)	23 (3)
O(29)	2490 (5)	5040 (15)	95 (14)	43 (4)
O(30)	3021 (6)	4876 (18)	2635 (14)	48 (5)
O(31)	4502 (3)	147 (9)	−8384 (10)	14 (2)
O(32)	4006 (4)	5106 (12)	2783 (12)	26 (3)
O(33)	1012 (3)	−171 (9)	4093 (10)	10 (2)
O(34)	0	−201 (12)	4079 (14)	14 (3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

of In atoms show interesting patterns of variable M–M distances correlated with the M–O distances.

In–In and In–O. To start with the In atoms first, the In–In distances decrease slightly from 266 to 262 pm in the In_5 chain and 269 to 265 pm in the In_6 chain when moving from the end to the centers of the chains. The top-to-bottom distances between atoms of different chains are 333 pm.

The In–In distances in the In_5 and In_6 units are the shortest known. The distances compare with those in In_6S_7 (274.1 pm),[30] In_6Se_7(276),[31] and γ-InSe (277 pm),[32] where In_2 pairs occur and in In_4Se_3,[33] where bent In units ($\angle$(In(3)–In(2)–In(1)) = 157.8°) are found and discussed as In_3^{5+} ions (275.6 and 277.6 pm).

As with the In_3^{5+} ion the chains of atoms are also bent in the In_5 and In_6 units of $In_{11}Mo_{40}O_{62}$ ($\angle$(In(1)–In(2)–In(3)) = 163° in the In_6 chain and $\angle$(In(4)–In(5)–In(6)) = 158° in the In_5 chain).

The bending has the consequence that the atoms In(3) and In(4) at the ends of the chains come close to three oxygen atoms each. The approximate tetrahedral (three O and one In) environment allows a description as In^{2+} for these atoms. The chains of In atoms in $In_{11}Mo_{40}O_{62}$ can therefore be formulated as $In^{2+}{}_2In^{+}{}_3 = In_5^{7+}$ and $In^{2+}{}_2In^{+}{}_4 = In_6^{8+}$. A more quantitative picture of the bonding is gained from bond length–bond strength calculations. Using $s_i(\text{In–O}) = [d(\text{In–O})/1.959]^{-7.0}$ to derive partial bond orders s_i,[29] one gets the following individual bond-order sums $\sum s_i$: In(1), 1.0; In(2), 1.25; In(3), 1.6; In(4), 1.7; In(5), 1.3; In(6), 1.0. According to this calculation, the In_5 chain composed of In(4), In(5), and In(6) has to be formulated as In_5^{7+} and the In_6 chain composed of In(1), In(2), and In(3) as $In_6^{7.7+} \approx In_6^{8+}$ in accordance with the assumption above.

Usually In^+ ions have a lone-pair configuration, but in the case of $In_{11}Mo_{40}O_{62}$ a number of structural details clearly indicate that the In^+ ions use all their valence electrons for metal–metal bonding. First, all In–In distances within the In_5 and In_6 units are extremely short. Second, the In^+ ions do not have the asymmetric coordination that is expected for a lone-pair ion. The central atom In(6) in the In_5 unit has an environment of four oxygen atoms in an exactly planar arrangement. According to the bond-order sum $\sum s_i(\text{In–O}) = 1.0$ this atom has to be formulated as In^+. But it is strongly bonded to two neighbors of the type In(5) via single bonds. Assuming that all valence electrons of In(6) are used in hetero- as well as homonuclear bonds, the discussion of bonding can be extended to In(5), which is capable of forming a bond with $s \approx 0.7$ to In(4), and following this line of argument, the valence electrons of In(4) are not entirely used for In–In bonding ($s \approx 0.7$) and In–O bonding ($\sum s_i = 1.7$). The interaction between In(4) and In(3), which belongs to the adjacent In_6 unit, is essentially nonbonding (d = 333 pm). This interpretation of bonding in the In_5 unit is also valid for the In_6 unit and accounts both for the sequence of In–In distances and for the specific variations of the coordination polyhedra around all In atoms. The In–In bonds found in the chainlike In_5^{7+} and In_6^{8+} ions add further evidence to the assumption[8] that strong In–In bonds also occur in the chains of In atoms in the structure of $InMo_4O_6$, somewhat resembling the bonding in the chains of mercury atoms in $Hg_{2.86}AsF_6$.[34]

