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The Crystal Structure of the Cesium Bronze $Cs(Mo_{0.95}W_{0.05})_7O_{21}$

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The crystal structure of $Cs(Mo_{0.95}W_{0.05})_7O_{21}$ has been determined from a single-crystal X-ray diffraction experiment. The crystal is orthorhombic (space group *Pnma*), with a = 17.638(5), b = 5.448(1), c = 17.945(7)Å, and Z = 4, for a formula unit $Cs(Mo_{0.95}W_{0.05})_7O_{21}$. The intensities ($I$) of 1431 reflections, for which $I > 3\sigma(I)$, were considered observed. The structure was solved by direct and Fourier methods and refined by least squares to a value of 0.019 for the conventional R factor. It is based on the corner sharing of molybdenum coordination polyhedra, forming chains of five very distorted "octahedra" and two terminal tetrahedra. These chains, similar to those found in the structures of γ- and η-Mo_4O_{11}, pack to form a three-dimensional network, thus generating voids in which the Cs atoms are located with a coordination number of 12.

1. Introduction

Many transition-metal oxides of the type MO_{n-x} and so-called bronze oxides of the type A_xMO_n (A is typically an alkali-metal atom) show metallic conduction, based on partial filling of a π^* band with a strong d character derived from the d orbitals of the transition metal (*1*). When the transition metal is molybdenum the conductive features of this class of compounds seem to depend on the effective charges of the transition-metal atoms and therefore on the Mo–O distances in a sensitive way. For this reason accurate refinements of the crystal structures are required, when correlations are sought between those effective charges and the conduction properties of these compounds.

The structures of most molybdenum oxides are based on the linking of oxygen-distorted coordination octahedra and tetrahedra by corner and edge sharing. In the bronze oxides insertion of metal A may modify the type of linking. Three basic types of linking have been found: one essentially based on edge sharing, as found, e.g., in MoO_3 (*2*), one characteristic of the structures of compounds of general type $Mo_n O_{3n-1}$, derived from that of ReO_3 by crystallographic shearing (*3*), and a third one based on corner sharing of octahedra and tetrahedra, found, e.g., in γ-Mo_4O_{11} (*4*) and in η-Mo_4O_{11} (*5*). The present study started when a Cs–Mo bronze oxide, prepared by a new

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TABLE I

Positional and Isotropic Equivalent Thermal Parameters with Their Estimated Standard Deviations. Multiplicities Are Also Given

Atom	X	Y	Z	B(Å^2)	Multiplicity
Cs	0.13276(3)	0.250	0.60728(3)	1.86(1)	0.50
Mo1	0.33855(4)	0.250	0.95066(4)	0.69(1)	0.50
Mo2	0.04283(3)	0.250	0.37597(3)	0.48(1)	0.54
Mo3	−0.04932(4)	0.250	0.76688(4)	0.55(1)	0.50
Mo4	0.43111(3)	0.750	0.59379(3)	0.62(1)	0.54
Mo5	0.35314(3)	0.250	0.47381(4)	0.51(1)	0.50
Mo6	0.15876(3)	0.250	0.82915(3)	0.390(8)	0.63
Mo7	0.27441(4)	0.750	0.74841(4)	0.57(1)	0.50
O1	0.2678(3)	0.250	0.8816(3)	1.3(1)	0.50
O2	0.2006(3)	0.750	0.5370(3)	1.3(1)	0.50
O3	0.1026(2)	0.4849(8)	0.4423(2)	1.18(7)	1.00
O4	0.0367(4)	0.750	0.5717(3)	1.5(1)	0.50
O5	−0.0231(2)	0.0028(8)	0.6859(2)	1.39(8)	1.00
O6	0.0782(3)	0.250	0.7735(3)	0.9(1)	0.50
O7	−0.1433(3)	0.250	0.7510(4)	1.6(1)	0.50
O8	−0.0427(2)	0.0013(8)	0.8360(2)	1.26(7)	1.00
O9	0.5152(3)	0.750	0.5466(3)	1.0(1)	0.50
O10	0.3778(2)	0.5023(8)	0.5377(2)	1.08(7)	1.00
O11	0.2572(3)	0.250	0.4792(4)	1.5(1)	0.50
O12	0.3624(2)	0.4978(8)	0.3894(2)	1.19(7)	1.00
O13	0.2130(2)	0.4892(8)	0.7561(2)	1.09(7)	1.00
O14	0.3219(3)	0.750	0.6632(3)	1.1(1)	0.50
O15	0.1603(3)	0.250	0.3208(3)	1.3(1)	0.50

Note. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as

$$\tfrac{4}{3}\,[a^2 B(1,1) + b^2 B(2,2) + c^2 B(3,3) + a\,b\cos\gamma\, B(1,2) + a\,c\cos\beta\, B(1,3) + b\,c\cos\alpha\, B(2,3)].$$

method (*6*), showed a powder diffraction pattern different from all those expected for previously determined structures of this type (*1*).

