Monatshefte für Chemie 110, 311—320 (1979)

Monatshefte für Chemie

Mean Amplitudes of Vibration for $PMo_{12}O_{40}^{3-}$ and Its Fragments

S. J. Cyvin[a, *], **L. Lyhamn**[b], and **B. N. Cyvin**[a]

[a] Division of Physical Chemistry, The University of Trondheim, N-7034 Trondheim-NTH, Norway

[b] Department of Inorganic Chemistry, The University of Umeå, S-901 87 Umeå, Sweden

(Received 3 April 1978. Accepted 26 April 1978)

Mean amplitudes of vibration (l) are calculated for all 80 distance types in $PMo_{12}O_{40}^{3-}$. The values are discussed and some of them compared with the corresponding values calculated for five different fragments of the structure. Reasonable l values (< 0.12 Å at 298 K) are found even for extremely long distances, e.g. 0.078 Å at 298 K for the longest oxygen—oxygen distance (10.4 Å). The l values for bonded distances as well as a number of nonbonded distances have comparable magnitudes in the fragments and the whole structure; in other cases the fragment values are substantially higher.

(Keywords: Force field, calculation of mean amplitudes of vibration; $PMo_{12}O_{40}^{3-}$; *Vibration, mean amplitudes of)*

Mittlere Schwingungsamplituden für $PMo_{12}O_{40}^{3-}$ *und Fragmente*

Mittlere Schwingungsamplituden (l) für alle 80 Typen von Abständen in $PMo_{12}O_{40}^{3-}$ wurden berechnet. Die Werte werden diskutiert und einige werden mit denen von fünf verschiedenen Fragmenten der untersuchten Struktur verglichen. Es wurden auch für extrem große Distanzen plausible l-Werte ($< 0{,}12$ Å bei 298 K) gefunden (z. B. 0,078 Å bei 298 K für die größte O—O-Distanz 10,4 Å). Die l-Werte für Bindungslängen und auch für einige Abstände von nicht aneinander gebundenen Atomen weisen in den Fragmenten und in der Gesamtstruktur vergleichbare Größe auf; in anderen Fällen sind die Fragment-Werte allerdings bedeutend höher.

Introduction

A vibrational analysis of $PMo_{12}O_{40}^{3-}$ (T_d symmetry) has been described previously[1, 2]. In the present work the force field described in Ref.[1] was used to calculate the mean amplitudes of vibration (l)[3] for the

0026-9247/79/0110/0311/$ 02.00

$PMo_{12}O_{40}^{3-}$ ion. The quantities are defined as

$$l = < (\Delta r)^2 >^{\frac{1}{2}}$$

i.e. the root-mean-square deviations of interatomic distance as a result of molecular vibrations. The mean value is taken both in the quantum-mechanical and the statistical-mechanical sense. Hence the l values are temperature-dependent quantities. For further details the standard reference[3] may be consulted.

To our knowledge this is the largest structure (53 atoms) for which the computations of mean amplitudes have been successfully completed from a complete analysis according to the theory of small harmonic vibrations[3, 4]. Since the considered structure is an ion the calculated mean amplitudes are not the subject of immediate application in gas electron diffraction studies. Nevertheless they are supposed to be of special interest for several other reasons: (1) The results give us the opportunity to study, in general terms, the behaviour of mean amplitudes for very long nonbonded interatomic distances, namely up to 10.4 Å. (2) Calculated mean amplitudes for different fragments of the structure may be compared with the results for the corresponding distances in the whole ion. Thus it is possible to judge the validity of transfering mean amplitudes from fragments to the whole compound in cage structures like the one of the present investigation. (3) Finally the calculated mean amplitudes for ions as well as molecules are of general interest because they are physical quantities associated with the different bonded and nonbonded atom pairs. Those of the bonded pairs reflect the bond strength generally in a more meaningful way than the force constants.

In the present work the mean amplitudes (l values) were calculated at the temperatures of absolute zero and 298 K. Simultaneously the perpendicular amplitude correction coefficients (K values)[3, 5] were obtained. For sake of brevity only the l values at 298 K are reported and discussed here.