Mo–O. The formal description of the bonding in $In_{11}Mo_{40}O_{62}$ as $(In_5)^{+7}(In_6)^{8+}(Mo_{40}O_{62})^{15-}$ has to be supported by the corresponding bond order sum for all Mo–O bonds. As pointed out by McCarley,[35] the function $s_i(\text{Mo–O}) = [d(\text{Mo–O})/1.882]^{-6.0}$ accounts well for a number of ternary molybdenum oxides with condensed clusters. Using this function, one gets a formal charge of 16.5− for the anions instead of 15− (assuming O^{2-} ions), which is in reasonably good agreement. Dividing the formal charge 16.5− as derived from the analysis of Mo–O bonds between the two anionic clusters, 8.85 and 7.65 for $Mo_{22}O_{34}$ and $Mo_{18}O_{28}$, respectively, leads to the (expected) result that the larger cluster has a slightly higher charge.

The calculation of bond orders for Mo–O bonds leads to a further interesting result. The bond-order sum $\sum s_i(\text{Mo–O})$ for the $Mo_{18}O_{28}$ cluster is 48.35, and for the $Mo_{22}O_{34}$ cluster it is 59.15. The difference of 10.80 corresponds to the bond-order sum of a fragment Mo_4O_6. The octahedra chain in the compound $InMo_4O_6$ is built up of such fragments only, leading to a de-

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Table III. Interatomic Distances ($d \leqslant 340$ pm) in the Structure of $In_{11}Mo_{40}O_{62}$[a]