2. Experimental

During the preparation of bronze oxides by a general method (*6*), based on the heating in a vacuum of mixtures of a metal halide, WO_2, and a transition-metal oxide, a small amount of crystals of the title compound was obtained, according to the reaction scheme

$$x\mathrm{CsCl} + x/2\ \mathrm{WO_2} + \mathrm{MoO_3} \rightarrow \mathrm{Cs}_x\mathrm{MoO_3} + x/2\ \mathrm{WO_2Cl_2}\uparrow .$$

WO_2 was used in the amount necessary for obtaining a compound with $x = 0.25$. The result of this attempt was a partial exchange Mo↔W (see below) and the formation of $Cs(Mo_{0.95}W_{0.05})_7O_{21}$, with $x = 0.14$.

The crystal is orthorhombic (space group *Pnma*), with $a = 17.638(5)$, $b = 5.448(1)$, $c = 17.945(7)$Å, and $Z = 4$, for a formula unit $Cs(Mo_{0.95}W_{0.05})_7O_{21}$.

A total of 4387 reflections were measured (Mo$K\alpha$) by the ω-scan technique on a CAD4 NONIUS X-ray four-circle diffractometer and were corrected for Lorentz, polarization, and absorption effects. Out of 2664

TABLE II

General Temperature Factor Expressions—*B*s.

Name	*B*(1, 1)	*B*(2, 2)	*B*(3, 3)	*B*(1, 2)	*B*(1, 3)	*B*(2, 3)
Cs	2.63(2)	1.75(2)	1.22(2)	0	0.29(2)	0
Mo1	0.75(2)	0.74(2)	0.59(2)	0	0.03(2)	0
Mo2	0.62(2)	0.45(2)	0.37(2)	0	0.04(2)	0
Mo3	0.56(2)	0.45(2)	0.65(2)	0	−0.06(2)	0
Mo4	0.57(2)	0.87(2)	0.44(2)	0	0.04(2)	0
Mo5	0.58(2)	0.39(2)	0.55(2)	0	−0.00(2)	0
Mo6	0.39(2)	0.42(2)	0.36(2)	0	0.02(1)	0
Mo7	0.56(2)	0.61(2)	0.54(2)	0	0.07(2)	0
O1	1.1(2)	1.1(2)	1.7(2)	0	−0.6(2)	0
O2	1.8(2)	1.5(3)	0.8(2)	0	−0.3(2)	0
O3	1.3(1)	1.2(2)	1.1(1)	−0.1(1)	0.0(1)	−0.3(1)
O4	1.8(2)	1.2(2)	1.6(2)	0	0.3(2)	0
O5	1.4(1)	1.1(2)	1.6(2)	−0.2(2)	−0.0(1)	−0.0(2)
O6	0.8(2)	0.9(2)	1.1(2)	0	−0.2(2)	0
O7	1.0(2)	2.2(3)	1.7(2)	0	−0.5(2)	0
O8	1.4(1)	1.2(2)	1.2(1)	−0.0(1)	0.2(1)	0.1(2)
O9	1.4(2)	0.7(2)	0.8(2)	0	0.2(2)	0
O10	1.2(1)	1.4(2)	0.6(1)	−0.3(1)	−0.1(1)	−0.0(1)
O11	0.8(2)	1.8(3)	1.9(2)	0	0.0(2)	0
O12	1.4(1)	1.4(2)	0.8(1)	0.1(1)	−0.1(1)	0.2(2)
O13	1.0(1)	1.0(2)	1.2(1)	0.0(1)	0.0(1)	0.3(2)
O14	1.1(2)	1.4(2)	0.8(2)	0	0.4(2)	0
O15	1.5(2)	1.3(2)	1.2(2)	0	−0.0(2)	0

Note. The form of the anisotropic thermal parameter is

$$\exp[-\tfrac{1}{4}\,(h^2\overset{*}{a}{}^2B(1,1) + k^2\overset{*}{b}{}^2B(2,2) + l^2\overset{*}{c}{}^2B(3,3) + 2hk\overset{*}{a}\overset{*}{b}B(1,2) + 2hl\overset{*}{a}\overset{*}{c}B(1,3) + 2kl\overset{*}{b}\overset{*}{c}B(2,3))]$$

independent reflections, 1431 intensities were found larger than 3σ and, on this basis, were considered observed. The structure was solved by direct and Fourier methods and refined by least squares to a value of 0.019 for the conventional *R* factor.