Molecular Model

A tetrahedral model (T_d; see Fig. 1) was assumed for the $PMo_{12}O_{40}^{3-}$ ion (a). It is an idealization of a structure deduced from single crystal data[6]. The central atom, P, is surrounded tetrahedrally by four oxygen atoms, O (P); see Fig. 2 (b). Each of the O (P) atoms forms the apex of a trigonal Mo_3O_7 group as shown in Fig. 2 (d). This fragment contains a puckered Mo_3O_3 ring. The four Mo_3O_7 groups are linked together by Mo—O—Mo bonds, which may be referred to as interligand bridges if the Mo_3O_7 groups are interpreted as ligands. It should be mentioned that the concept of ligands in this case was introduced from a mathematical viewpoint rather than a chemical one[2]. The oxygen atoms of the in-

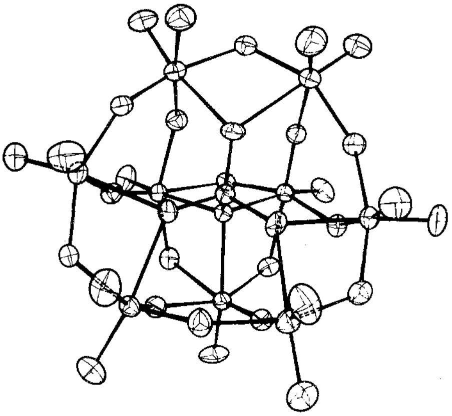

Fig. 1. The tetrahedral model (symmetry T_d) of the $PMo_{12}O_{40}^{-3}$ ion. It is designated *a* in the text

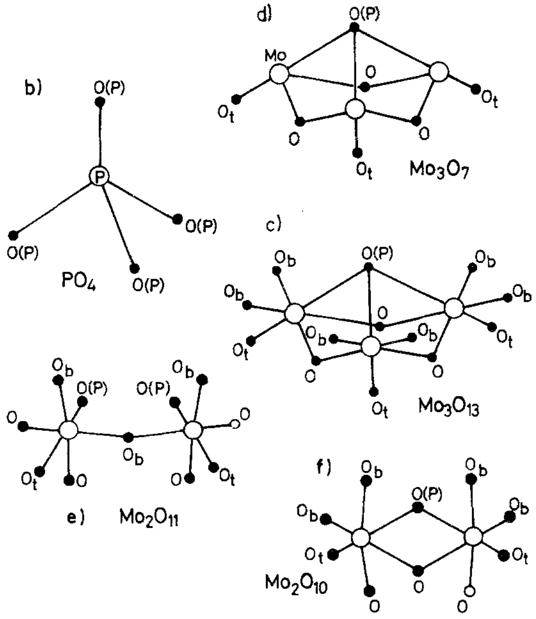

Fig. 2. Five fragments of the *a* $PMo_{12}O_{40}^{3-}$ ion (T_d): *b* PO_4 (T_d), *c* Mo_3O_{13} (C_{3v}), *d* Mo_3O_7 (C_{3v}), *e* Mo_2O_{11} (C_s) and *f* Mo_2O_{10} (C_s)

terligand bridges are designated O_b (see Fig. 2). Another type of oxygen atoms, O_t, is present in the terminal Mo—O bonds. Fig. 2 shows altogether five fragments, (b)-(f), distinguished by selecting groups of atoms from the whole $PMo_{12}O_{40}^{3-}$ complex (a).

The 80 different types of interatomic distances in $PMo_{12}O_{40}^{3-}$ may be grouped according to the types of atoms. Four types of oxygen atoms have been defined and are designated O (P), O, O_b and O_t according to the previous conventions[1].

Normal Coordinate Analysis

Spectroscopically active frequencies ($9\,A_1 + 13\,E + 22\,F_2$) from an approximate force field for $PMo_{12}O_{40}^{3-}$ were communicated elsewhere[1]. The force field adopted in the present work is a slight modification of the force field from another normal coordinate analysis, which was reported in more details[2]. Also the principles of transferring the force field to the different fragments along with calculated vibrational frequencies for the fragments have been published[7].

Results and Discussion

Bonded Distances

For the P—O (P) [1.54] distance the values of 0.0408 and 0.0439 Å were calculated for (a) the whole ion and (b) the PO_4 fragment, respectively. The figures in brackets here and throughout indicate the interatomic separations in Å. The four remaining types of bond distances occur in most of the fragments except (b). The l values are found in Table 1. The l values for the bonded Mo-oxygen distances in the whole complex were found to increase with the interatomic distance in a roughly linear way; $l \approx 0.0202 \cdot r$.

Table 1. *Mean amplitudes* ($l \cdot 10^2$ *in* Å) *at 298 K for bonded* Mo—O *distances in* $PMo_{12}O_{40}^{3-}$ *(a) and its fragments (c)-(f)*

Distance	[r/Å]	(a)	(c)	(d)	(e)	(f)
Mo—O_t	[1.68]	3.62	3.62	3.62	3.62	3.62
Mo—O_b	[1.91]	4.14	4.32	—	4.32 4.25	4.32 4.32
Mo—O	[1.92]	4.14	4.17	4.18	4.32 4.32	4.19 4.32
Mo—O(P)	[2.43]	5.15	5.88	5.98	7.80	6.61

Nonbonded Distances Other than Oxygen-Oxygen

The nonbonded distances involving the P atom do not exist in any one of the fragments considered here. The following mean amplitudes (l in Å) at 298 K were calculated for the whole complex: P···Mo [3.56] 0.0505, P···O_b [3.39] 0.0709, P···O [3.97] 0.0598, P···O_t [5.22] 0.0621.