In(1): –In(1′) = 266.7; –In(2) = 266.0; –O(4′) = 245.8; –O(5) = 250.7; –O(16‴) = 245.3; –O(17‴) = 244.4
In(2): –In(1) = 266.0; –In(3) = 268.9; –O(8) = 226.9; –O(13) = 249.0; –O(23‴) = 255.1; –O(27‴) = 225.2
In(3): –In(2) = 268.9; –In(4) = 332.9; –O(20‴) = 214.7; –O(21‴) = 223.9; O(26) = 227.6; –O(23‴) = 290.6; –O(24) = 292.9
In(4): –In(3) = 332.9; –In(5) = 266.4; –O(20′) = 222.1; –O(25) = 298.8; –O(26) = 215.9; –O(30‴) = 218.5; –O(32‴) = 297.4;
In(5): –In(4) = 266.4; –In(6) = 262.4; –O(6′) = 243.2; –O(14) = 229.5; –O(15‴) = 222.7; –O(32) = 250.0
In(6): –In(5) = 262.4; –In(5′) = 262.4; –O(1‴) = 233.7; –O(3) = 261.8; –O(7‴) = 233.9; –O(9‴) = 269.3
Mo(1): –Mo(2) = 277.3; –Mo(4) = 278.5; –Mo(5) = 276.3; –Mo(6) = 278.2; –O(21) = 200.8; –O(22‴) = 196.4; –O(25) = 215.3; –O(26) = 200.6; –O(28‴) = 221.2
Mo(2): –Mo(1) = 277.3; –Mo(3) = 281.2; –Mo(5) = 283.6; –Mo(6) = 280.9; –Mo(7) = 283.96; –Mo(9) = 274.0; –Mo(10) = 273.4; –O(13) = 203.6; –O(22‴) = 211.6; –O(23) = 205.8; O(33‴) = 197.4
Mo(3): –Mo(2) = 281.3; –Mo(4) = 276.9; –Mo(5) = 277.9; –Mo(6) = 281.8; –Mo(8) = 281.9; –Mo(9) = 272.4; –Mo(10) = 272.9; –O(8) = 210.0; –O(10) = 198.2; –O(11) = 206.6; –O(27) = 207.9
Mo(4): –Mo(1) = 278.5; –Mo(3) = 276.9; –Mo(5) = 283.5; –Mo(6) = 264.0; –O(11) = 189.1; –O(24) = 212.9; –O(25) = 206.1; –O(29) = 198.2; –O(30) = 224.0
Mo(5): –Mo(1) = 276.3; –Mo(2) = 283.6; –Mo(3) = 277.9; –Mo(4) = 283.95; –Mo(10) = 267.1; –O(8) = 207.6; –O(21) = 209.3; –O(22) = 209.9; –O(23) = 199.7
Mo(6): –Mo(1) = 278.2; –Mo(2) = 280.9; –Mo(3) = 281.8; –Mo(4) = 264.0; –Mo(9) = 274.9; –O(11‴) = 211.8; –O(13) = 201.6; –O(26) = 208.7; –O(27) = 208.3; –O(29) = 203.1
Mo(7): –Mo(2) = 283.6; Mo(7′) = 284.4; –Mo(8) = 273.4; –Mo(9) = 282.7; –Mo(10) = 287.6; –Mo(11) = 277.3; –Mo(12) = 277.6; –O(4′) = 203.4; –O(16) = 203.8; –O(33‴) = 211.1; –O(34‴) = 204.7
Mo(8): –Mo(3) = 281.9; –Mo(7) = 273.4; –Mo(8′) = 283.6; –Mo(9) = 284.7; –Mo(10) = 285.0; –Mo(11) = 277.3; –Mo(12) = 276.8; –O(5) = 206.3; –O(10) = 201.7; –O(12) = 199.8; –O(17) = 207.1
Mo(9): –Mo(2) = 274.0; –Mo(3) = 272.4; –Mo(6) = 274.9; –Mo(7) = 282.7; –Mo(8) = 284.7; –Mo(11) = 293.8; –O(4′) = 204.7; –O(10‴) = 212.7; –O(13) = 204.7; –O(17) = 210.6; –O(27) = 203.3
Mo(10): –Mo(2) = 273.4; –Mo(3) = 272.9; –Mo(5) = 267.1; –Mo(7) = 287.6; –Mo(8) = 285.0; –Mo(12) = 300.2; –O(5) = 210.7; –O(8) = 208.2; –O(16) = 208.2; O(23) = 206.4; –O(33) = 210.1
Mo(11): –Mo(7) = 277.3; –Mo(7′) = 277.3; –Mo(8) = 277.3; –Mo(8′) = 277.3; –Mo(9) = 293.8; –Mo(9) = 293.8; –O(4) = 201.5; –O(4′) = 201.5; –O(12‴) = 216.1; –O(17) = 203.1; –O(17′) = 203.1
Mo(12): –Mo(7) = 277.6; –Mo(7‴) = 277.6; –Mo(8) = 276.8; –Mo(8) = 276.8; –Mo(10) = 300.2; –Mo(10′) = 300.2; –O(5) = 201.3; –O(5′) = 201.3; –O(16) = 203.6; –O(16′) = 203.6; –O(34) = 211.4
Mo(13): –Mo(14) = 276.1; –Mo(16) = 278.2; –Mo(17) = 277.1; –Mo(18) = 279.5; –O(18‴) = 192.4; –O(20‴) = 202.2; –O(24) = 210.6; –O(29‴) = 223.6; –O(30) = 203.6
Mo(14): –Mo(13) = 276.1; –Mo(15) = 283.0; –Mo(17) = 281.3; –Mo(18) = 282.2; –Mo(20) = 282.6; –Mo(21) = 273.3; –Mo(22) = 272.9; –O(2‴) = 197.7; –O(6‴) = 207.4; –O(18‴) = 208.8; –O(32) = 207.4
Mo(15): –Mo(14) = 283.0; –Mo(16) = 275.8; –Mo(17) = 275.6; –Mo(18) = 283.2; –Mo(19) = 279.8; –Mo(21) = 271.6; –Mo(22) = 271.1; –O(14) ; 206.1; –O(15) = 206.3; –O(19) = 209.9; –O(31) = 199.2
Mo(16): –Mo(13) = 278.2; –Mo(15) = 275.8; –Mo(17) = 283.8; –Mo(18) = 265.0; –O(13) = 193.7; –O(21) = 217.4; –O(24) = 209.4; –O(25) = 211.7; –O(28) = 192.0
Mo(17): –Mo(13) = 277.1; –Mo(14) = 281.3; –Mo(15) = 275.6; –Mo(16) = 283.8; –Mo(22) = 265.1; –O(14) = 203.0; –O(18) = 214.3; –O(25) = 215.2; –O(30) = 200.8; –O(32) = 208.2
Mo(18): –Mo(13) = 279.5; –Mo(14) = 282.2; –Mo(15) = 283.2; –Mo(16) = 265.0; –Mo(21) = 267.5; –O(6‴) = 210.6; –O(15) = 204.1; –O(19‴) = 203.4; –O(20‴) = 213.9; –O(28) = 214.6
Mo(19): –Mo(15) = 279.7; –Mo(15′) = 279.7; –Mo(20) = 267.6; –Mo(21) = 284.2; –Mo(21′) = 284.2; –Mo(22) = 282.6; –Mo(22′) = 282.6; –O(3) = 206.3; –O(9) = 203.7; –O(31) = 210.6; –O(31′) = 210.6
Mo(20): –Mo(14) = 282.6; –Mo(14′) = 282.6; –Mo(19) = 267.6; –Mo(21) = 284.0; –Mo(21′) = 284.0; –Mo(22) = 284.0; –Mo(22′) = 284.0; –O(1‴) = 206.6; –O(2″) = 208.7; –O(2‴) = 208.7; –O(7) = 206.8
Mo(21): –Mo(14) = 273.3; –Mo(15) = 271.6; –Mo(18) = 267.5; –Mo(19) = 284.2; –Mo(20) = 284.0; –Mo(21′) = 310.1; –O(1‴) = 212.2; –O(6‴) = 210.0; –O(9) = 205.1; –O(15) = 209.2; –O(31‴) = 207.6
Mo(22): –Mo(14) = 272.9; –Mo(15) = 271.1; –Mo(17) = 265.1; –Mo(19) = 282.6; –Mo(20) = 284.0; –Mo(22′) = 312.5; –O(2) = 212.1; –O(3) = 206.9; –O(7) = 209.8; –O(14) = 202.4; –O(32) = 201.1