The atomic fractional coordinates and the isotropic equivalent thermal parameter values are given in Table I and the anisotropic temperature factors in Table II. A list of observed and calculated structure factors has been submitted as supplementary material.

A projection of the structure along the *b* axis is presented in Fig. 1.

At the end of the least-squares refinement we found for the occupancies of three Mo sites (Mo(2), Mo(4), and Mo(6), see Table I) values larger than 0.5. (This value takes into account the multiplicity factor due to the site symmetry). In particular, for Mo(6), the refinement occupancy parameter is 0.63, a value very significantly higher than 0.5. This result can be explained by the statistical presence of W atoms in this site (see above), as confirmed by the microprobe analysis of many crystals belonging to the same batch of the crystal used in the diffraction experiment, and by the fact that the Mo(6) isotropic thermal parameter (B = 0.39 Å^2) is significantly smaller than the others. Unfortunately it was not possible to perform the microprobe analysis on the particular crystal used in the structural analysis, since it

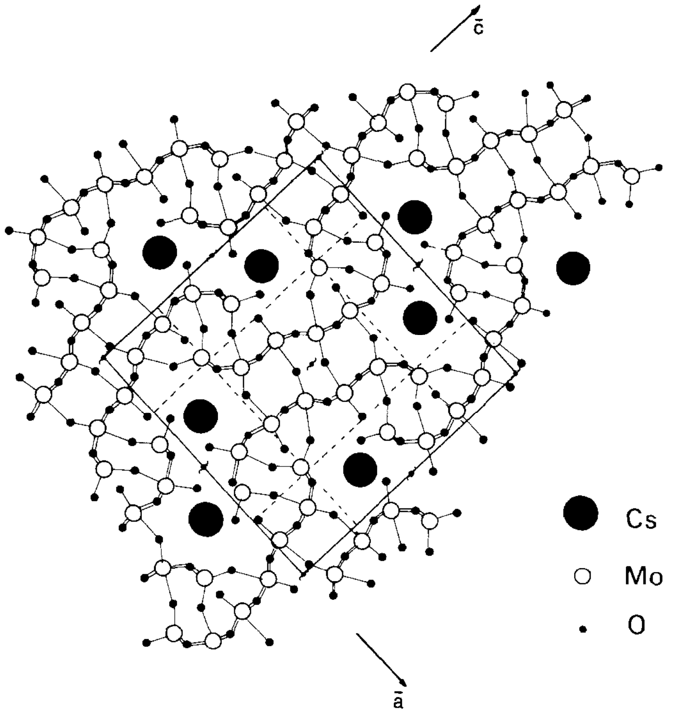

FIG. 1. Projection of the structure along the *b* axis of the orthorhombic unit cell.

was lost soon after the diffraction experiment, while undergoing the preparatory manipulations in the SEM laboratory.

3. Results

The crystal structure is based on the corner sharing of molybdenum coordination polyhedra (tetrahedra and octahedra), forming chains of five octahedra and two terminal tetrahedra (See Fig. 2, and Table III).

All these polyhedra are distorted and their approximate symmetry is T_d for Mo(1) and Mo(7), C_{3v} for Mo(2), Mo(3), Mo(5), and Mo(6), and C_{4v} for Mo(4), the distortion being much more severe in the case of the five octahedra.

The chains of polyhedra are linked in couples by corner sharing of four octahedra and the couples are bound to each other by the coordination tetrahedra of Mo(1) and Mo(7) (hereafter the coordination polyhedron of Mo(*n*) will be referred to as the Mo(*n*) polyhedron) (Fig. 2).

The Mo(1) tetrahedron bridges the Mo(2) and the Mo(6) octahedra and the Mo(7) tetrahedron shares corners with the latter two octahedra and with the Mo(4) octahedron.

The couples of chains, due to the periodicity along the *b* axis, generate infinite slabs whose inner cores have a very distorted ReO_3 type of structure (Fig. 3). As shown in Fig. 1, the resulting three-dimensional network of coordination polyhedra creates voids in which the Cs atoms are located with a coordination number (C.N.) = 12.