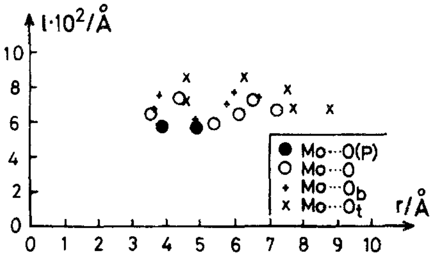

Fig. 3. Mean amplitudes (l at 298 K) of nonbonded Mo—oxygen distances in the whole complex

Table 2. *Mean amplitudes* ($l \cdot 10^2$ *in* Å) *at 298 K for nonbonded* Mo···O- *and* Mo···Mo-*distances in* $PMo_{12}O_{40}{}^{3-}$ *(a) and its fragments (c)-(f)*

Distance	[r/Å]	(a)	(c)	(d)	(e)	(f)
Mo···O	[3.57]	6.48	6.96	7.40	—	14.85
Mo···O	[4.39]	7.43	—	—	14.61	—
Mo···O	[5.39]	5.87	—	—	9.80	—
Mo···O_b	[3.65]	6.71	—	—	15.74	—
Mo···O_b	[3.83]	7.49	10.94	—	—	14.49
Mo···O_b	[4.85]	6.21	7.66	—	—	7.90
Mo···O_t	[4.60]	8.65	—	—	12.37	—
Mo···O_t	[4.64]	7.28	7.51	8.55	—	7.74
Mo···O (P)	[3.90]	5.71	—	—	21.07	—
Mo···Mo	[3.42]	4.27	4.53	4.61	—	4.78
Mo···Mo	[3.70]	4.41	—	—	5.68	—

The l values for nonbonded Mo···oxygen distances for the whole complex are plotted versus the interatomic distances in Fig. 3. No gross trend of variation in the l values is observed throughout the substantial range [3.57–8.78 Å] of interatomic distances. On the contrary the l values are remarkably constant, most of them within 0.07 ± 0.01 Å. The types which also occur in one or more of the fragments are listed in Table 2.

Also the l values of Mo···Mo distances have roughly characteristic values, slightly lower than the Mo···O mean amplitudes. Two of the types

Table 3. *Mean amplitudes ($l \cdot 10^2$ in Å) at 298 K for nonbonded* O (P) ··· O-*distances in* $PMo_{12}O_{40}^{3-}$ *(a) and its fragments (c)-(f)*

Distance	[r/Å]	(a)	(c)	(d)	(e)	(f)
O (P) ··· O	[2.61]	5.80	6.25	6.39	10.26 10.26	6.46 11.71
O (P) ··· O	[4.17]	7.28	—	—	49.98	—
O (P) ··· O_b	[2.92]	7.15	9.69	—	10.38 10.39	10.01 10.02
O (P) ··· O_b	[3.89]	7.30	—	—	69.46	—
O (P) ··· O_b	[4.91]	6.48	—	—	31.33	—
O (P) ··· O_t	[4.10]	6.14	6.69	6.75	8.53	7.38
O (P) ··· O_t	[5.41]	7.45	—	—	18.48	—

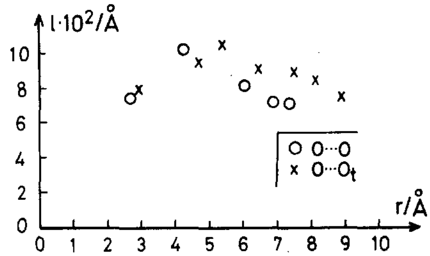

Fig. 4. Mean amplitudes (l at 298 K) of O ··· O- and O ··· O_t-distances in the whole complex

are included in Table 2. The l values (in Å) of three additional types, which only are found in the whole complex, are: [5.04] 0.0594, [6.17] 0.0551 and [7.12] 0.0578.

The Nonbonded Oxygen-Oxygen Distances

Most of the nonbonded distances involve oxygen—oxygen atoms of some types.