[a] Distances to equivalent atoms are assigned according to the following notation: single prime, $\bar{x}$, y, z; double prime, $\bar{x}$, $\bar{y}$, $z + {}^1/_2$; triple prime, x, $\bar{y}$, $z + {}^1/_2$. The standard deviations for d(In–In) and d(Mo–Mo) are 0.1–0.2 pm, and for d(In–O) and d(Mo–O) they are 0.9–2.2 pm.

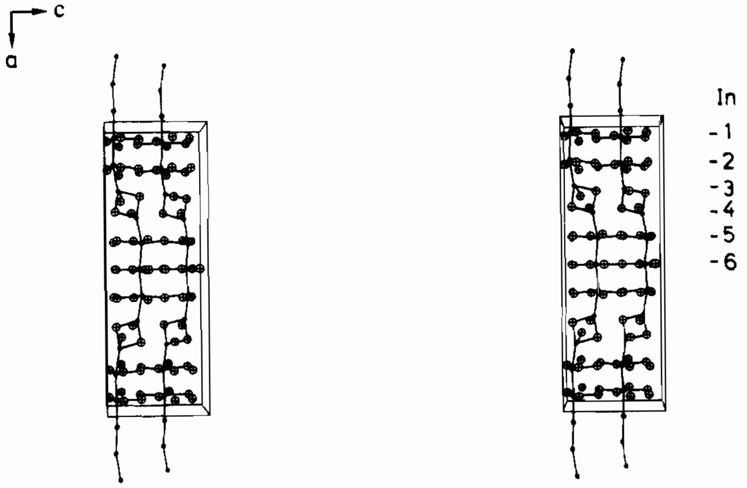

Figure 4. Stereoview of a part of the unit cell content of $In_{11}Mo_{40}O_{62}$ along [010]. Only the In atoms with their oxygen coordination are shown. The In atoms are labeled according to Table IIa.

scription as $In^{1.2+}Mo_4O_6^{1.2-}$, in very good agreement with the description $In^{1.15+}Mo_4O_6^{1.15-}$ found from an analysis of Mo–O distances in the actual compound by McCarley.[8]