4. Discussion

The structure of the title compound may be related to those of γ-Mo_4O_{11} (*4*), and η-Mo_4O_{11} (*5*), these oxides being also formed

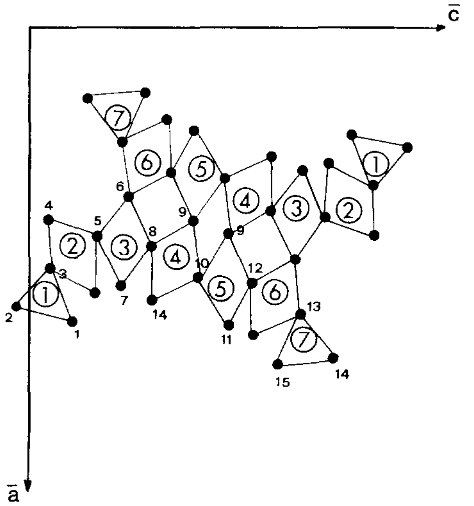

FIG. 2. Projection along the *b* axis of a couple of chains of coordination polyhedra with labeling of the Mo atoms.

by chains of corner-sharing polyhedra (six octahedra and two final tetrahedra). Indeed the similarity between the three structures is strong and the following matrix notation fairly accurately represents the transformation from the unit cell of γ-Mo_4O_{11} or from that of the strictly related η phase (*5*) to that of the present crystal.

$$\begin{bmatrix} a' \\ b' \\ c' \end{bmatrix} = \begin{bmatrix} 1/2 & 0 & -2 \\ 0 & 1 & 0 \\ 1/2 & 0 & 2 \end{bmatrix} \begin{bmatrix} a \\ b \\ c \end{bmatrix} .$$

The similarity is not only formal, since also in γ-Mo_4O_{11} and in η-Mo_4O_{11} slabs of ReO_3-type coordination polyhedra run parallel to the *b* axis (b = 5.45 Å for the three crystals). However, in the two oxides the slabs are not based on couples of chains as in the title compound. They are based on sets of parallel chains and have infinite extension also in the *c* axis direction, thus constituting layers normal to [100].

Thus the present crystal structure can be described as a deformed γ-Mo_4O_{11} (or η-Mo_4O_{11}) structure with wide tunnels running parallel to the *b* axis and accommodating the cesium atoms in sites of C.N. = 12. One can describe this deformation as a two-step process (Fig. 4):

(i) the cesium atom, when entering the structure, is included at the end of a couple of chains that open like a zip-fastener;

(ii) these deformed couples pack together in order to obtain the maximum number of oxygen atoms bridging them and a maximum coordination number (C.N. = 12) for Cs.

This possible deformation mechanism, allowing the insertion of Cs atoms, is in agreement with the most distinctive feature of this structure, i.e., the particular bridging action of one of the two terminal tetrahedra, linking not only two different chains but also two octahedra (Mo(2) and Mo(4)) belonging to the same neighboring chain. In this way this bridging action favors the formation of the parenthesis shape characteristic of these polyhedra chains.

Thus the structure of the title compound is based on the third type of linking of coordination polyhedra mentioned in the Introduction. This type of linking was never found in W oxides of similar stoichiometry and was reported only in structures in which at least one of the Mo atoms has its oxidation number in the range 5.0 to 5.8.

In this respect it is interesting to note that in the hexagonal Cs molybdenum bronze of similar composition ($Cs_{0.14}MoO_3$), also studied by us (*7*) and where no Mo atom has an oxidation number less than 5.85, the structure is based on both corner and edge-sharing of MoO_6 octahedra.

Bond strength calculations (*8*) based on the formula $s = (R/R_0)^{-N}$, where R_0 = 1.882 Å and N = 6, give for the oxidation numbers, v, of the Mo atoms in the asymmetric unit (a single chain) the values reported in Table IV. Consideration of this table and of Table III, where the mean square-root deviation ξ is taken as an index of deformation of a coordination polyhedra, suggests a