The O (P) ··· O (P) [2.52] type occurs only in the whole complex (a), the PO_4 fragment (b) and the Mo_2O_{11} fragment (e). The calculated mean amplitudes (in Å) are (a) 0.0534, (b) 0.0657 and (e) 0.3162, respectively. The other O (P) ··· oxygen distances are listed in Table 3. Two of the types are not included in the table because they do not occur in any one of the fragments. They are (with l values in Å): O (P) ··· O_b [4.82] 0.0760 and O (P) ··· O_t [6.56] 0.0657. Most of the l values for O (P) ··· oxygen in the whole complex are found within 0.07 ± 0.01 Å.

The rest of the oxygen $\cdots$ oxygen distances are collected into three groups: (i) The $O \cdots O$ and $O \cdots O_t$ distances, for which the l values in the complex (a) are shown as functions of the interatomic distance in Fig. 4. The magnitudes are found to be generally larger than those of the O (P) $\cdots$ oxygen distances, namely between 0.07 and 0.11 Å. Comparisons with l values calculated for the different fragments are found in Table 4. (ii) The l values of $O \cdots O_b$ and $O_b \cdots O_b$ distances for the whole complex are found in Fig. 5. The magnitudes are within 0.08 ± 0.01 Å for all of them except for the two types $O \cdots O_b$ [3.75] 0.0577 and $O_b \cdots O_b$ [3.21] 0.0993 Å. Comparisons with fragments are found in Table 5. (iii) Fig. 6 shows the graphical representation of the l values for the $O_b \cdots O_t$ and $O_t \cdots O_t$ distances in the complex. They are spread over a large range of magnitudes, especially those of $O_t \cdots O_t$, which range from 0.078 to 0.137 Å. For comparisons with the calculated l values for the different fragments, see Table 6.

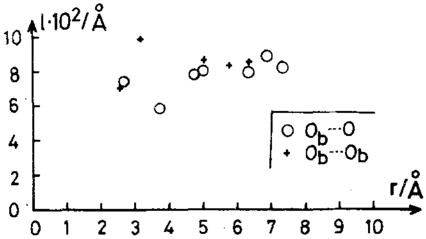

Fig. 5. Mean amplitudes (l at 298 K) of $O_b \cdots O$- and $O_b \cdots O_b$-distances in the whole complex

Table 4. *Mean amplitudes* ($l \cdot 10^2$ *in* Å) *at 298 K for nonbonded* $O \cdots O$- *and* $O \cdots O_t$-*distances in* $PMo_{12}O_{40}{}^{3-}$ *(a) and its fragments (c)-(f)*

Distance	[r/Å]	(a)	(c)	(d)	(e)	(f)
$O \cdots O$	[2.64]	7.41	8.02	8.63	8.95	7.90 27.02
$O \cdots O$	[4.21]	10.18	—	—	24.08	—
$O \cdots O$	[5.99]	8.12	—	—	26.19	—
$O \cdots O_t$	[2.78]	7.88	8.13	9.47	8.32 8.32	8.14 8.47
$O \cdots O_t$	[4.71]	9.50	10.41	11.87	—	18.76
$O \cdots O_t$	[5.35]	10.54	—	—	18.93	—
$O \cdots O_t$	[6.46]	9.17	—	—	15.46	—

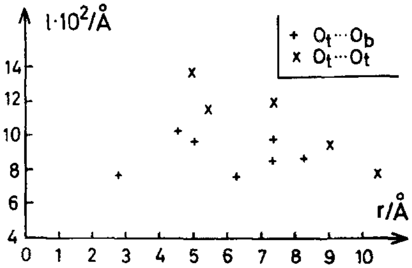

Fig. 6. Mean amplitudes (l at 298 K) of $O_t\cdots O_b$- and $O_t\cdots O_t$-distances in the whole complex

Table 5. *Mean amplitudes* ($l\cdot 10^2$ *in* Å) *at 298 K for nonbonded* $O\cdots O_b$*- and* $O_b\cdots O_b$*-distances in* $PMo_{12}O_{40}{}^{3-}$ *(a) and its fragments (c)-(f)*

Distance	[r/Å]	(a)	(c)	(d)	(e)	(f)
$O\cdots O_b$	[2.68]	7.43	8.79	—	8.88 8.92	8.79 8.82
$O\cdots O_b$	[3.75]	5.77	6.08	—	6.28 6.32	6.11 6.42
$O\cdots O_b$	[4.75]	7.77	9.31	—	—	11.00 19.41
$O\cdots O_b$	[5.01]	8.00	—	—	26.19 29.58	—
$O\cdots O_b$	[6.86]	8.78	—	—	16.54	—
$O_b\cdots O_b$	[2.61]	7.01	8.97	—	9.03 23.12	8.97
$O_b\cdots O_b$	[3.21]	9.93	18.03	—	—	28.29
$O_b\cdots O_b$	[5.05]	8.64	14.04	—	—	19.11
$O_b\cdots O_b$	[5.83]	8.32	12.18	—	—	12.44