Although the bond length–bond strength concept works remarkably well for reduced ternary molybdenum oxides on the basis of averaged values, a discussion of bond-order sums for individual atoms suffers considerably from uncertainties of the oxygen positions. For example, independent refinements of the atomic parameters in $In_{11}Mo_{40}O_{62}$ result in oxygen positions that in some cases differ by twice the standard deviations, leading to an uncertainty of 10% in the bond-order sum for an individual oxygen atom in its metal environment. In spite of these uncertainties the differences in the bond-order sums of oxygen atoms of different functionality on the whole seem to be real: O(20) and O(26) are atoms of the type X^i, which are both coordinated to two In atoms each. The values $\sum s_i(O–Mo) = 1.12$ and 1.21 are very low but add up to approximately 2.0 with the corresponding contributions $\sum s_i(O–In) = 0.95$ and 0.86, respectively. In contrast O(24) and O(25) (both X^{i-i}) have no In contacts and are characterized by $\sum s_i(O–Mo) = 1.91$ and 1.96. The same holds for O(11) and O(19), both of the type X^{i-a}, in equivalent positions of the $(M_6)_5$ and $(M_6)_4$ units (2.03 and 1.99, respectively). The average bond-order sum 1.82 for all O atoms of the type X^{i-a} is reasonable due to the fact that further small contributions (≈ 0.06) might come from more distant ($330 \leq d(In–O) \leq 400$ pm) In atoms. The range of 1.71–2.03 for individual oxygen atoms of the kind X^{i-a} reflects, however, positional uncertainties. A scatter of values (1.54–1.89) is observed for $\sum s_i(O–Mo)$ for the atoms of the kind X^i, which are coordinated to only one close In neighbor, adding $\sum s_i(O–In)$ from 0.44 to 0.14.

As a rule both contributions supplement each other to yield values near 2.0. The averaged values 1.73 (O–Mo) and 0.29 (O–In) are in excellent agreement with expectation.

Mo–Mo. The Mo–Mo distances in the $(M_6)_4$ andd $(M_6)_5$ units cover a broad spectrum from 264 to 312 pm. The longest distances within the clusters are only slightly shorter than the intercluster Mo–Mo distances (320 pm). The variations of bond lengths in the $(M_6)_4$ and $(M_6)_5$ units follow very similar patterns insofar as the shared edges of the central octahedron in the $(M_6)_5$ unit as well as the central shared edge in the $(M_6)_4$ unit are short (273 and 268 pm, respectively), followed by parallel edges that are long (281 and 283 pm) and short edges again at the ends of the chains (278 pm in both units). All other distances in the octahedral bases decrease steadily in the direction from the center to the ends of the cluster chains. A remarkable variation of distances between apex atom occurs. The apex atoms at the ends of the chains are very close to each other (267 and 265 pm for the $(M_6)_4$ unit and 267 and 275 pm for the $(M_6)_5$ unit), whereas the separation between apex atoms of the central octahedra are large (310 and 312 pm in the $(M_6)_4$ unit and 300 and 294 pm in the $(M_6)_5$ unit). The specific distortion of the Mo octahedra in the short chains of $In_{11}Mo_{40}O_{62}$ displays a close relationship to the distortion in the infinite chains occurring in $ZnMo_8O_{10}$.[35] In the structure of that compound, octahedra are coupled pairwise to form short bonds between their apex atoms whereas the bond lengths of the shared edges increased.