TABLE III

COORDINATION DISTANCES

	M–O		Average M–O (ξ)[a]
Tetrahedron	Mo–O1	1.758(6)	1.756
Mo(1)	Mo–O2	1.696(6)	(0.042)
	Mo–O3 × 2	1.785(5)	
Octahedron	Mo–O3 × 2	2.041(4)	
Mo(2)	Mo–O4	1.688(7)	1.945
	Mo–O5 × 2	1.803(5)	(0.223)
	Mo–O15	2.296(7)	
Octahedron	Mo–O5 × 2	2.034(5)	
Mo(3)	Mo–O6	2.251(6)	1.947
	Mo–O7	1.683(6)	(0.200)
	Mo–O8 × 2	1.841(5)	
Octahedron	Mo–O8 × 2	1.917(5)	
Mo(4)	Mo–O9	1.708(6)	1.949
	Mo–O10 × 2	1.928(4)	(0.189)
	Mo–O14	2.293(6)	
Octahedron	Mo–O9	2.351(6)	
Mo(5)	Mo–O10 × 2	1.842(4)	1.965
	Mo–O11	1.683(6)	(0.232)
	Mo–O12 × 2	2.035(5)	
Octahedron	Mo–O1	2.142(6)	
Mo(6)	Mo–O6	1.738(6)	1.936
	Mo–O12 × 2	1.788(5)	(0.183)
	Mo–O13 × 2	2.081(4)	
Tetrahedron	Mo–O13 × 2	1.792(4)	1.766
Mo(7)	Mo–O14	1.744(6)	(0.030)
	Mo–O15	1.736(7)	
Polyhedron	Cs–O2 × 2	3.231(4)	
Cs	Cs–O3 × 2	3.268(5)	
	Cs–O4 × 2	3.271(4)	3.265
	Cs–O5 × 2	3.371(4)	(0.067)
	Cs–O6	3.134(6)	
	Cs–O11	3.186(7)	
	Cs–O13 × 2	3.291(5)	

[a] ξ is the mean square root deviation, assumed in the text as an index of distortion of the coordination polyhedra.

correlation between ξ and v, with the smallest values found for atom Mo(4) (0.189 and 5.64, respectively) in the middle of the chain. The apparent violation observed for Mo(6) (with ξ and v values of 0.183 and 5.89) can possibly be explained by the important presence of W in this site (See the Experimental section).

Similar structures, based on chains of corner-sharing polyhedra or on more or less extended slabs of the ReO_3 type are given by the purple bronzes $K_{0.9}Mo_6O_{17}$ (*9*) and $Li_{0.9}Mo_6O_{17}$ (*10*), where the basic chain is formed by four octahedra and one terminal tetrahedron, and by $D_{0.99}MoO_3$ and β'-MoO_3 studied by neutron diffraction (*11*). In all these structures the oxidation number of at least one Mo atom is significantly smaller

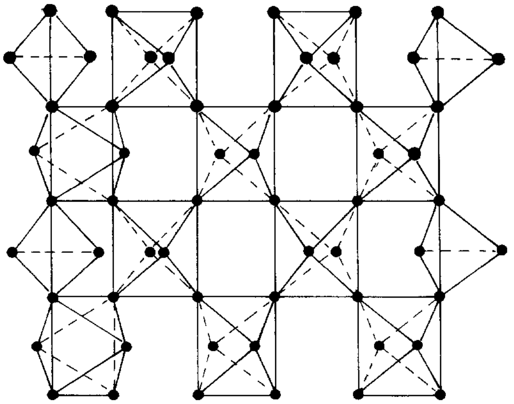

FIG. 3. Slab of coordination polyhedra showing the distorted ReO_3 type of structure. The vertical direction is parallel to the *b* axis.

than 5.8. In the case of the purple bronzes, the correlation between ξ and v is also verified, with the smallest values found in the middle of the chains. This appears to be a general rule (See also the cases of γ- and η-Mo_4O_{11}) (*4, 5*) and one may speculate on its relevance to the well known fact that the conduction properties of some of these materials are associated with the low oxidation numbers of the Mo atoms in the middle of the slabs formed by polyhedra chains.

Thus, not considering the "special" case of Mo(6) (see above), the less distorted octahedron in the chain is that of Mo(4), showing an approximate symmetry $C_{4}v$. In this respect it is worthwhile to note that the thermal ellipsoid of atom Mo(4) is strongly anisotropic, with its longest axis parallel to *b* ($B(2, 2) = 0.87$ Å^2), while for all the other Mo atoms the anisotropic thermal parameters are very close to each other. This feature may possibly be explained by a tendency of Mo(4) to distribute itself between two almost tetrahedral sites along a direction parallel to the *b* axis, as if it were trying to leave its "regular" octahedral position. This explanation can be proposed if one takes into account the fact that molybdenum often shows in oxygen compounds a tendency toward tetrahedral coordination, as pointed out by Kihlborg (*2*) and confirmed by our own results and by those obtained by others for comparable structures (*4, 5, 8, 9*), where the tetrahedra are much less distorted than the octahedra.