Table 6. *Mean amplitudes* ($l\cdot 10^2$ *in* Å) *at 298 K for nonbonded* $O_b\cdots O_t$*- and* $O_t\cdots O_t$*-distances in* $PMo_{12}O_{40}{}^{3-}$ *(a) and its fragments (c)-(f)*

Distance	[r/Å]	(a)	(c)	(d)	(e)	(f)
$O_b\cdots O_t$	[2.81]	7.77	8.06	—	8.16 8.20	8.07 8.35
$O_b\cdots O_t$	[4.57]	10.23	—	—	35.16	—
$O_b\cdots O_t$	[5.05]	9.69	13.27	—	—	17.20
$O_b\cdots O_t$	[6.31]	7.73	8.43	—	—	8.72
$O_t\cdots O_t$	[4.96]	13.68	—	—	20.73	—
$O_t\cdots O_t$	[5.47]	11.55	12.20	14.91	—	12.57

General Discussion

The calculated mean amplitudes for the whole 53-atomic ion all display magnitudes within the usual orders of magnitude[3]. A general tendency of increasing mean amplitudes with increasing interatomic separation for the same atom pairs has been studied[8–11]. Here we find many exceptions to this tendency for the nonbonded distances. In many cases this relationship seems consistently to be reversed. For instance for the $O_t \cdots O_t$ distances the mean amplitudes (l) decrease with the increasing separation (r) in all cases but one (cf. Fig. 6). For the $O \cdots O$ and $O \cdots O_t$ distances (cf. Fig. 4) the mean amplitudes start to increase up to a maximum value and then decrease when r is increased. A closer inspection reveals that the l values tend to be smaller than expected from the interatomic separation when the connecting chain of bonds between the atom pair in question is nearly linear. The same feature has been observed many times before. It accounts for instance for the magnitudes of l for the nonbonded distances in benzene[3].

When comparing the calculated mean amplitudes for the whole ion with those of different fragments (cf. Tables 1–6) we find both similarities and large deviations. Application of fragments for approximate calculations of mean amplitudes must therefore not be used without great precaution. The largest deviations are found as expected among mean amplitudes for nonbonded distances, and especially when the fragment is "loose", i.e. when it contains few bridging atoms. In some instances this "loosening" of bridges has a tremendous effect on the mean amplitudes. The most drastic examples are found among the fragments Mo_2O_{11} (e) and Mo_2O_{12} (f). To quote only one extreme example (cf. Table 3): The l value of 0.695 Å for O (P) $\cdots O_b$ in Mo_2O_{11} is not at all comparable with the value of 0.073 Å for the corresponding distance in the whole ion.

Acknowledgement

Financial support to *B. N. Cyvin* from The Norwegian Research Council for Science and the Humanities is gratefully acknowledged.

References

[1] *L. Lyhamn, S. J. Cyvin, B. N. Cyvin,* and *J. Brunvoll,* Spectroscopy Letters **9**, 859 (1976).

[2] *L. Lyhamn, S. J. Cyvin, B. N. Cyvin,* and *J. Brunvoll,* Z. Naturforsch. **31 a**, 1589 (1976).

[3] *S. J. Cyvin,* Molecular Vibrations and Mean Square Amplitudes. Oslo: Universitetsforlaget/Amsterdam: Elsevier. 1968.

[4] *E. B. Wilson, jr., J. C. Decius,* and *P. C. Cross,* Molecular Vibrations. New York: McGraw-Hill. 1955.

[5] *S. J. Cyvin* (ed.), Molecular Structures and Vibrations. Amsterdam: Elsevier. 1972.

[6] *R. Strandberg*, Acta Chem. Scand. **A 29**, 359 (1975).

[7] *L. Lyhamn* and *S. J. Cyvin*, Spectroscopy Letters, in press.

[8] *V. S. Mastryukov* and *S. J. Cyvin*, J. Mol. Struct. **29**, 15 (1975).

[9] *S. J. Cyvin* and *V. S. Mastryukov*, J. Mol. Struct. **30**, 333 (1976).

[10] *E. L. Osina, V. S. Mastryukov, L. V. Vilkov*, and *S. Cyvin*, Zh. Strukt. Khim. **16**, 1065 (1975).

[11] *V. S. Mastryukov, E. L. Osina, L. V. Vilkov*, and *S. Cyvin*, Zh. Strukt. Khim. **17**, 80 (1976).