The above mentioned distortions cannot be explained in terms of local strains due to the interconnection as in the chains of $ZnMo_8O_{10}$ or due to any distorted environments of the cluster units in $In_{11}Mo_{40}O_{62}$. The distortions are likely to be of electronic origin. According to extended Hückel calculations[18] the number of electrons entering metal–metal bonding states in a Mo_4O_6 chain is approximately 13 per Mo_4 fragment. Exceeding this electron concentration leads to the occupation of band states involving the $d_{x^2-y^2}$ orbitals of the apex atoms, and these states are antibonding with respect to the interactions between these atoms. Careful analysis of bond order sums ($\sum s_i(Mo–O) + \sum s_i(Mo–Mo)$) performed by McCarley[35] indeed give clear evidence for a critical value of the valence electron concentration beyond which electrons occupy metal–metal antibonding states. As a consequence the chains of octahedra become distorted. A rather qualitative argument allows a first understanding of the characteristic distortions in the $(M_6)_4$ and $(M_6)_5$ units of $In_{11}Mo_{40}O_{62}$. The bonding between the apex atoms in these units can be discussed in terms of MO schemes for chains of four and five atoms. Linear combinations of the $d_{x^2-y^2}$ orbitals lead to sequences of two bonding and two antibonding states in the case of the M_4 chains and two bonding, one nonbonding, and two antibonding states for the M_5 chain. Occupation of all bonding orbitals and the nonbonding orbitals results in the formation of bonds with the atoms at the ends of the chains with their neighbors but with effectively nonbonding interactions of the atoms in the chain centers. Other structural details of the $(M_6)_4$ and $(M_6)_5$ units, e.g. the short distances of 265 and 276 pm, involving Mo(16) and Mo(18) and Mo(1) and Mo(5), call for a complete MO calculation.

The Pauling type formula $d = 261.4 - 60 \log s^{8,36}$ has been used to calculate Mo–Mo bond-order sums to yield an average value of $\sum s_i(Mo–Mo) = 3.1$ per Mo atom in $In_{11}Mo_{40}O_{62}$. Together with the average value $\sum s_i(Mo–O) = 2.7$, this adds up to a total bond order of 5.8 for one Mo atom. This value is in a good agreement with the range of total bond-order sums 5.8–6.0 calculated[35] for systems with infinite Mo_4O_6 chains. From a formula $In_{11}{}^{15+}Mo_{40}O_{62}{}^{15-}$ an average value $\sum s_i(Mo–Mo) = 3.3$ is expected. The difference from the 3.1 value indicates that not all Mo valence electrons are involved in Mo–Mo bonding interactions. In an alternative interpretation one might argue that the rigid framework of the structure does not allow a free approach between Mo atoms. (Similar arguments might hold for the In atoms.)

A detailed analysis of the bond-order sums for the Mo atoms in $In_{11}Mo_{40}O_{62}$ shows that most of the atoms have values between 5.5 and 6.0. Highest values are found for those atoms (Mo(2), Mo(3), Mo(14), and Mo(15) that belong to the stretched edges shared between octahedra (6.0, 6.1, 6.0, and 6.3, respectively). The high value of 6.3, which of course is chemically unreasonable, provides a hint for the possible error of these bond-order sums. On the other hand we are convinced that the unusually low values found for the atoms at the ends of the $(M_6)_4$ unit (Mo(13), Mo(16)) and the $(M_6)_5$ unit (M(1), Mo(4)) are relevant. The bond-order sums of M(4) and Mo(16) can be raised to 5.8 by assuming some bonding with (three) Mo atoms of an adjacent unit at distances near 320 pm. Such additional bonding, though, cannot be taken into account for Mo(1) and Mo(13), which both have a bond-order sum of 5.1. The contribution of Mo–O bonding is high (near 3.0) for both atoms. It is the contribution of Mo–Mo bonding that is very low. We chose different approaches to calculate the Mo–Mo bond orders, e.g. the exponent-type expression used to analyse distances in Chevrel phases.[37] But there exist no values for the reference distance and the exponent, as can be shown in a systematic way, where the bond-order sums for Mo(1) and Mo(13) equal the average bond-order sum of the other Mo atoms. The low values for Mo(1) and Mo(13) are difficult to understand. Do they indicate some interaction with (three) In atoms in the distance range 330–350 pm? Do they indicate nonbonding electrons in the shells of these atoms? Can these atoms be replaced by niobium atoms?

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Registry No. $In_{11}Mo_{40}O_{62}$, 103691-57-2; MoO_2, 18868-43-4; Mo, 7439-98-7; In, 7440-74-6.

Supplementary Material Available: Table IIb, anisotropic thermal parameters (2 pages); a listing of observed and calculated structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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(38) (a) $F = \sum |F_o - |F_c|| / \sum F_o$. (b) $R = \sum (|F_o - |F_c|| w^{1/2}) / \sum F_o w^{1/2}$; $w = 1/\sigma^2(I)$. (c) $F^* = F(1 - XF^2/(\sin \theta))$; $X = 2 \times 10^{-4}$.