The average Cs–O distance is 3.265 Å (C.N. = 12) in very good agreement with the value of 3.269 Å found in cesium pentamolybdate, $Cs_2Mo_5O_{16}$ (*12*), for a comparable coordination number of 10, but significantly longer than the value of 3.125 Å ($Cs_{0.33}MoO_3$, C.N. = 8) (*13*), 3.16 Å

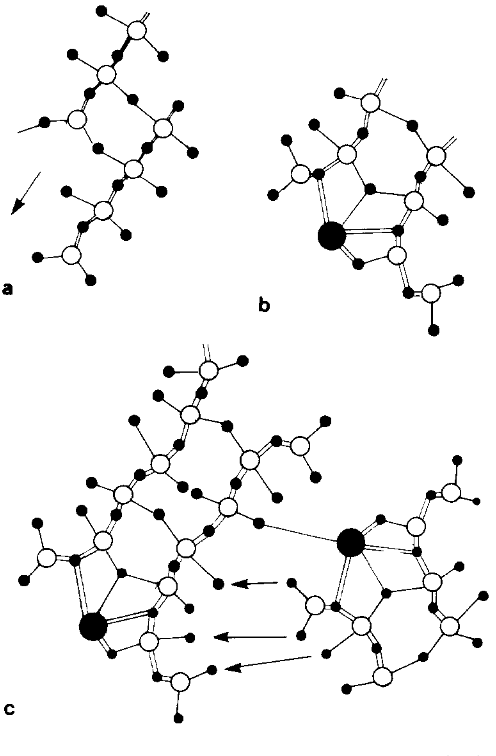

FIG. 4. (a) Two parallel chains in a structure similar to that of η- or γ-Mo_4O_{11} with the arrow indicating the direction along which the two slide relative to each other before opening like a zip-fastener for accommodating a Cs atom. (b) A Cs Atom inserted at the end of a couple of chains. (c) Two couples of chains pack together forming bonds as indicated by the arrows, in order to maximize the number of bridging oxygen atoms and the coordination number of cesium (C.N. = 12).

TABLE IV

COORDINATION BOND STRENGTHS[a] AND OXIDATION STATES (v) OF THE Mo ATOMS

	Mo1	Mo2	Mo3	Mo4	Mo5	Mo6	Mo7
O1	1.51					0.46	
O2	1.87						
O3 × 2	1.37	0.61					
O4		1.92					
O5 × 2		1.29	0.63				
O6			0.34			1.61	
O7			1.96				
O8 × 2			1.14	0.90			
O9				1.79	0.26		
O10 × 2				0.87	1.14		
O11					1.96		
O12 × 2					0.63	1.36	
O13 × 2						0.55	1.34
O14				0.31			1.58
O15		0.30					1.62
v	6.12	6.02	5.84	5.64	5.76	5.89	5.88

[a] Calculated on the basis of the Brown's formula $s_i = (R_i/R_0)^{-N}$, where $R_0 = 1.882$ Å and $N = 6$ (*8*). $v = \Sigma s_i$.

($Cs_{0.25}MoO_3$, C.N. = 8) (*14*), and 3.221 Å ($Cs_2Mo_7O_{22}$, C.N. = 9) (*12*) found for smaller coordination numbers.

5. Conclusions

It is well known that in any MoO_6 unit six hybrid metal orbitals overlap with six orbitals of the oxygen atoms to give a set of six bonding σ and six antibonding σ^* orbitals, while three metal $4d(t_{2g})$ orbitals overlap with three oxygen $p\pi$ orbitals, forming bonding π and antibonding π^* orbitals. These π bonding orbitals are responsible for the possible formation of localized Mo–O double bonds leading to distortion of the coordination polyhedron from its "regular" O_h symmetry. When Mo is in a lower oxidation state this distortion can be partly relieved by the extra electrons filling the π^* antibonding orbitals and thereby opening some of the Mo–O double bonds, giving rise to a more regular octahedron. This is the case of the Mo(4) octahedron in which only one Mo–O distance is shorter than 1.9 Å, while in all the other MoO_6 units in the chain there are three very short Mo–O distances leading to distorted octahedra of approximately symmetry C_{3v}.

This is a possibly interesting consideration, giving a physical basis to the observed correlation (see Discussion) between the distortion parameter, ξ, and v, the oxidation state of a given Mo atom in a MoO_6 unit. In this connection it is worthwhile to note that the electrons in the π^* antibonding orbitals are also those responsible for the conduction properties of some of these materials.

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